

論文 / 著書情報
Article / Book Information

題目(和文)	酸をプロモーターとするラクトン、環状カーボネート類の開環重合挙動
Title(English)	Acid Promoted Ring-Opening Polymerization Behavior of Cyclic Carbonates and Lactones
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出典(和文)	学位:工学博士, 学位授与機関:東京工業大学, 報告番号:甲第4405号, 授与年月日:2000年3月26日, 学位の種別:課程博士, 審査員:
Citation(English)	Degree:Doctor of Engineering, Conferring organization: Tokyo Institute of Technology, Report number:甲第4405号, Conferred date:2000/3/26, Degree Type:Course doctor, Examiner:
学位種別(和文)	博士論文
Type(English)	Doctoral Thesis

**Acid Promoted Ring-Opening Polymerization
Behavior of Cyclic Carbonates and Lactones**

**A Thesis Presented
to
Tokyo Institute of Technology**

Yuji Shibasaki

Yokohama, 2000

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Chapter 1

General Introduction

Chapter 1.
General Introduction

Introduction

Living polymerization is one of the most rapidly developing fields in polymer chemistry. It has been originally considered that a growing polymer retains indefinitely the propensity of growth and the propagation proceeds without termination and chain transfer.¹ Recently, the first definition has somewhat changed. We shall refer it as a living polymer,² when the end group retains the propensity of growth for at least a period for completion of an intended synthesis, or any other desired task. Hence:

- i) Initiation is faster or equal compared to propagation.
- ii) The exchange between species of different reactivities is faster than propagation.
- iii) The rate of depropagation is substantially lower than propagation.
- iv) The system is homogeneous and the rate of diffusion is sufficiently fast.

Living polymerization can provide synthetic polymer chemists with various useful opportunities. It can control the molecular mass of produced polymers. It can prepare block copolymers free from homopolymers, having a desired sequence and a block size. The reactivity of the end groups permits their conversion into requested functional groups, i.e., allows for the preparation of functional and bifunctional telechelic polymers with desired end groups. By this procedure, macromers can be produced using properly synthesized reagents. "Linking reagents" convert bifunctional linear living polymers into macrocyclics. Modification of these procedures yields star- and comb-shaped polymers. The application of living polymerization has developed numerous new macromolecules of considerable technological value as well as provided researchers with materials allowing precise studies of various properties of polymers, especially those depending on their molecular mass.

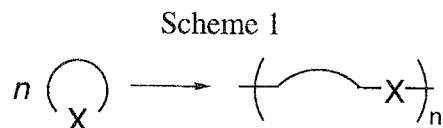
Ring-opening polymerization is an important method for macromolecular synthesis, although the contribution to the synthetic plastics

rubbers, and fibers is not so large compared to the other methods such as vinyl polymerization and polycondensation. In fact, ring-opening polymerization commercially produces several elastoplastics, and engineering thermoplastics such as polyethylene oxide and nylon-6.

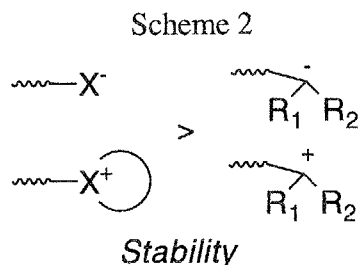
The ring-opening polymerization of cyclic monomers is an equilibrium reaction between polymers, monomers, and cyclic oligomers. When the ceiling temperature of the polymerization is rather low, the obtained polymers undergo depolymerization to regenerate the original monomers. The theoretical basis on the ring formation has been established by Jacobson and Stockmayer³ which has been generally corroborated by a number of systems.⁴ After replacing the random flight model by Jacobson and Stockmayer into the rotational isomeric state model Flory and Smelyen⁵ have deduced conformational parameters from the equilibrium concentration of the rings.

Ring-opening polymerization has several advantages compared to vinyl polymerization as following.

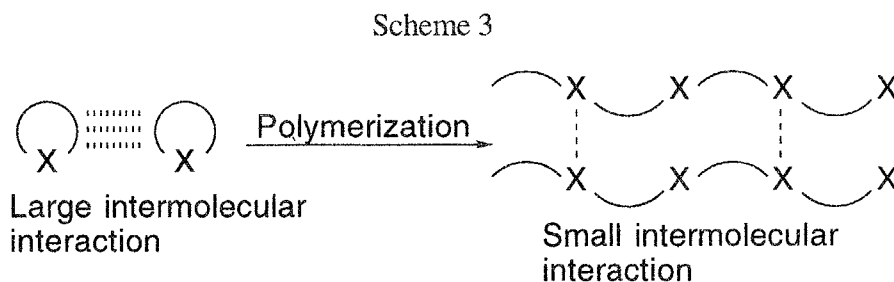
i) Functional groups can be introduced into the main chain of the polymers (Scheme 1). This can be also achieved by polycondensation, however, this method is usually accompanied by elimination of small molecules such as HCl and H₂O, which makes it difficult to apply the polymerization to the fine material synthesis. Furthermore, it is difficult to achieve narrow polydispersity ratios, ordered sequences, and stereocontrol of polymers by polycondensation.



ii) The polymerization can be easily controlled due to the stable propagating structure (Scheme 2). The propagating center in ring-opening polymerization is a nucleophile of a heteroatom or an onium ion, commonly more stable compared to a carbanion or a carbocation in vinyl polymerization.

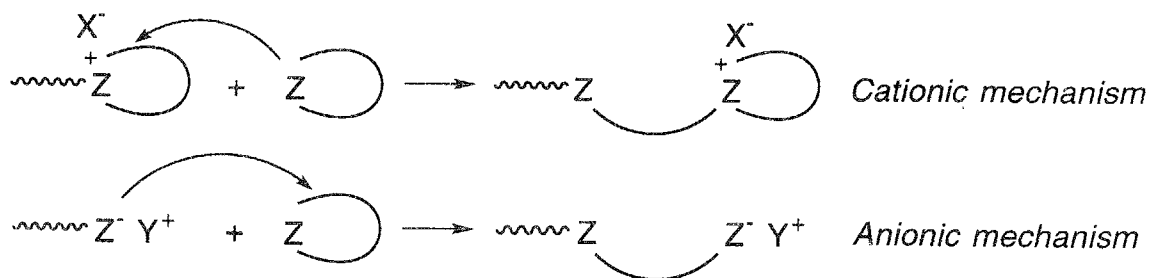


iii) The volume change during polymerization is small,^{6a} which is useful for molding materials, thermosetting resins, and adhesives. The volume shrinkage from monomeric compound to polymeric one is usually around 15 ~ 20 % in vinyl polymerization. The phenomena can be improved by ring-opening polymerization, which is explained by differences of bond length and distance between molecules on polymerization.^{6a} Oxabicyclic and oxaspirocyclic monomers such as spiro orthoesters, bicyclo orthoesters, and spiro orthocarbonates undergo cationic double ring-opening polymerization in the presence of Lewis acid like $\text{BF}_3 \cdot \text{Et}_2\text{O}$, with the result that volume expansion on polymerization are observed.^{6b} In the case of cyclic carbonates, volume expansion during polymerization has been reported due to the favorable formation of more compact structure in monomeric state (e. g. +1.1 ~ 7.7% volume change on the polymerization of a non-substituted six-membered cyclic carbonate^{6c}) (Scheme 3).



The propagating reaction in cationic polymerization involves fission of a carbon-onium bond to provide better leaving groups, while in anionic polymerization carbon-heteroatom bond is broken (Scheme 4).

Scheme 4

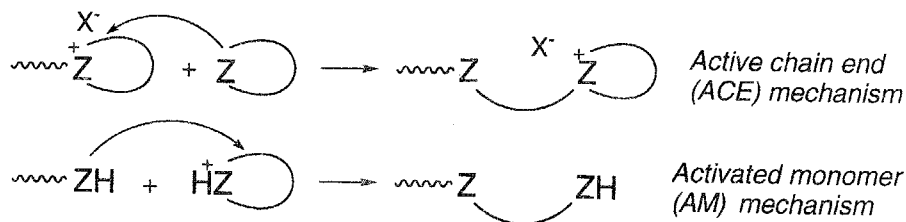


Despite a great number of monomers which can polymerize in cationic manner, the cationic mechanism has been supposed to be more difficult than anionic one to achieve living polymerization. The following generalities are formulated for cationic ring-opening polymerization.

- i) Propagating center is highly solvated where the monomer and polymer are strongest solvating agents. This is comparable with anionic polymerization, whose counter ion is solvated possessing the possibility of stabilization of the propagating center with some additives like Lewis acids.
- ii) The stereo chemistry of the growing species is not affected by the counter anion due to the solvation as described in i).
- iii) Covalent species are usually less reactive than their ionic counter parts. However, sterically hindered onium ions may add the puckered cyclic monomers more slowly than the respective covalent species.

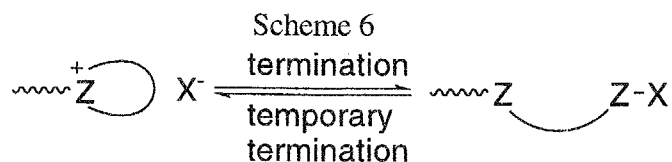
Cationic ring-opening polymerization proceeds either by nucleophilic attack of the monomer molecules on the onium ion of propagating chain end, namely active chain end (ACE) mechanism,⁷ or by nucleophilic attack of the chain end on the monomer molecules bearing a positive charge, activated monomer (AM) mechanism⁸ as shown in Scheme 5.

Scheme 5

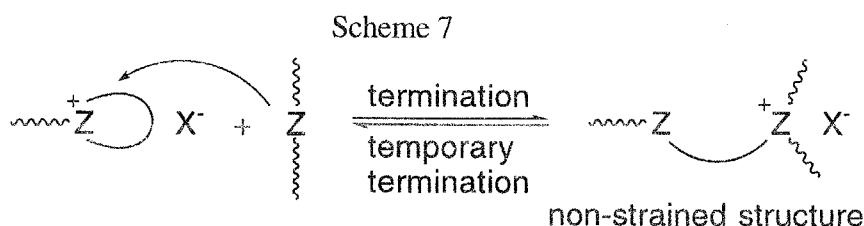


In the ACE mechanism, the counter ion has possibility to cause the ring-opening reaction with onium structure in polymer chain end to afford a linear

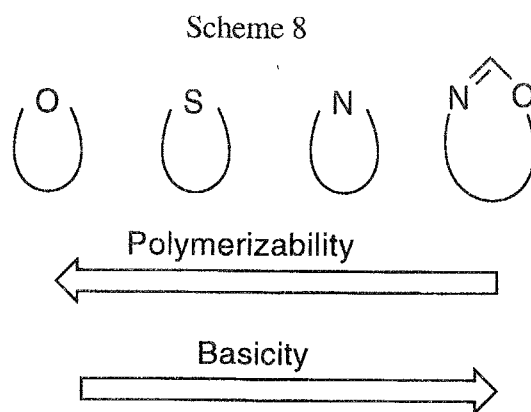
polymer with covalent bond. The tendency of this reaction is strongly depended on the nature of the counter ion and stability of onium ion. Depending on the stability of the covalent bond between carbon and counter ion, the reaction becomes termination or temporary termination (Scheme 6).



The ring-opening of the active species by a heteroatom of the polymer chain results in a nonstrained onium ion which also cause termination or temporary termination (Scheme 7).

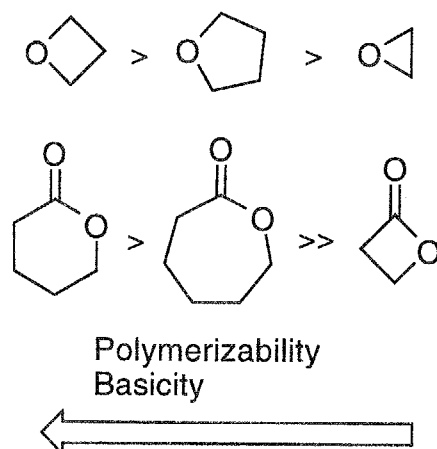


The ACE mechanism proceeds via nucleophilic substitution reaction, and it has known that the rate of propagation is mainly determined by the difference in reactivities of the corresponding active species; lower the basicity of the parent monomer and higher the ring strain of the active species (Scheme 8).



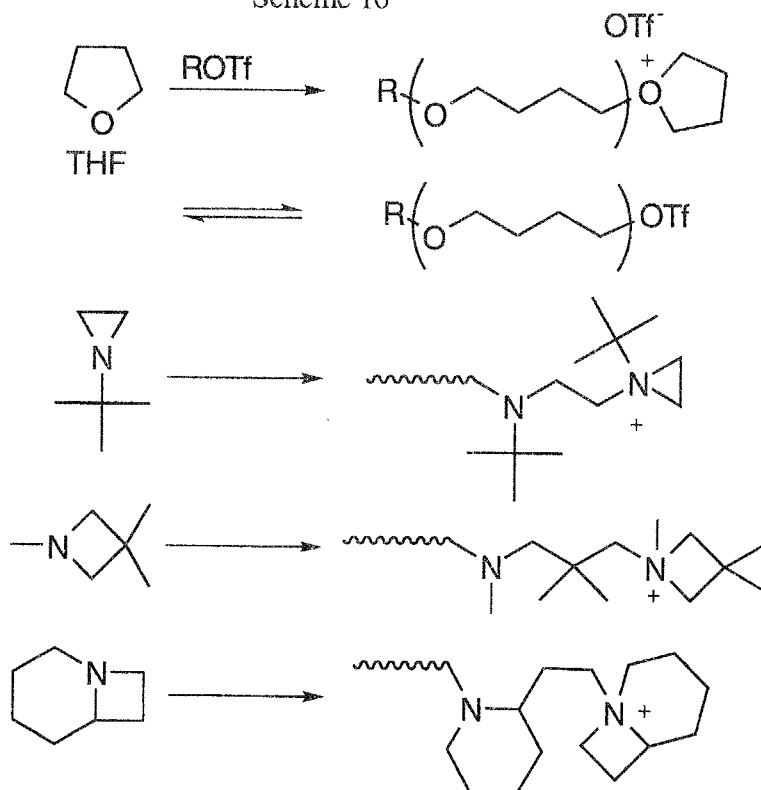
However, the basicity of the monomer strongly affects the mode of the reactions of growing species, since as the linear ether group in the polymer chain and the counter anion at the growing end, are also present in reaction systems, and thus the chain growth competes with various side reactions. The polymerizability of cyclic ethers and esters are shown in Scheme 9.

Scheme 9



The living cationic nature was found in some systems such as tetrahydrofuran (THF),⁹ cyclic sulfides (particularly those which are substituted and four-membered),¹⁰ aziridines,¹¹ azetidines,¹² and oxazolines¹³ via an ACE mechanism after careful choice of the conditions (Scheme 10).

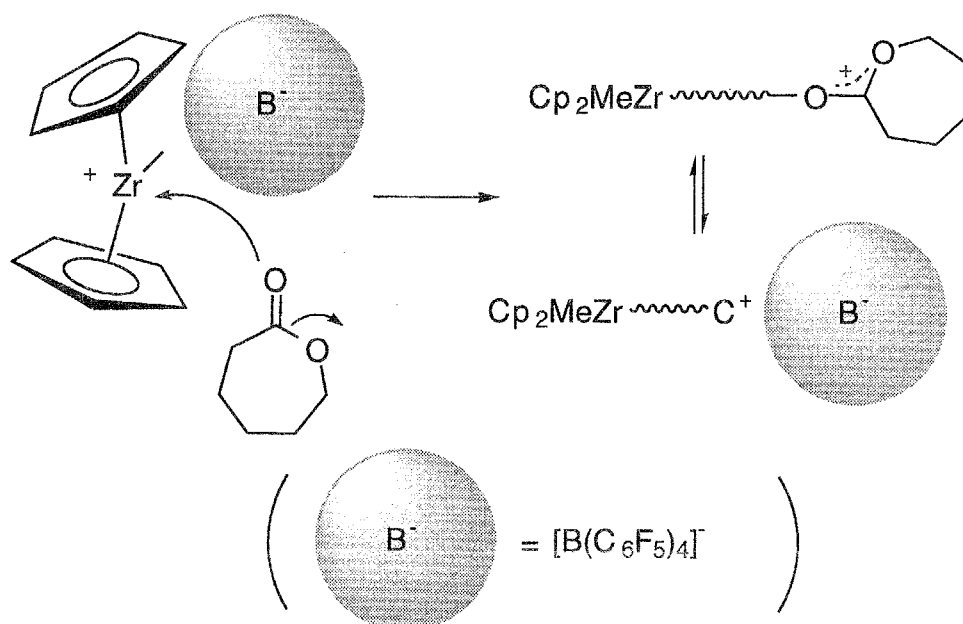
Scheme 10



The use of zirconocene complex with bulky non-nucleophilic counter ion, $[\text{Cp}_2\text{ZrMe}^+][\text{B}(\text{C}_6\text{F}_5)_4]^-$ has been successful to conduct living polymerization of lactones and cyclic carbonates. Narrow polydispersity polymers of ϵ -

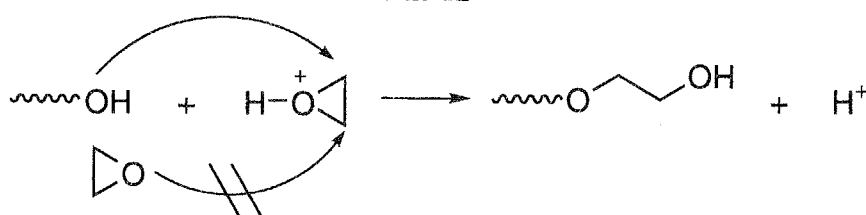
caprolactone ($M_w/M_n \sim 1.08$) and of 1,3-dioxepan-2-one ($M_w/M_n \sim 1.18$) can be obtained quantitatively via an ACE mechanism (Scheme 11).¹⁴

Scheme 11



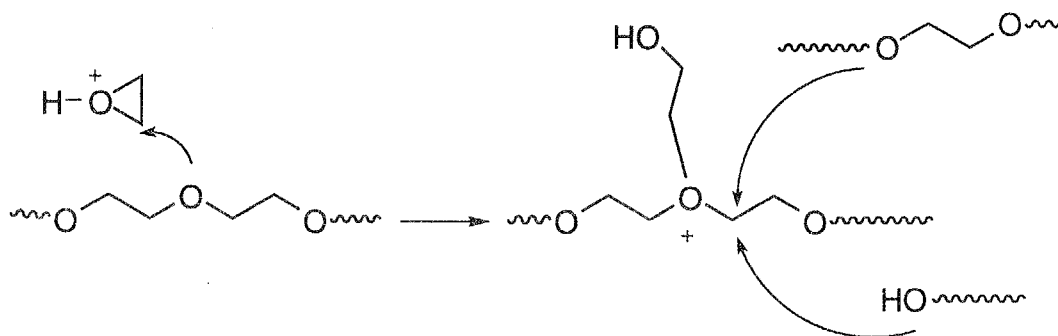
The other mechanism, AM polymerization has been first discovered by Kuzaev et al. in the polymerization of epichlorohydrin with $\text{BF}_3 \cdot \text{THF}$ in the presence of ethylene glycol, where no cyclic oligomer has been detected at the early stage of the polymerization.¹⁵ Penczek et al. have revealed that the polymerization can be switched from the ACE into AM mechanism to afford a linear polymer ($M_n \sim 4000$) with a narrow $M_w/M_n (< 1.16)$.¹⁶ Polymerization of ethylene oxide with a super acid, which is usually accompanied by back-biting reaction, has been also found to proceed by AM mechanism in diluted conditions by Penczek et. al. ($M_n \sim 4000$, $M_w/M_n \sim 1.2$). The activated (e.g. by HSbF_6) monomer addition to the hydroxyl end group of polyethylene oxide may dominate the conventional mechanism (ACE mechanism) when the hydroxyl group is much more nucleophilic than the monomer (Scheme 12).¹⁷

Scheme 12



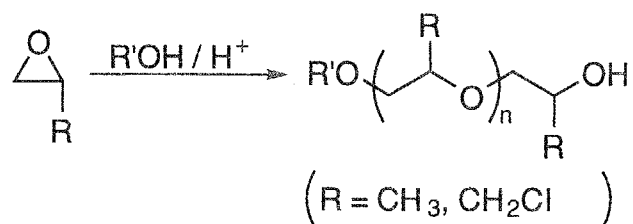
Polymerization of ethylene oxide via an AM mechanism has the advantage of preventing the formation of cyclic oligomers, on the other hands, it is difficult to obtain a high M_n polymer mainly because of scrambling reactions (Scheme 13).¹⁸

Scheme 13



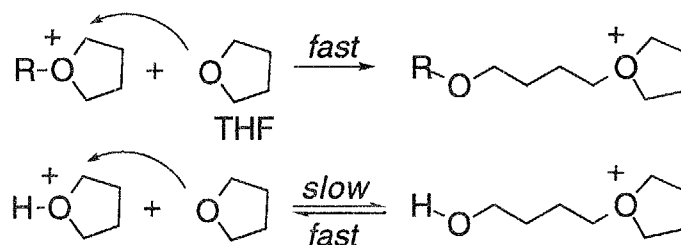
The substituted oxirane can tend to avoid such unfavorable reactions, especially in epichlorohydrin polymerization. The reaction between the oxygen in the polymer chain and activated monomer can be negligible due to the electron with-drawing effect of chlorine atoms (Scheme 14).¹⁹

Scheme 14



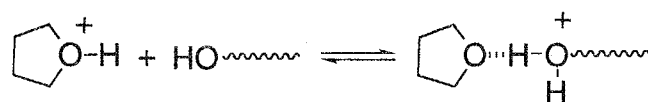
The AM polymerization cannot be applied for THF homopolymerization, because protonic acids in the presence of alcohols do not initiate the polymerization of THF. Super acids such as triflic acid initiate THF polymerization, although the rate constant of initiation is much lower than that by alkylating agents (e. g., trialkyloxonium ion) and lower than that of propagation (Scheme 15).^{7a} Furthermore, the formation of cycles by the end to end cyclization is observed when the polymerization is initiated by protonic acids.

Scheme 15



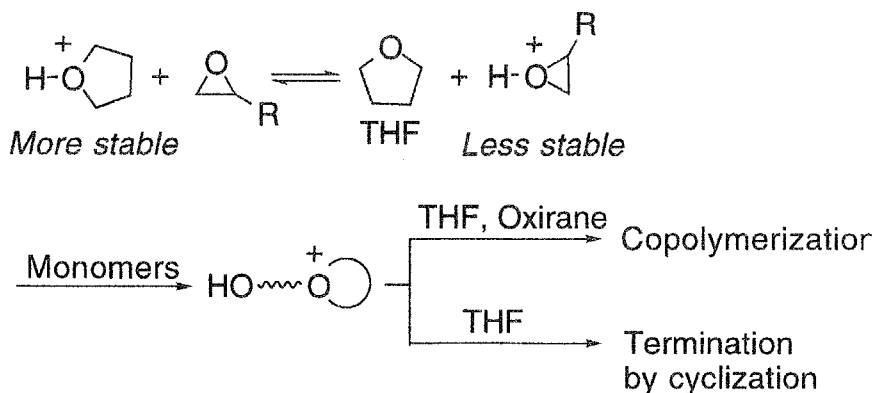
The low reactivity of protonated THF stems from hydrogen bonding with a primary alcohol produced in initiation step (Scheme 16).

Scheme 16



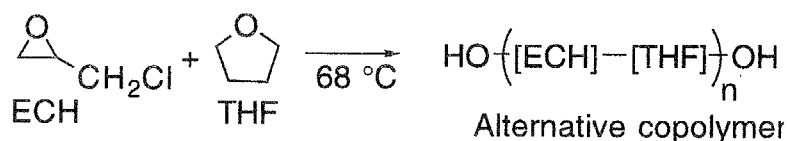
The low reactivity of protonated THF is due to the low ring strain of the five-membered ring. Thus the addition of oxiranes (e. g., epichlorohydrin) enhances the polymerization by increasing considerably the rate of initiation to afford the copolymer.²⁰ The polymerization stops when the oxirane is entirely consumed (Scheme 17).⁸

Scheme 17



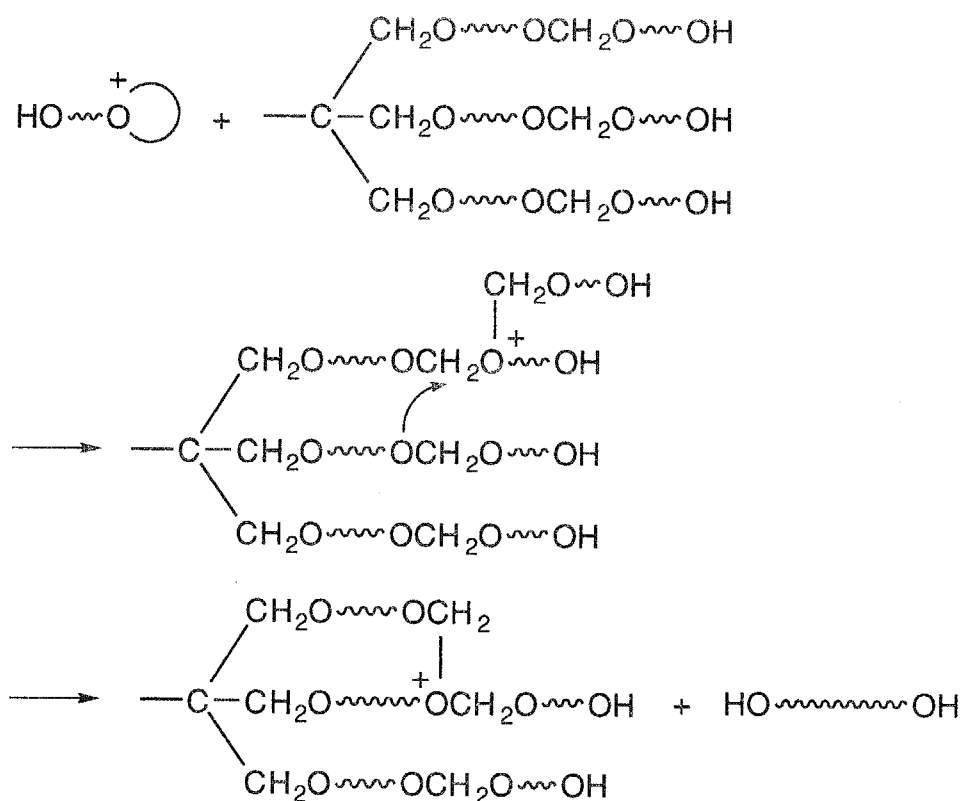
The microstructure of the polymer chain in AM polymerization of oxiranes is governed exclusively by the kinetic control, while in the copolymerization of oxiranes (e. g., epichlorohydrin) with THF or with 1,4-dioxane the distribution of comonomer units depends on both kinetic and thermodynamic factors. The alternative copolymer of epichlorohydrin with THF has been successfully prepared by kinetic and thermodynamic controls (Scheme 18).⁸

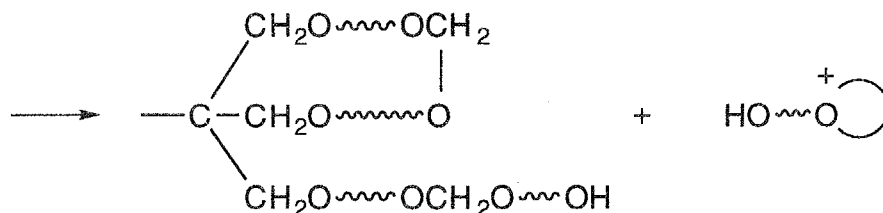
Scheme 18



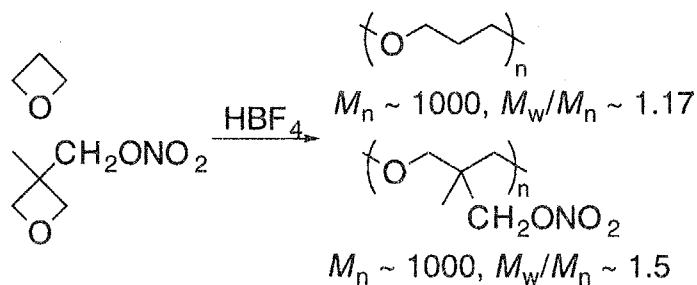
The AM mechanism has been applied to the polymerization of cyclic acetal such as 1,3-dioxolane and 1,3-dioxepane to afford a high M_n polymer (~ 20000) free from cyclic oligomers, but the M_w/M_n is broad (~ 1.4) because of transacetalization.²¹ The star-shaped poly1,3-dioxepane has been prepared with triflic acid in the presence of polyols, whereas the formation of cyclic oligomers is detected probably due to accessibility of oxonium ion in one arm with the acetal moiety of the neighboring chain in the same molecules of the polymer (Scheme 19).²²

Scheme 19

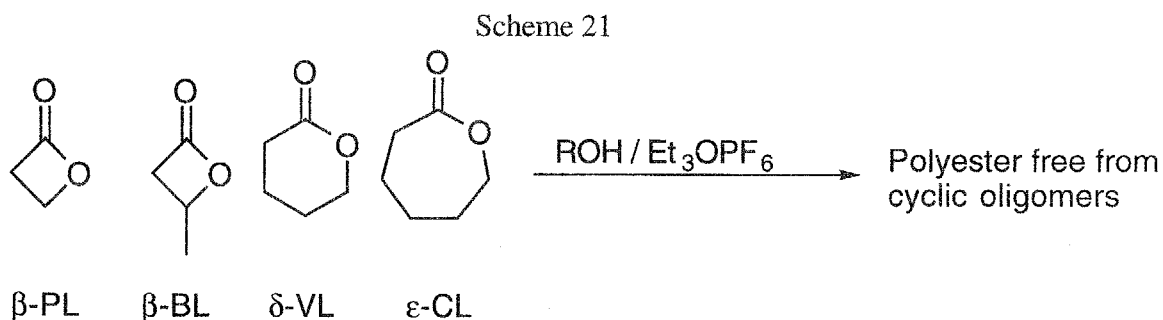




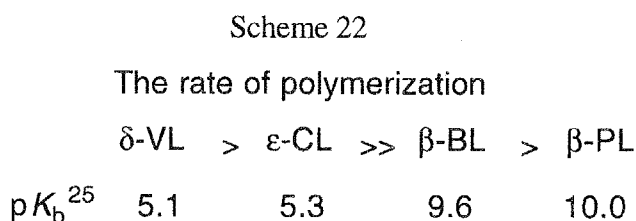
Amass et al. have reported the polymerization of a substituted oxetane by HBF_4 in the presence of an alcohol to give a linear polyether ($M_n \sim 1000$, $M_w/M_n \sim 1.5$) free from cyclic compounds (Scheme 20).²³



Okamoto et al. have reported that the combination of a protonic acid and an alcohol is an effective initiator for the ring-opening polymerization of lactones to afford the polymers with controlled M_n s (< 3000), but the M_w/M_n s are broad (~ 1.3) (Scheme 21).²⁴



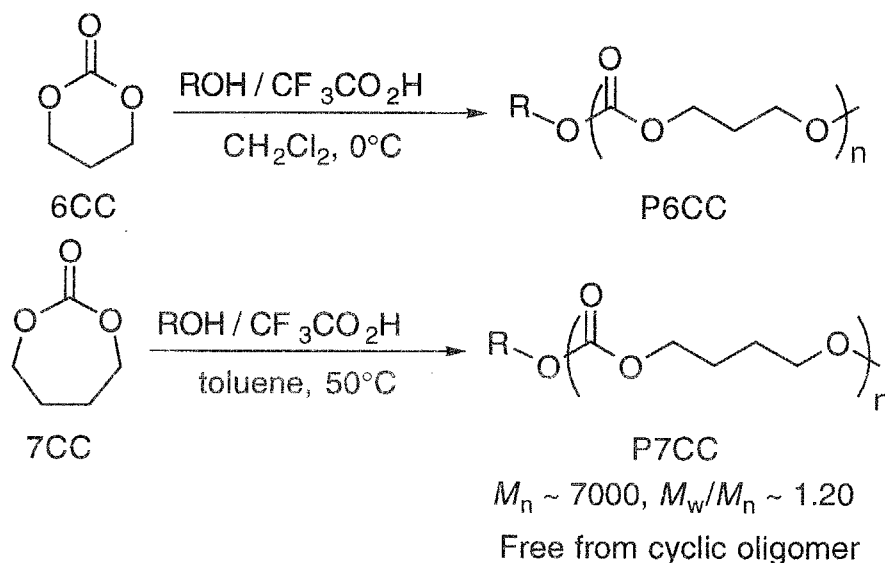
The rates of polymerization are comparable with their basicities as shown in Scheme 22.



These study have been applied to preparation of block copolymers, graft copolymers like of hydroxyl terminated polybutadiene with polytetramethylene oxide²⁶ and of polyethylene glycol with ϵ -caprolactone.²⁷

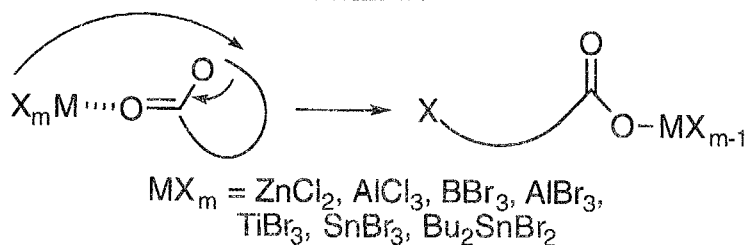
Ring-opening polymerization of six- and seven-membered cyclic carbonates with an alcohol in the presence of trifluoroacetic acid has been investigated.²⁸ The corresponding polycarbonates with relatively narrow polydispersity ratios are obtained free from cyclic oligomers ($M_n \sim 7000$, $M_w/M_n \sim 1.20$) (Scheme 23).

Scheme 23



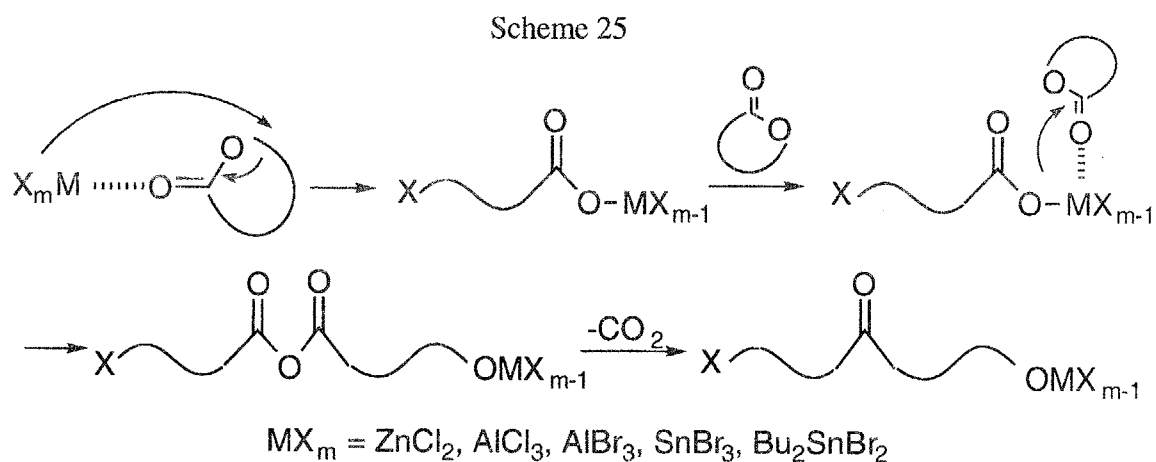
Ring-opening cationic polymerization with Lewis acids is one of the most common and convenient methods for general use, whereas the mechanism usually is complicated with side reactions. Ring-opening polymerization of lactones and cyclic carbonates with various Lewis acids has been investigated by several groups. The polymerization proceeds generally via a conventional (ACE) and insertion mechanism depending on the catalysts. The stoichiometric reaction between lactones with various metalhalides (MX_m) such as ZnCl_2 , AlCl_3 , and BBr_3 has been studied, where ω -halogenatedcarboxylic acids form in all cases (Scheme 24).²⁹

Scheme 24



Consequently, Lewis acids with energetically favorable d-orbitals like SnBr_4 and ZnBr_2 , metal-oxygen bonds are formed to produce high M_n polymer (~ 70000) via an insertion mechanism at least above 60°C (Scheme 25).³⁰

However, due to such fierce conditions, the exact mechanism has not been revealed both in initiation and transfer. The obtained polymer has halogen and hydroxyl groups at the both ends, but the ratio is not equal. To obtain a controlled M_n polymer, the conditions are required to choose carefully to avoid inter and intramolecular transesterification which broadens the M_w/M_n of the polymer (~ 1.7).

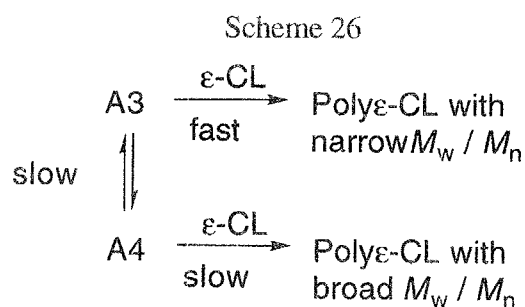


⇌ Insertion polymerization

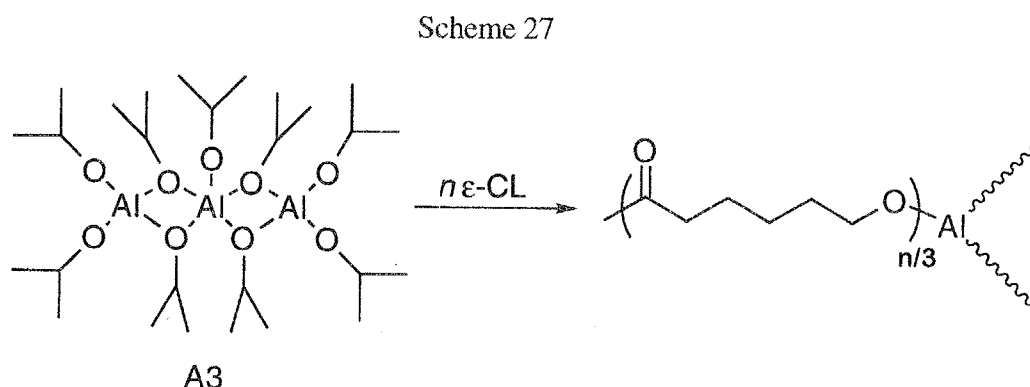
Tin compounds such as tin(II) 2-ethylhexanoate,³¹ Bu_3SnOMe ,³² $\text{Bu}_2\text{Sn}(\text{OMe})_2$,³³ BuSnCl_3 ,³⁴ Bu_2SnO ,³⁵ and the spirocyclic tin compounds³⁷ have been investigated for the polymerization of lactide and lactones.

Kricheldorf et al. have studied the polymerization mechanism of metal alkoxide-initiated polymerization $[\text{Mt}(\text{OR})_n]$: ($\text{Mt} = \text{Mg}, \text{Al}, \text{Zn}, \text{Ti}, \text{Zr}, \text{Sn}$), ($\text{R} = \text{alkyl}$) of lactide and lactones to find all the metal alkoxides serve as coordination initiators.³⁷ The difference of activity depends on the central metal and the reaction temperature. The degree of intramolecular transesterification have been observed as follows; $\text{Bu}_2\text{Sn}(\text{OR})_2 > \text{Ti}(\text{OR})_4 > \text{Zn}(\text{OR})_2 > \text{Al}(\text{OR})_3$.^{37(a)} Poly lactones with small polydispersity ratios and predictable M_n s are synthesized by aluminum alkoxides.³⁷ They exist at least as dimers, trimers, and tetramers, which is the general problem in initiation with

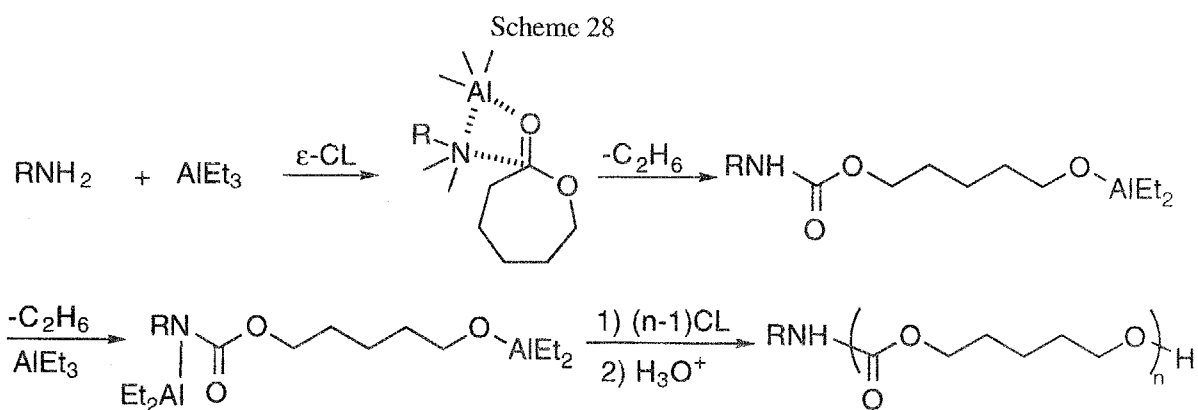
easily aggregating metal alkoxides.⁴¹ The number of components in the starting initiators depends on the size of substituents, solvents, and concentration.⁴² $\text{Al}(\text{O-}i\text{Pr})_3$ exists mostly as a mixture of trimers (A3) and tetramers (A4). These aggregates are much stronger and much less labile than the aggregates of $\text{R}_2\text{Al}(\text{OR})$ because the two oxygen atom bridges are available, linked to one aluminum atom. Based on the analysis of the M_n measurements, ^{27}Al NMR, and the kinetics of polymerization this number goes up to six in the central Al atom in A4.⁴³ Thus, the $\text{A3} \leftrightarrow \text{A4}$ interconversion is slow in comparison with $\epsilon\text{-CL}$ propagation. The rate constants of the reaction between the trimer and $\epsilon\text{-CL}$, and the tetramer and $\epsilon\text{-CL}$ have been measured to find out that the reactivity of tetramer is so much slower than trimer that if the mixture of A3 and A4 is used, then there is not enough time allowed for A4 to participate in initiation (Scheme 26).



Thus, on average, usually less than three O-*i*Pr groups per one Al atom reacts if the A3/A4 mixture is used, where A3 has been known to initiate the polymerization with quantitative efficiency and the aggregation is broken off during propagation as shown in Scheme 27.

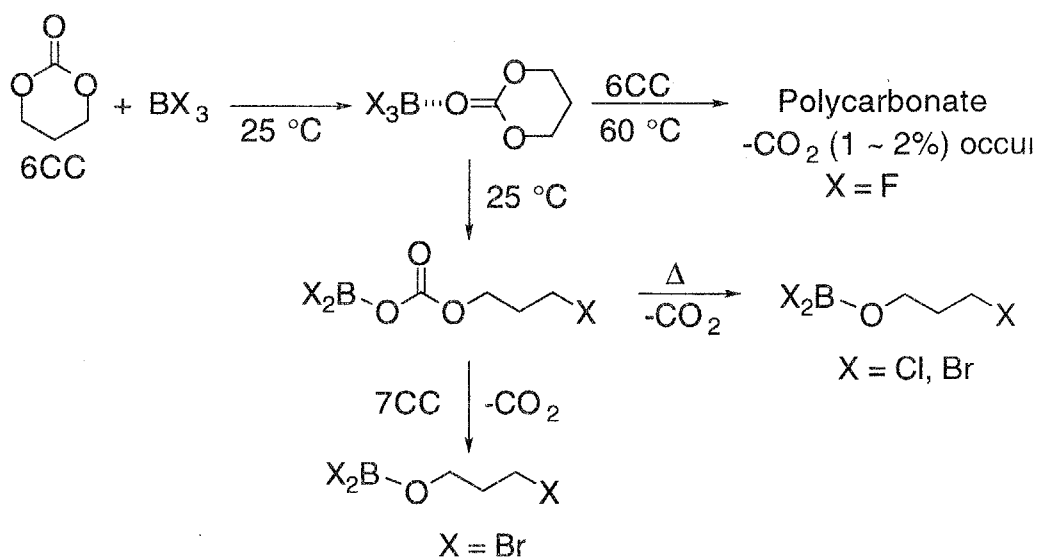


Monomers less reactive than ϵ -CL such as β -lactone and lactide,⁴⁴ requiring higher polymerization temperatures may give A4 enough time to be consumed before the monomer polymerized completely. Therefore, the rate constants of the polymerizations with A3 and A4 are different (~ 50), and the M_w/M_n become broader. Aluminum dialkylalkoxides and trialkylalkoxides carrying functional groups have been applied as initiators in polymerization of ϵ -caprolactone for the purpose of preparing selectively end functionalized poly(ϵ -caprolactone) with amino, bromo, allyl, thiol, or methacryloyl groups.^{38,39} Combination of primary amines with triethylaluminum serves as a good initiator for poly ϵ -CL (Scheme 28).⁴⁰



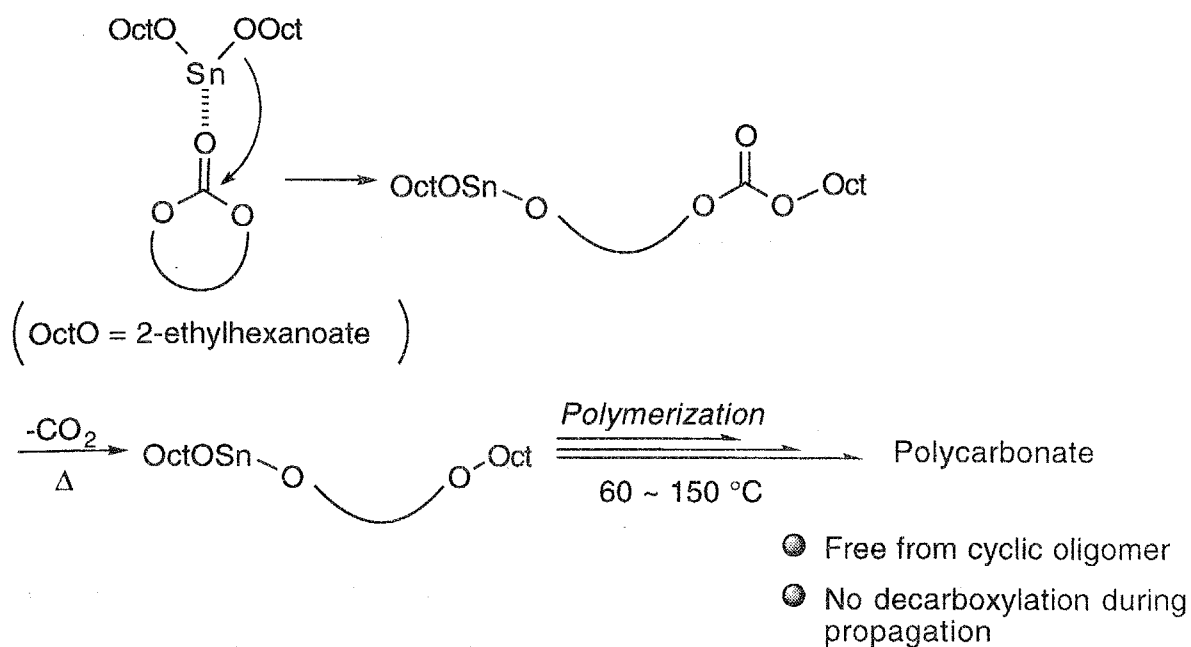
Al(OR)_3 , however, is not effective for the polymerization of a cyclic carbonate to obtain the polycarbonate with a small polydispersity ratio.⁴⁵ Aluminum-porphyrine complexes act as good initiator for the polymerization of cyclic carbonates as well as of lactones to provide high M_n polymers in slow reaction at 50 °C.⁴⁶ The reaction of substituted and unsubstituted six-membered cyclic carbonates (6CCs) with boron halogenides has been investigated.⁴⁷ The equimolar reaction provides the corresponding complexes at 25 °C. With $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at 60 °C, the further addition of the monomer leads to polymerization producing the polycarbonate containing 1 ~ 2% of ether units due to decarboxylation. On the other hand, BCl_3 and BBr_3 react with 6CCs to give boron ω -halogenobutylcarbonates after the formation of complexes similar to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and 6CC. However these compounds show no polymerizability for the monomers. (Scheme 29).

Scheme 29



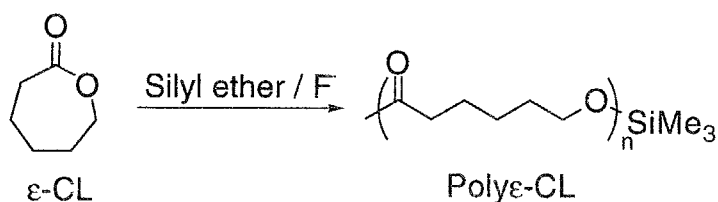
The insertion mechanism on ring opening polymerization of non-substituted six-membered cyclic carbonates has been demonstrated using TiCl_4 ,⁴⁸ and several Tin compounds such as $\text{R}_n\text{SnX}_{4-n}$,^{49a} SnX .^{49b} Very high M_n (150,000) polycarbonate can be synthesized free from ether units when the polymerization is conducted with SnI_4 at 60 °C, whereas the M_n of the obtained polymer does not agree with a calculated value and the M_w/M_n is large (> 1.8).^{49b} A substituted six-membered cyclic carbonate also undergo ring-opening polymerization by using $\text{R}_n\text{SnX}_{4-n}$ and $\text{Sn}(\text{Oct})_2$ with the result that the corresponding polycarbonates with high M_n (150,000) are obtained (Scheme 30).^{49c} Polymerization of cyclobis(octamethylene carbonate) with BuSnCl_3 and $\text{Sn}(\text{Oct})_2$ was reported ($M_w \sim 95000$), where the property of the obtained polymer was discussed by DSC, TGA, and WAXD measurements.^{49d} Hematin also initiates the polymerization of six-membered cyclic carbonates to give corresponding polycarbonates in bulk at 100 °C.^{49e}

Scheme 30



Polymerization initiated with some non-metallic systems, e.g., a silylketene acetal in conjunction with nucleophiles such as fluoride, bifluoride, cyanide, azide, and benzoate provides living polyacrylates, so called group transfer polymerization (GTP).⁵⁰ This polymerization has been applied to ring-opening polymerization of oxiranes,⁵¹ lactones,⁵² and cyclic carbonates.⁵³ In the polymerization of ϵ -caprolactone, the initiator, silyl ether / fluoride like Bu_4NF and CsF gives the corresponding polymer ($M_n \sim 15000$), whereas the initiation efficiency is not quantitative and the polydispersity ratio is rather broad (1.2 ~ 1.8) (Scheme 31).⁵²

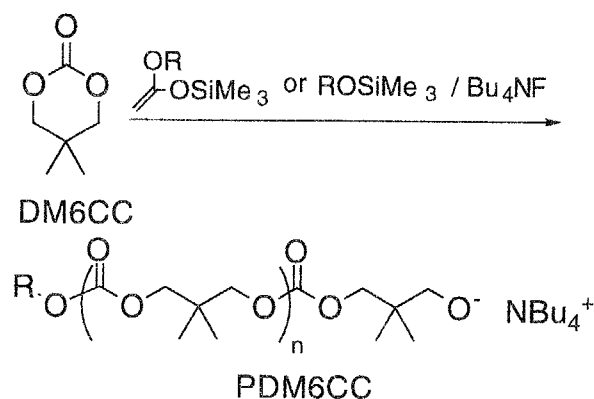
Scheme 31



In the polymerization of a substituted six-membered cyclic carbonate (DM6CC), the corresponding polycarbonate can be obtained with silylketene acetal or silyl alkoxide in conjunction with $\text{Bu}_4\text{NF} \cdot 3\text{H}_2\text{O}$ in a good yield, where the M_n is influenced by the amount of $\text{Bu}_4\text{NF} \cdot 3\text{H}_2\text{O}$ and the M_w/M_n

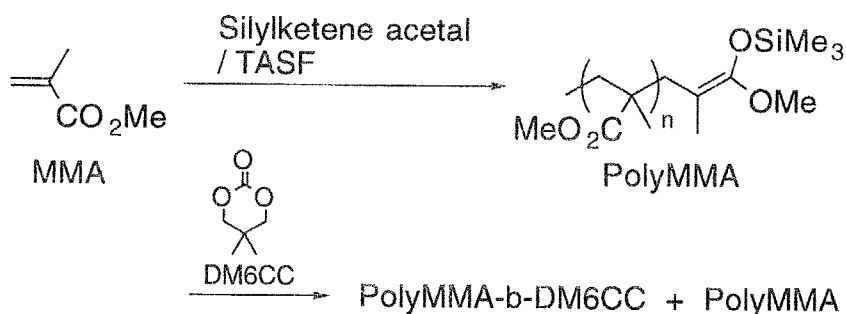
ratio was narrow (~ 1.05).⁵³ Thus, this polymerization does not proceed via GTP mechanism, but metal free anionic one (Scheme 32).

Scheme 32



The block copolymerization of MMA with DM6CC has been achieved by silylketene acetal / trimethylsilyldifluoride (TASF) as an initiator (Scheme 33).⁵⁴

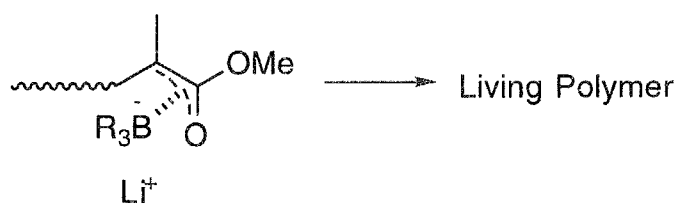
Scheme 33



However, the block efficiency is not quantitative, and the formation of polyMMA is detected.

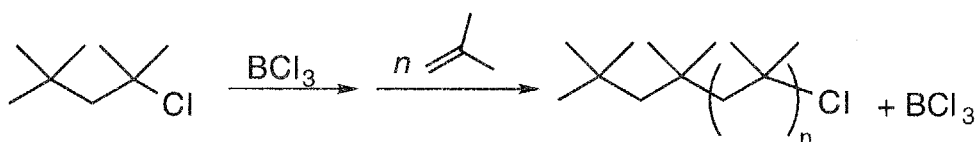
Organoborons are useful for polymer chemistry as well as organochemistry. There are many reports of polymer synthesis utilizing organoborons such as in polycondensation,⁵⁵ polyaddition,⁵⁶ radical polymerization,⁵⁷ and metallocene-catalyzed olefin polymerization.⁵⁸ Living anionic polymerization of *tert*-butyl acrylate was achieved by alkyllithium in the presence of alkylboron (Scheme 34).⁵⁹

Scheme 34

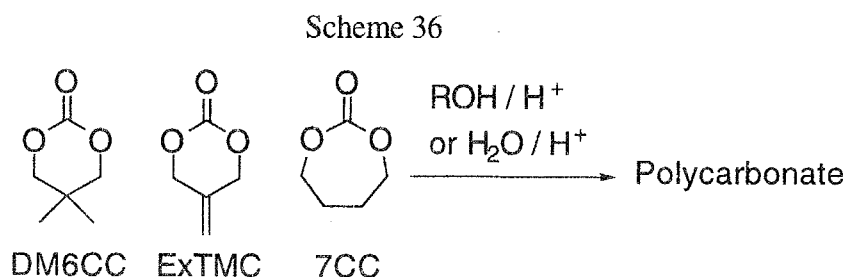


Living cationic polymerization of isobutylene was demonstrated by an alkyl chloride with BCl_3 as an activator.⁶⁰

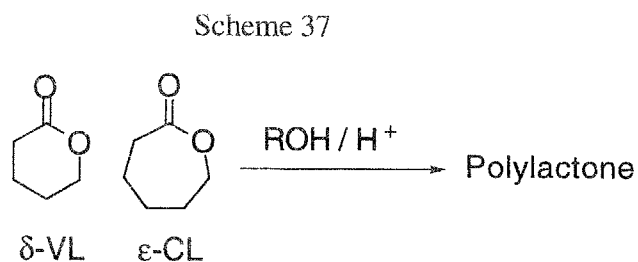
Scheme 35



Chapter 2 describes ring-opening polymerization of cyclic carbonates, 5,5-dimethyl-1,3-dioxan-2-one (DM6CC), 5-exomethylene-1,3-dioxan-2-one (Ex6CC), and 1,3-dioxepan-2-one (7CC) with alcohol / acid and H₂O / acid initiator systems (Scheme 36).

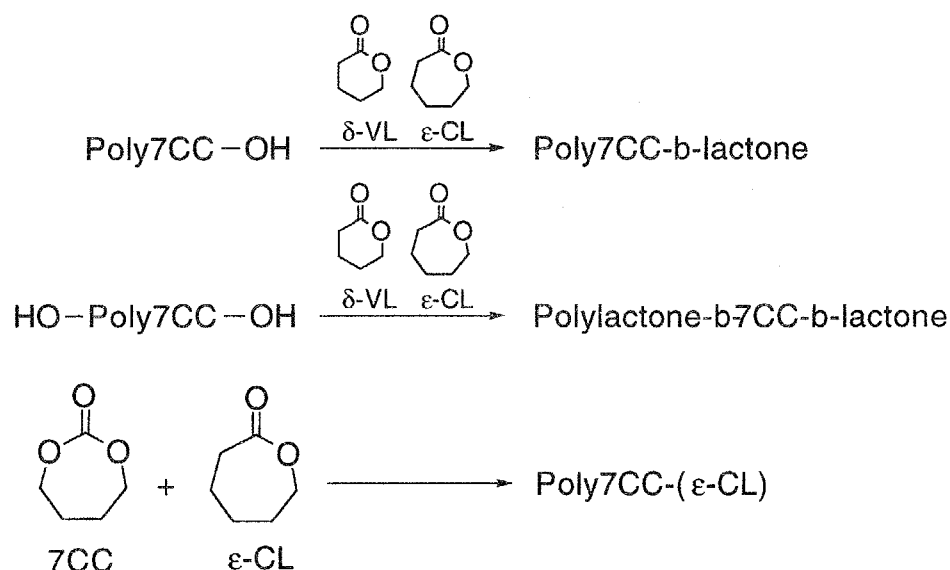


Chapter 3 describes activated monomer cationic ring-opening polymerization of ϵ -caprolactone (ϵ -CL) and δ -valerolactone (δ -VL) with *n*-butyl alcohol / HCl•Et₂O initiator system (Scheme 37).



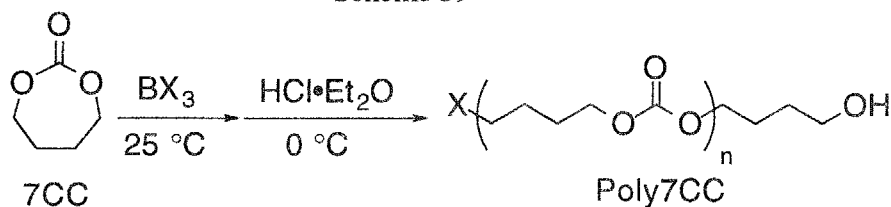
Chapter 4 describes syntheses of di-, triblock, and random copolymers of a seven-membered cyclic carbonate (7CC) and lactones (ϵ -caprolactone and δ -valerolactone) with *n*-butyl alcohol / HCl•Et₂O and H₂O / HCl•Et₂O initiator systems (Scheme 38).

Scheme 38



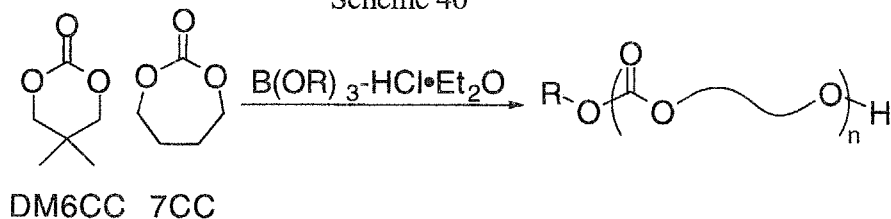
Chapter 5 describes ring-opening polymerization of a seven-membered cyclic carbonate, 1,3-dioxepan-2-one (7CC) with a novel initiator system, $\text{BX}_3\text{-HCl}\cdot\text{Et}_2\text{O}$ ($\text{X} = \text{Cl}$ and Br) (Scheme 39).

Scheme 39

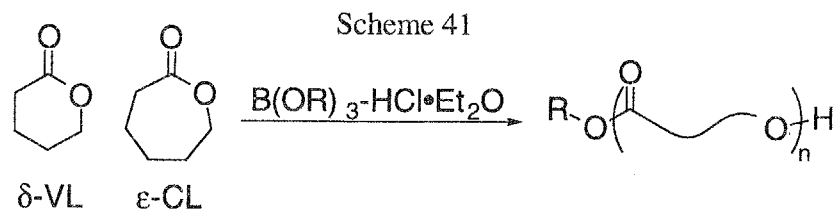


Chapter 6 describes ring-opening polymerization of cyclic carbonates (1,3-dioxepan-2-one and 5,5-dimethyl-1,3-dioxan-2-one) with triethyl and triisopropyl borates as initiators promoted by hydrogen chloride (Scheme 40).

Scheme 40



Chapter 7 describes acid promoted ring-opening polymerization of ϵ -caprolactone (ϵ -CL) and δ -valerolactone (δ -VL) with triethylborate $[\text{B}(\text{OEt})_3]$ (Scheme 41).



Chapter 8 summarizes this thesis and describes the prospect of the study.

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Chapter 2

Activated Monomer Cationic Polymerization of Cyclic Carbonates

2-1 ABSTRACT

Ring-opening polymerization of cyclic carbonates, 5,5-dimethyl-1,3-dioxan-2-one (DM6CC), 5-exomethylene-1,3-dioxan-2-one (Ex6CC), and 1,3-dioxepan-2-one (7CC) with alcohol / acid and H₂O / acid initiator systems was investigated. The use of HCl•Et₂O as an activator was quite effective to control the polymerization. The molecular weights (M_n s) of the obtained polymers could be controlled by the amount of alcohol or water in the range of $10^2 \sim 10^4$ maintaining narrow polydispersity ratios ($M_w/M_n \sim 1.15$). The second portion of the monomer after completion of the first polymerization was converted quantitatively to give the corresponding polymer with a narrow M_w/M_n . The kinetic and ¹H NMR spectroscopic studies suggested that the nucleophilic attack of water to the monomer activated with hydrogen chloride afforded α -hydroxyl- ω -carboxylic acid, followed by decarboxylation reaction to give α, ω -dihydroxyl compound. It was suggested that the chain growth in this system was the attack of the terminal hydroxyl group to the monomer activated with hydrogen chloride.

2-2 Introduction

Living polymerization has been established by stabilization of a propagating center to avoid unfavorable reactions such as chain transfer and termination. Living polymerization attracts much attention in ring-opening polymerization as well as in vinyl polymerization, because it provides polymers with controlled molecular weights (M_n s) and polydispersities (M_w/M_n s). Living ring-opening polymerization of lactones and cyclic carbonates has been reported by several groups. Penczek et al. have reported the living polymerization of β -propiolactone initiated with sodium acetate in conjunction with crown ether.¹ The living polymerization of ϵ -caprolactone with aluminum alkoxide has been established by Teyssie et al., where $(R_2AlO)_2Zn$ ($R = \text{alkyl}$) serves as an initiator preventing the formation of cyclic oligomers to provide polycaprolactone with a narrow M_w/M_n ratio.² Inoue and Aida have reported an exceptionally clean coordination process based on aluminum-porphirines for the polymerization of cyclic ethers,³ lactones,⁴ and cyclic carbonates⁵ to yield living polymers. On the other hand, the controlled ring-opening polymerization of cyclic ethers,⁶ lactones,⁷ and cyclic carbonates⁸ has been reported on the basis of activated monomer cationic polymerization. These initiator systems are very effective to suppress the formation of cyclic oligomers, however they usually provide relatively low M_n polymers, and the M_w/M_n s are not very small. In this chapter, I describe the controlled polymerization of cyclic carbonates with alcohol and water catalyzed by $HCl \cdot Et_2O$ for the preparation of high M_n polymers with small polydispersities.

2-3 Study of Several ROHs and Acids on 1,3-Dioxepan-2-one (7CC) Polymerization

Scheme 1 and Table 1 summarize the conditions and results of the polymerization of 1,3-dioxolan-2-one (7CC) with various primary alcohol and H₂O in the presence of acetic acid (CH₃CO₂H), trifluoroacetic acid (CF₃CO₂H), and HCl•Et₂O in CH₂Cl₂ at 0 and 25 °C.

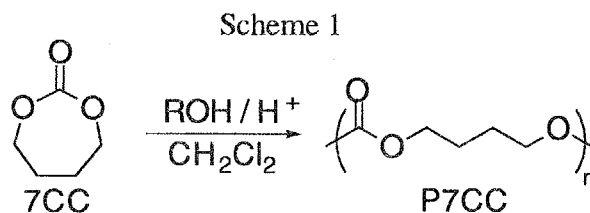
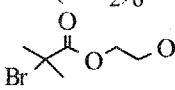


Table 1 Polymerization of 7CC^a

run	ROH	H ⁺	[M] ₀ / [I] ₀ ^b	[H] ₀ / [I] ₀	temp (°C)	time (h)	yield ^c (%)	M _n ^d	M _w /M _n ^d
1	<i>n</i> -BuOH	CH ₃ CO ₂ H	20	1	25	12	0 ^e	— ^f	— ^f
2	<i>n</i> -BuOH	CF ₃ CO ₂ H	20	0.2	0	30	92	3700	1.23
3	<i>n</i> -BuOH	HCl	20	1	25	12	85	2300	1.11
4	<i>n</i> -BuOH	HCl	60	1	25	12	89	7000	1.18
5	<i>n</i> -BuOH	HCl	90	1	25	12	92	9900	1.15
6	HO(CH ₂) ₄ OH	HCl	15	1	25	12	85	2100	1.09
7	H ₂ O	HCl	30	1	25	4	89	4700	1.15
8	Cl(CH ₂) ₄ OH	HCl	30	1.5	25	4	79	3500	1.10
9	Br(CH ₂) ₆ OH	HCl	25	1	25	4	99 ^e	2200	1.15
10		HCl	25	1	25	4	99 ^e	2600	1.22

^a Conditions: [M]₀ = 1 mol/L in CH₂Cl₂ / (CH₃CH₂)₂O. ^b The feed ration of the monomer to initiator (alcohol and water). ^c Methanol / *n*-hexane (1 / 1 volume ratio)-insoluble part. ^d Determined by GPC (THF, polystyrene standards). ^e Conversion. ^f Not determined.

The reaction of 7CC and *n*-butanol (*n*-BuOH) in the presence of CH₃CO₂H did not proceed at all as well as the polymerization of 7CC (run 1). The addition of CF₃CO₂H was effective to produce the polymer quantitatively, whereas the M_w/M_n of the polymer (P7CC) was somewhat broad even at 0 °C (1.23) as shown in run 2. The activator, HCl•Et₂O was quite useful to afford the P7CC quantitatively with small M_w/M_n values (~ 1.11) (run 3). The M_n of P7CC could be tailored varying with the feed ratio of the monomer to initiator (M_n < 10⁴) (runs 3~5). Instead of *n*-BuOH, 1,4-butanediol and H₂O

served as initiators of the polymerization of 7CC to produce the controlled polymer as well (runs 6 and 7). The alcohol with chlorine (or bromine) moiety also worked as an initiator to give telechelic P7CC having chlorine (or bromine) and hydroxyl moieties at the both ends with a relatively narrow M_w/M_n (runs 8 ~ 10).

2-4 Ring-Opening Polymerization of Six-Membered Cyclic Carbonates [5,5-Dimethyl-1,3-Dioxan-2-One (DM6CC) and 5-Exomethylene-1,3-Dioxan-2-One (Ex6CC)] by ROH / HCl•Et₂O Initiator System

Scheme 2 and Table 2 summarize the results of the polymerization of 5,5-dimethyl-1,3-dioxan-2-one (DM6CC) and 5-exomethylene-1,3-dioxan-2-one (Ex6CC) with several alcohols and H₂O in the presence of HCl•Et₂O in CH₂Cl₂ at 25 °C.

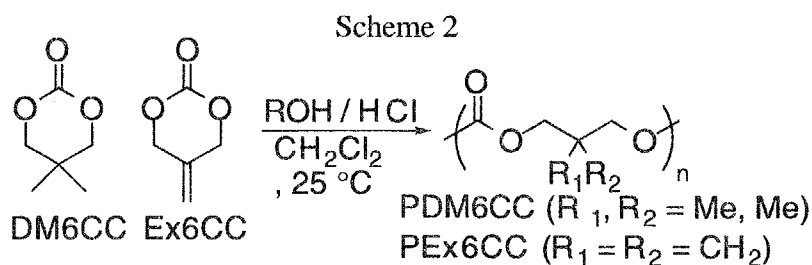


Table 2 Polymerization of DM6CC and ExTMC^a

run	monomer	ROH	$\frac{[\text{M}]_0}{[\text{I}]_0}$ ^b	$\frac{[\text{H}]_0}{[\text{I}]_0}$	time (h)	conv ^c (%)	yield ^d (%)	M_n ^e	M_w/M_n ^e
1	DM6CC	BuOH	30	30	48	94	84	3600	1.16
2	DM6CC	BuOH	60	30	96	91	81	7500	1.15
3	DM6CC	BuOH	90	30	96	91	81	12000	1.19
4	DM6CC	H ₂ O	30	30	48	92	82	3100	1.14
5	Ex6CC	BuOH	30	1	72	87	66	4300	1.05
6	Ex6CC	H ₂ O	34	1	66	89	66	3100	1.07
7	Ex6CC		30	1.5	43	98	87	2500	1.19

^aConditions: $[\text{M}]_0 = 1 \text{ mol/L}$ in CH₂Cl₂ / (CH₃CH₂)₂O. ^bThe feed ration of monomer to initiator (alcohol or water). ^cDetermined by ¹H NMR.

^dIsolated yield. ^eDetermined by GPC (polystyrene standards, THF).

HCl•Et₂O was used as an activator for the polymerization of DM6CC and Ex6CC. In every case, the polymer was obtained in a relatively good yield. Varying the feed ratio of the monomer to initiator (BuOH) provided PDM6CC with the corresponding M_n s and narrow M_w/M_n s (runs 1 ~ 3). H₂O also served as an initiator to afford PDM6CC with a narrow M_w/M_n (run 4). The cationic polymerization of Ex6CC with Lewis acids such as BF₃•Et₂O, SnCl₄, and TiCl₄ has been reported that the corresponding polycarbonates are obtained with high M_n s (~ 30000), probably due to the contribution of the

exomethylene group to stabilize the propagating cationic end, whereas the M_n was not precisely predictable and the M_w/M_n was somewhat broad (1.2 ~ 3.0).⁹ In this work, the polymerization of Ex6CC with BuOH / HCl initiator system was effective to yield PEx6CC with a controlled M_n and a narrow M_w/M_n ratio (run 5). Water instead of *n*-BuOH was also successful to provide the controlled polymer (run 6). A brominated alcohol also served as an initiator to give the polymer with a relatively narrow M_w/M_n ratio (run 7).

Figure 1 depicts the ^1H NMR spectrum of PEx6CC obtained in run 7 in Table 2. Signals *b* and *c* assignable to α -methylene protons of a carbonate moiety and exomethylene protons were observed at 4.68 and 5.37 ppm. Signals *a* and *f* assignable to methyl protons adjacent to a bromine group and α -methylene protons of a terminal hydroxyl group were observed at 1.95 and 4.20 ppm, respectively. The integration ration of *a* to *f* was exactly 6/2, which agreed well with an expected value.

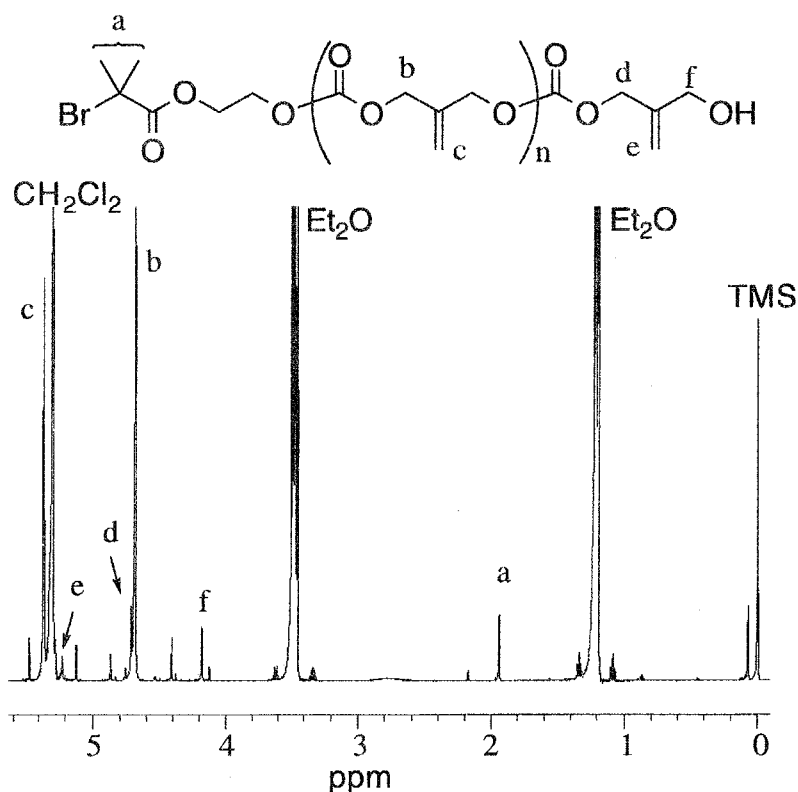


Figure 1. ^1H NMR spectrum (300MHz, CDCl_3) of PEx6CC obtained in run 2 in Table 2.

Figure 2 illustrates the ^1H NMR spectrum of PEx6CC obtained by the cationic ring-opening polymerization of Ex6CC initiated with Et_3OBF_4 in

CH_2Cl_2 at 25 °C for 24 h ($[\text{Ex6CC}]_0 = 2 \text{ mol/L}$, $[\text{Ex6CC}]_0 / [\text{Et}_3\text{OBF}_4]_0 = 40$), followed by precipitation with diethyl ether.

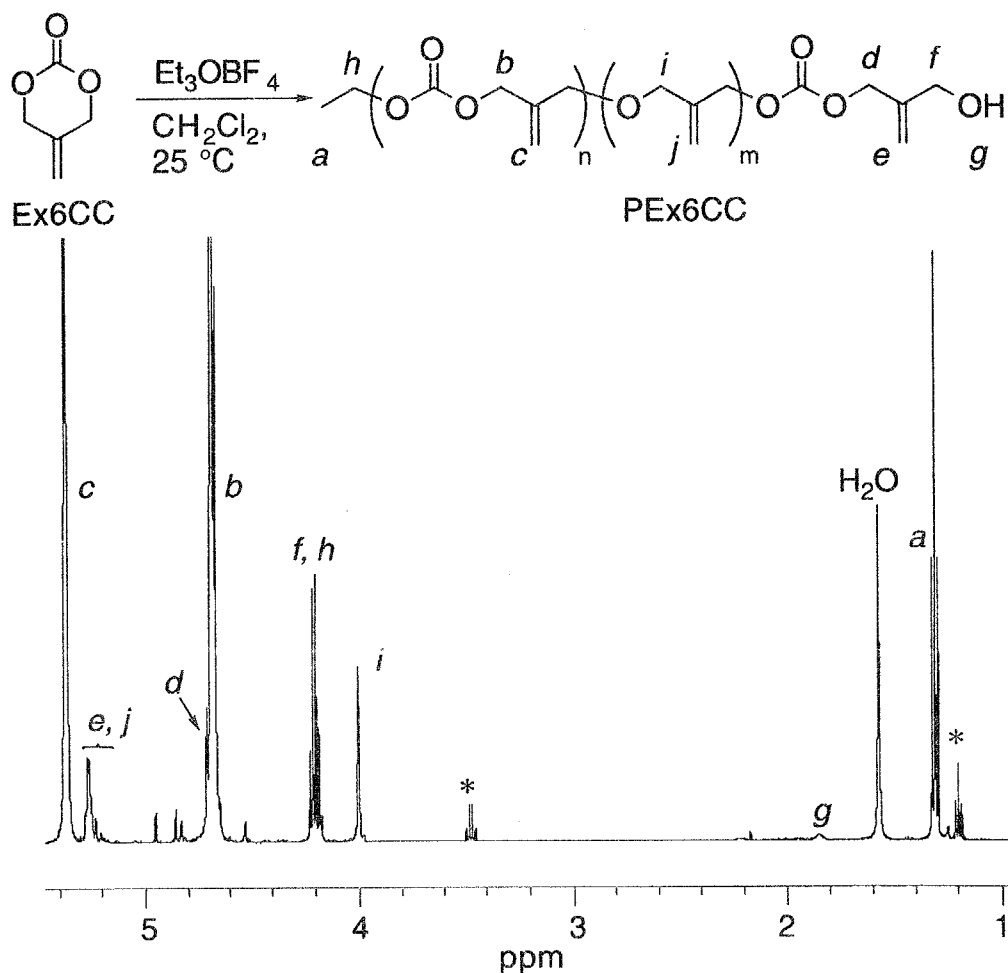
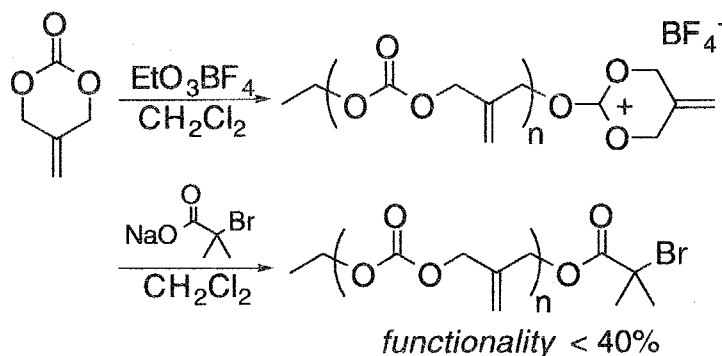


Figure 2. ^1H NMR spectrum (300MHz, CDCl_3) of PEx6CC obtained by the ring-opening polymerization of Ex6CC with Et_3OBF_4 in CH_2Cl_2 at 25 °C for 24 h ($[\text{Ex6CC}]_0/[\text{Et}_3\text{OBF}_4]_0 = 40$, $[\text{Ex6CC}]_0 = 2 \text{ mol/L}$). *: Signal derived from diethylether.

The polymer was obtained in 88% isolated yield, but the M_w/M_n ratio was large (1.39). The ^1H NMR spectrum showed signals *a* and *h* assignable to methyl and methylene protons of the initiating ethyl group at 1.30 and 4.20 ppm in addition to the signals *b* ~ *f* assignable to polycarbonate units. It also showed the signal *i* assignable to methylene protons adjacent to an ether-oxygen moiety at 4.00 ppm. The ether segment was derived from decarboxylation of the carbonate group, and the degree of decarboxylation was estimated as 0.7% by the integration ratio of signals *b* and *i*. The end

functionality of the polymer quenched with sodium isobutyrate was below 40% (Scheme 3).

Scheme 3



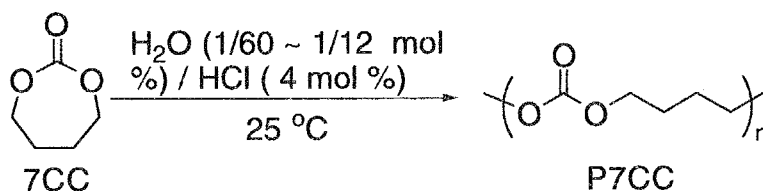
Consequently, I can concluded that the activated monomer polymerization is superior to obtain well-defined telechelic polycarbonates with small M_w/M_n ratios suppressing decarboxylation, compared with traditional cationic polymerization.

2-5 H₂O / HCl•Et₂O Initiator System.

~ Mechanistic Study of the Polymerization

Table 3 summarizes the results of the polymerization of 7CC with H₂O / HCl•Et₂O initiator system at 25 °C (Scheme 4).

Scheme 4

Table 3 Polymerization of 7CC with H₂O / HCl^a

run	[M] ₀ : [H ₂ O] ₀	time (h)	solvent	yield ^b (%)	M _n ^c	M _w /M _n ^c
1	30 : 0	4	CH ₂ Cl ₂	0	— ^d	— ^d
2	15 : 1	4	CH ₂ Cl ₂	95	3000	1.17
3	30 : 1	4	CH ₂ Cl ₂	96	4700	1.15
4	45 : 1	4	CH ₂ Cl ₂	98	6000	1.17
5	60 : 1	4	CH ₂ Cl ₂	98	10000	1.11
6	15 : 1	0.5	CH ₂ Cl ₂	61 ^e	— ^d	— ^d
7 ^e	15 : 1	0.5	CH ₂ Cl ₂ / Et ₂ O	98	2800	1.15
8	12 : 1	15	THF	90	2600	1.11

^aConditions: 25 °C, [M]₀ = 1 mol/L, [HCl]₀ = 0.04 mol/L. ^b*n*-Hexane / MeOH (1/1 volume ratio)-insoluble part. ^cDetermined by GPC (THF, polystyrene standards). ^dNot determined. ^eConversion.

^f[HCl]₀ = 0.5 mol/L, CH₂Cl₂ / Et₂O = 1 / 1 (vol / vol).

In the presence of water, the polymers (P7CC) with narrow M_w/M_n s (1.11 ~ 1.17) were obtained in almost quantitative yields, where the M_n could be tailored by changing the ratio between [M]₀ and [H₂O]₀ (runs 2 ~ 5). No polymer was obtained in the absence of water, indicating that HCl•Et₂O had no ability to polymerize 7CC by itself (run 1). When [HCl]₀ increased from 0.04 to 0.5 mol/L, the propagation rate was accelerated to give the polymer for 0.5 h quantitatively (runs 6 and 7). The polymerization also proceeded quantitatively in THF instead of CH₂Cl₂ without incorporation of THF unit into the polymer for 15 h (run 8).

Table 4 shows the ^1H and ^{13}C NMR chemical shifts of the α - and β -methylene protons of the carbonate group, and the carbonyl carbon on 7CC in the absence and presence of Et_2O in dry CDCl_3 at 25°C as well as pK_a values with various protonic acids. No signal assignable to a ring-opened structure of 7CC was observed.

Scheme 5

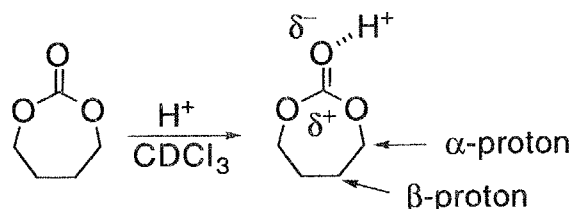


Table 4 ^1H and ^{13}C NMR Chemical Shifts of 7CC in the Absence and Presence of $\text{HCl}\cdot\text{Et}_2\text{O}$ in CDCl_3 at 25°C ^a

run	additive	α -proton (ppm)	β -proton (ppm)	$^{13}\text{C}=\text{O}$ (ppm)	pK_a
1	none	4.210	1.950	155.40 (154.49) ^b	
2	$\text{CH}_3\text{CO}_2\text{H}$	4.220	1.956	— ^c	4.75
3	$\text{BrCH}_2\text{CO}_2\text{H}$	4.228	1.960	156.24	2.69
4	$\text{CF}_3\text{CO}_2\text{H}$	4.282	1.989	159.40 (155.01) ^b	0.23
5	$\text{HCl}\cdot\text{Et}_2\text{O}$	4.211 ^b	1.953 ^b	(154.54) ^b	-3.70

^aConditions; $[\text{7CC}]_0 = 0.10\text{ M}$, $[\text{HCl}]_0 = 0.11\text{ M}$. ^bIn Et_2O and CDCl_3 (1 / 1 volume ratio). ^cNot measured.

The signals shifted into lower field due to the electron localization by added protonic acids, and the degree was influenced by the pK_a ¹⁰ values (runs 2 ~ 4). In the case of $\text{HCl}\cdot\text{Et}_2\text{O}$, however, despite of its stronger acidity than the others, the chemical shifts in ^1H and ^{13}C NMR spectra were not so large (run 5). In addition, the chemical shift of the carbonyl carbon at 154.54 ppm in ^{13}C NMR spectrum was still small compared with that with $\text{CF}_3\text{CO}_2\text{H}$ in CDCl_3 / Et_2O ($\delta = 155.01$ ppm). Anyhow, these signals shifted to lower fields compared to 7CC alone to support that $\text{HCl}\cdot\text{Et}_2\text{O}$ might activate the monomer, probably by coordination at the carbonyl oxygen.

Table 5 summarizes the results of a cationic ring-opening polymerization of 7CC with the $\text{HCl}\cdot\text{Et}_2\text{O}$ besides $\text{CH}_3\text{CO}_2\text{H}$, $\text{CH}_2\text{BrCO}_2\text{H}$, $\text{CF}_3\text{CO}_2\text{H}$ in the presence and absence of H_2O at $25\text{ }^\circ\text{C}$ in CH_2Cl_2 for 3 h.

Table 5 Polymerization of 7CC with Protonic Acids in the Presence and Absence of Water^a

run	initiator	conv. ^b (%)
1	$\text{CH}_3\text{CO}_2\text{H}$	0
2	$\text{CH}_3\text{CO}_2\text{H} / \text{H}_2\text{O}$	0
3	$\text{CH}_2\text{BrCO}_2\text{H}$	0
4	$\text{CH}_2\text{BrCO}_2\text{H} / \text{H}_2\text{O}$	0
5	$\text{HCl}\cdot\text{Et}_2\text{O}$	0
6	$\text{HCl}\cdot\text{Et}_2\text{O} / \text{H}_2\text{O}$	100
7	$\text{CF}_3\text{CO}_2\text{H}$	44
8	$\text{CF}_3\text{CO}_2\text{H} / \text{H}_2\text{O}$	100

^a Conditions: $25\text{ }^\circ\text{C}$, 3 h, $[\text{M}]_0 = 1\text{ M}$, $[\text{H}^+]_0 = 0.04\text{ M}$, $[\text{H}_2\text{O}] = 0.05\text{ M}$, solvent; CH_2Cl_2 .^b

Determined by $^1\text{H-NMR}$.

Although $\text{CF}_3\text{CO}_2\text{H}$ polymerized 7CC even in the absence of H_2O probably through a conventional cationic mechanism, other acids showed no activity for 7CC polymerization except for the case of $\text{HCl}\cdot\text{Et}_2\text{O}$ with H_2O . This tendency may be explained in conjunction with the acidity of the additives. The initiator activity increased according to the acidity.¹⁰

Figure 1 depicts the dependence of M_n values of P7CC obtained by the polymerization of 7CC initiated with $H_2O / HCl \cdot Et_2O$ and H_2O / CF_3CO_2H in CH_2Cl_2 at 0 and 25 °C, respectively (Scheme 6).

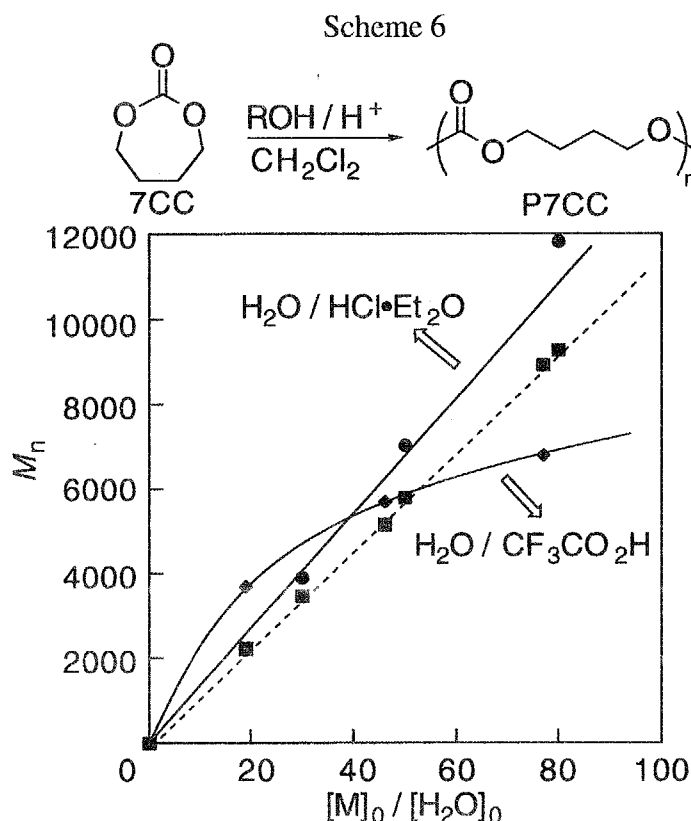


Figure 1. Relationships between $[M]_0 / [H_2O]_0$ and M_n of P7CC obtained by the polymerization of 7CC; (●) with $H_2O / HCl \cdot Et_2O$ at 25 °C for 4 h, (◆) with H_2O / CF_3CO_2H at 0 °C for 12 h, (■) theoretical. $[M]_0 = 1$ mol/L in CH_2Cl_2 , $[H^+]_0 = 0.04$ mol/L.

Using $HCl \cdot Et_2O$ along with H_2O , the M_n of the obtained polymer increased linearly as the $[M]_0 / [H_2O]_0$ ratio, keeping close to the theoretical values. Using CF_3CO_2H along with H_2O , the M_n increased as the $[M]_0 / [H_2O]_0$ ratio, but did not show good agreement with the theoretical value. Considering these results, the role of $HCl \cdot Et_2O$ on the polymerization of 7CC in the presence of water should be definitely only an activator of the monomer. As the results, monodisperse P7CC was obtained *via* a single propagation mechanism.

To confirm the living nature of the present system, 30 equiv of 7CC was first polymerized to obtain the polymer of $M_n = 5000$ in a quantitative conversion ($[M]_0 = 1 \text{ mol/L}$) (Scheme 7).

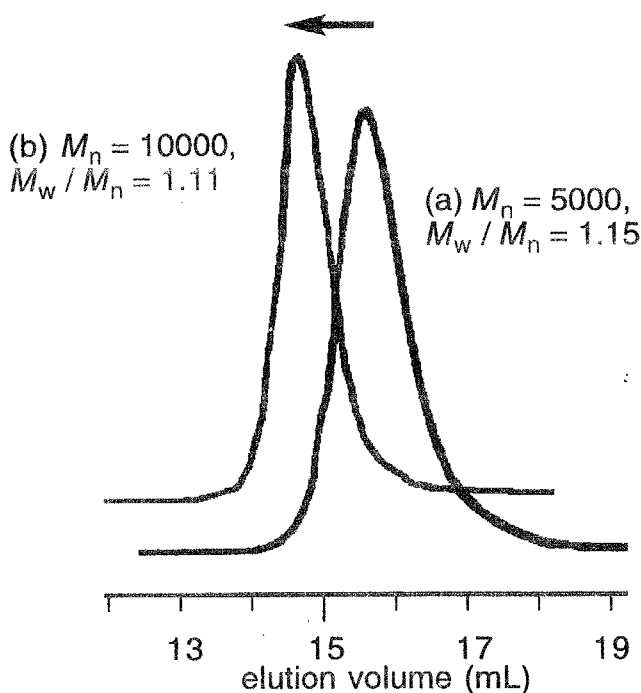
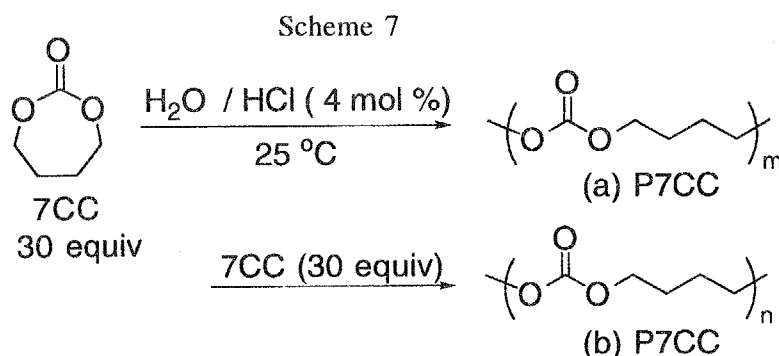


Figure 2. GPC traces of P7CC obtained by the polymerization with $\text{H}_2\text{O} / \text{HCl} \cdot \text{Et}_2\text{O}$ in CH_2Cl_2 at $25\text{ }^\circ\text{C}$; (a) 30 equiv. of 7CC for 4 h, (b) and the further addition of 30 equiv. of 7CC for 24 h.

After 24 h, the GPC profile of the polymer showed the same M_n and M_w/M_n to indicate that there was no side reaction even in the absence of monomer. Then, a same amount of monomer was charged into the reaction mixture to restart again the polymerization. The GPC curve completely shifted to a higher M_n field, where the M_n of the final polymer was twice of the starting polymer keeping a small M_w/M_n ratio (Figure 2). These results clearly showed that the propagating center did not react with the carbonate moieties in

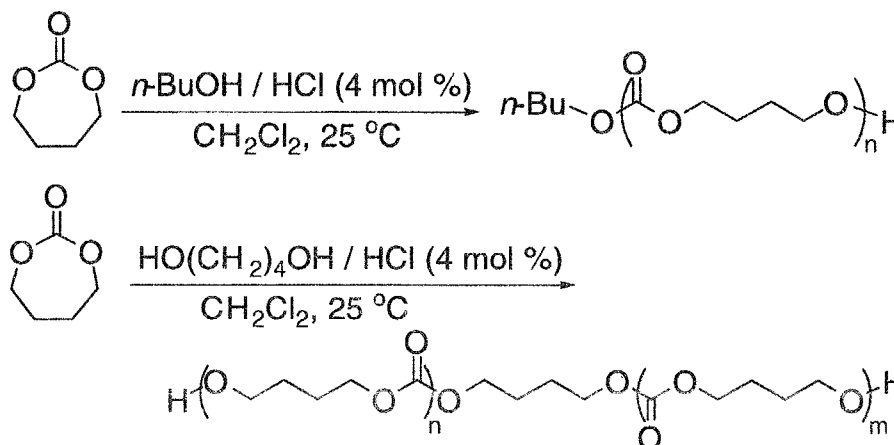
the polymer back bone, and the active site was still "living" even for 24 h after the monomer was entirely converted into the polymer.

Figure 3 shows the kinetic plots of the polymerization (Scheme 8) with HO(CH₂)₄OH / HCl•Et₂O, H₂O / HCl•Et₂O, and *n*-BuOH / HCl•Et₂O in CH₂Cl₂ at 25 °C based on a first order equation as follows.

$$-d[M] / dt = k_p[ROH]_0[M] \quad (ROH = H_2O, BuOH, \text{ and } HO(CH_2)_4OH)$$

$$-[ROH]_0^{-1} \cdot \ln\{[M] / [M]_0\} = k_p t$$

Scheme 8



$$-\frac{d[M]}{dt} = k_p[ROH]_0[M]$$

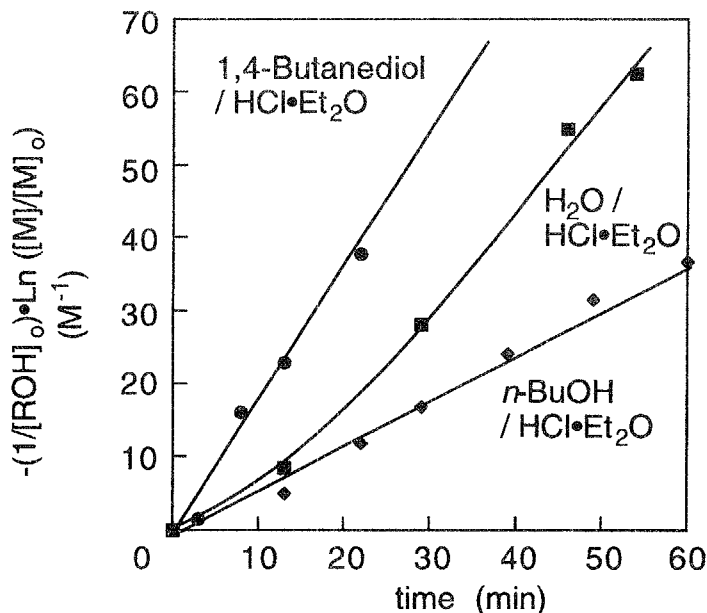


Figure 3. Relationships between time and $-(1/[ROH]_0) \cdot \ln([M] / [M]_0)$ in the polymerization of 7CC in CH₂Cl₂ ([M]₀ = 1 mol/L, [HCl•Et₂O]₀ = 0.04 mol/L) at 25 °C initiated with (●) Bu(OH)₂ / HCl•Et₂O, (■) H₂O / HCl•Et₂O, (◆) BuOH / HCl•Et₂O.

The polymerization behavior with $\text{H}_2\text{O} / \text{HCl} \cdot \text{Et}_2\text{O}$ seems similar to that with $n\text{-BuOH} / \text{HCl} \cdot \text{Et}_2\text{O}$ in the early stage (< 15 min), but as the result of acceleration, it showed the similar tendency to the $\text{HO}(\text{CH}_2)_4\text{OH} / \text{HCl} \cdot \text{Et}_2\text{O}$ initiator system.

Figure 4 illustrates the time-dependence of the ^1H NMR spectra of P7CC obtained in the polymerization with $\text{H}_2\text{O} / \text{HCl}$ catalyst in CH_2Cl_2 at 25°C for 4 h.

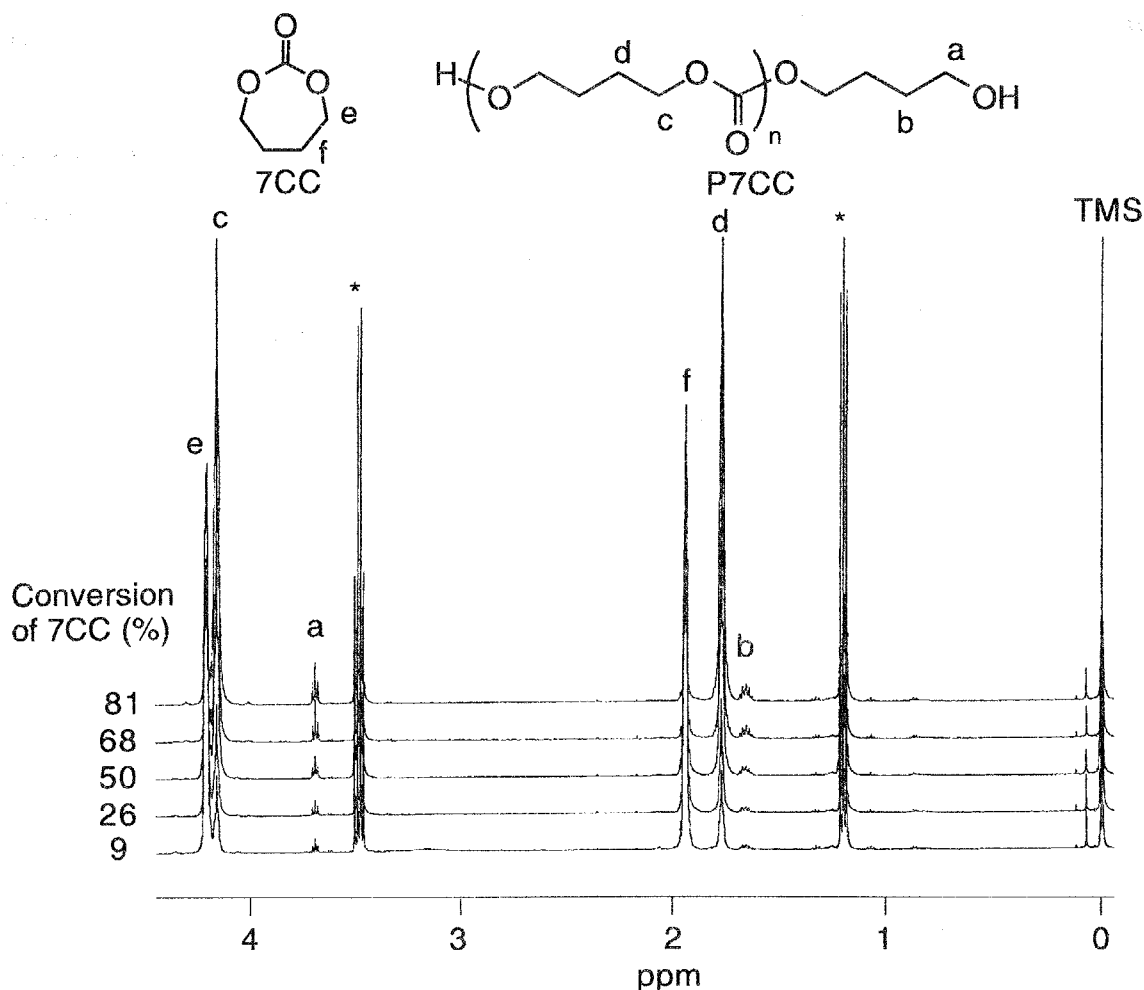


Figure 4. ^1H NMR spectra (500 MHz, CDCl_3) of P7CC obtained the polymerization with $\text{H}_2\text{O} / \text{HCl} \cdot \text{Et}_2\text{O}$ in CH_2Cl_2 ($[\text{M}]_0 = 1 \text{ mol/L}$, $[\text{HCl} \cdot \text{Et}_2\text{O}]_0 = 0.04 \text{ mol/L}$) at 25°C . *; signals due to diethyl ether.

Signals *a* and *b* assignable to α - and β -methylene protons of a terminal hydroxyl group were observed at 3.68 and 1.66 ppm, respectively, in addition to the signals *c* and *d* of the P7CC unit. No signal was observed at 3.40 ~ 3.46 ppm assignable to methylene protons adjacent to an ether unit, indicating that the polymerization was not accompanied by random decarboxylation, a typical side reaction in the cationic ring-opening polymerization of cyclic carbonates.¹² It is noticeable that the intensities of the α and β -proton signals of the terminal OH group increased during the polymerization. Its

observation would be explained by selective decarboxylation reaction at the carbonic acid polymer end, because the obtained polymer showed narrow M_w/M_n . Considering the increase of -OH group, the kinetic plot of polymerization of 7CC with $H_2O / HCl \cdot Et_2O$ in Figure 3 can be re-illustrated as Figure 5, exhibiting a linear relationship, i.e., good obedience to a first order reaction in any region ($-[ROH]^{-1} \cdot \ln\{[M] / [M]_0\} = k_p t$). This result might also suggest the single active site of the polymerization of 7CC in this system.

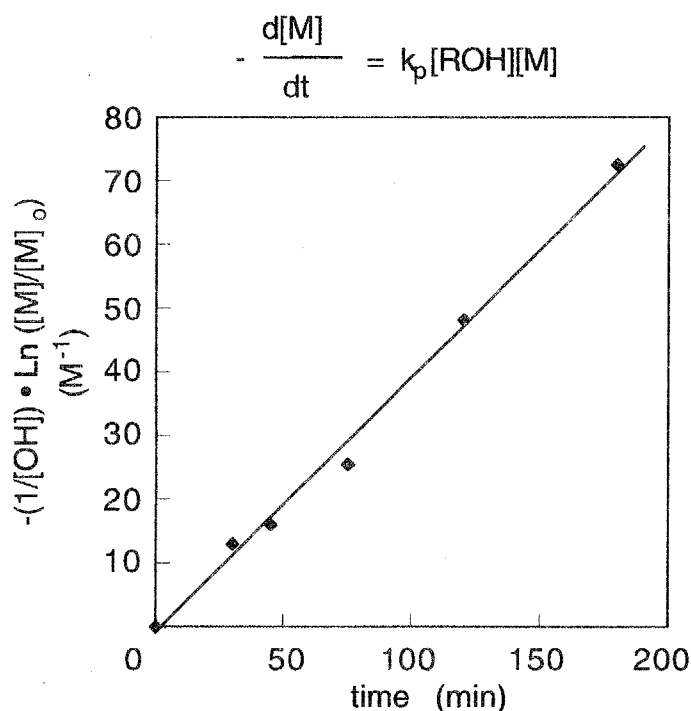
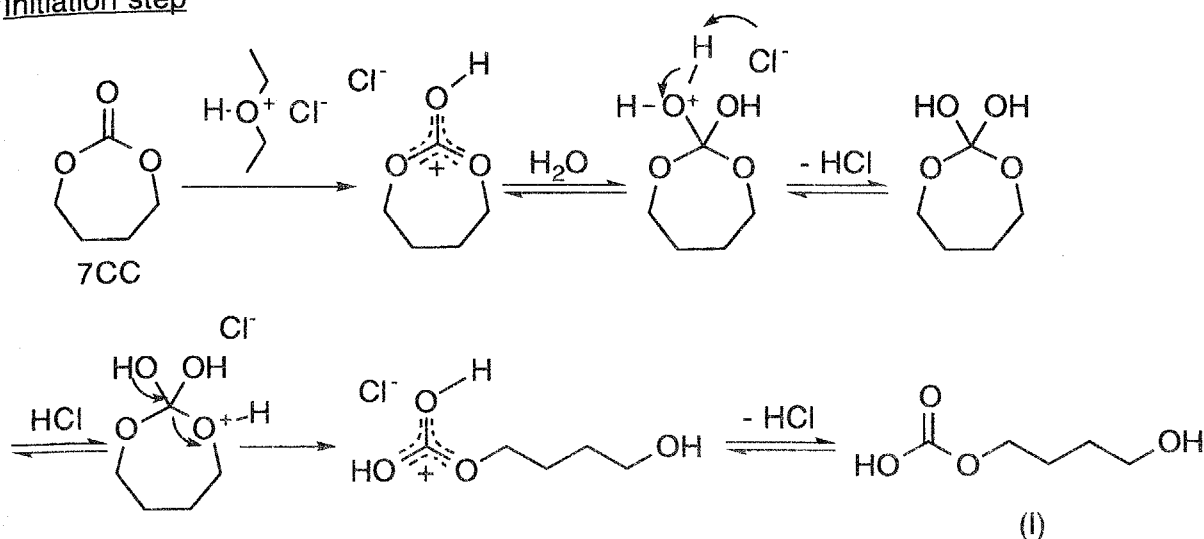


Figure 5. Relationship between time and $-[OH]^{-1} \cdot \ln([M] / [M]_0)$ in the polymerization of 7CC with $H_2O / HCl \cdot Et_2O$ in CH_2Cl_2 ($[M]_0 = 1 \text{ mol/L}$, $[HCl \cdot Et_2O]_0 = 0.04 \text{ mol/L}$) at $25 \text{ }^\circ\text{C}$.

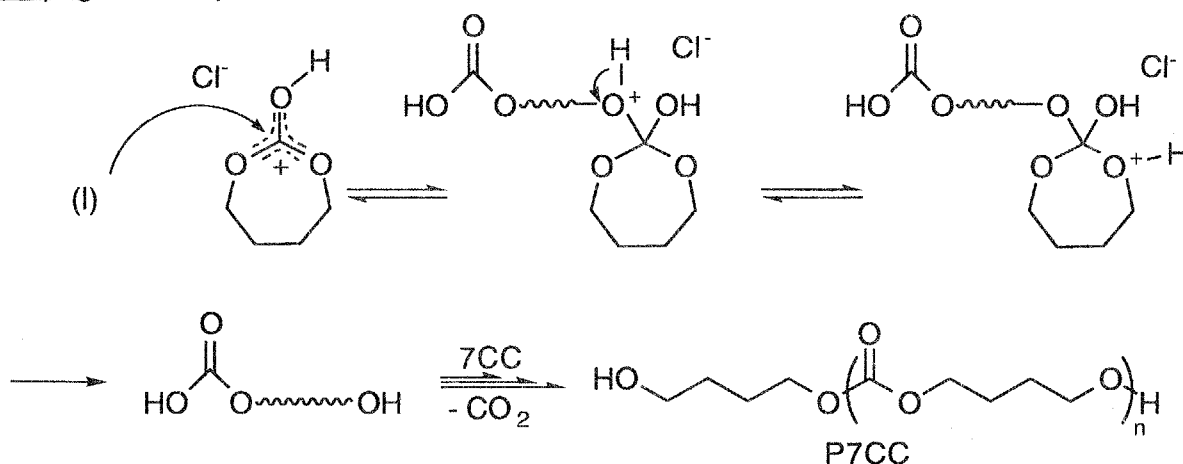
Scheme 9 illustrates a plausible polymerization mechanism of 7CC in this system.

Scheme 9

Initiation step



Propagation step



H_2O may attack to the monomer activated by $\text{HCl} \cdot \text{Et}_2\text{O}$ to form the adduct (I). The hydroxyl group of the adduct (I) initiates the polymerization by the attack to the activated monomer. The propagation involves the activated monomer mechanism, which is accompanied by the transformation of the carbonic acid end of the adduct (I) into a hydroxyl group *via* decarboxylation. $\text{HCl} \cdot \text{Et}_2\text{O}$ has some possibilities to coordinate the carbonyl group of the polymer like that of monomer, but it causes no cleavage of any covalent bonds by the nucleophilic attack of the terminal OH group in the polymer probably due to the lack of basicity of the OH group. $\text{HCl} \cdot \text{Et}_2\text{O}$ may favorably coordinate the

monomer carbonyl group rather than the polymer one, probably due to the higher basicity and smaller sterical hindrance of the former. This may suppress a back-biting reaction, resulting in the living character of the polymerization.

2-6 Summary

In this chapter, I have demonstrated controlled ring-opening polymerizations of cyclic carbonates, 5,5-dimethyl-1,3-dioxan-2-one (DM6CC), 5-exomethylene-1,3-dioxan-2-one (Ex6CC), and 1,3-dioxepan-2-one (7CC) based on the simple combinations of alcohol / $\text{HCl}\cdot\text{Et}_2\text{O}$ and H_2O / $\text{HCl}\cdot\text{Et}_2\text{O}$ initiator systems, and studied the mechanistic aspects of the polymerization of 7CC with H_2O / $\text{HCl}\cdot\text{Et}_2\text{O}$. The M_n of the polymers could be controlled by the amount of alcohol or water in the range of $10^2 \sim 10^4$ maintaining a narrow M_w/M_n (1.11 \sim 1.17). The polymer propagating end was still active for 24 h after the complete consumption of the monomer. Kinetic and ^1H NMR spectroscopic studies suggested that a single active species of -OH group selectively attacked the monomer activated with hydrogen chloride to proceed the controlled polymerization.

2-7 Experimental Section

Materials. CH_2Cl_2 , CHCl_3 , and CDCl_3 were distilled sequentially over CaH_2 and P_2O_5 under nitrogen. THF was dried over sodium and distilled before use under nitrogen. Water was distilled prior to use. *n*-Butyl alcohol (BuOH) and 1,4-butanediol (Bu(OH)_2) was distilled over CaH_2 under nitrogen. A 1.0 mol/L triethyloxonium tetrafluoroborate (Et_3OBF_4) solution in CH_2Cl_2 7CC was purchased from Aldrich and used without further purification. DM6CC were prepared according to the literature and stored at $-20\text{ }^\circ\text{C}$ under nitrogen atmosphere.¹³ Acetic acid, bromoacetic acid, and trifluoroacetic acid were dried over P_2O_5 , and then distilled under nitrogen. A 1.0 M HCl solution in diethyl ether (Et_2O) and 2-methylene-1,3-propanediol were purchased from Aldrich and used without further purification. Antipyrine and triphosgen were purchased from Tokyo Kasei and used without further purification.

Measurements. $^1\text{H-NMR}$ spectra were recorded with a JEOL Lambda-500 spectrometer. Number and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Tosoh HLC-8120 system equipped with two consecutive polystyrene gel columns (G2500HXL and G4000HXL) eluted with tetrahydrofuran (THF) at a flow rate of $1.0\text{ mL}\cdot\text{min}^{-1}$ calibrated by standard polystyrene samples. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-14B equipped with FID detector using *n*-dodecane as an internal standard (column packing SE-30, gradient temperature of $100\text{-}230\text{ }^\circ\text{C}$, $15\text{ }^\circ\text{C}/\text{min}$).

Synthesis of Ex6CC. This compound have been first synthesized by Takata et al. by flush vacuum pyrolysis of the cyclic carbonates having norbornene moiety at $400\text{-}450\text{ }^\circ\text{C}$ in 77 % yield.⁹ Here, I chose more convenient method in milder condition as following. 2-methylene-1,3-propanediol (5.00 g, 56.8

mmol) in dry CHCl_3 (1.0 L) and antipyrine (21.5 g, 114 mmol) placed in two-necked flask equipped with dropping funnel under nitrogen. The CHCl_3 100 mL solution of triphosgene (5.60 g, 18.9 mmol) was slowly dropwisely into the mixture for 1 h with warming at 45 °C by oil bath. At the end of the addition, the oil bath was removed and the reaction allowed to keep with stirring for another 12 h. The solution was carefully poured into the HCl aq (1 N, 300 mL), and washed. The organic layer was rewashed with brine (300 mL), dried over MgSO_4 for 1 h, and removed solvents under reduced pressure. The collected pale yellow viscous oil was passed through silicagel column chromatography (ethyl acetate / *n*-hexane = 3 / 1 volume ratio), and the separated white crystal was recrystallized from ether. Yield 3.24g 50%, m.p. 55 - 58 °C, IR (KBr) 1730, 1630, 1190, 1105, 940 cm^{-1} , ^1H NMR (CDCl_3) δ = 5.33 (m, 2H), 4.87 (t, 4H) ppm, ^{13}C NMR (CDCl_3) δ = 149.4, 132.5, 114.6, 70.9 ppm.

Polymerization. All polymerization reactions were carried out with the following general procedure: All glass vessels were heated in vacuo before use, filled with and handled in a stream of dry nitrogen. To 0.80 g (5.0 mmol) of 7CC were added 0.0045 g (0.25 mmol) of water, and 4.8 mL of CH_2Cl_2 . The polymerization was initiated by the addition of 250 μL (0.25 mmol) of HCl solution (1 M) in Et_2O at 25 °C. After a set time, the reaction mixture was poured into 300 mL of methanol / *n*-hexane (50 / 50, volume ratio) containing 5 mL of triethylamine to precipitate a polymer. The precipitate was filtered, washed sequentially with methanol (5 mL) and *n*-hexane (5 mL), and dried at 25 °C for 5 h in vacuo.¹⁴

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- (14) In DM6CC polymerization, the reaction mixture was diluted with CH_2Cl_2 , washed with Na_2CO_3 aq, and dried in vacuo at 25 °C for 5h. In EXTMC, the reaction mixture was poured into ether to precipitate the polymer, and filtered. The white polymeric compound was collected, and dried in vacuo at 25 °C for 5 h.

Chapter 3.

Activated Monomer Cationic Polymerization of Lactones using $\text{HCl}\cdot\text{Et}_2\text{O}$

Chapter 3

Cationic Precisely Controlled Ring-Opening Polymerization of Lactones through Activated Monomer Mechanism

3-1 ABSTRACT

Activated monomer cationic ring-opening polymerization of ϵ -caprolactone (ϵ -CL) and δ -valerolactone (δ -VL) with *n*-butyl alcohol / $\text{HCl}\cdot\text{Et}_2\text{O}$ initiator system was investigated. Corresponding poly ϵ -CLs with small polydispersity (M_w/M_n) ratios were obtained at 25°C quantitatively. The polymerization of δ -VL showed typical equilibrium polymerization behavior between the monomer and polymer chain. Poly δ -VLs with controlled M_n and small M_w/M_n values were obtained by the polymerization of δ -VL at -40 °C. The molecular weights of the polymers could be controlled with the feed ratio of the monomer and initiator. The post polymerization was successfully achieved, keeping small M_w/M_n s to indicate that the polymerization proceeded in living fashion.

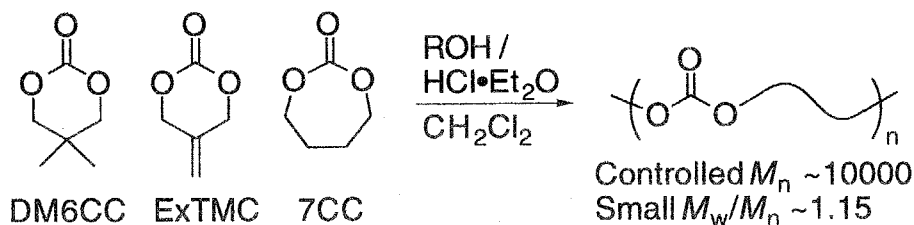
3-2 Introduction

Ring-opening polymerization of lactones and cyclic carbonates attracts much attention because the resulting polymers are applicable to drug delivery and biodegradable materials.¹ Recent development of living ring-opening polymerization has enabled us to obtain polymeric materials with controlled molecular weights (M_n s) and polydispersity indexes (M_w/M_n s). One of the most powerful method to control cationic ring-opening polymerization is "activated monomer cationic polymerization" reported by Penczek et al.,² which can suppress unfavorable reactions such as back-biting and deproportionation. This method has been applied to the polymerization of epichlorohydrin and propylene oxide to give the linear polymers free from cyclic oligomers.³ Okamoto has reported that the combination of an alcohol and triethyloxonium hexafluorophosphate is effective for ring-opening polymerization of β -propiolactone, δ -valerolactone (δ -VL), and ϵ -caprolactone (ϵ -CL) to give the corresponding polymers with controlled M_n (< 3000), but the M_w/M_n s are relatively large (~ 1.4).⁴ These methods have been also applied to prepare the block copolymers using the hydroxy terminated prepolymers such as poly(tetramethylene oxide).⁵ In chapter 2, I have demonstrated a controlled ring-opening polymerization of 1,3-dioxepan-2-one (7CC) with an alcohol / HCl•Et₂O initiator gives the corresponding polycarbonate ($M_n < 10000$) with narrow polydispersity ($M_w/M_n \sim 1.15$). I describe here the controlled ring-opening polymerization of ϵ -CL and δ -VL by *n*-butyl alcohol / HCl•Et₂O initiator system.

3-3 Controlled Polymerization of ϵ -Caprolactone (ϵ -CL) by *n*-BuOH / $\text{HCl}\cdot\text{Et}_2\text{O}$

In chapter 2, I have described the controlled ring-opening polymerizations of cyclic carbonates with alcohols and H_2O in the presence of $\text{HCl}\cdot\text{Et}_2\text{O}$, and the mechanistic study on the polymerization of a seven-membered cyclic carbonate (7CC) with H_2O / $\text{HCl}\cdot\text{Et}_2\text{O}$ initiator system (Scheme 1). The M_n s can be varied with the feed ratio of the monomer to initiator ($10^3\sim 10^4$) and M_w/M_n s are narrow (~ 1.15). The key feature of this polymerization may be the acidity of the added protonic acid, which is not as large to polymerize the monomer by itself but is sufficient to activate the monomer.

Scheme 1



To extend this facile method to other cyclic esters, I investigated the ring-opening polymerization of ϵ -CL to examine the M_n and M_w/M_n of the polymer.

Scheme 2 and Table 1 summarize the results of the polymerization of ϵ -CL with *n*-butyl alcohol (*n*-BuOH) in the presence of $\text{HCl}\cdot\text{Et}_2\text{O}$. Although the polymerization did not proceed with *n*-butyl alcohol alone (run 1), the addition of $\text{HCl}\cdot\text{Et}_2\text{O}$ was quite effective to give poly ϵ -CL quantitatively (runs 2 ~ 6). The increase of HCl amount did not affect the M_n of the obtained polymer, and the M_w/M_n was small (runs 2 and 3). These results indicated that HCl did not serve as an initiator, but an activator in this system, similar to the polymerization of 7CC. The M_n value agreed well with that calculated from the feed ratio of the monomer to initiator in every case, keeping a narrow polydispersity ratio (runs 2, 4, 5, and 6).

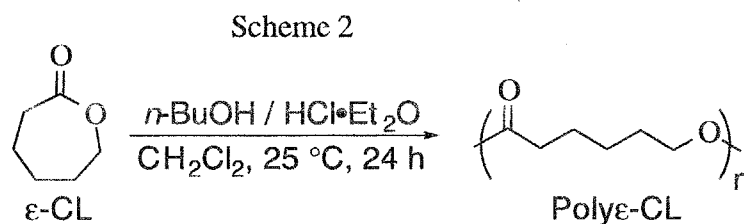


Table 1 Ring-opening polymerization of ϵ -CL^a

run	$[\text{CL}]_0 / [\text{BuOH}]_0$	$[\text{HCl}]_0 / [\text{BuOH}]_0$	conv ^b (%)	yield ^c (%)	M_n^d	M_w / M_n^d
1	20	0	0	— ^c	— ^c	— ^c
2	20	1	100	99	3000	1.08
3	20	10	99	78	2700	1.17
4	40	1	100	99	6500	1.13
5	75	4	95	87	7900	1.14
6	100	5	94	82	10300	1.15

^aPolymerization was carried out in CH_2Cl_2 at 25°C for 24 h. $[\epsilon\text{-CL}]_0 =$

1 mol / L. ^bDetermined by ^1H NMR. ^c*n*-Hexane-insoluble part.

^dDetermined by GPC(polystyrene standard, THF). ^eNot determined.

Figure 1 illustrates the ^1H NMR spectrum of poly ϵ -CL obtained by the polymerization of ϵ -CL with 1/10 equiv of *n*-BuOH / $\text{HCl}\cdot\text{Et}_2\text{O}$ initiator system in CH_2Cl_2 at 25°C for 5 h ($[\epsilon\text{-CL}]_0 = 1$ mol / L). In addition to signals *b* ~ *f* on the basis of α -, β -, γ -, δ -, and ϵ -methylene protons of the ester carbonyl moiety at 2.31, 1.65, 1.39, 1.65, and 4.06 ppm, signals *a* and *g* assignable to terminal methyl and α -methylene proton signals of a hydroxyl

group were observed at 0.94, 3.65 ppm, respectively. The integration ratio of the signals *a* to *g* was exactly 3 / 2, which agreed well to the expected value.

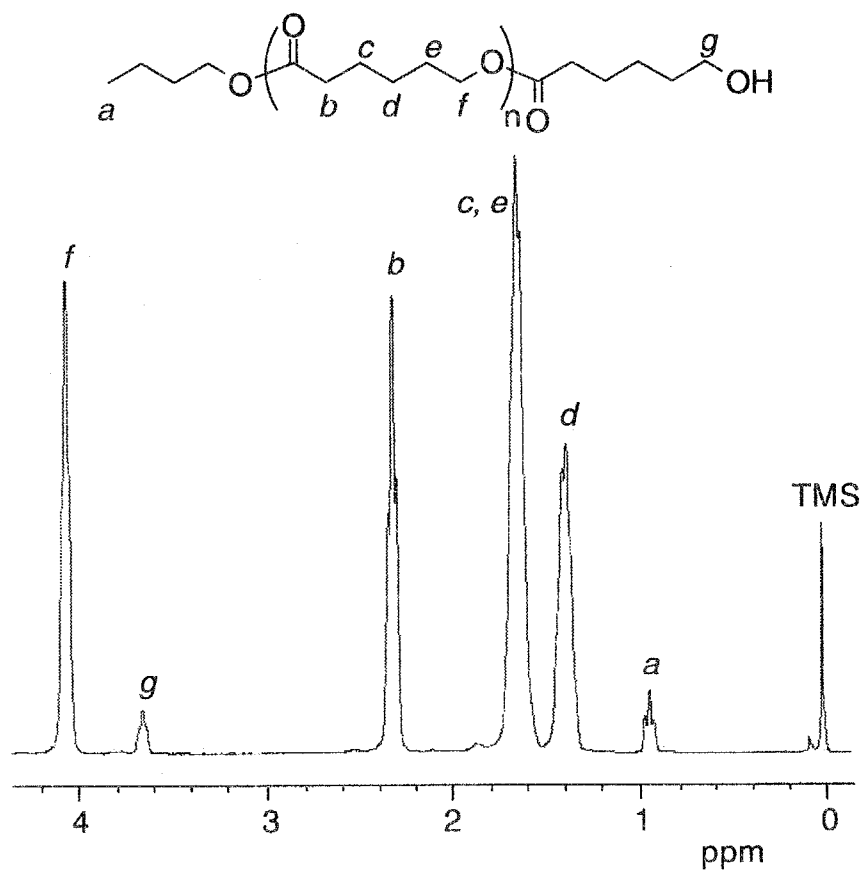


Figure 1. ^1H NMR spectrum (300 MHz, CDCl_3) of poly ϵ -CL obtained by the polymerization of ϵ -CL with *n*-BuOH / $\text{HCl}\cdot\text{Et}_2\text{O}$ initiator system in CH_2Cl_2 at 25 °C. $[\epsilon\text{-CL}]_0 = 1 \text{ mol / L}$, $[n\text{-BuOH}]_0 = [\text{HCl}]_0 = 0.1 \text{ mol / L}$.

Figure 2 illustrates the dependence of M_n , M_w/M_n of poly ϵ -CL on the feed ratio $[\epsilon\text{-CL}]_0 / [n\text{-BuOH}]_0$ in the polymerization in CH_2Cl_2 at 25°C . The M_n increased almost linearly with increasing the feed ratio of the monomer to initiator, keeping narrow polydispersity.

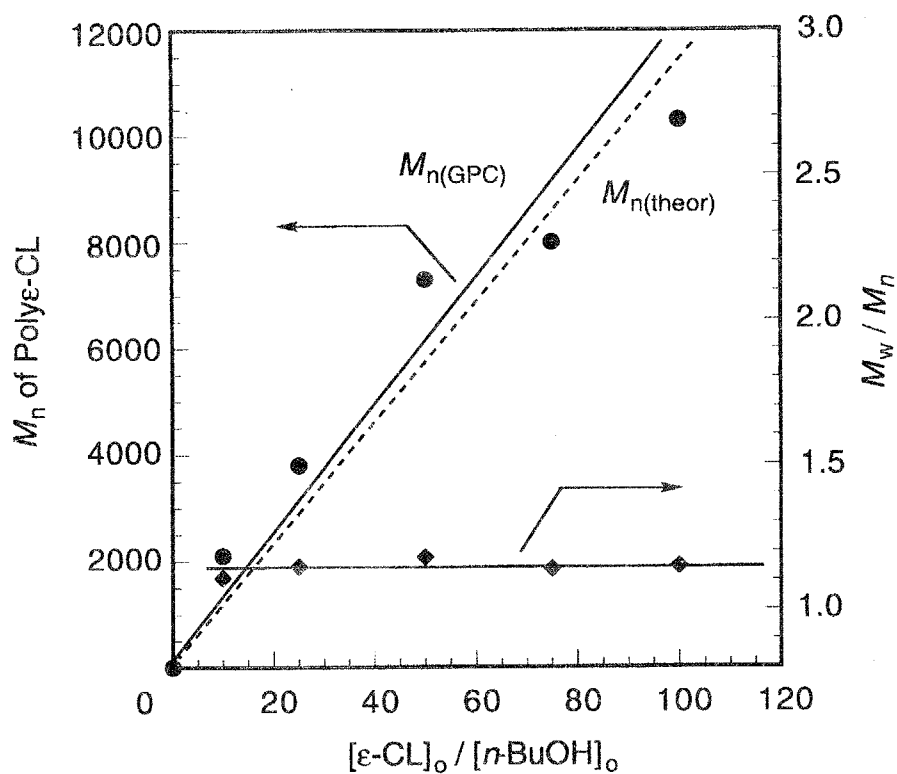


Figure 2. Dependence of M_n and M_w/M_n of poly ϵ -CL on $[\epsilon\text{-CL}]_0 / [n\text{-BuOH}]_0$ obtained by the polymerization of $\epsilon\text{-CL}$ in CH_2Cl_2 at 25°C for 24 h. $[\epsilon\text{-CL}]_0 = 1 \text{ mol/L}$, $[\text{HCl}]_0 / [n\text{-BuOH}]_0 = 1$.

Figure 3 illustrates the kinetic plots for the polymerization of $\epsilon\text{-CL}$ by $n\text{-BuOH}$ varying with $\text{HCl}\cdot\text{Et}_2\text{O}$ (20, 10, 0.50, 0.25 equiv to initiator) in CH_2Cl_2 at 25°C . The $-\text{[BuOH]}_0^{-1}\cdot\text{Ln}(\text{[M]} / \text{[M]}_0)$ versus time plots exhibited linear variations, illustrative of a first order reaction in monomer. The rate of polymerization k_p was greatly affected by the ration of $[\text{H}^+]_0 / [\text{I}]_0$, indicating that HCl served as an activator in the polymerization. The values of k_p in $\epsilon\text{-CL}$ polymerization with $n\text{-BuOH}$ activated by $\text{HCl}\cdot\text{Et}_2\text{O}$ (20, 10, 0.50, 0.25 equiv to initiator) were estimated as follows; $k_p = 77, 48, 12, 9 \text{ mol}^{-1}\cdot\text{L}\cdot\text{h}^{-1}$, respectively.

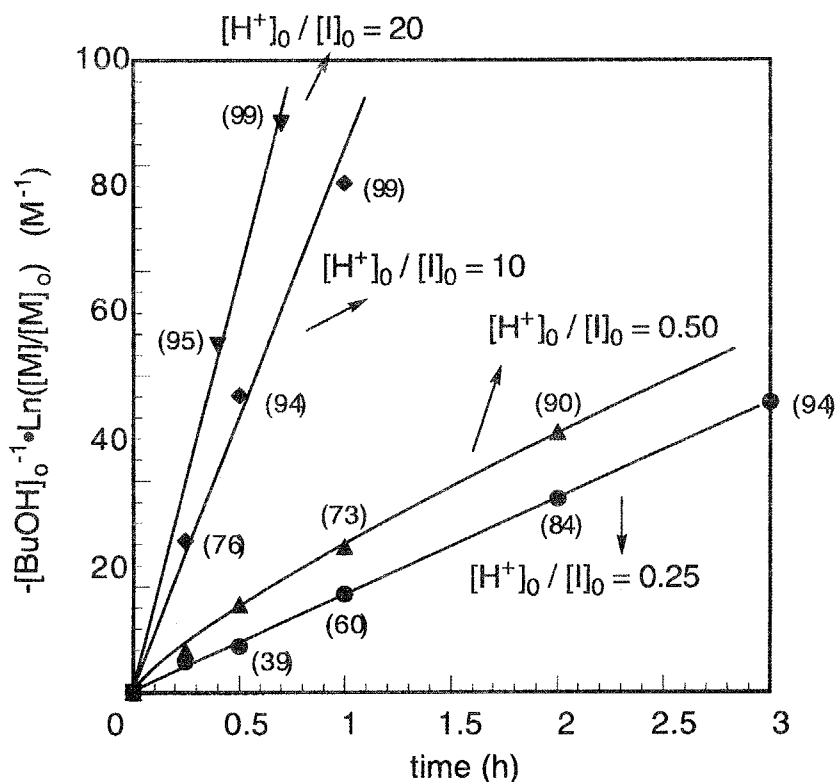


Figure 3. Time-conversion curves for the PCL. $[\text{M}]_0 = 1 \text{ mol} / \text{L}$ in CH_2Cl_2 at 25°C . $[\text{HCl}]_0 / [n\text{-BuOH}]_0 = 20, 10, 0.5, 0.25$. The data in parentheses were monomer conversion (%).

Figure 4 shows the result of a second-feed experiment to confirm the living nature of the polymerization. First, $\epsilon\text{-CL}$ was polymerized with 1/40 equiv of $n\text{-BuOH} / \text{HCl}\cdot\text{Et}_2\text{O}$ initiator system in CH_2Cl_2 at 25°C for 12 h.

After confirming the quantitative monomer conversion, the same amount of monomer was fed into the polymerization mixture to conduct post polymerization. The GPC elution peak shifted to the higher M_n region maintaining a narrow polydispersity. These results suggest that no termination or chain transfer occurs, namely this polymerization proceeds via *living* fashion.

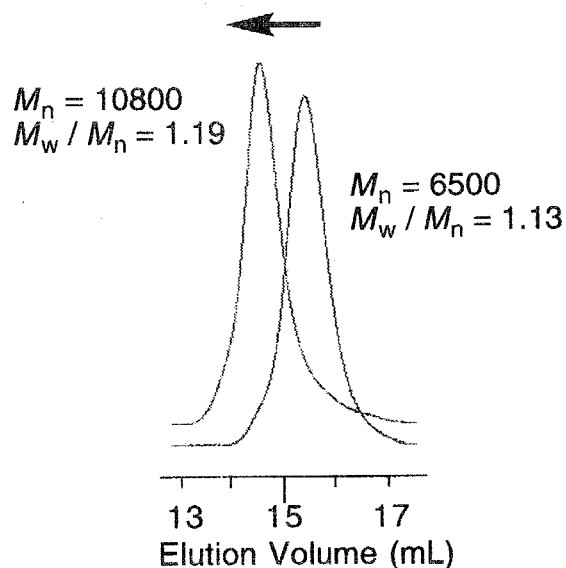


Figure 4. GPC traces of the prepolymer obtained by the polymerization of ϵ -CL with 1/40 equiv of n -BuOH / $\text{HCl}\cdot\text{Et}_2\text{O}$ in CH_2Cl_2 at 25 °C ($[\epsilon\text{-CL}]_0 = 1 \text{ mol / L}$, $[\text{HCl}]_0 / [n\text{-BuOH}]_0 = 1$), and the post polymer obtained by the further addition of same amount of monomer.

3-4 Controlled Polymerization of δ -Caprolactone (δ -CL) by Activated Monomer Mechanism

Scheme 3 and Table 2 summarize the ring-opening polymerization of δ -VL with *n*-BuOH catalyzed by various acids.

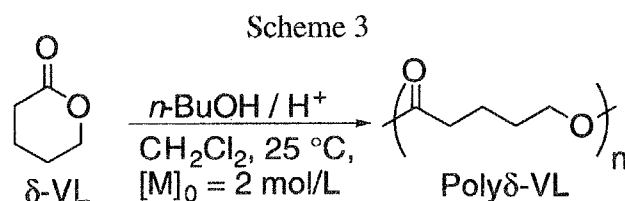


Table 2 Ring-opening polymerization of δ -VL^a

run	Catalyst	$[\delta\text{-VL}]_0/[\text{BuOH}]_0$	$[\text{H}^+]$ (M)	time (h)	yield ^b (%)	M_n^c	M_w/M_n^c
1	$\text{CF}_3\text{CO}_2\text{H}$	20	0.1	10	65	1900	1.71
2	$\text{CCl}_3\text{CO}_2\text{H}$	25	0.3	16	91	3700	1.45
3	$\text{HCl}\cdot\text{Et}_2\text{O}$	30	1.5	0.5	77	2700	1.27
4	$\text{HCl}\cdot\text{Et}_2\text{O}$	30	1.5	0.5	76	6000	1.61
5	CSA ^d	10	0.2	20	68	1400	2.59

^aPolymerization was carried out in CH_2Cl_2 at 25 °C. $[\delta\text{-VL}]_0/[\text{BuOH}]_0 = 30$, $[\text{M}]_0 = 2\text{ mol/L}$. ^b*n*-Hexane-insoluble part. ^cDetermined by GPC(polystyrene standard, THF). ^dCamphorsulfonic acid.

The polymers were obtained in high yields in the presence of $\text{CF}_3\text{CO}_2\text{H}$, $\text{CCl}_3\text{CO}_2\text{H}$, $\text{HCl}\cdot\text{Et}_2\text{O}$, and camphorsulfonic acid (CSA). However, the M_w/M_n values of the obtained polymers were somewhat large (1.27 ~ 2.59) probably due to back-biting reaction.

Scheme 4 and Table 3 summarize the ring-opening polymerization of δ -VL with *n*-butyl alcohol in the presence of $\text{HCl}\cdot\text{Et}_2\text{O}$ at 25 ~ -40 °C. The polymerization of δ -VL provided the polymer in high yield at 25 °C, but the M_w/M_n was somewhat large (run 1). At 0 °C, poly δ -VL with a small M_w/M_n was obtained in a high yield (run 2). The M_w/M_n became smaller as the temperature decreased (runs 2 ~ 4).

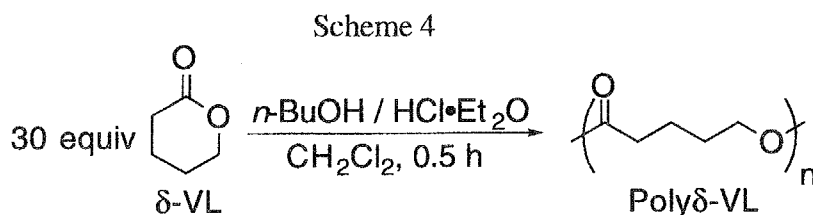


Table 3 Ring-opening polymerization of $\delta\text{-VL}^a$

run	temp (°C)	conv ^b (%)	yield ^c (%)	M_n^d	M_w / M_n^d
1	25	92	77	2700	1.27
2	0	95	86	3200	1.17
3	-10	95	82	2800	1.17
4	-40	94	85	2700	1.10

^aPolymerization was carried out in CH_2Cl_2 for 0.5 h. $[\text{M}]_0 / [\text{BuOH}]_0 = 30$, $[\text{H}]_0 / [\text{BuOH}]_0 = 1.5$, $[\text{M}]_0 = 2 \text{ mol/L}$. ^bDetermined by $^1\text{H NMR}$. ^c*n*-Hexane-insoluble part. ^dDetermined by GPC(polystyrene standard, THF).

Figure 5 depicts the dependence of the M_n and M_w / M_n of poly $\delta\text{-VL}$ on the feed ratio of $[\delta\text{-VL}]_0 / [n\text{-BuOH}]_0$ in the polymerization in CH_2Cl_2 at -40°C . The M_n increased linearly with the monomer feed ratio, keeping a narrow polydispersity ($M_w / M_n \leq 1.11$). The experimental M_n values agreed well with theoretical ones calculated from the feed ratio of the monomer to initiator.

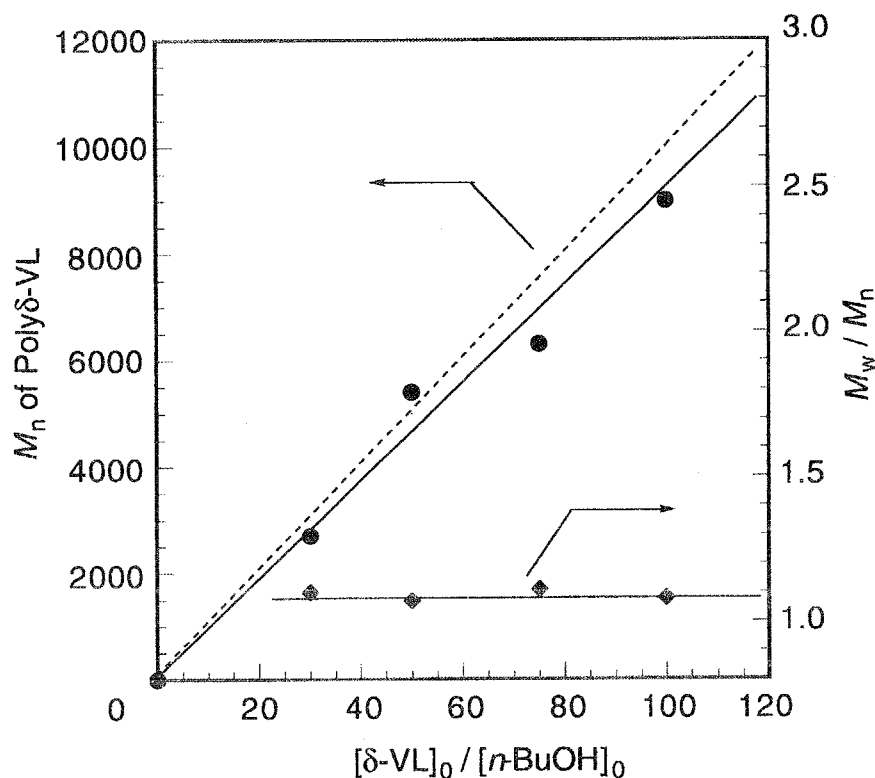


Figure 5. Dependence of the M_n and M_w / M_n of poly $\delta\text{-VL}$ on $[\delta\text{-VL}]_0 / [n\text{-BuOH}]_0$ in the polymerization of $\delta\text{-VL}$ in CH_2Cl_2 at -40°C . $[\delta\text{-VL}]_0 = 2 \text{ mol / L}$, $[\text{HCl}]_0 / [n\text{-BuOH}]_0 = 1.5$.

Figure 6 depicts the results of second-feed experiment to confirm the living nature of the polymerization of $\delta\text{-VL}$. First, 30 equiv of $\delta\text{-VL}$ was polymerized with $n\text{-BuOH} / \text{HCl}\cdot\text{Et}_2\text{O}$ initiator system in CH_2Cl_2 at -40°C for 2 h. After the quantitative monomer conversion, the same amount of monomer was recharged into the polymerization mixture to conduct a post polymerization. The elution peak in GPC shifted to the higher M_n region maintaining a narrow M_w/M_n . As in the case of $\epsilon\text{-CL}$, these results suggest that this polymerization system proceed via *living* fashion.

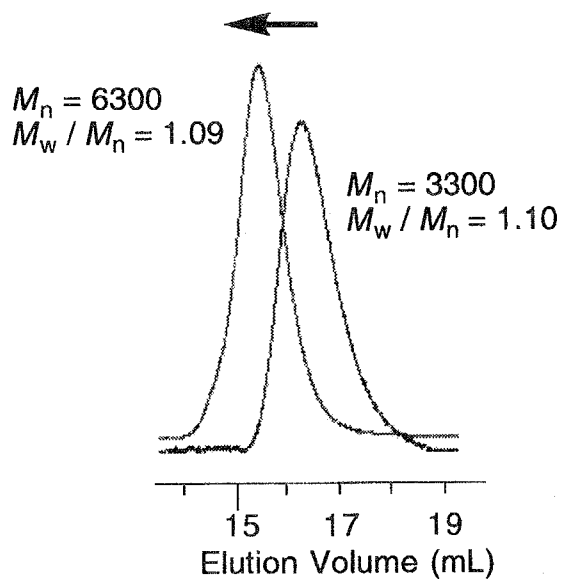


Figure 6. GPC traces of the prepolymer obtained by the polymerization of δ -VL (30 equiv) with n -BuOH / $\text{HCl}\cdot\text{Et}_2\text{O}$, and the post polymer obtained by the further addition of same amount of monomer

3-5 Summary

In this chapter, I have demonstrated the ring-opening polymerizations of ϵ -CL and δ -VL by use of *n*-BuOH / $\text{HCl}\cdot\text{Et}_2\text{O}$ initiator system for controlled polymer synthesis. The corresponding polylactones with small polydispersities (~ 1.1) were obtained quantitatively both in the polymerization of ϵ -CL and δ -VL. These polymerizations proceeded in living fashion as like the polymerization of cyclic carbonates described in Chapter 2. The terminal structures of the obtained polymers were *n*-butyl and hydroxyl moieties, which suggested that the polymerization proceeded via activated monomer mechanism similar to the polymerization of cyclic carbonates.

3-6 Experimental Section

Materials. CH_2Cl_2 was distilled sequentially over P_2O_5 and CaH_2 under nitrogen. $\epsilon\text{-CL}$ and $\delta\text{-VL}$ were purchased from Aldrich and distilled over CaH_2 under nitrogen prior to use. *n*-Butyl alcohol was dried over CaH_2 and distilled under nitrogen. A 2.0 mol/L HCl solution in diethyl ether (Et_2O) was purchased from Aldrich and used without further purification. $\text{CF}_3\text{CO}_2\text{H}$ and $\text{CCl}_3\text{CO}_2\text{H}$ were distilled prior to use. Camphorsulfonic acid (CSA) and 3-(4-methoxybenzoyl)propionic acid were recrystallized from ethyl acetate and THF/toluene, respectively.

Measurements. ^1H NMR spectra were recorded with a JEOL Lambda-300 spectrometer. Number and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Tosoh HLC-8120 system equipped with two consecutive polystyrene gel columns (G2500HXL and G4000HXL) eluted with tetrahydrofuran (THF) at a flow rate of $1.0\text{ mL}\cdot\text{min}^{-1}$ calibrated by standard polystyrenes.

Polymerization of $\epsilon\text{-CL}$ and $\delta\text{-VL}$. A typical procedure: All glass vessels were heated in vacuo before use, filled with and handled in a stream of dry nitrogen. To a solution of $\epsilon\text{-CL}$ (0.58 g, 5.0 mmol) in CH_2Cl_2 (4.5 mL) was added *n*-butyl alcohol (9.3 mg, 0.13 mmol). The polymerization was initiated by the addition of 65 μL (0.13 mmol) of HCl solution (2 mol / L) in Et_2O at a set temperature. After a set time the reaction mixture was poured into 300 mL of *n*-hexane to precipitate a polymer. The precipitate was filtered, and dried at $25\text{ }^\circ\text{C}$ for 5 h in vacuo to give a white powder.

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Chapter 3.

Activated Monomer Cationic Polymerization of Lactones using $\text{HCl}\cdot\text{Et}_2\text{O}$

Chapter 4

Synthesis of Well-Defined Copolymers of Cyclic Carbonate with Lactone via Activated Monomer Mechanism

4-1 ABSTRACT

This chapter deals with syntheses of di-, triblock, and random copolymers of a seven-membered cyclic carbonate (7CC) and lactones (ϵ -caprolactone and δ -valerolactone) with *n*-butyl alcohol / HCl•Et₂O and H₂O / HCl•Et₂O initiator systems. The corresponding di- and triblock copolymers with small polydispersity ratios (1.08 ~ 1.16) were obtained quantitatively in one pot. The molecular weights and composition of the block copolymers could be controlled with varying the feed ratio of the monomer to initiator, and the first monomer to second one, respectively.

4-2 Introduction

Block copolymerization possesses various properties of macromolecules by way of the chain length control of the blocks as well as the choice of the monomers in each segments. Since the finding of living polymerization by Szwarc in the early sixties, sequential anionic polymerization has been recognized as a powerful tool for the synthesis of well-defined block copolymers. This finding was followed by the tremendous strides in living polymerization techniques including living cationic, radical and group-transfer polymerizations that have supplied a wide range of block copolymers.¹ On the biomedical and agricultural demands, many efforts have been made to synthesis and investigate the biodegradable polymers such as polysaccharides, polypeptides, polyesters, polyamides, polyurethanes, polyureas, and polyanhydrides.² Polyesters and copolyesters of several α -, β -, and ω -hydroxyacids have been found as a versatile family of materials with interesting applications in surgery and pharmacology due to their biocompatibility and biodegradability.³ Thus, the polymers and copolymers of ϵ -caprolactone, lactides, and glycolide have been used in medical materials as biocompatible sutures, artificial skins, and drug delivery materials, where their properties are strongly dependent on chemical structures, molecular weights, and crystallinities.⁴

Several groups have demonstrated the living ring-opening polymerization of ϵ -caprolactone (ϵ -CL) initiated with aluminum alkoxide initiators, which has been applied to poly ϵ -CL based biodegradable macromonomers functionalized with amino, bromo, allyl, and methacryloy groups.⁵ The aluminum alkoxide initiating polymerization, however, is not effective to obtain aliphatic polycarbonates with small polydispersity ratios.⁶ In chapters 2 and 3, I have demonstrated a versatile synthesis of polycarbonates and polylactones with controlled M_n and small M_w/M_n ratios by activated monomer polymerization. As a part of the research, I describe

here the copolymerization of a seven-membered cyclic carbonate with ϵ -caprolactone and δ -valerolactone using *n*-butyl alcohol / $\text{HCl}\cdot\text{Et}_2\text{O}$ and H_2O / $\text{HCl}\cdot\text{Et}_2\text{O}$ initiator systems.

4-3 Synthesis of diblock copolymers of 7CC with lactones.

The combination of *n*-butyl alcohol and HCl•Et₂O could provide controlled polymers of a seven-membered cyclic carbonate (7CC), ϵ -caprolactone (ϵ -CL) and δ -valerolactone (δ -VL) as described in Chapters 2 and 3. To develop this facile method to copolymer synthesis, I first examined diblock copolymerization of ϵ -caprolactone and δ -valerolactone with 7CC, undergoing controlled polymerization (Scheme 1). Table 1 summarizes the yield, M_n , M_w/M_n , and composition of the block copolymers obtained by the copolymerization.

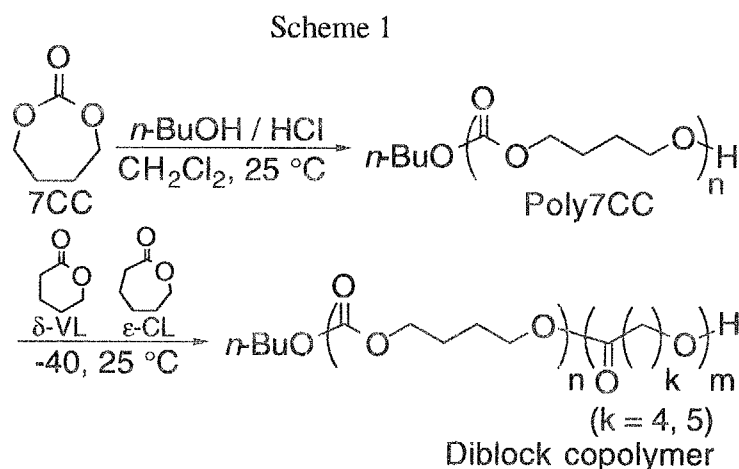


Table 1 Synthesis of diblock copolymer of 7CC with lactones

run	homopolymerization ^a			triblock copolymerization							
	$[7CC]_0 / [BuOH]_0$	M_n^b	M_w/M_n^b	monomer	$[M]_0 / [BuOH]_0$	time (h)	temp (°C)	yield ^c (%)	M_n^b	M_w/M_n^b	7CC : lactone ^d
1	10	1500	1.15	ϵ -CL	30	24	25	96	6600	1.16	22 : 78
2	30	3500	1.13	ϵ -CL	30	24	25	92	6800	1.12	49 : 51
3	60	6200	1.15	ϵ -CL	30	24	25	88	9500	1.13	74 : 26
4	10	1900	1.14	δ -VL	30	3	-40	99	6900	1.14	22 : 78
5	30	4200	1.14	δ -VL	30	1.5	-40	99	6900	1.14	48 : 52
6	60	6600	1.12	δ -VL	30	3	-40	84	8600	1.14	70 : 30

^aConditions; in CH₂Cl₂ at 25 °C for 24 h, $[7CC]_0 = 1$ mol/L, $[HCl]_0/[BuOH]_0 = 1.5$.

All runs achieved above 98% monomer conversions. ^bDetermined by GPC

(polystyrene standards, THF). ^c*n*-Hexane-insoluble part. ^dDetermined by ¹H NMR.

The second monomer conversion was almost quantitative in every case.

The polydispersities of the post polymers were narrow ($M_w/M_n \leq 1.16$) similar to the prepolymers. The composition of the copolymer could be varied with the feed ratio of the first and second monomers.

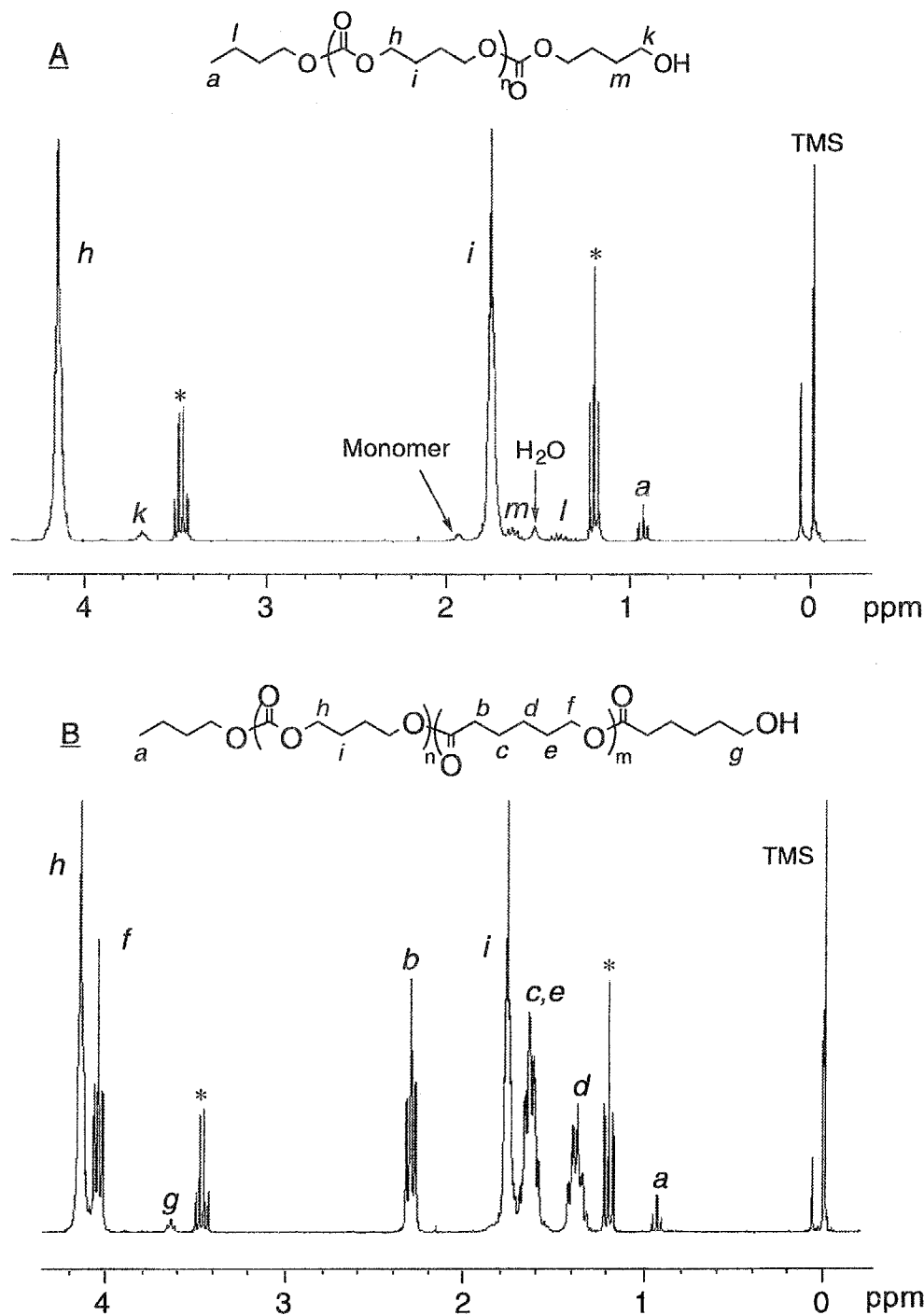
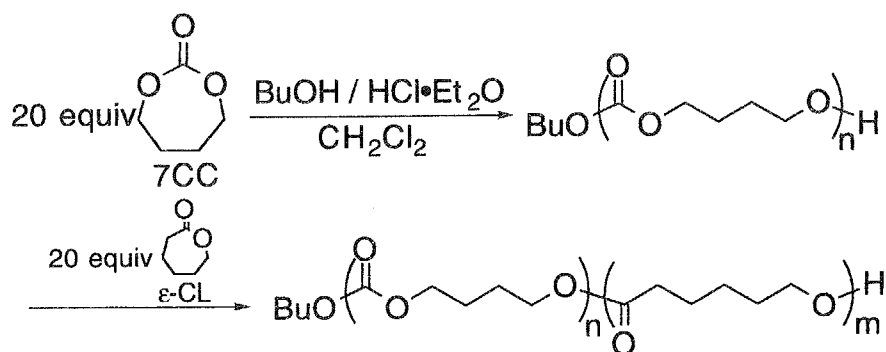


Figure 1. ^1H NMR spectra (300 MHz, CDCl_3) of (A) homo poly7CC obtained by the polymerization of 7CC (30 equiv) with $n\text{-BuOH} / \text{HCl} \cdot \text{Et}_2\text{O}$ initiator system in CH_2Cl_2 at 25 $^\circ\text{C}$ ($[\text{7CC}]_0 = 1 \text{ mol/L}$, $[\text{HCl}]_0 / [n\text{-BuOH}]_0 = 1$), and (B) diblock copolymer obtained by the further addition of $\epsilon\text{-CL}$ (30 equiv) into the polymer mixture (A). *: signals due to Et_2O .

Figure 1 depicts ^1H NMR spectra of (A) the prepolymer (poly7CC), and (B) the diblock copoly7CC-*b*- ϵ -CL obtained in run 2 in Table 1. In addition to signals *h* and *i* assignable to α - and β -methylene protons of the carbonate moiety at 4.17 and 1.75 ppm, signals *a* and *k* assignable to terminal methyl and α -methylene proton signals of a hydroxyl group were observed at 0.94 and 3.70 ppm, respectively (Figure 1A). After the post polymerization, new signals *b*, *c*, *d*, *e* and *f* appeared at 2.31, 1.65, 1.39, 1.65, and 4.06 ppm which were assignable to α -, β -, γ -, δ -, and ϵ -methylene protons of the ester carbonyl moiety (Figure 1B). The terminal methylene signal *k* disappeared, and a new signal *g* assignable to α -methylene protons of a hydroxyl moiety at the poly ϵ -CL terminal unit appeared at 3.65 ppm, supporting the formation of a diblock copolymer free from homo poly7CC. The integration ratio of the signals *a* to *g* was exactly 3 / 2, which agreed well to the expected value. The unit ratio of 7CC and the comonomer in the resulted polymer was calculated by the ^1H NMR integration ratio of signals *h* and *b* in Figure 1B, which agreed well with the feed ratio.

Figure 2 shows the GPC traces of homo poly7CC and the resulted diblock copolymer before precipitation with *n*-hexane (Scheme 2). The elution peak shifted to higher molecular weight region maintaining a narrow polydispersity after copolymerization. This indicates the satisfactory formation of a diblock copolymer.

Scheme 2



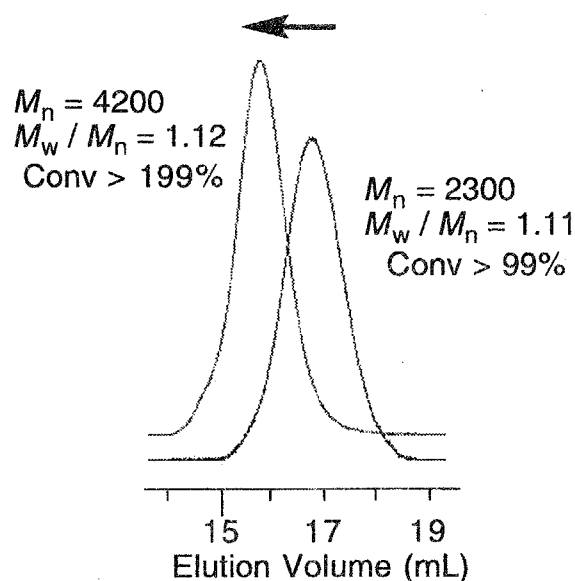


Figure 2. GPC traces of homo poly7CC obtained by the polymerization of 7CC (20 equiv) with *n*-BuOH / HCl•Et₂O in CH₂Cl₂ at 25 °C ([7CC]₀ = 1 mol / L, [HCl]₀ / [*n*-BuOH]₀ = 1), and the diblock copolymer obtained by further addition of ε-CL (20 equiv).

4-4 Synthesis of Triblock Copolymer of 7CC with ε-CL and δ-VL

When H₂O was employed instead of *n*-butyl alcohol as the initiator on 7CC polymerization in the presence of HCl, the initiating carbonic acid polymer end smoothly changed into a hydroxyl group by rapid decarboxylation to form a polycarbonate diol as described in Chapter 2 (Scheme 3).

Scheme 3

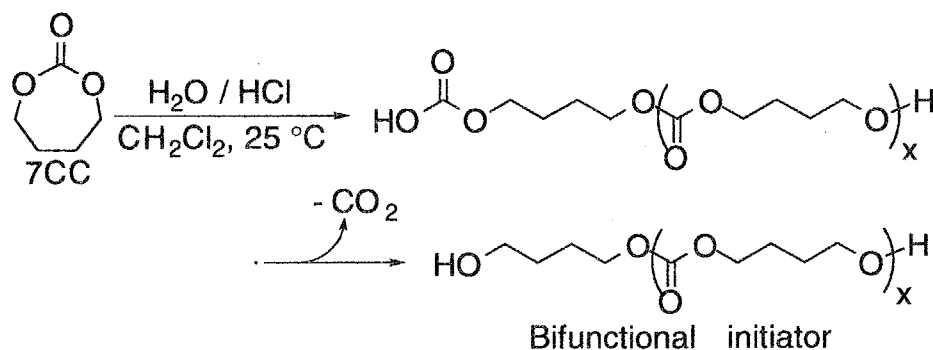


Table 2 summarizes the results of triblock copolymerization of 7CC, ϵ -CL, and δ -VL with $\text{H}_2\text{O} / \text{HCl} \cdot \text{Et}_2\text{O}$ initiator system utilizing the above bisfunctional initiator (Scheme 4). The corresponding triblock copolymers with narrow polydispersities were obtained in good yields. The copolymer composition determined by ^1H NMR agreed well with the expected value.

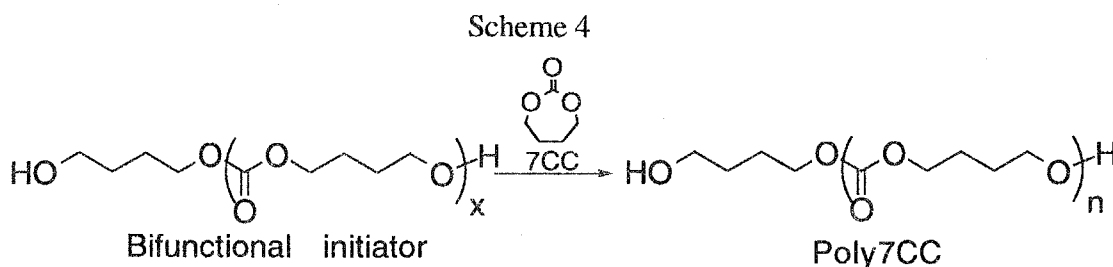


Table 2 Synthesis of triblock copolymer of 7CC with lactones

run	homopolymerization ^a				triblock copolymerization							
	$[\text{7CC}]_0 / [\text{H}_2\text{O}]_0$	$[\text{M}]_0$ (mol/L)	M_n^c	M_w/M_n^c	monomer	$[\text{M}]_0 / [\text{H}_2\text{O}]_0$	time (h)	temp (°C)	yield ^d (%)	M_n^c	M_w/M_n^c	7CC : lactone ^b
1	30	1	3100	1.14	ϵ -CL	30	24	25	92	5900	1.10	46 : 54
2	30	1	3500	1.14	ϵ -CL	45	24	25	98	9400	1.12	38 : 62
3	60	1	9300	1.23	ϵ -CL	120	24	25	83	21100	1.16	33 : 67
4	30	2	3500	1.13	δ -VL	30	1.5	-40	85	6300	1.08	54 : 46

^aConditions; in CH_2Cl_2 at 25 °C for 4 h, $[\text{HCl}]_0 / [\text{H}_2\text{O}]_0 = 1.5$. ^bDetermined by ^1H NMR.

All runs achieved above 98% monomer conversion ^cDetermined by GPC(polystyrene standards, THF). ^d*n*-Hexane-insoluble part.

Figure 3 depicts a ^1H NMR spectrum of the triblock copolymer obtained in run 2 in Table 2, where no signal was observed corresponding to α -methylene protons of a hydroxyl group of poly7CC end at 3.70 ppm but a signal *g* assignable to α -methylene protons of a hydroxyl group of poly ϵ -CL end at 3.65 ppm was observed. This indicated that all homo poly7CC participated the copolymerization. The molecular weights of the triblock copolymers calculated by the integration ratio of signal *g* and the other signals *h* and *b* in Figure 3 showed good agreement with the value estimated by GPC ($M_{n(\text{NMR})} / M_{n(\text{GPC})} = 5700 / 5900$ and $5500 / 6300$, respectively).

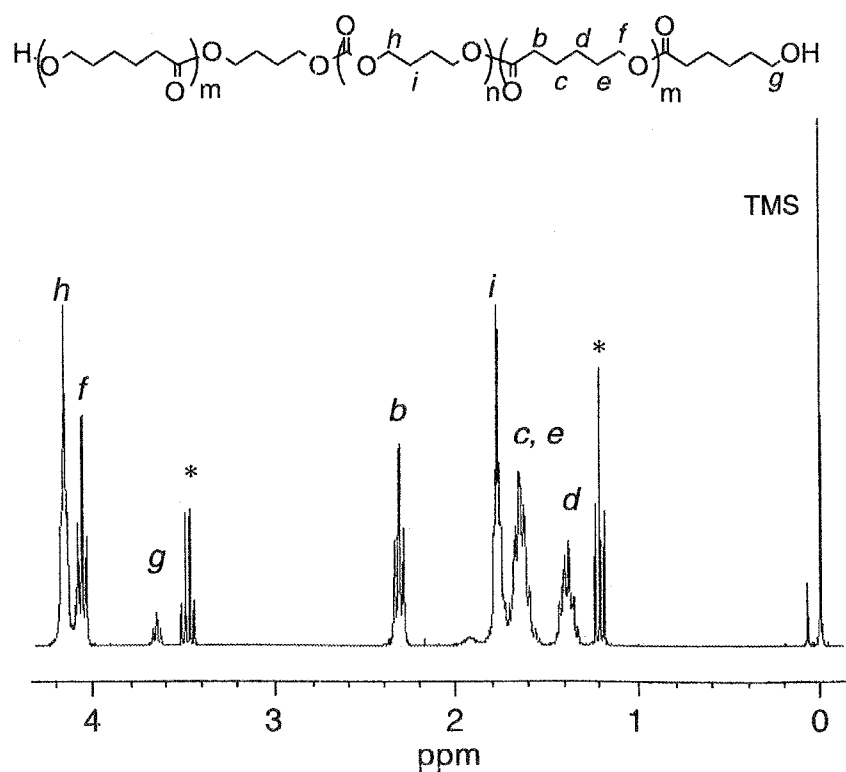


Figure 3. ^1H NMR spectrum (300 MHz, CDCl_3) of the triblock copolymer obtained by the polymerization of 7CC (30 equiv) with $\text{H}_2\text{O} / \text{HCl} \cdot \text{Et}_2\text{O}$ initiator system in CH_2Cl_2 at 25°C ($[\text{7CC}]_0 = 1 \text{ mol/L}$, $[\text{HCl}]_0 / [\text{H}_2\text{O}]_0 = 1$), followed by the further addition of $\epsilon\text{-CL}$ (30 equiv). *; signals due to diethyl ether.

Figure 4 illustrates the GPC traces of homo poly7CC and the resulted triblock copolymer before precipitation with *n*-hexane (Scheme 5). The elution peak shifted to higher molecular weight region maintaining a narrow polydispersity after copolymerization. The GPC curve of the copolymer showed complete participation of homo poly7CC to the initiation of $\epsilon\text{-CL}$.

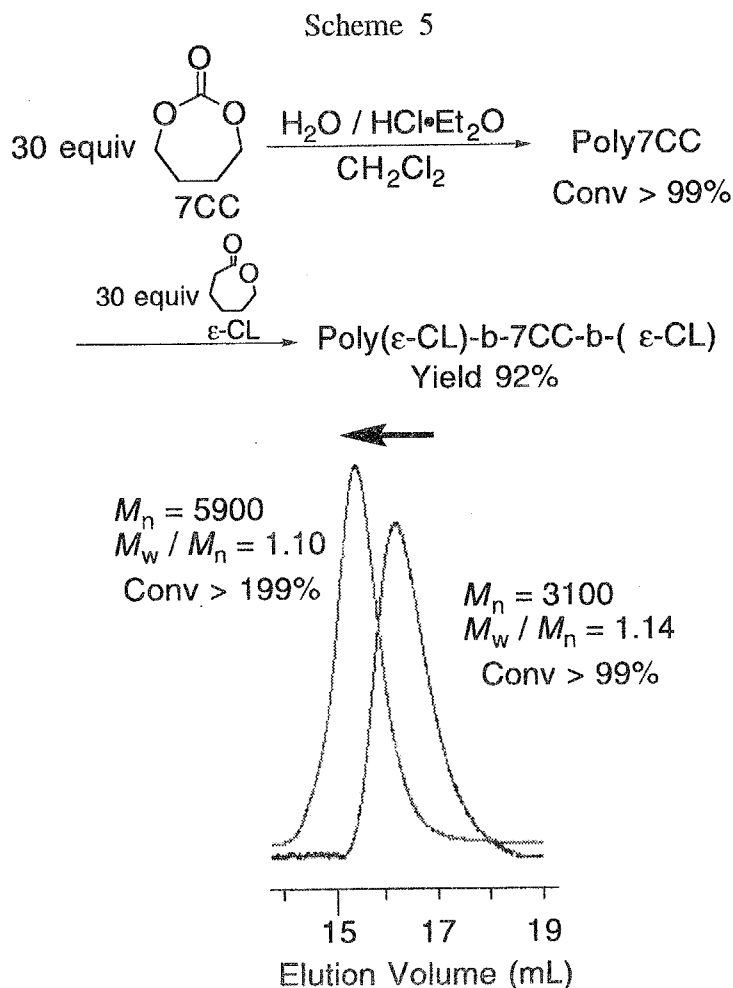
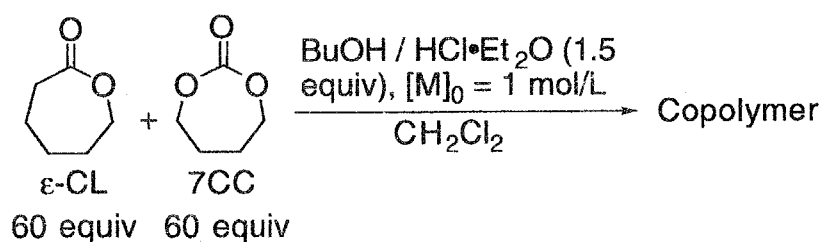


Figure 4. GPC traces of homo poly7CC obtained by the polymerization of 7CC (30 equiv) with $\text{H}_2\text{O} / \text{HCl} \cdot \text{Et}_2\text{O}$ in CH_2Cl_2 at 25°C ($[\text{7CC}]_0 = 1 \text{ mol/L}$, $[\text{HCl}]_0 / [\text{H}_2\text{O}]_0 = 1$), and the triblock copolymer obtained by further addition of $\epsilon\text{-CL}$ (30 equiv).

4-5 Copolymerization on One-Shot Monomer Feeding

Next, the copolymerization of 7CC with $\epsilon\text{-CL}$ was carried out in one-shot feeding of the both monomers to examine the difference. It was initiated by the addition of HCl (1.5 equiv) into the solution of these monomers (60 equiv) and *n*-BuOH in CH_2Cl_2 at 25°C (Scheme 6).

Scheme 6



The copolymer with a small polydispersity ratio (1.14) was obtained quantitatively ($\text{Conv}_{7\text{CC}} > 99\%$, $\text{Conv}_{\epsilon\text{-CL}} = 93\%$) free from cyclic oligomers, which was confirmed by GPC, where the $M_{n(\text{GPC})}$ (11000) showed good agreement with theoretical one ($M_{n(\text{theor})} = 13400$) calculated from the feed ratio of the monomer to initiator.

Figure 5 depicts a ^1H NMR spectrum of the copolymer before the precipitation into *n*-hexane ($\text{Conv}_{7\text{CC}} > 99\%$, $\text{Conv}_{\epsilon\text{-CL}} = 93\%$).

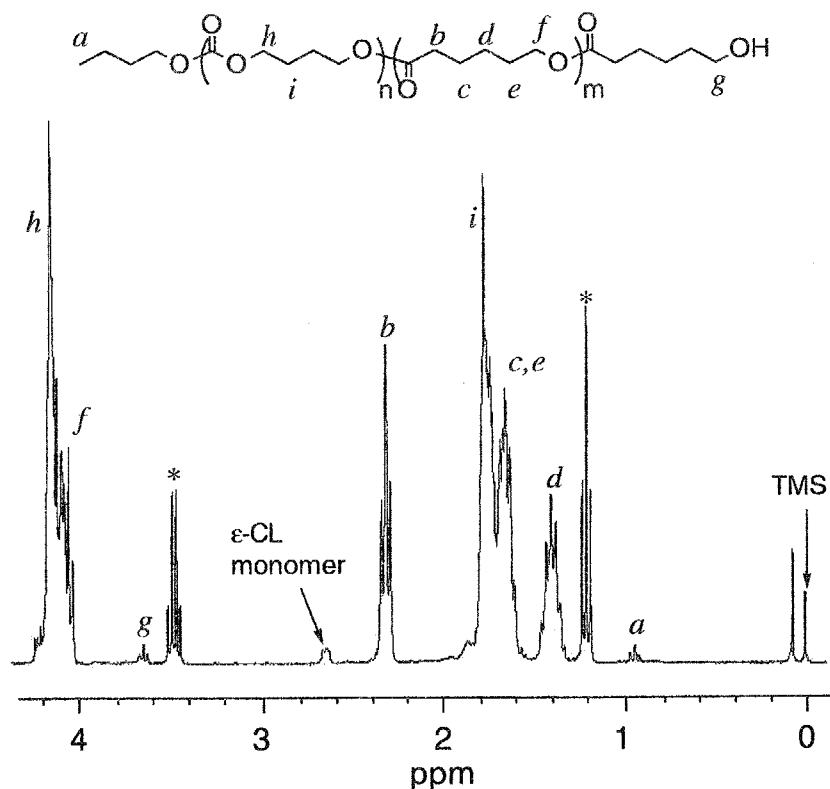


Figure 5. ^1H NMR spectrum (300 MHz, CDCl_3) of random copolymer obtained by the polymerization of 7CC (60 equiv) and $\epsilon\text{-CL}$ (60 equiv) with $\text{BuOH}/\text{HCl} \cdot \text{Et}_2\text{O}$ (1.5 equiv) initiator system in CH_2Cl_2 at 25°C ($[\text{7CC}]_0 = [\epsilon\text{-CL}]_0 = 1 \text{ mol/L}$).

Signals $a \sim f$ and $h \sim i$ were identical with diblock copolymer as shown in Figure 3. It showed signal g assignable to α -methylene protons of a

hydroxyl group at poly ϵ -CL end at 3.65 ppm, which indicated that all 7CC was incorporated into the copolymer before the consumption of ϵ -CL.

Figure 6 illustrates a first order kinetic plots of the copolymerization of 7CC and ϵ -CL as well as those of homopolymerization of 7CC and ϵ -CL in CH_2Cl_2 at 25 °C.

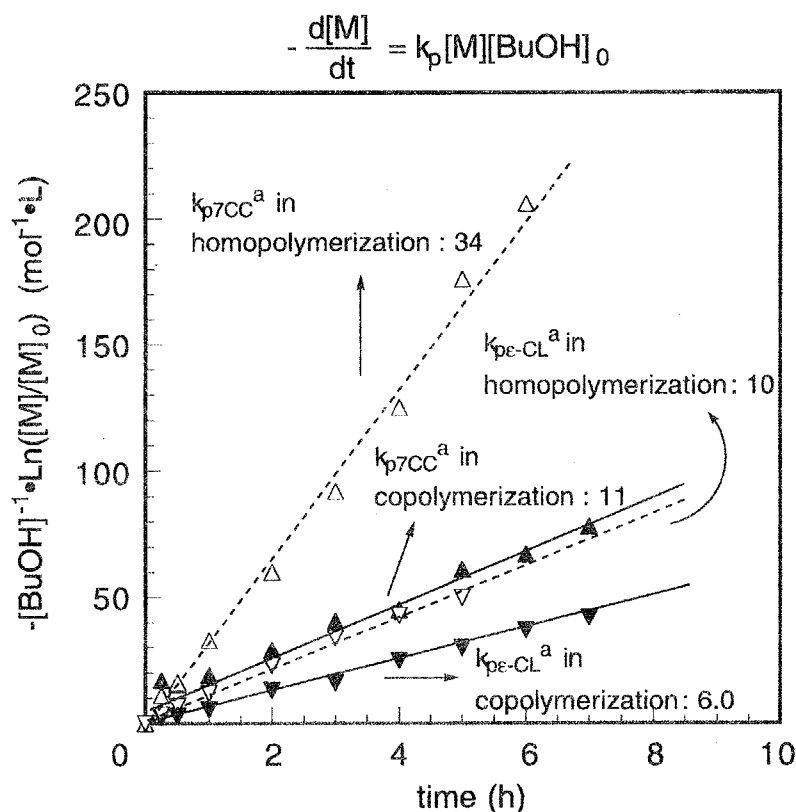


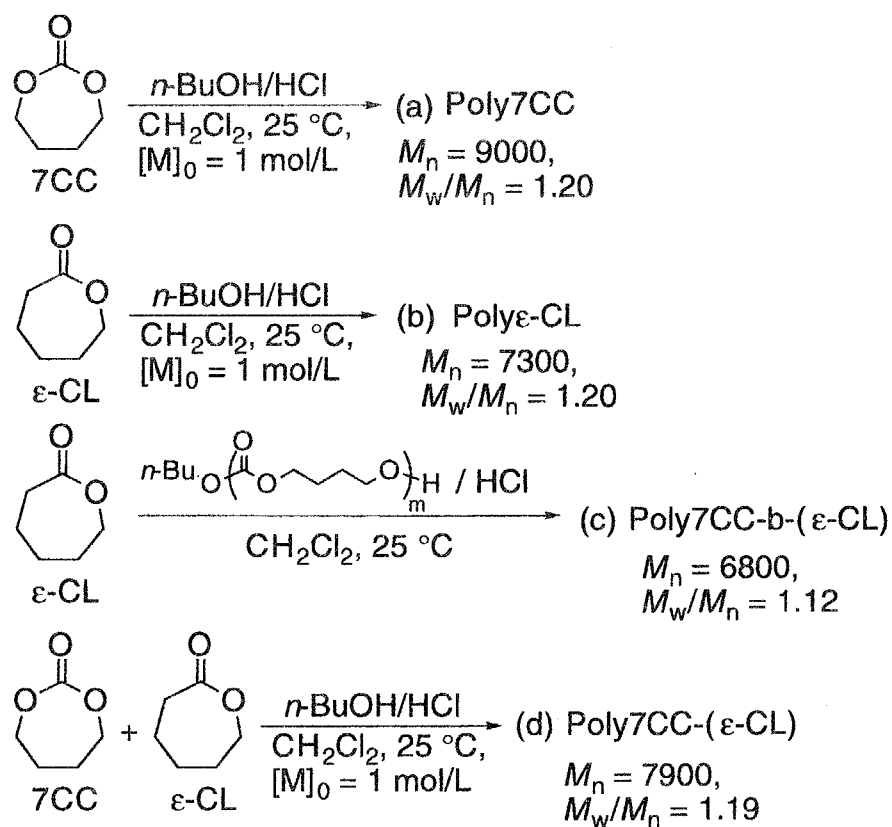
Figure 6. First order kinetic plots for the copolymerization of 7CC with ϵ -CL, and homopolymerizations of 7CC and ϵ -CL in CH_2Cl_2 at 25 °C. $[\text{M}]_0 = 1 \text{ mol/L}$, $[\text{M}]_0/[\text{BuOH}]_0 = 60$, $[\text{HCl}]_0/[\text{BuOH}] = 1.5$. ^a Rate constant ($\text{mol}^{-1} \cdot \text{L} \cdot \text{h}^{-1}$)

The rate constant values were smaller in the copolymerization of 7CC with ϵ -CL compared with those in their homopolymerizations, probably due to the increase of medium basicity which might restrain this cationic polymerization. As the results, random copolymer was produced. The terminal unit exclusively dominated by ϵ -CL, because the conversion of ϵ -CL was 92% when that of 7CC reached quantitatively. This supported the ^1H NMR spectroscopic data, where all the terminal hydroxyl group was

assigned as a poly ϵ -CL terminal unit (Figure 5).

Figure 7 depicts a comparison of the DSC traces of (a) poly7CC, (b) poly ϵ -CL, (c) poly7CC-b-(ϵ -CL), and (d) poly7CC-(ϵ -CL) obtained by the polymerization of 7CC with *n*-BuOH/HCl, ϵ -CL with *n*-BuOH/HCl, ϵ -CL with poly7CC macroinitiator, and ϵ -CL with 7CC by one-shot monomer feeding, respectively (Scheme 7). The melting endothermic processes of poly ϵ -CL and poly7CC were observed at 66.7 and 62.2 °C, respectively ($\Delta H_m = 59.6$ and 78.8 J/g). The DSC traces of the copolymer (c), prepared by sequential monomer addition after the quantitative conversion of the first monomer, showed two melting temperatures ($T_m = 56.9$ and 49.5 °C), supporting the formation of a block copolymer ($\Delta H_m = 77.6$ J/g). In contrast, the copolymer (d), prepared by one-shot monomer feeding, showed only one lower T_m (21.1 °C) indicating the absence of block structures ($\Delta H_m = 49.5$ J/g). These supports the results of kinetic study mentioned above (Figure 6).

Scheme 7



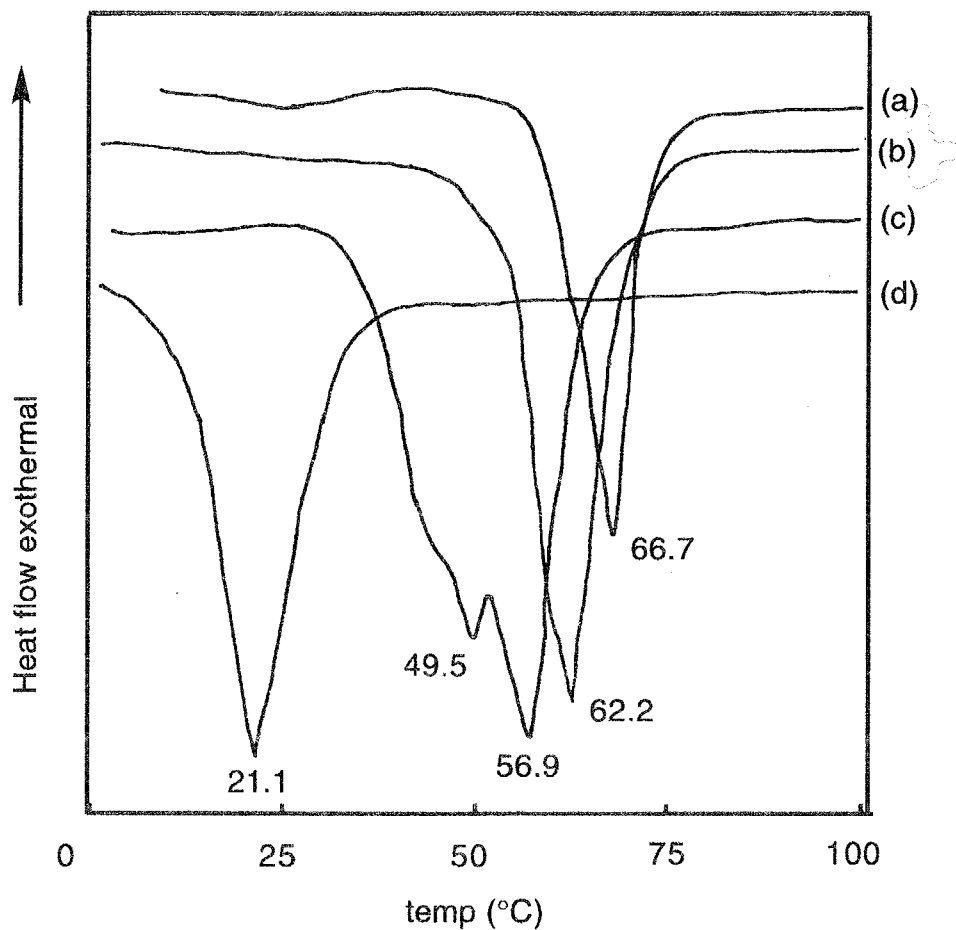


Figure 7. DSC traces of homo- and copolymers. (a) poly7CC ($M_n = 9000, M_w/M_n = 1.20$), (b) poly ϵ -CL ($M_n = 7300, M_w/M_n = 1.18$), (c) poly7CC-b- ϵ -CL ($M_n = 6800, M_w/M_n = 1.12$), (d) poly7CC-(ϵ -CL) ($M_n = 7900, M_w/M_n = 1.19$).

4-6 Summary

In this chapter, I have demonstrated the synthesis of well-defined copolymers of a seven-membered cyclic carbonate (7CC) and lactones (ϵ -CL and δ -VL) initiated with n -BuOH / HCl•Et₂O and H₂O / HCl•Et₂O initiator systems. The corresponding di- triblock, and random copolymers with narrow polydispersities were obtained quantitatively. As far as I know, this is one of the most convenient and successful block copolymer synthesis, using common and cheap reagents; n -butyl alcohol, H₂O, and HCl•Et₂O.

4-7 Experimental Section

Materials. CH_2Cl_2 was distilled sequentially over P_2O_5 and CaH_2 under nitrogen. ϵ -CL and δ -VL were purchased from Aldrich and distilled over CaH_2 under nitrogen prior to use. 7CC was prepared according to the literature and stored at $-20\text{ }^\circ\text{C}$ under nitrogen.⁷ *n*-Butyl alcohol was dried over CaH_2 and distilled under nitrogen. H_2O was distilled prior to use. A 2.0 mol/L HCl solution in diethyl ether (Et_2O) was purchased from Aldrich and used without further purification.

Measurements. ^1H NMR spectra were recorded with a JEOL Lambda-300 spectrometer. Number- and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Tosoh HLC-8120 system equipped with two consecutive polystyrene gel columns (G2500HXL and G4000HXL) eluted with tetrahydrofuran (THF) at a flow rate of 1.0 mL / min calibrated by standard polystyrenes. Differential scanning calorimetry (DSC) was performed with a SEIKO SSC-5200DSC-220C instrument. Samples were previously heated up to $150\text{ }^\circ\text{C}$ and slowly cooled down to $-100\text{ }^\circ\text{C}$. The melting enthalpies (ΔH_m) and melting temperatures (T_m) were then determined from the DSC endotherms recorded from -100 to $150\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

Polymerization of ϵ -CL and δ -VL. A typical procedure: All glass vessels were heated in vacuo before use, filled with and handled in a stream of dry nitrogen. To a solution of ϵ -CL (0.58 g, 5.0 mmol) in CH_2Cl_2 (4.5 mL) was added *n*-butyl alcohol (9.3 mg, 0.13 mmol). The polymerization was initiated by the addition of 65 μL (0.13 mmol) of HCl solution (2 mol / L) in Et_2O at $25\text{ }^\circ\text{C}$. After 4 h, the reaction mixture was poured into 300 mL of *n*-hexane to precipitate a polymer. The precipitate was filtered, and dried at $25\text{ }^\circ\text{C}$ for 5 h in vacuo to give 0.57 g of white powdery polymer (yield 99%).

Block Copolymerization. A typical procedure: To a solution of 7CC (0.58 g, 5.0 mmol) in CH_2Cl_2 (4.5 mL) was added *n*-butyl alcohol (13 mg, 0.17 mmol). The polymerization was initiated by the addition of 130 μL (0.26 mmol) of HCl solution (2 mol / L) in Et_2O at 25 °C. After confirming a quantitative conversion of 7CC by ^1H NMR, the copolymerization was conducted initiated by charging 0.57 g (5.0 mmol) of ϵ -CL into the reaction mixture with vigorous stirring. After the polymerization, the mixture was poured into 300 mL of *n*-hexane to precipitate a polymer. The precipitate was filtered, and dried at 25 °C for 5 h in vacuo to give 1.06 g of a white powdery copolymer (yield 92%).

Copolymerization on One-Shot Monomer Feeding. A typical procedure: To a solution of 7CC (0.23 g, 2.0 mmol) and ϵ -CL (0.23 g, 2.0 mmol) in CH_2Cl_2 (1.8 mL) were added *n*-butyl alcohol (28 mg, 0.34 mmol). The polymerization was initiated by the addition of 25 μL (0.50 mmol) of HCl solution (2 mol/L) in Et_2O at 25 °C for 36 h. After the polymerization, the mixture was poured into 300 mL of *n*-hexane to precipitate a polymer. The precipitate was filtered, and dried at 25 °C for 5 h in vacuo to give 0.44 g of a white viscous copolymer (yield 95%).

4-8 References

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Chapter 4.

Synthesis of Well-Defined Copolymers of Cyclic Carbonate with Lactone via Activated Monomer Mechanism

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Chapter 5

Novel Acid Promoted Living Ring-Opening Polymerization of Cyclic Carbonates Initiated with Borontrihalide

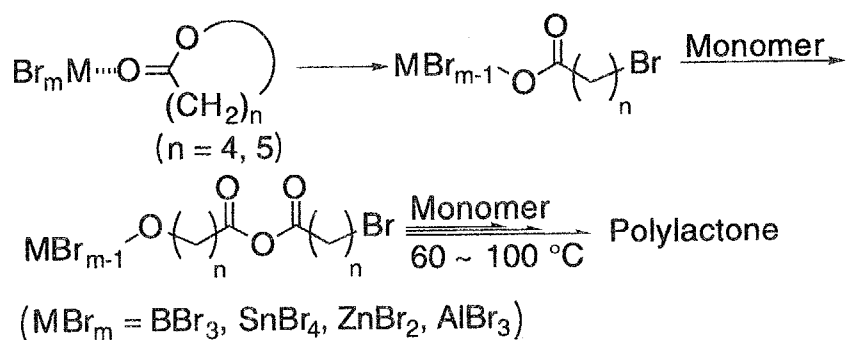
5-1 ABSTRACT

Ring-opening polymerization of a seven-membered cyclic carbonate, 1,3-dioxepan-2-one (7CC) was investigated with a novel initiator system, $\text{BX}_3 \cdot \text{HCl} \cdot \text{Et}_2\text{O}$ ($\text{X} = \text{Cl}$ and Br). After treatment of 7CC with BCl_3 in CH_2Cl_2 for 24 h, the addition of $\text{HCl} \cdot \text{Et}_2\text{O}$ promoted the controlled polymerization giving a corresponding polycarbonate quantitatively with a relatively narrow polydispersity (~ 1.15) at 0°C . The molecular weights of the obtained polymers showed good agreement with the values calculated from one-third of the feed ratio of the monomer to initiator, indicating that all the chlorine groups of BCl_3 initiated and propagated the polymerization of 7CC.

5-2 Introduction

Lewis acids are convenient and effective initiators for ring-opening polymerization of lactones,¹ lactides,² and cyclic carbonates.³ However, Lewis-acid-initiated ring-opening polymerization is usually accompanied by back-biting reactions forming cyclic oligomers, which makes it difficult to control the molecular weight of the polymers, especially at elevated temperature.⁴ Several attempts have been made to achieve controlled ring-opening polymerization by the combination of bulky substituents and Lewis acids.⁵ Endo et al. have recently reported the living ring-opening polymerization of a seven-membered cyclic carbonate, 1,3-dioxepan-2-one (7CC) by titanium bisphenolate complexes to produce the corresponding polycarbonate with a controlled molecular weight (M_n) and narrow polydispersity (M_w/M_n).^{5a} The resulting polymer has hydroxyl groups at the both ends, indicating that the initiator is an water and the polymerization proceeds via an activated monomer mechanism. Kricheldorf et al. have examined the polymerization of lactones with several Lewis acids in detail. They have suggested that some metal bromides with vacant p- or d-orbitals react with lactones to give ω -bromoalkanoic acids via complexation at the exocyclic oxygen and cleavage of the alkyl-oxygen bond. Consequently, the metal bromides with energetically favorable d-orbitals like SnBr_4 and ZnBr_2 , metal-oxygen bonds are formed to cause polymerization reactions via an insertion mechanism at 60 °C, where the M_w/M_n of the obtained polymers is ca. 1.7 (Scheme 1).⁶ The insertion mechanism of the ring-opening polymerization of a six-membered cyclic carbonate (6CC) has been also studied using TiCl_4 ^{3c} and several alkyltin (IV) chlorides^{3d} at 60 °C, where the M_n of the obtained polymer does not agree with a calculated value and the M_w/M_n is large (> 1.8). With aluminum alkoxide as an initiator for the insertion polymerization of 6CC at 100 °C, however, neither M_n nor M_w/M_n is controlled.^{3e}

Scheme 1



The reaction of substituted and unsubstituted six-membered cyclic carbonates (6CCs) with boron halogenides has been investigated.⁷ The equimolar reaction provides the corresponding complexes at 25 °C. With $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at 60 °C, the further addition of the monomer leads to polymerization producing the polycarbonate containing 1 ~ 2% of ether units due to decarboxylation. On the other hand, BCl_3 and BBr_3 react with 6CCs to give boron ω -halogenobutylcarbonates after the formation of complexes similar to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and 6CC. However these compounds show no polymerizability for the monomers. I describe here the ring-opening polymerization of 7CC with a novel initiator system, i.e., BX_3 ($\text{X} = \text{Cl}$ and Br) catalyzed by $\text{HCl} \cdot \text{Et}_2\text{O}$ to obtain the polycarbonate with controlled M_n and small M_w/M_n under mild conditions.

5-3 Polymerization of 7CC with borontrihalide

Scheme 2 and Table 1 summarize the conditions and results of the polymerization of 7CC in CH_2Cl_2 at 25 °C for 24 and 96 h with BX_3 ($\text{X} = \text{Cl}$ and Br) / $\text{HCl}\cdot\text{Et}_2\text{O}$. Addition of equimolar amount of $\text{HCl}\cdot\text{Et}_2\text{O}$ was not effective although 7CC was pretreated with BCl_3 at 25 °C for 24 h (run 1). On the other hand, P7CC was obtained in 69% conversion in BBr_3 in conjunction with an equiv of HCl for 24 h at 25 °C (run 6). The polymerization of 7CC proceeded quantitatively by charging 40 equiv of $\text{HCl}\cdot\text{Et}_2\text{O}$ after the reaction of 7CC with BCl_3 at 25 °C for 24 h, but the M_w/M_n s were broad (runs 2 ~ 4). The polymerization of 7CC with BBr_3 / $\text{HCl}\cdot\text{Et}_2\text{O}$ initiator system provided the P7CC in a good yield, and especially in the case of high feed ratio of the monomer to initiator, the M_w/M_n ratio was relatively small (run 7).

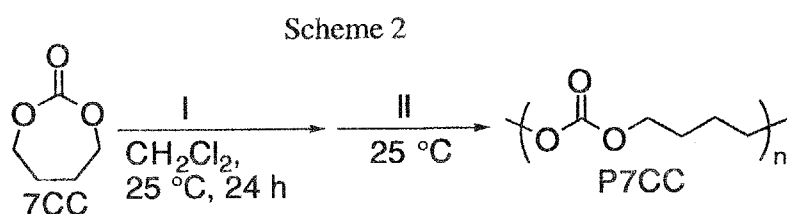


Table 1. Polymerization of 7CC^a

run	initiator system		temp (°C)	$[\text{M}]_0 / [\text{BCl}_3]_0$	time ^b (h)	conv ^c (%)	yield ^d (%)	M_n^e	M_w/M_n^e
	I (eq)	II (eq)							
1	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (1)	25	20	96	9	— ^f	— ^f	— ^f
2	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (40)	25	20	24	99	75	2200	1.26
3	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (40)	25	60	24	99	88	3300	1.29
4	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (40)	25	100	24	99	87	3500	1.43
5	BBr_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (30)	25	20	24	99	85	1300	1.39
6	BBr_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (1)	25	50	24	69	55	1400	1.17
7	BBr_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (30)	25	100	24	99	86	2300	1.16

^a $[\text{M}]_0 = 1 \text{ mol}\cdot\text{L}^{-1}$ in CH_2Cl_2 . ^bTime after the addition of II. ^cDetermined by ^1H NMR. ^dMethanol / *n*-hexane (1/1 vol/vol)-insoluble part. ^eDetermined by GPC (THF, polystyrene standards). ^fNot determined.

Figure 1 illustrates a first order kinetic plot for the polymerization of 7CC with $\text{BCl}_3\text{-HCl}\cdot\text{Et}_2\text{O}$ in CH_2Cl_2 at $25\text{ }^\circ\text{C}$ ($[\text{M}]_0 = 1\text{ mol/L}$, $[\text{HCl}]_0 / [\text{BCl}_3]_0 = 40$). It deviated from a linear relation at the early stage of the polymerization, which made the M_w/M_n much broader (1.29) than in the case of $\text{BBr}_3\text{-HCl}\cdot\text{Et}_2\text{O}$ initiator system. This acceleration might be attributed to the slow initiation in the system.

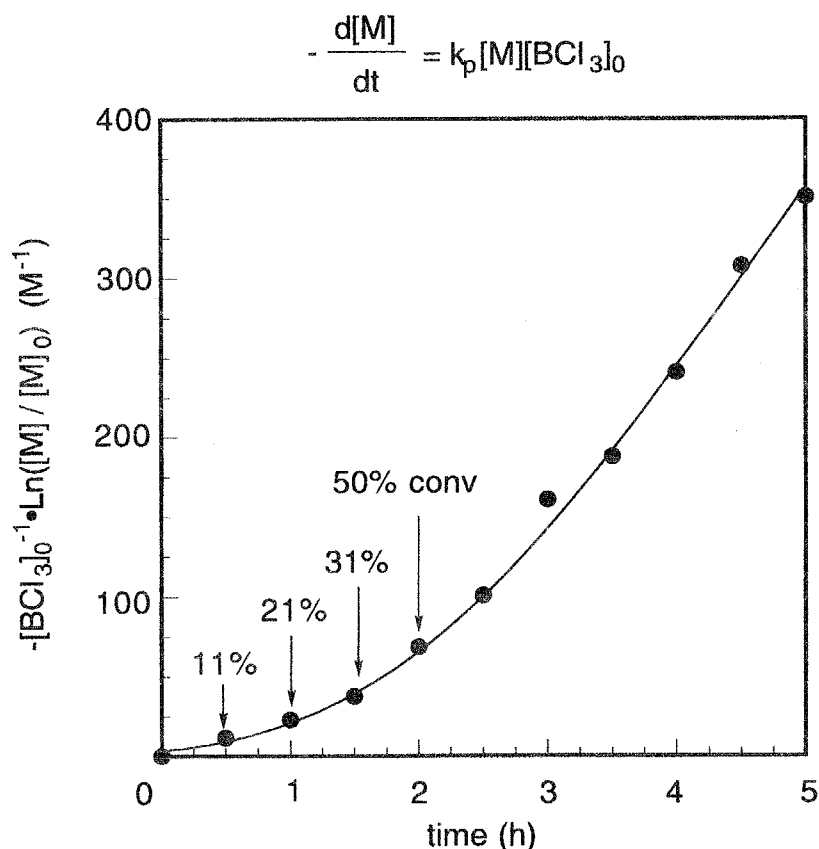


Figure 1. The first order kinetic plot for P7CC initiated with $\text{BCl}_3\text{-HCl}\cdot\text{Et}_2\text{O}$ at $25\text{ }^\circ\text{C}$

Figure 2 illustrates a first order kinetic plot for the polymerization of 7CC in CH_2Cl_2 at $0\text{ }^\circ\text{C}$ ($[\text{M}]_0 = 1\text{ mol/L}$, $[\text{HCl}]_0 / [\text{BCl}_3]_0 = 40$). The kinetic curve showed almost linear variation with small deviation at the early stage of the polymerization, different from Figure 1. In this case, the polymer was obtained quantitatively with a narrow M_w/M_n (1.15). The rate constant k_p was estimated as $10\text{ mol}^{-1}\cdot\text{L}\cdot\text{h}^{-1}$ ($[\text{H}^+]_0 / [\text{BCl}_3]_0 = 40$ at $0\text{ }^\circ\text{C}$), much smaller than that calculated in the polymerization of 7CC with $\text{B(OEt)}_3 / \text{HCl}\cdot\text{Et}_2\text{O}$ initiator system ($80\text{ mol}^{-1}\cdot\text{L}\cdot\text{h}^{-1}$, $[\text{H}^+]_0 / [\text{B(OEt)}_3]_0 = 20$ at $0\text{ }^\circ\text{C}$). This indicates that the

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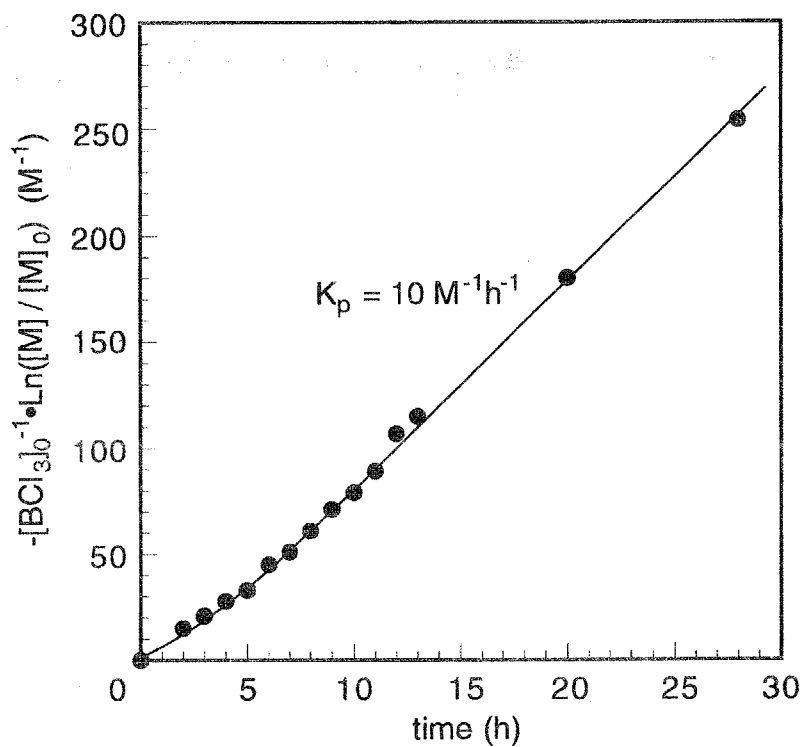


Figure 2. The first order kinetic plot for P7CC with $\text{BCl}_3\text{-HCl} \cdot \text{Et}_2\text{O}$ initiator system at 0°C

Scheme 3 and Table 2 summarize the results of the polymerization of 7CC with BCl_3 in CH_2Cl_2 at 0°C .

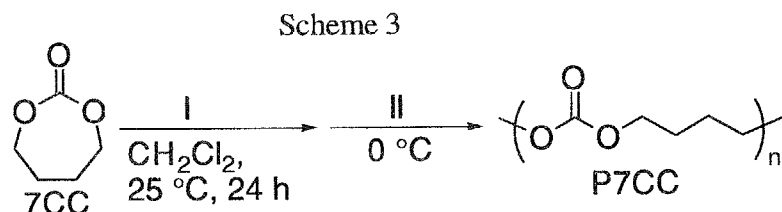


Table 2 Polymerization of 7CC^a

run	initiator system		$[\text{M}]_0 / [\text{BCl}_3]_0$	time ^b (h)	conv ^c (%)	yield ^d (%)	M_n^e	M_w/M_n^e
	I (eq)	II (eq)						
1	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (20)	100	48	39	— ^f	— ^f	— ^f
2	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (20)	100	96	92	85	4200	1.19
3	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (30)	100	48	93	83	4100	1.16
4	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (40)	60	24	99	92	3100	1.14
5	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (40)	100	48	99	85	3800	1.18
6	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (100)	200	48	99	90	6600	1.19
7	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (100)	400	96	99	90	11700	1.19

^a $[\text{M}]_0 = 1 \text{ mol}\cdot\text{L}^{-1}$ in CH_2Cl_2 . ^b Time after the addition of II. ^c Determined by ^1H NMR. ^d Methanol / *n*-hexane (1/1 vol/vol)-insoluble part. ^e Determined by GPC (THF, polystyrene standards). ^f Not determined.

Twenty equiv of $\text{HCl}\cdot\text{Et}_2\text{O}$ promoted 7CC polymerization to achieve 39% conversion for 48 h (run 1). The monomer was converted quantitatively for 96 h to provide the P7CC with relatively narrow M_w/M_n (1.19) (run 2). The amount of $\text{HCl}\cdot\text{Et}_2\text{O}$ slightly affected the M_n (runs 2, 3, and 5), while varying the feed ratio of 7CC to BCl_3 enabled a control of the M_n keeping narrow M_w/M_n (runs 4 ~ 7).

Figure 3 shows the dependence of the observed molecular weight $M_{n(\text{GPC})}$ and theoretical value ($M_{n(\text{theor})}$) calculated from one-third of $[\text{M}]_0 / [\text{BCl}_3]_0$ feed ratio as well as M_w/M_n ratio of the polymer on the monomer conversion. These were obtained in CH_2Cl_2 at 0°C initiated with 50 equiv of $\text{HCl}\cdot\text{Et}_2\text{O}$ into the mixture of 100 equiv of 7CC and BCl_3 .

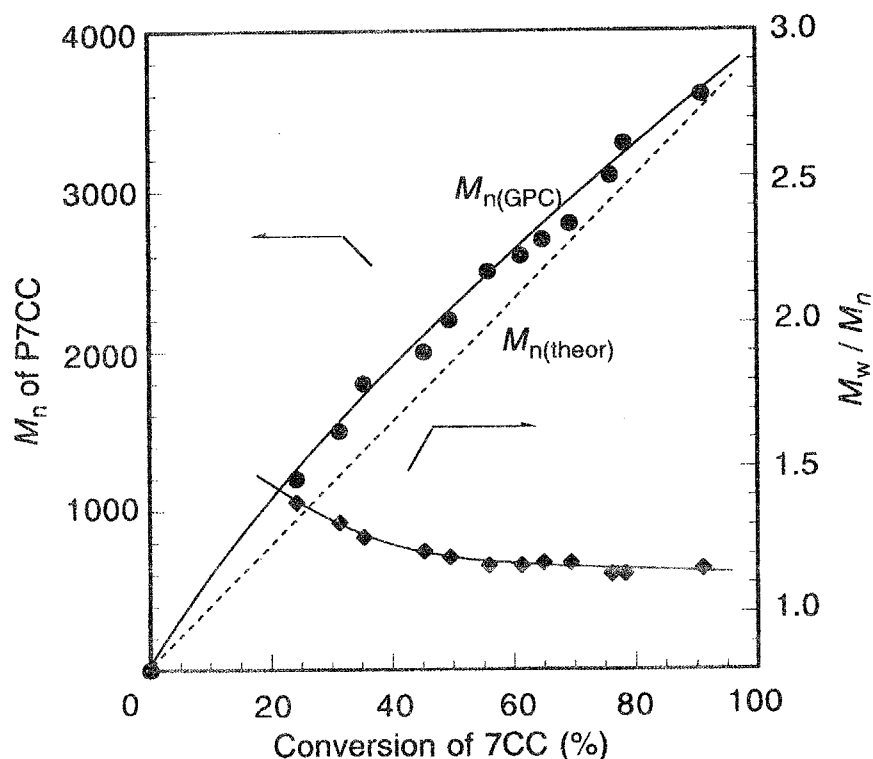
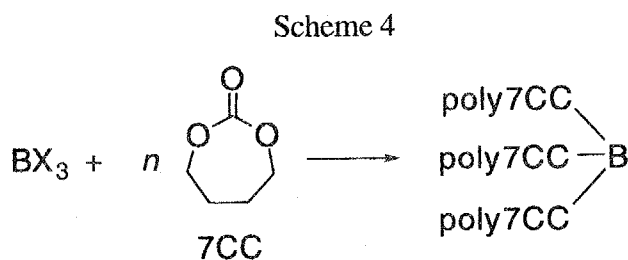


Figure 3. The dependence of the observed $M_{n(\text{GPC})}$ and theoretical $M_{n(\text{theor})}$ as well as M_w/M_n of the polymer on the 7CC conversion

The M_n value of the polymer increased with monomer conversion, whereas the M_w/M_n decreased from 1.38 to 1.13. The experimental plots showed relatively good agreement with theoretical ones ($M_{n(\text{theor})}$) calculated from one third of the monomer-boron feed ratio. Thus, three active sites of the polymer chain should be assembled on one boron compound as shown in Scheme 4.

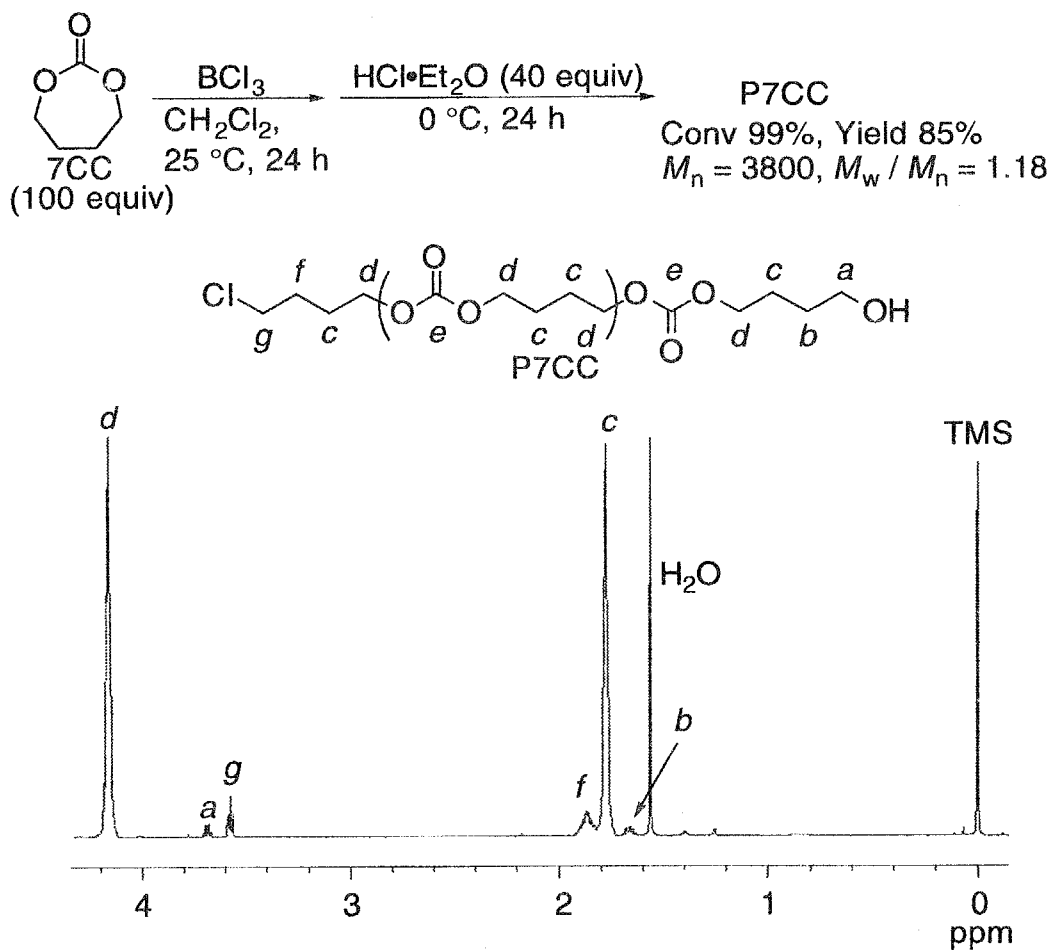


However, the observed M_n values were slightly higher than the theoretical ones, and the M_w/M_n was large (~ 1.38) in a low 7CC conversion, suggesting

Novel Acid Promoted Living Ring-Opening Polymerization of Cyclic Carbonates Initiated with Borontrihalide the slow initiation. These results were also supported the existence of small deviation in the kinetic study demonstrated in Figure 2.

Figure 4 depicts ^1H and ^{13}C NMR spectra of P7CC obtained by the polymerization of 7CC initiated with $\text{BCl}_3\text{-HCl}\cdot\text{Et}_2\text{O}$ in CH_2Cl_2 at $0\text{ }^\circ\text{C}$ (Scheme 5).

Scheme 5



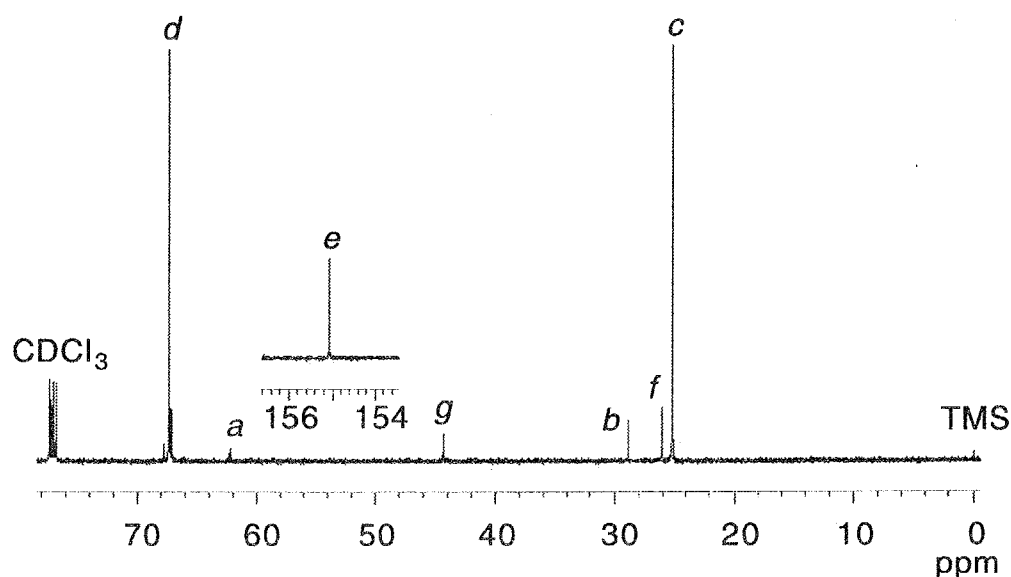


Figure 4. ^1H and ^{13}C NMR spectra (CDCl_3 at $25\text{ }^\circ\text{C}$) of P7CC initiated with $\text{BCl}_3\text{-HCl}\cdot\text{Et}_2\text{O}$ in CH_2Cl_2 at $0\text{ }^\circ\text{C}$

The ^1H NMR spectrum showed signals *a* and *b* assignable to α - and β -methylene protons of $-\text{OH}$ moiety at 3.69 and 1.66 ppm in addition to the signals *c* and *d* assignable to β - and α -methylene protons of carbonate group at 1.77 and 4.18 ppm. It also showed signals *f* and *g* assignable to β - and α -methylene protons of $-\text{Cl}$ moiety at 1.87 and 3.58 ppm. The ^{13}C NMR spectrum showed the corresponding signals *a* ~ *d*, *f*, and *g* at 62.16, 28.79, 25.06, 67.20, 26.01, and 44.30 ppm, respectively, along with signal *e* derived from a carbonyl carbon at 155.09 ppm. Contamination of polyether unit caused by decarboxylation could be negligible, because no signal was observed at 3.40 ~ 3.46 ppm at all in the ^1H NMR spectrum.⁸

To elucidate the living nature, the polymerization of 7CC was carried out with $\text{BCl}_3\text{-HCl}\cdot\text{Et}_2\text{O}$ initiator system in CH_2Cl_2 at $0\text{ }^\circ\text{C}$ ($[\text{M}]_0 = 1\text{ mol/L}$, $[\text{M}]_0 / [\text{BCl}_3]_0 = 100$, $[\text{HCl}]_0 / [\text{BCl}_3]_0 = 40$). After the quantitative monomer conversion, further addition of the same amount of monomer was recharged to conduct the postpolymerization. The elution peak in GPC shifted to the higher molecular weight region ($M_n = 7000$) than those of the starting polymer ($M_n = 3600$) without the formation of cyclic oligomers, where the M_w/M_n kept small value ($M_w / M_n = 1.17$) as shown in Figure 5.

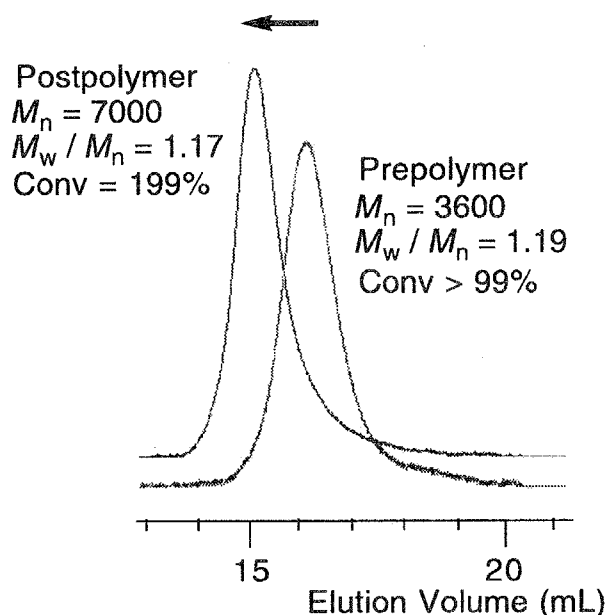


Figure 5. GPC profiles of the prepolymer obtained by the polymerization of 100 equiv of 7CC with $\text{BCl}_3\text{-HCl}\cdot\text{Et}_2\text{O}$ at 0°C , and the post polymer obtained by the further addition of same amount of 7CC

As shown in Table 3, the order of addition of the initiator components was the key feature for the controlled polymerization of 7CC. Premixing of $\text{HCl}\cdot\text{Et}_2\text{O}$ with 7CC, followed by BCl_3 charging caused the slow polymerization rate giving the polymer with broad M_w/M_n , probably due to the conventional cationic mechanism (runs 2 and 3).

Table 3 Polymerization of 7CC^a

run	initiator system		temp ($^\circ\text{C}$)	$[\text{M}]_0/[\text{BCl}_3]_0$	time ^b (h)	conv ^c (%)	yield ^d (%)	M_n^e	M_w/M_n^e
	I (eq)	II (eq)							
1	BCl_3 (1)	$\text{HCl}\cdot\text{Et}_2\text{O}$ (40)	0	60	24	99	92	3100	1.14
2	$\text{HCl}\cdot\text{Et}_2\text{O}$ (40)	BCl_3 (1)	0	60	24	18	— ^f	— ^f	— ^f
3	$\text{HCl}\cdot\text{Et}_2\text{O}$ (40)	BCl_3 (1)	0	60	89	99	86	3400	1.47

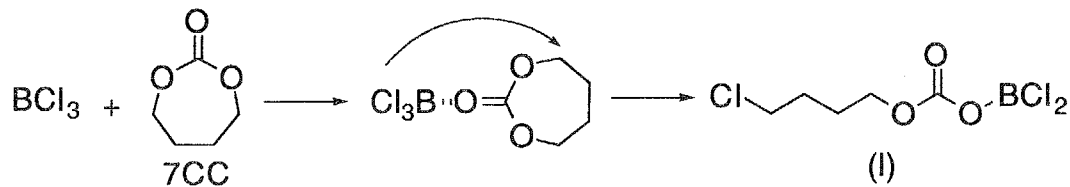
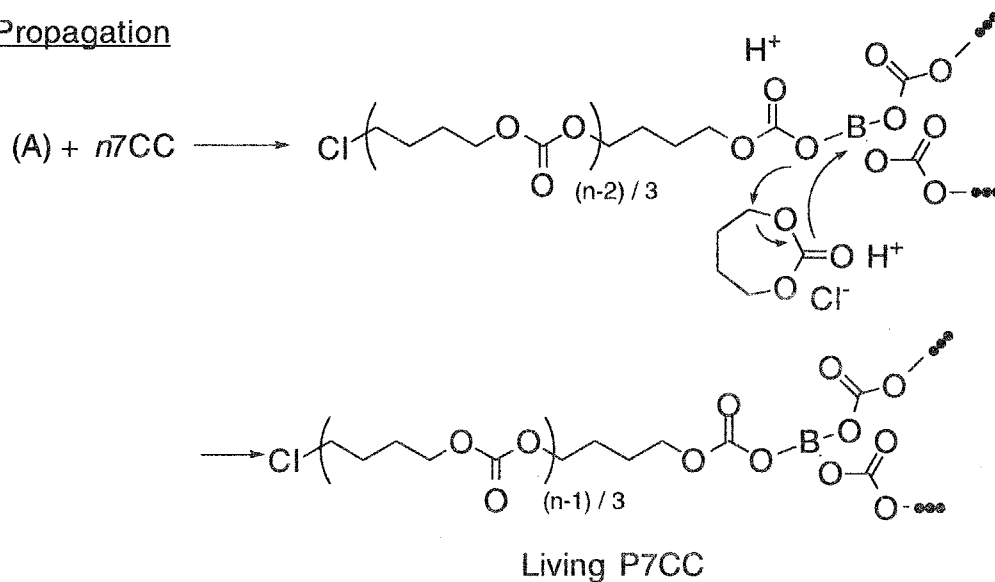
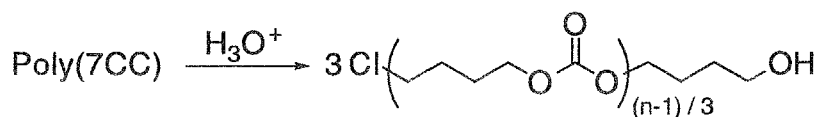
^a $[\text{M}]_0 = 1 \text{ mol/L}$ in CH_2Cl_2 . ^b Time after the addition of II. ^c Determined by $^1\text{H-NMR}$. ^d Methanol / *n*-hexane (1/1 vol/vol)-insoluble part.

^e Determined by GPC (THF, polystyrene standards). ^f Not determined.

Scheme 6 illustrates a plausible mechanism of the polymerization of 7CC with $\text{BCl}_3\text{-HCl}\cdot\text{Et}_2\text{O}$ in CH_2Cl_2 at 25°C . The coordination of the monomer to BCl_3 in its vacant site may be followed by the cleavage of the carbon-oxygen bond to give a boron ω -chlorobutylcarbonate (A) having insufficient initiating activity. The addition of $\text{HCl}\cdot\text{Et}_2\text{O}$ may promote the sequential monomer insertion between the boron-oxygen bond by the

Novel Acid Promoted Living Ring-Opening Polymerization of Cyclic Carbonates Initiated with Borontrihalide activation of the monomer, and/or loosening the boron-carbonate bond by coordination to the carbonate oxygen in the polymer propagating end.

Scheme 6

InitiationPropagationQuenching

5-4 Summary

In this Chapter, I demonstrated living ring-opening polymerization of a seven-membered cyclic carbonate (7CC) with $BX_3 \cdot HCl \cdot Et_2O$ ($X = Cl$ and Br) initiator system to obtain a monodisperse ($M_w/M_n \leq 1.19$) α -hydroxy- ω -halogenated polycarbonate (M_n 2000 ~ 12000). The addition of $HCl \cdot Et_2O$ into the mixture of 7CC and BCl_3 promoted the monomer insertion polymerization enable to produce the corresponding polycarbonate with a controlled M_n and narrow M_w/M_n as well as preventing decarboxylation reaction.

5-5 Experimental Section

Materials. BCl_3 solution in dichloromethane (1.0 mol/L) and HCl solution in diethyl ether (1.0 mol/L) were purchased from Aldrich and used without purification. 7CC was prepared according to the literature.⁹ Dichloromethane was washed with water, pre-dried with MgSO_4 , and sequentially distilled from P_2O_5 and CaH_2 .

Measurements. ^1H and ^{13}C NMR spectra were recorded with a JEOL Lambda-300 spectrometer. Number and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Tosoh HLC-8120 system equipped with two consecutive polystyrene gel columns eluted with tetrahydrofuran (THF) at a flow rate of 1.0 mL/min calibrated by standard polystyrenes.

Procedure. All manipulations were carried out in dry nitrogen atmosphere. A typical procedure was following: Into a 30 mL baked glass flask equipped with a three-way stopcock were placed 0.58 g (5.0 mmol) of 7CC and 3 mL of CH_2Cl_2 . To the resulted solution was added 50 μL (0.05 mmol) of BCl_3 solution in CH_2Cl_2 (1.0 mol/L) with a micro syringe, and the resulting mixture was stirred vigorously at 25 °C for 24 h. After that, the solution was cooled to 0 °C, then 2 mL (2.0 mmol) of HCl solution in Et_2O (1.0 mol/L) was added to the mixture and it was stirred for another 24 h. The reaction mixture was poured into 300 mL of methanol / hexane (1 / 1, volume ratio) to precipitate a polymer. The precipitate was filtered, and dried at 25 °C for 5 h *in vacuo*.

5-6 References

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Chapter 6.

Novel Acid Promoted Living Ring-Opening Polymerization of Cyclic Carbonates Initiated with Borontrialkoxide

Chapter 6

Novel Acid Promoted Living Ring-Opening Polymerization of Cyclic Carbonates Initiated with Borontrialkoxide

6-1 ABSTRACT

Ring-opening polymerization of cyclic carbonates (1,3-dioxepan-2-one and 5,5-dimethyl-1,3-dioxan-2-one) with triethyl and triisopropyl borates as initiators promoted by hydrogen chloride were investigated. The molecular weights of the obtained polymers could be controlled by the amount of alkylborates, and their polydispersity ratios were narrow (~ 1.15). The polymerization obeyed good first order kinetics throughout the reaction. After the monomers were completely consumed, the polymerization took place again when the same amount of monomers were introduced into the polymerization mixtures. ^1H and ^{13}C NMR spectroscopic studies confirmed that the polymerization proceeded in a living manner via insertion of the monomer to the boron-oxygen bond.

6-2 Introduction

Lewis acids play an important role in cationic ring-opening polymerization of cyclic monomers as well as of vinyl monomers. Though their versatility, these catalysts generally cause back biting reaction forming cyclic oligomers which makes it difficult to control the molecular weights (M_n s) and polydispersity ratios (M_w/M_n s) of the polymers.¹ The stoichiometric reaction between lactones with various Lewis acids has been studied, where ω -halogenated carboxylic acids are formed in all cases.² Especially, Lewis acids with energetically favorable d-orbitals like SnBr_4 and ZnBr_2 produce high M_n polymers (~ 70000) via an insertion mechanism at 60°C , although the M_w/M_n s of the formed polymers are broad (~ 1.7). Metal alkoxides have been investigated for ring-opening polymerizations of lactones as initiators.³ Intermolecular transesterification and backbiting reactions are negligible during the polymerization of ϵ -caprolactone when the polymerization is initiated with aluminum alkoxide, thus the linear polymer can be obtained free from cyclic oligomers.^{3a} Narrow M_w/M_n poly ϵ -caprolactone have been synthesized by aluminum triisopropoxide trimer as an initiator in quantitative yield.⁴ However, these aluminum complexes are not effective to obtain aliphatic polycarbonates with narrow M_w/M_n ratios via a ring-opening process.⁵ Ring-opening insertion polymerizations of six-membered cyclic carbonates with TiCl_4 ⁶ and alkyltin (IV) chloride initiators⁷ have been investigated to give the corresponding polycarbonates without decarboxylation reaction, but the M_n s can not be precisely controlled by changing the feed ratios, and the M_w/M_n s are broad (~ 1.7). The reaction of substituted and unsubstituted six-membered cyclic carbonates (6CC) with boron halogenides (F, Cl, Br), and the polymerization with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ have been investigated.⁸ All the boron compounds reacted with 6CC to give the crystalline complexes at 25°C , especially in the case of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ the further addition of the monomer at 60°C led to polymerization producing the polycarbonate containing 1 ~ 2% of polyether unit due to the decarboxylation reaction. BCl_3 and BBr_3 reacted with 6CC to give boron ω -halogenobutylcarbonates after the

Novel Acid Promoted Living Ring-Opening Polymerization of Cyclic Carbonates Initiated with Borontrialkoxide formation of complexes similar to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and 6CC. In Chapter 5, the study on BX_3 ($\text{X} = \text{Cl}$ or Br) for the polymerization of a non-substituted seven-membered cyclic carbonate (7CC) has revealed that the propagating species is stabilized with boron to afford a living polymer. However, the polymerization requires to premixing BX_3 and 7CC before initiation by charging $\text{HCl} \cdot \text{Et}_2\text{O}$, and therefore, the available monomers were somewhat restricted. I describe here a novel method for ring-opening polymerization of cyclic carbonates with boron alkoxides in the presence of $\text{HCl} \cdot \text{Et}_2\text{O}$ under mild conditions to give controlled M_n and M_w/M_n ratio polymers in high yields suppressing side reactions such as decarboxylation and back biting.

6-3 Living ring-opening polymerization of 7CC with $B(OEt)_3$ and $B(O-iPr)_3$ in the presence of $HCl \cdot Et_2O$

Scheme 1 and Table 1 summarize the results of the ring-opening polymerization of a non-substituted seven-membered cyclic carbonate (7CC) with $B(OEt)_3-HCl \cdot Et_2O$ and $B(O-iPr)_3-HCl \cdot Et_2O$ initiator systems in CH_2Cl_2 at 25 °C.

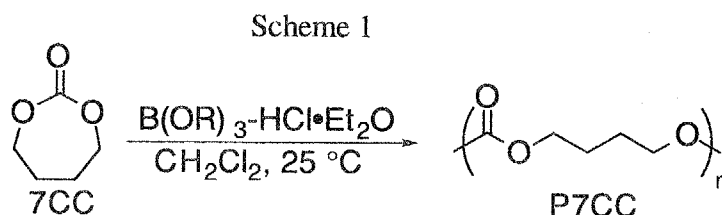


Table 1 Polymerization of 7CC initiated with trialkyl borates ^a

run	initiator system	$[M]_0 / [B^{3+}]_0$	$[HCl]_0 / [B^{3+}]_0$	conv ^b (%)	yield ^c (%)	M_n^d	M_w/M_n^d
1	$B(OEt)_3$	40	0	1	— ^e	— ^e	— ^e
2	$B(OEt)_3 / HCl \cdot Et_2O$	40	20	98	90	1900	1.19
3	$B(OEt)_3 / HCl \cdot Et_2O$	38	10	98	91	1800	1.16
4	$B(OEt)_3 / HCl \cdot Et_2O$	90	10	98	85	3500	1.17
5	$B(OEt)_3 / HCl \cdot Et_2O$	135	10	98	92	6500	1.14
6	$B(OiPr)_3$	40	0	0	— ^e	— ^e	— ^e
7	$B(OiPr)_3 / HCl \cdot Et_2O$	40	10	99	90	1700	1.15
8	$B(OiPr)_3 / HCl \cdot Et_2O$	55	10	99	92	2100	1.15

^aConditions; $[M]_0 = 1$ mol / L in CH_2Cl_2 at 25 °C for 24 h.

^bDetermined by ¹H NMR. ^cMethanol / *n*-hexane (1 / 1

volume ratio)-insoluble part. ^dDetermined by GPC

(THF, polystyrene standards). ^eNot determined.

In Chapter 2, I examined $HCl \cdot Et_2O$ as an initiator for the polymerization of 7CC in CH_2Cl_2 at 25 °C, but it did not work effectively. $B(OEt)_3$ alone did not serve as an initiator for the polymerization (run 1). The combination of $B(OEt)_3$ and $HCl \cdot Et_2O$ provided the polymer of 7CC quantitatively (runs 2 ~ 5). The M_n varied with the ratio of the borate to the monomer, but did not with the amount of $HCl \cdot Et_2O$ (runs 2 and 3). $B(O-iPr)_3$ also did not work as an initiator by itself (run 6). In the presence of 10 equiv of $HCl \cdot Et_2O$, it initiated the polymerization smoothly, where the M_n and M_w/M_n could be controlled (runs 7 and 8). Thus in these polymerizations, it

Novel Acid Promoted Living Ring-Opening Polymerization of Cyclic Carbonates Initiated with Borontrialkoxide was confirmed that $\text{HCl}\cdot\text{Et}_2\text{O}$ only served as a promoter for the polymerization of 7CC.

6-4 Living Polymerization of DM6CC with $\text{B}(\text{OEt})_3/\text{HCl}\cdot\text{Et}_2\text{O}$

Scheme 2 and Table 2 summarize the results of the polymerization of dimethyl substituted trimethylene carbonate (DM6CC) with $\text{B}(\text{OEt})_3\text{-HCl}\cdot\text{Et}_2\text{O}$ initiator system in CH_2Cl_2 at 25 °C.

Scheme 2

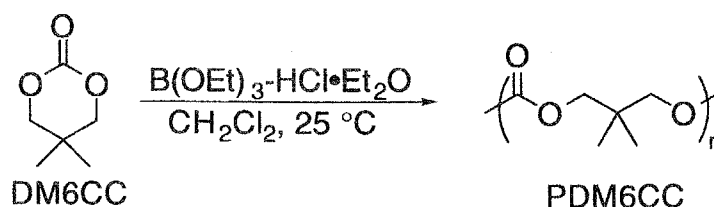


Table 2 Polymerization of DM6CC initiated with triethyl borate^a

run	initiator	$[\text{M}]_0 / [\text{B}^{3+}]_0$	$[\text{HCl}]_0 / [\text{B}^{3+}]_0$	time (h)	conv ^b (%)	yield (%)	M_n^c	M_w/M_n^c
1	$\text{B}(\text{OEt})_3$	30	0	48	0	— ^d	— ^d	— ^d
2	$\text{B}(\text{OEt})_3 / \text{HCl}\cdot\text{Et}_2\text{O}$	60	10	48	15	— ^d	— ^d	— ^d
3	$\text{B}(\text{OEt})_3 / \text{HCl}\cdot\text{Et}_2\text{O}$	30	20	48	86	81	1570	1.12
4	$\text{B}(\text{OEt})_3 / \text{HCl}\cdot\text{Et}_2\text{O}$	60	30	96	82	75	2200	1.11
5	$\text{B}(\text{OEt})_3 / \text{HCl}\cdot\text{Et}_2\text{O}$	90	30	96	91	83	2700	1.16
6	$\text{B}(\text{OEt})_3 / \text{HCl}\cdot\text{Et}_2\text{O}$	120	30	96	90	83	3100	1.11

^aConditions; $[\text{M}]_0 = 1 \text{ mol/L}$ in CH_2Cl_2 at 25 °C. ^bDetermined by ^1H NMR. ^cDetermined by GPC (THF, polystyrene standards). ^dNot determined.

Although $\text{B}(\text{OEt})_3$ showed no polymerizability (run 1), in the presence of more than 20 equiv of $\text{HCl}\cdot\text{Et}_2\text{O}$ to $\text{B}(\text{OEt})_3$ the corresponding polymers were obtained in high yield where the M_n s could be tailored varying with the monomer / initiator ratios keeping narrow M_w/M_n s (runs 3 ~ 6). The decrease of the $\text{HCl}\cdot\text{Et}_2\text{O}$ amount (10 equiv to $\text{B}(\text{OEt})_3$) resulted in significant decrease of monomer conversion (run 2). Again, these results suggested that $\text{HCl}\cdot\text{Et}_2\text{O}$ acted a promoter in this system.

6-5 Mechanistic Study

Figure 1 illustrates the first order kinetic plots for the polymerization of 7CC with $B(OEt)_3$ - $HCl \cdot Et_2O$ initiator system in CH_2Cl_2 at 25 °C varying with the amount of $HCl \cdot Et_2O$; $[HCl \cdot Et_2O]_0 / [B(OEt)_3]_0 = 5, 20, \text{ and } 50$.

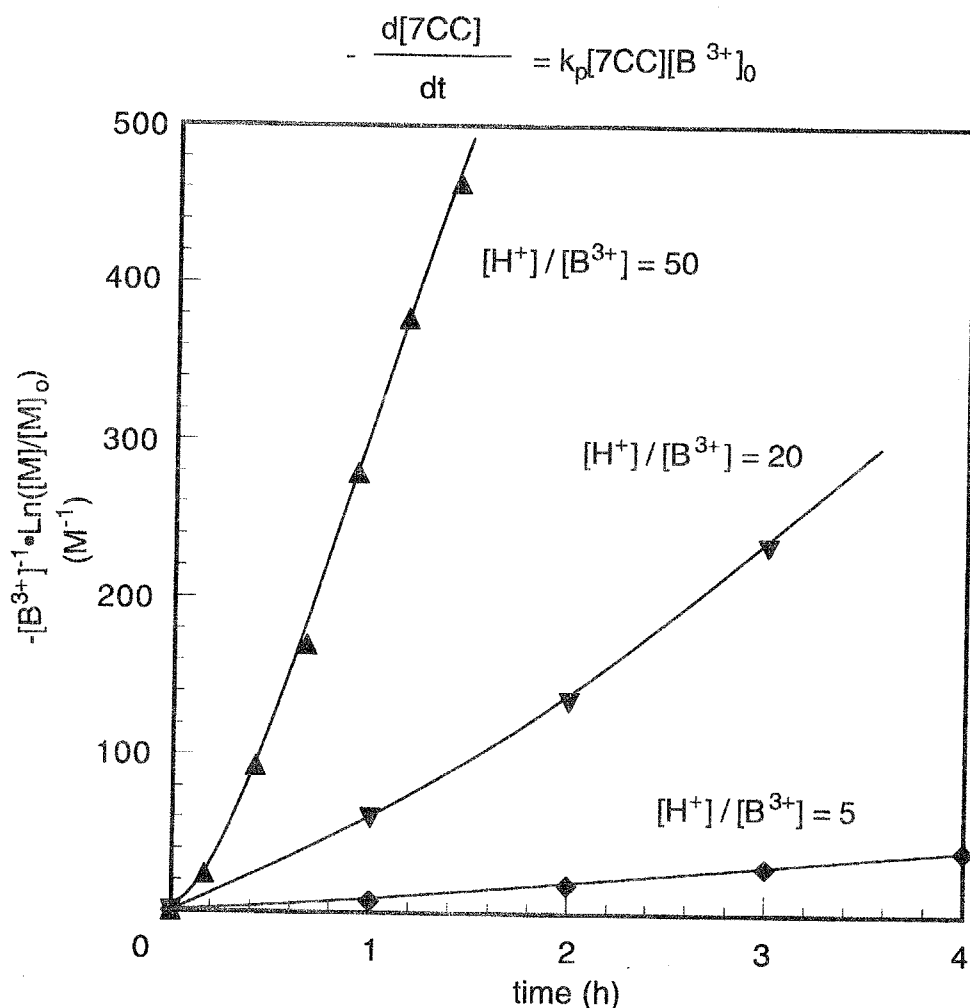


Figure 1. First order kinetic plots for the polymerization of 7CC. Conditions; in CH_2Cl_2 at 25 °C, $[M]_0 = 1 \text{ mol/L}$, $[HCl \cdot Et_2O]_0 / [B(OEt)_3]_0 = 5, 20, \text{ and } 50$.

They showed some acceleration in early stage becoming a linear variation to indicate that the absence of termination reaction, but slow initiation in the polymerization. The rate constants (k_p) of the 7CC polymerization above were estimated as 10, 87, and 340 $\text{mol}^{-1} \cdot \text{L} \cdot \text{h}^{-1}$, respectively. Figure 2 illustrates the first order kinetic plots for the DM6CC polymerization with $B(OEt)_3$ - $HCl \cdot Et_2O$ initiator system in CH_2Cl_2 at 25 °C,

Novel Acid Promoted Living Ring-Opening Polymerization of Cyclic Carbonates Initiated with Borontrialkoxide showing a linear variation to indicate the absence of termination. The rate constant (k_p) of the DM6CC polymerization at 25 °C ($[\text{HCl}\cdot\text{Et}_2\text{O}]_0 / [\text{B}(\text{OEt})_3]_0 = 20$) was estimated as $1.6 \text{ mol}^{-1}\cdot\text{L}\cdot\text{h}^{-1}$, much smaller than those of 7CC.

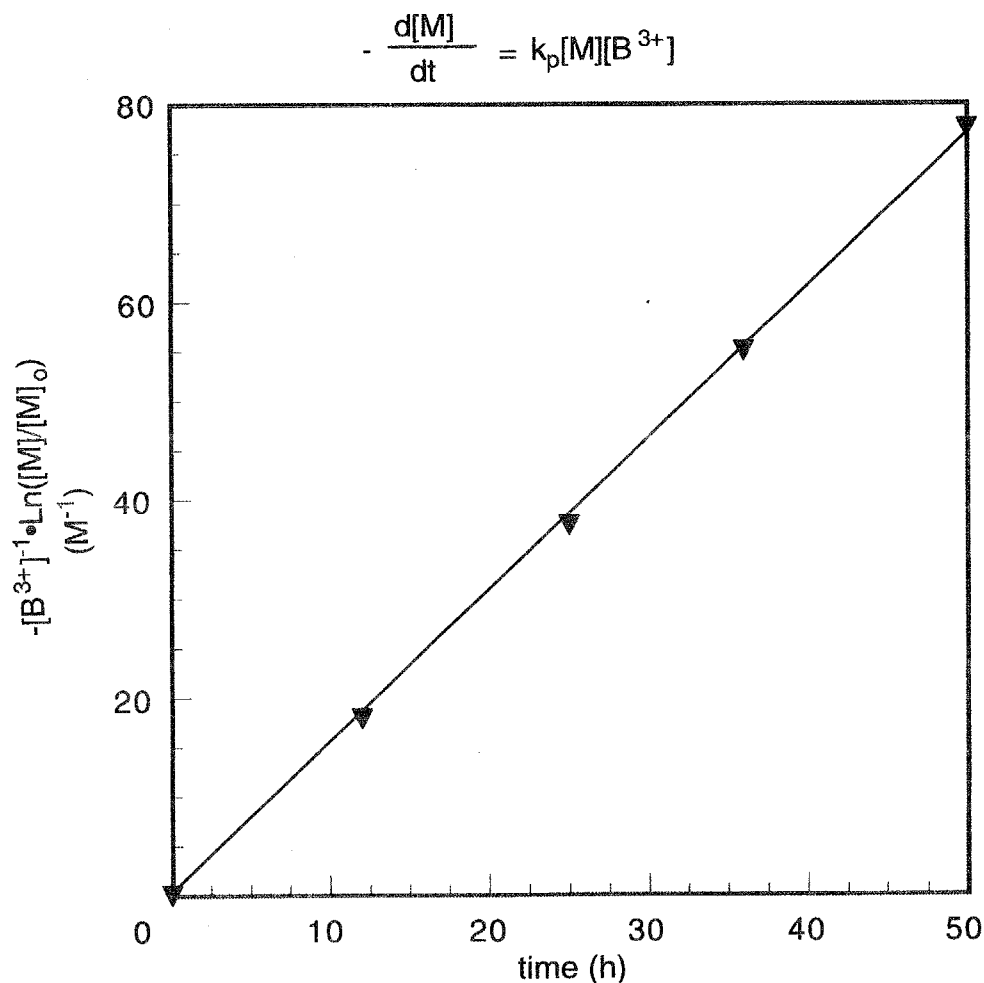


Figure 2. First order kinetic plot for the polymerization of DM6CC. Conditions; in CH_2Cl_2 at 25 °C, $[\text{M}]_0 = 1 \text{ mol/L}$, $[\text{HCl}\cdot\text{Et}_2\text{O}]_0 / [\text{B}(\text{OEt})_3]_0 = 20$.

To verify the living nature, the second feed experiments were carried out in the polymerization of 7CC and DM6CC. First, 90 and 60 equiv of 7CC and DM6CC were polymerized with $\text{B}(\text{OEt})_3\text{-HCl}\cdot\text{Et}_2\text{O}$ initiator system in CH_2Cl_2 to obtain the prepolymers, respectively. After the quantitative consumption of the first monomers confirmed by ^1H NMR, the polymerization mixtures were kept stirring for another 24 h. Then, the same amounts of the monomers were recharged into the polymerization mixtures to conduct the

Novel Acid Promoted Living Ring-Opening Polymerization of Cyclic Carbonates Initiated with Borontrialkoxide post polymerization, respectively. In both cases the elution peaks in GPC shifted to the higher M_n region without the formation of cyclic oligomers, where the M_w/M_n values kept small (Figure 3).

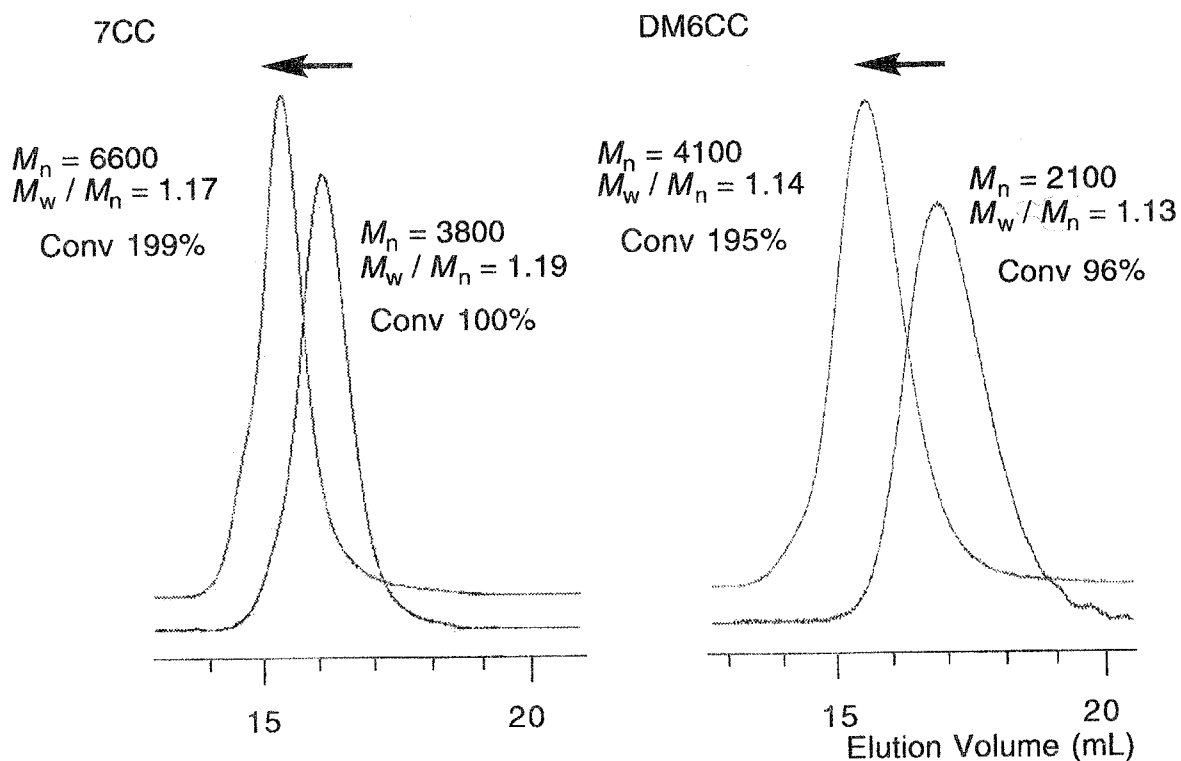


Figure 3. GPC profiles of the prepolymers obtained by the polymerization of 90 equiv of 7CC and 60 equiv of DM6CC with $B(OEt)_3$ in the presence of $HCl \cdot Et_2O$ (10 and 30 equiv vs $B(OEt)_3$), and the postpolymers obtained by the addition of the same amounts of the monomers.

Figure 4 (A) illustrates the ^1H NMR spectrum of P7CC obtained by the polymerization in run 3 in Table 1. In addition to signals *c* and *d* assignable to α - and β -methylene protons of the carbonate moiety at 4.17 and 1.75 ppm, signals *a* and *f* assignable to terminal methyl and α -methylene proton signals of a hydroxyl group were observed at 1.30 and 3.68 ppm respectively. The integration ratio of the signals *a* to *f* was 3 / 2, which agreed well to the theoretical value.

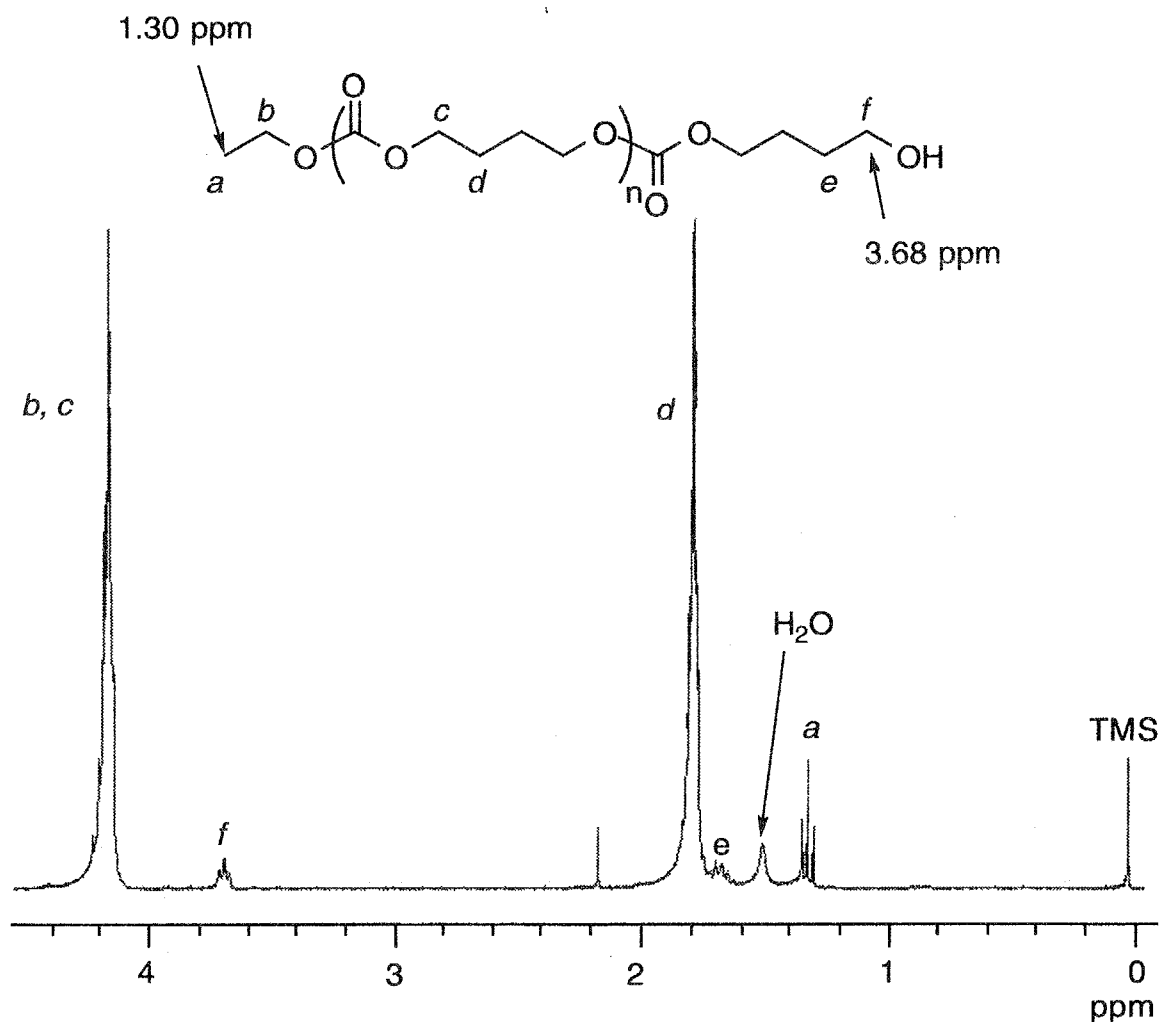


Figure 4 (A). ^1H NMR spectrum (300 MHz, CDCl_3) of P7CC obtained by the polymerization in run 3 in Table 1.

Figure 4 (B) illustrates the ^1H NMR spectrum of PDM6CC obtained by the polymerization in run 3 in Table 2. In addition to signals *c* and *d* assignable to α -methylene and γ -methyl protons of the carbonate moiety at 3.98 and 1.00 ppm, signals *a* and *f* assignable to terminal methyl and α -methylene proton signals of a hydroxyl group were observed at 1.30 and 3.36 ppm respectively. The integration ratio of the signals *a* to *f* was 3 / 2, which agreed well to the theoretical value.

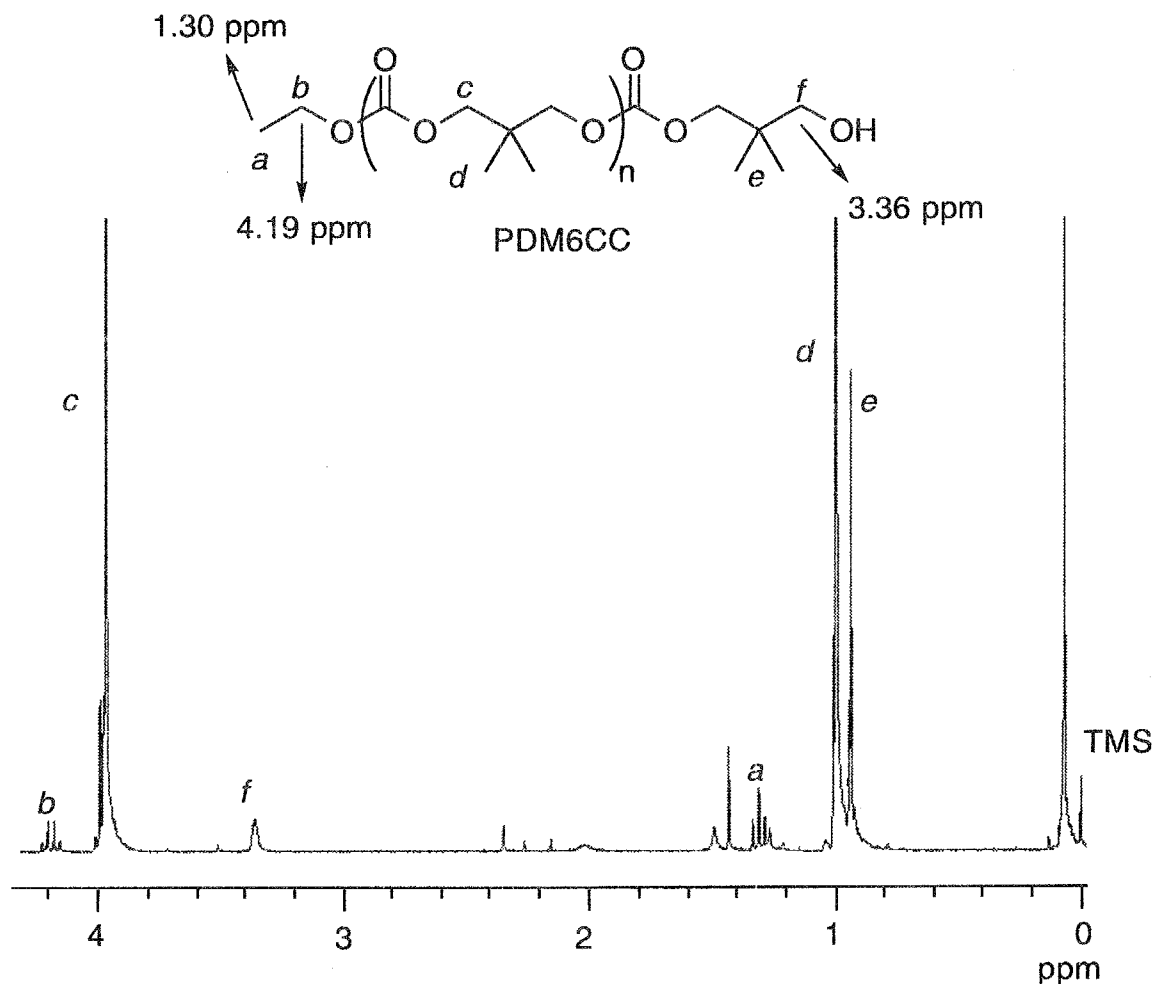


Figure 4 (B) ^1H NMR spectrum (300 MHz, CDCl_3) of PDM6CC obtained by the polymerization in run 3 in Table 2.

Table 3 summarizes the dependence of the average unit number of the oligo 7CC estimated by ^1H NMR ($x_{(\text{NMR})}$) and GPC ($x_{(\text{GPC})}$) on the feed ratio of the monomer to initiator. The both values almost agreed with 1 / 3 of the $[\text{M}]_0 / [\text{B}(\text{OEt})_3]_0$, suggesting that all the three ethoxide moieties on the boron initiated the polymerization.

Table 3 Polymerization of 7CC^a

run	$[M]_0 / [B(OEt)_3]_0$	conv ^b (%)	$x_{(NMR)}$ ^c	$x_{(GPC)}$ ^d	M_w / M_n ^d
1	9	99	3.7	3.8	1.37
2	18	99	5.2	9.8	1.20
3	27	99	7.3	13	1.15
4	45	91	14	18	1.14
5	50	99	17	21	1.14

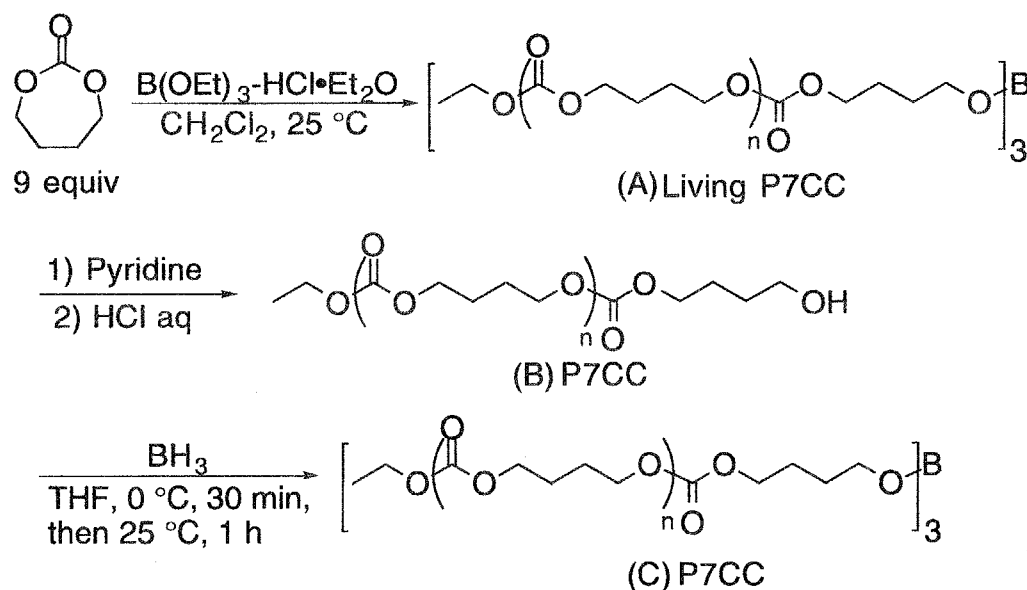
^aConditions; in CH₂Cl₂ at 25 °C for 24 h, $[M]_0 = 1$ mol/L,

$[HCl]_0/[B(OEt)_3]_0 = 10$. ^bDetermined by ¹H NMR.

^cAverage unit number calculated by ¹H NMR. ^dAverage unit number calculated by GPC (polystyrene standards, THF).

Figure 5 illustrates the ¹³C NMR spectra of (A) living P7CC obtained by the polymerization of 7CC with B(OEt)₃-HCl·Et₂O initiator system, (B) P7CC obtained by quenching the living P7CC with pyridine, followed by washing with HCl aq and subsequent extraction with toluene, (C) and P7CC treated with BH₃ in THF at 0 °C for 30 min, then 25 °C for 1 h (Scheme 3).

Scheme 3



Signals *a* ~ *d* assignable to terminal ethyl group and α - and β -methylenes of the carbonate moiety were observed in all the samples.

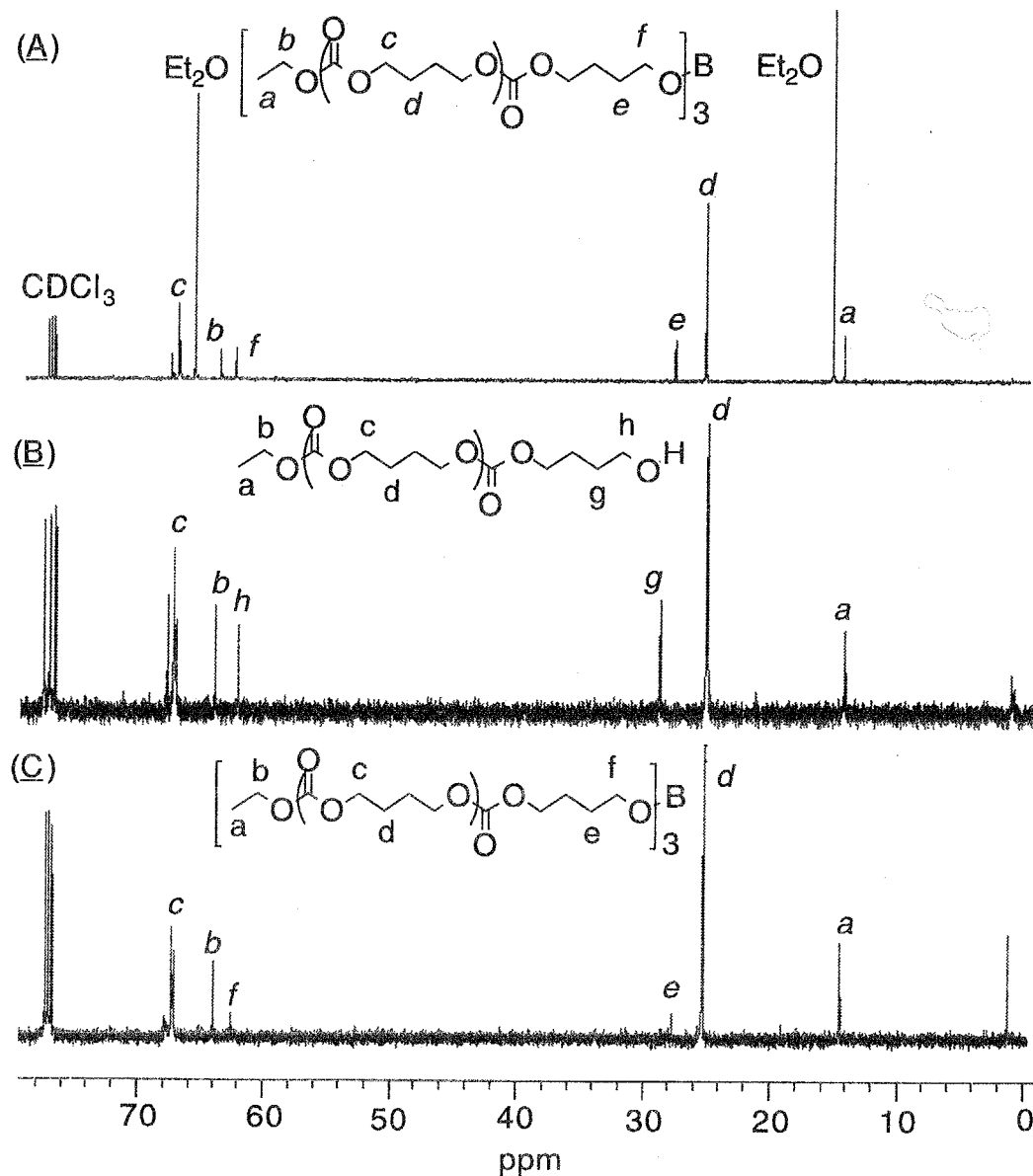


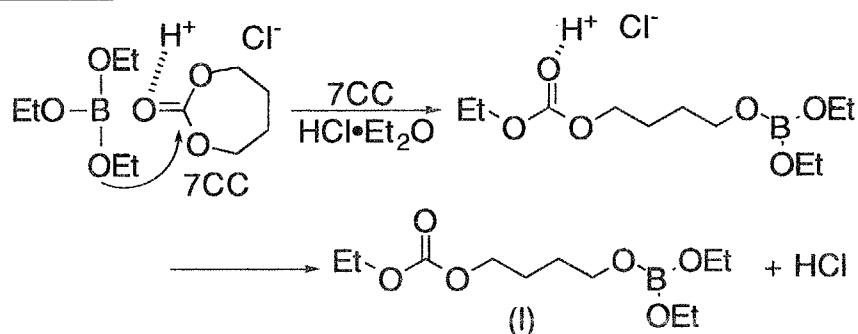
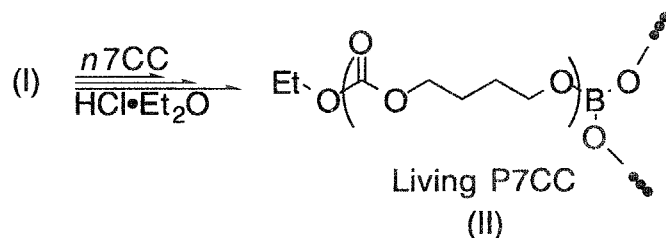
Figure 5. ^{13}C NMR spectra (75 MHz, CDCl_3) of (a) living P7CC obtained by the polymerization of 7CC (9 equiv) with $\text{B}(\text{OEt})_3 \cdot \text{HCl} \cdot \text{Et}_2\text{O}$ (1 / 10 molar ratio) in CDCl_3 at 25 °C for 12 h, (b) P7CC obtained by quenching the living P7CC with pyridine, followed by washing with HCl aq and subsequent extraction with toluene, (c) and P7CC treated with BH_3 in THF at 0 °C for 30 min, then 25 °C for 1 h.

In Figure 5A, signals *e* and *f* adjacent to a borate moiety were observed at 27.3 and 62.3 ppm, respectively. In Figure 5B, the two signals disappeared while signals *g* and *h* assignable to β - and α -methylenes of a hydroxyl group appeared at 28.8 and 62.1 ppm, respectively. In Figure 5C, signals *e* and *f* assignable to the β - and α -methylenes of the terminal borate moiety appeared again at 27.5 and 62.5 ppm, respectively. These results indicate that the

Novel Acid Promoted Living Ring-Opening Polymerization of Cyclic Carbonates Initiated with Borontrialkoxide propagating polymer end should be a stable borate structure. The formation of a hydroxyl chain end by protonation of the terminal borate with HCl was negligible by these results.

Scheme 4 depicts the possible mechanism of the polymerization of 7CC with $B(OEt)_3 \cdot HCl \cdot Et_2O$ initiator system.

Scheme 4

InitiationPropagation

The ethoxide group of the borate attacks the monomer activated with $HCl \cdot Et_2O$ to reproduce the borate structure (I). The propagation proceeds via the activated monomer insertion to the B-O bond. Consequently, the polymer isolated after hydrolysis by HCl aq has ethyl carbonate and hydroxyl groups as the initial and terminal units, respectively.

6-6 Summary

In this Chapter, I have demonstrated the novel HCl promoted controlled ring-opening polymerization of a non-substituted seven-membered (7CC) and dimethyl substituted six-membered cyclic carbonates (DM6CC) with $B(OR)_3$ ($R = Et$ and iPr) as the initiator to obtain monodisperse ($M_w/M_n < 1.15$) living polymers. The addition of $HCl \cdot Et_2O$ promoted the monomer insertion to the B-O bond at ambient temperature to produce the corresponding polymers with controlled M_n s and narrow M_w/M_n s.

6-7 Experimental Section

Materials. CH_2Cl_2 and CDCl_3 were distilled sequentially over P_2O_5 and CaH_2 under nitrogen. The monomers, 1,3-dioxepan-2-one (7CC)⁹ and 5,5-dimethyl-1,3-dioxan-2-one (DM6CC)¹⁰ were prepared according to the literature and stored at $-20\text{ }^\circ\text{C}$ under nitrogen. Triethyl borate [$\text{B}(\text{OEt})_3$] and triisopropyl borate [$\text{B}(\text{O-}i\text{Pr})_3$] were purchased from Aldrich and distilled under nitrogen before use. A 2.0 M HCl solution in diethyl ether (Et_2O) was purchased from Aldrich and used without further purification.

Measurements. ^1H and ^{13}C NMR spectra were recorded with a JEOL Lambda-300 spectrometer. Number and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Tosoh HLC-8120 system equipped with two consecutive polystyrene gel columns eluted with tetrahydrofuran (THF) at a flow rate of $1.0\text{ mL}\cdot\text{min}^{-1}$ calibrated by standard polystyrenes.

Polymerization. All manipulations were carried out under dry nitrogen. Typical procedure was following: Into a 30 mL baked glass flask equipped with a three-way stopcock was placed a solution of 0.116 g (1.0 mmol) of 7CC and 20 μL (0.010 mmol) of $\text{B}(\text{OEt})_3$ in 0.9 mL of CH_2Cl_2 . The polymerization was initiated by the addition of 50 μL (0.10 mmol) of a HCl solution (2 M) in Et_2O at $25\text{ }^\circ\text{C}$. After a set time the reaction mixture was poured into 100 mL of methanol / *n*-hexane (1 / 1 volume ratio) to precipitate a polymer.¹¹ The precipitate was filtered, washed sequentially with methanol (5 mL), *n*-hexane (5 mL), and dried in vacuo at $25\text{ }^\circ\text{C}$ for 5 h.

6-8 References and Notes

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- 11) In DM6CC polymerization, the reaction mixture was diluted with CH_2Cl_2 , washed with Na_2CO_3 aq, and dried in vacuo at 25 °C for 5 h.

Chapter 7

Novel Acid Promoted Living Ring-Opening Polymerization of Lactones Initiated with Borontrialkoxide

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7-1 ABSTRACT

Acid promoted ring-opening polymerization of ϵ -caprolactone (ϵ -CL) and δ -valerolactone (δ -VL) with triethylborate [$B(OEt)_3$] was investigated. Poly- ϵ -CL and poly δ -VL with controlled molecular weights (~ 12000) and small polydispersity ratios (1.05 \sim 1.20) were obtained quantitatively when the polymerization was conducted with $B(OEt)_3/HCl$ in CH_2Cl_2 and with $B(OEt)_3/CF_3CO_2H$ in tetrahydrofuran, respectively. The post polymerization of δ -VL after quantitative monomer conversion successfully proceeded keeping a narrow polydispersity ratio (1.07), which suggested that the polymerization proceeded via living fashion.

7-2 Introduction

Ring-opening polymerization is utilized for industrial production of nylon-6, polyepoxides, polyformaldehyde, polytetrahydrofuran, polylactones, and polyglycolides. Some of them can be synthesized by other methods like polycondensation, but it's generally difficult to obtain polymers with desired molecular weights and narrow polydispersity ratios. Aliphatic polylactones, polycarbonates, polylactide, and their copolymers are of great interest in applications to medical fields such as surgical sutures and drug delivery mediums. Many efforts have been made to prepare precisely controlled molecular weight polymer, because it plays an important role to control the rates of degradation rate and drug release *in vivo*.¹ A metal alkoxide is one of the most effective initiator for ring-opening polymerization of heterocyclic monomers such as lactones and lactide.² Intermolecular transesterification and backbiting are negligible during the polymerization of ϵ -caprolactone initiated with aluminum alkoxides, affording poly ϵ -caprolactone with a narrow polydispersity, free from cyclic oligomers.^{2c} Narrow M_w/M_n poly ϵ -caprolactone have been successfully synthesized by diethylaluminum ethoxide or aluminum isopropoxide trimer as an initiator in quantitative yield.³ However, aluminum alkoxides are not effective to obtain aliphatic polycarbonates with narrow polydispersities.⁴ In chapter 5, I demonstrated that a seven-membered cyclic carbonate (7CC) underwent controlled ring-opening polymerization with $\text{BCl}_3 / \text{HCl}\cdot\text{Et}_2\text{O}$ initiator to give the corresponding polycarbonate with predictable M_n and narrow M_w/M_n ratio. However, the initiator system required two-stage reaction, i.e., reaction of 7CC with BCl_3 followed by activation with $\text{HCl}\cdot\text{Et}_2\text{O}$, and the rate of propagation was rather slow due to its monomer insertion mechanism between boron and carbonate moieties. In chapter 6, I demonstrated a novel initiator system, borate in conjunction with $\text{HCl}\cdot\text{Et}_2\text{O}$, which polymerized six-membered as well as seven-membered cyclic carbonates in living fashion via monomer insertion mechanism between boron and alkoxide moieties. The

Chapter 7.

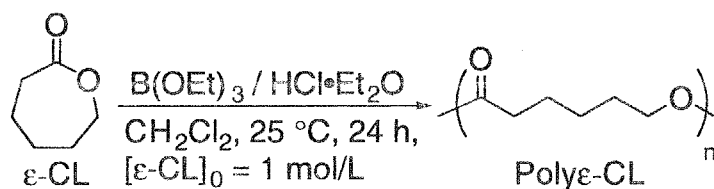
Novel Acid Promoted Living Ring-Opening Polymerization of Lactones Initiated with Borontrialkoxide

rate of polymerization was faster about ten times than that with $\text{BCl}_3 / \text{HCl} \cdot \text{Et}_2\text{O}$ initiator system. In this chapter, I describe the controlled ring-opening polymerization of ϵ -caprolactone and δ -valerolactone with $\text{B}(\text{OEt})_3$ promoted by protonic acid.

7-3 Ring-Opening Polymerization of ϵ -Caprolactone with $B(OEt)_3$ / $HCl \cdot Et_2O$ Initiator System

In chapter 6, I investigated the acid promoted ring-opening polymerization of cyclic carbonates initiated with $B(OEt)_3$ and $B(O-iPr)_3$ promoted with HCl to give the corresponding polycarbonates with controlled molecular weights and narrow polydispersities. Thus, HCl was first examined as an activator for the polymerization of ϵ -CL with $B(OEt)_3$ initiator. Table 1 summarizes the results of the ring-opening polymerization of ϵ -caprolactone (ϵ -CL) with $B(OEt)_3$ / $HCl \cdot Et_2O$ initiator system in CH_2Cl_2 at 25 °C (Scheme 1).

Scheme 1

Table 1 Polymerization of ϵ -CL with $B(OEt)_3$ / HCl ^a

run	$[\epsilon\text{-CL}]_0 / [B(OEt)_3]_0$	$[HCl]_0 / [B(OEt)_3]_0$	conv ^b (%)	yield ^c (%)	M_n^d	M_w/M_n^d
1	100	5	99	94	4600	1.13
2	100	50	98	93	4100	1.20
3	27	10	99	95	1500	1.17
4	60	10	99	95	2900	1.17
5	100	10	98	94	4000	1.11
6	120	10	99	94	5000	1.17
7	180	10	99	96	7700	1.19

^a $[\epsilon\text{-CL}]_0 = 1$ mol/L in CH_2Cl_2 at 25 °C for 24h.

^b Determined by ¹H NMR. ^c *n*-Hexane-insoluble part.

^d Determined by GPC (THF, polystyrene standards).

^e Not determined.

The combination of $B(OEt)_3$ and $HCl \cdot Et_2O$ initiated the polymerization of ϵ -CL to afford the polymers quantitatively, where the molecular weights (M_n) of the polymers could be varied with the ratio of the monomer to $B(OEt)_3$ (runs 3 ~ 6), not that to $HCl \cdot Et_2O$ (runs 1, 2, and 5). Thus, $HCl \cdot Et_2O$ only worked as a promoter for the polymerization of ϵ -CL in this system. Figure 1 illustrates the M_n dependence of poly ϵ -CL on the feed ratio of ϵ -CL to $B(OEt)_3$. The M_n increased with the feed ratio, and well agreed with one-third

of the value calculated from the feed ratio, keeping a narrow M_w/M_n . Thus, it was suggested that all the ethoxide moieties of the borate initiated and propagated the polymerization (Scheme 2).

Scheme 2

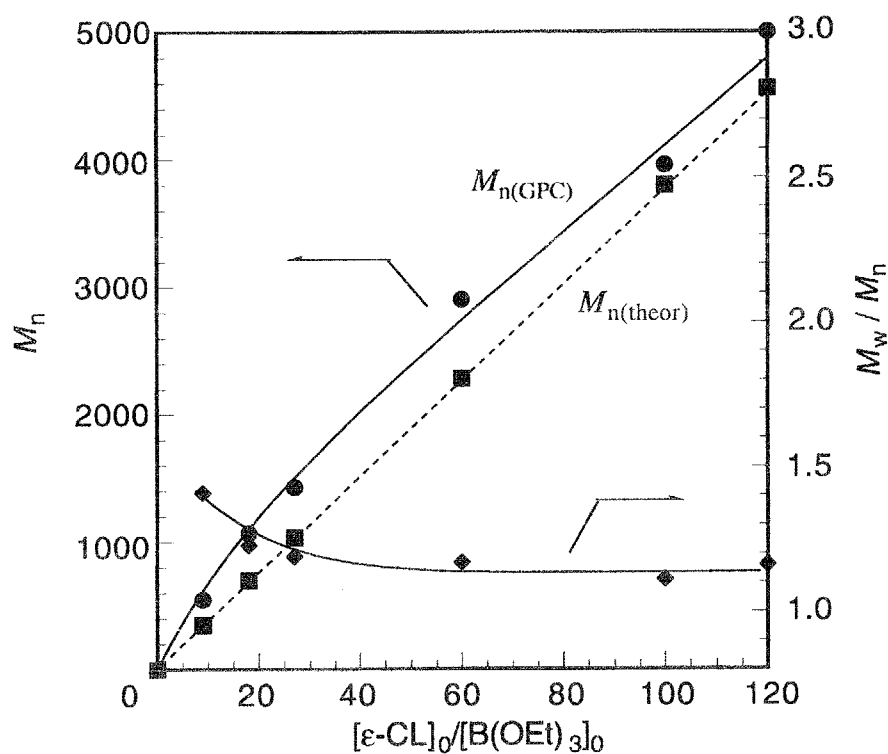
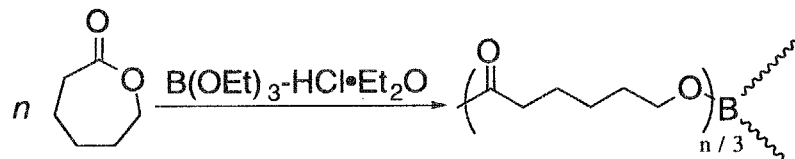


Figure 1. Dependence of M_n and M_w/M_n of poly- ϵ -CL on $[\epsilon\text{-CL}]_0/[\text{B}(\text{OEt})_3]_0$. Conditions; $[\epsilon\text{-CL}]_0=1$ mol/L in CH_2Cl_2 at 25 °C. $[\text{HCl}]_0/[\text{B}(\text{OEt})_3]_0=20$. $M_{n(\text{theor})} = \{[\text{M}]_0 / [\text{B}(\text{OEt})_3]_0 \times 114 \times \text{Conversion}\} / 3$

Figure 2 illustrates the first order kinetic plot for the polymerization of ϵ -CL with $B(OEt)_3$ -HCl \cdot Et₂O initiator system in CH₂Cl₂ at 25 °C ($[HCl]_0 / [B(OEt)_3] = 20$). A linear relationship was observed, where the rate constant was evaluated as $k_{p(CL)} = 31 \text{ mol}^{-1}\cdot\text{L}\cdot\text{h}^{-1}$ ($[M]_0 = 1 \text{ mol/L}$, 25 °C).

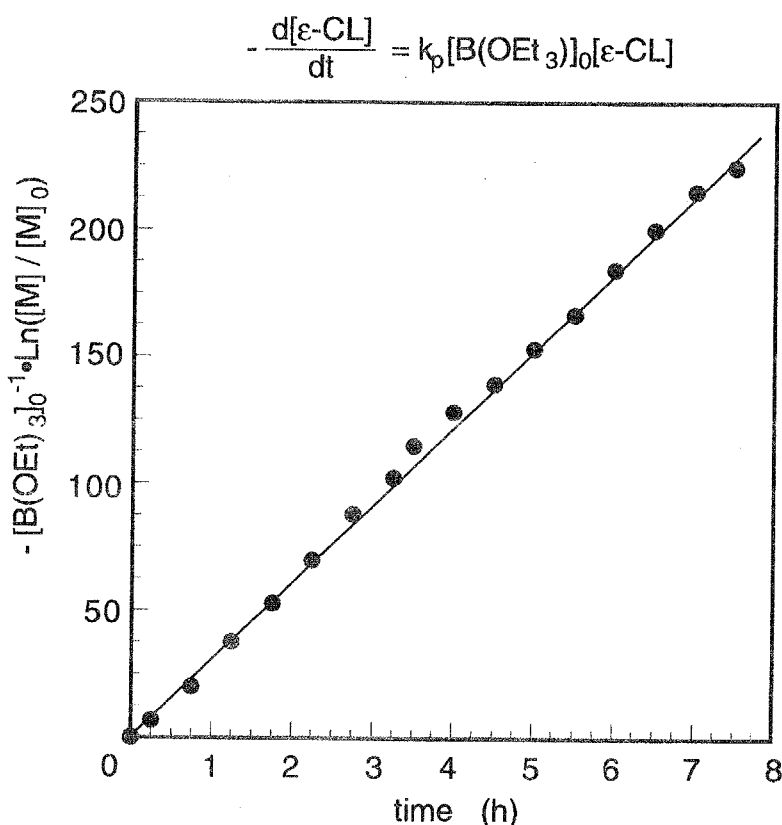


Figure 2. First order kinetic plot for the polymerization of ϵ -CL. Conditions; $[\epsilon\text{-CL}]_0 = 1 \text{ mol/L}$ in CH₂Cl₂ at 25 °C, $[\epsilon\text{-CL}]_0/[B(OEt)_3]_0 = 90$, $[HCl]_0/[B(OEt)_3]_0 = 20$.

To testify the living nature, 90 equiv of ϵ -CL was first polymerized with $B(OEt)_3$ -HCl \cdot Et₂O (20 equiv) initiator system in CH₂Cl₂ at 25°C ($[\epsilon\text{-CL}]_0 = 1 \text{ mol/L}$). After confirming the quantitative monomer conversion by ¹H NMR, the polymerization mixture was kept stirring for another 24 h. A back biting reaction was negligible because the M_n and M_w/M_n values unchanged in the period. Then the same amount of monomer was recharged to conduct the postpolymerization. Figure 3 depicts the GPC profiles of ϵ -CL prepolymer and postpolymer. The peak top shifted into a higher M_n region (7100) without the formation of cyclic oligomers. However, the M_w/M_n ratio became

somewhat broad (1.26), probably due to the partial deactivation of the polymer propagating end.

Scheme 3

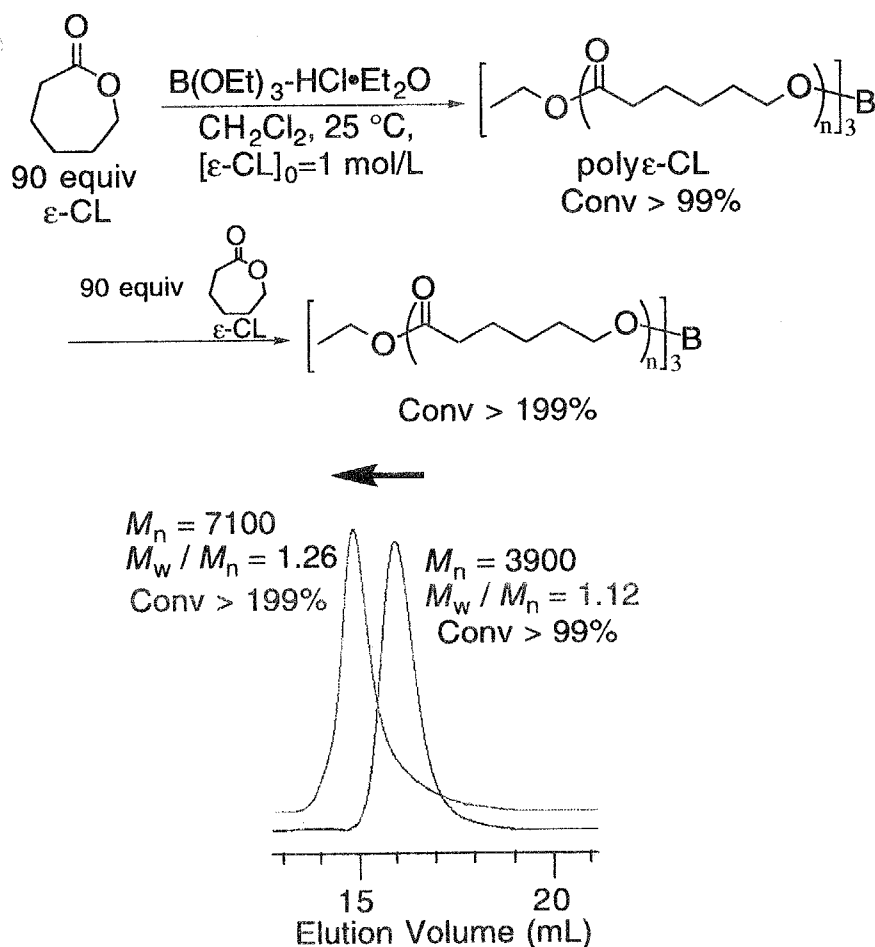


Figure 3. GPC traces of poly ϵ -CL obtained by the polymerization of ϵ -CL (90 equiv) with $B(OEt)_3$ in the presence of $HCl \cdot Et_2O$ (20 equiv) in CH_2Cl_2 at 25 °C ($[\epsilon\text{-CL}]_0 = 1 \text{ mol/L}$), and the post polymer obtained by charging the same amount of monomer.

Figure 4 illustrates the 1H NMR spectrum of poly ϵ -CL obtained by the polymerization of ϵ -CL in run 2 in Table 1. In addition to signals $c \sim g$ assignable to α - \sim ϵ -methylene protons of the ester carbonyl moiety at 2.30, 1.65, 1.40, 1.65, and 4.06 ppm, signals a , b , and h assignable to terminal methyl, methylene, and α -methylene protons of a hydroxyl group were observed at 1.25, 4.12, and 3.66 ppm, respectively. The integration ratio of the signals a to h was exactly 3 / 2, which agreed well with the expected value. The average unit number of the obtained polymer estimated by the integration

ratio of signals *a* and *c* showed good agreement with one-third of the feed ratio of $[\epsilon\text{-CL}]_0 / [\text{B}(\text{OEt})_3]_0$, which also indicated all of the ethoxide groups of the boron compound initiated the polymerization.

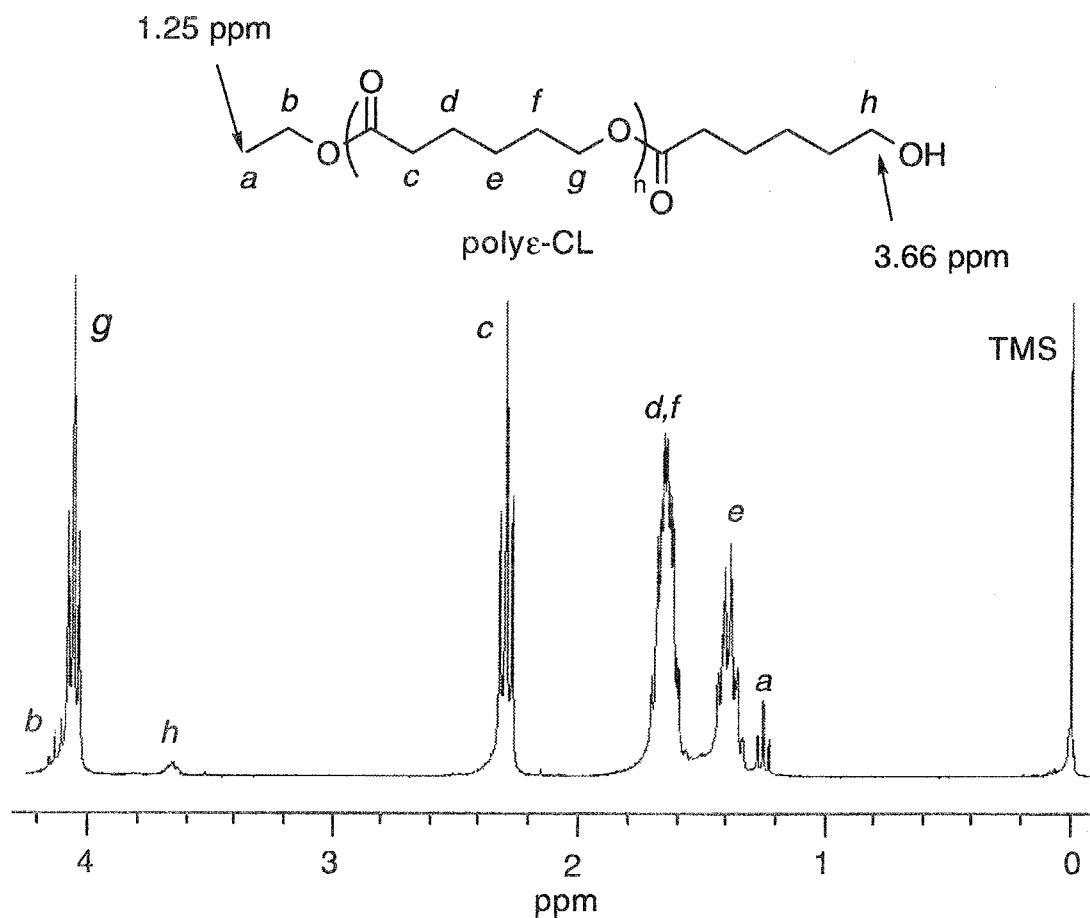
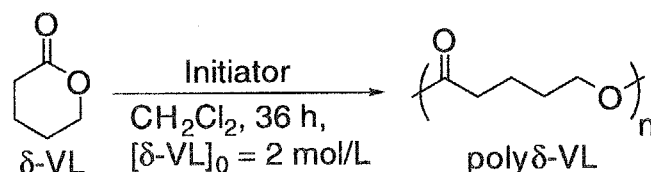


Figure 4. ^1H NMR spectrum (300 MHz, CDCl_3) of poly- ϵ -CL obtained by the polymerization in run 4 in Table 1.

7-4 Ring-Opening Polymerization of δ -Valerolactone with $B(OEt)_3$ Promoted by Protonic Acid

Next, polymerization of δ -VL was examined with the same initiator system as the preceding section, $B(OEt)_3$ -HCl•Et₂O in CH₂Cl₂ at 0 and 25 °C ($[\delta\text{-VL}]_0 = 2 \text{ mol/L}$).

Scheme 4

Table 2 Polymerization of δ -VL with $B(OEt)_3$ /HCl Initiator^a

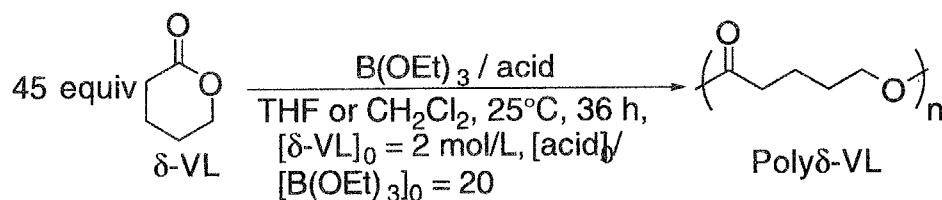
run	initiator	$[\text{HCl}]_0 / [\text{B}(\text{OEt})_3]_0$	temp (°C)	conv ^b (%)	yield ^c (%)	M_n^d	M_w/M_n^d
1	$B(\text{OEt})_3$	0	25	0	— ^e	— ^e	— ^e
2	$B(\text{OEt})_3 / \text{HCl}\cdot\text{Et}_2\text{O}$	10	25	79	70	2300	1.57
3	$B(\text{OEt})_3 / \text{HCl}\cdot\text{Et}_2\text{O}$	1	25	83	75	2000	1.52
4	$B(\text{OEt})_3 / \text{HCl}\cdot\text{Et}_2\text{O}$	10	0	92	79	2000	2.34

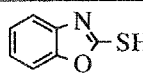
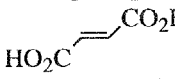
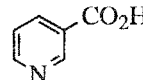
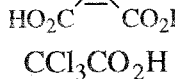
^a $[\delta\text{-VL}]_0 = 2 \text{ mol/L}$ in CH₂Cl₂ for 36 h, $[\delta\text{-VL}]_0 / [\text{B}(\text{OEt})_3]_0 = 40$.

^bDetermined by ¹H NMR. ^c*n*-Hexane-insoluble part. ^dDetermined by GPC (THF, polystyrene standards). ^eNot determined.

Although $B(\text{OEt})_3$ itself did not serve as an initiator for the polymerization of δ -VL, HCl promoted the polymerization to give poly δ -VL in good yields. However, the M_w/M_n ratios of the obtained polymers could not be controlled at a lower temperature (0 °C) or with smaller amount of HCl (runs 4 and 3), probably due to back biting reaction. Thus, HCl was not effective to obtain poly δ -VL with a narrow M_w/M_n ratio. Therefore, I attempted various protonic acids as the promotor to achieve more efficient $B(\text{OEt})_3$ -initiated δ -VL polymerization as summarized in Scheme 5 and Table 3.

Scheme 5

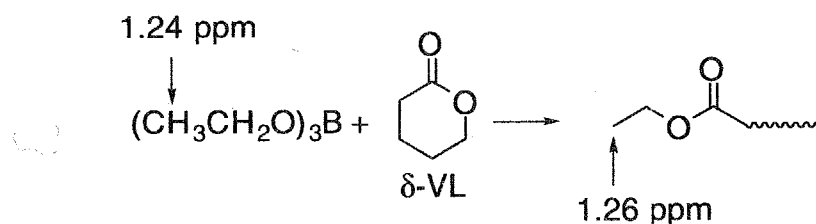
**Table 3** Polymerization of δ -VL with B(OEt)_3 / various acids^a

run	acid	pK _a	solvent	conv ^b (%)	M _n ^c	M _w /M _n ^c
1		~8.0	THF	4	— ^d	— ^d
2	CH ₃ CO ₂ H	4.75	CH ₂ Cl ₂	2	— ^d	— ^d
3		3.02	THF	6	— ^d	— ^d
4	CH ₂ (CO ₂ H) ₂	2.86	THF	63	1400	1.37
5		2.05	THF	3	— ^d	— ^d
6		1.92	THF	2	— ^d	— ^d
7	CCl ₃ CO ₂ H	0.89	CH ₂ Cl ₂	33	— ^d	— ^d
8	CCl ₃ CO ₂ H	0.89	THF	72	1600	1.20
9	CF ₃ CO ₂ H	0.23	CH ₂ Cl ₂	60	2100	1.39
10	CF ₃ CO ₂ H	0.23	THF	84	2000	1.17
11 ^c	HCl•Et ₂ O	-3.7	CH ₂ Cl ₂	83	1800	1.45
12 ^c	HCl•Et ₂ O	-3.7	THF	85	1900	1.38

^aConditions; $[\delta\text{-VL}]_0 = 2 \text{ mol/L}$ at 20°C for 36 h, $[\text{acid}]_0 / [\text{B(OEt)}_3]_0 = 20$. ^bDetermined by ¹H NMR. ^cDetermined by GPC (polystyrene standards, THF). ^dNot measured. ^e $[\text{acid}]_0 / [\text{B(OEt)}_3]_0 = 1$.

Several aliphatic carboxylic and aromatic acids such as acetic, fumaric, malonic, maleic, and nicotinic acids and mercaptobenzoxazole did not satisfactorily serve as initiators in conjunction with B(OEt)_3 for the polymerization of δ -VL. It was confirmed by ¹H NMR spectroscopy (Scheme 6) that fumaric and maleic acids, and mercaptobenzoxazole associated the addition of B(OEt)_3 ethoxy group with δ -VL to give ring-opened adducts, but the polymerization did not proceed at all probably due to lack of acidity.

Scheme 6



On the contrary, trichloroacetic acid, trifluoroacetic acid, and hydrogen chloride effectively promoted the polymerization of δ -VL in the presence of triethylborate to give the polymers in high monomer conversion. The small M_w/M_n (1.17) was achieved with $\text{CF}_3\text{CO}_2\text{H}$ in THF (run 10 in Table 3).

Table 4 summarizes the results of polymerization of δ -VL with various monomer feed ratios with $\text{B}(\text{OEt})_3$ - $\text{CF}_3\text{CO}_2\text{H}$ initiator system at 25°C ($[\delta\text{-VL}]_0 = 2 \text{ mol/L}$). The polymerization in CH_2Cl_2 afforded poly δ -VL with a large M_w/M_n (1.39 - 1.45) in a low monomer conversion (runs 1 - 2), while the polymer with very narrow M_w/M_n ratios could be obtained in high yields in THF (runs 3 - 8). The M_n was affected by the feed ratio of the monomer to $\text{B}(\text{OEt})_3$, not to HCl (runs 5 and 6) and the values could be varied with the feed ratio in the range of 1300 to 11000, where the M_w/M_n ratios were narrow (1.05 - 1.18). As observed in the polymerization of ϵ -CL with $\text{B}(\text{OEt})_3$ -HCl initiator system, the M_n values are in good agreement with one-third of those calculated by the feed ratio. Thus, it may be declared that all the ethoxide moieties of $\text{B}(\text{OEt})_3$ initiated and propagated the polymerization of δ -VL as depicted in Scheme 2.

Scheme 6

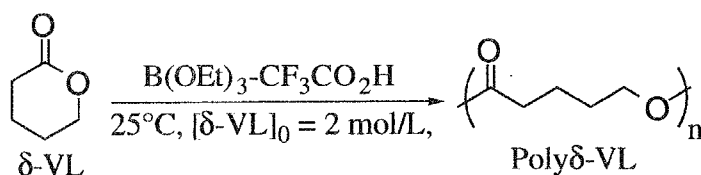


Table 4 Polymerization of δ -VL promoted by $\text{CF}_3\text{CO}_2\text{H}^a$

run	$[\delta\text{-VL}]_0 / [\text{I}]_0^b$	$[\text{H}^+]_0 / [\text{I}]_0^b$	solvent	time (h)	conv ^c (%)	yield ^d (%)	M_n^e	M_w/M_n^e
1	45	20	CH_2Cl_2	24	58	— ^f	2100	1.39
2	45	20	CH_2Cl_2	36	57	— ^f	1800	1.45
3	40	20	THF	36	73	68	1300	1.18
4	45	20	THF	36	84	75	2000	1.17
5	120	50	THF	48	95	89	4600	1.09
6	120	100	THF	48	90	80	4500	1.10
7	200	100	THF	96	90	83	6400	1.05
8	300	200	THF	120	93	85	11000	1.07

^aConditions; at 25 °C, $[\delta\text{-VL}]_0 = 2 \text{ mol/L}$. ^bThe initial concentration ratio of δ -VL to Initiator. ^cDetermined by ¹H NMR. ^d*n*-Hexane-insoluble part. ^eDetermined by GPC (polystyrene standards, THF). ^fNot determined.

Figure 5 depicts the second- feed experiment of δ -VL polymerization initiated with $\text{B}(\text{OEt})_3\text{-CF}_3\text{CO}_2\text{H}$ initiator system in THF at 25 °C ($[\delta\text{-VL}]_0 = 2 \text{ mol/L}$, $[\delta\text{-VL}]_0 / [\text{CF}_3\text{CO}_2\text{H}]_0 = 200$). Poly δ -VL was first prepared by the polymerization of 120 equiv of δ -VL with $\text{B}(\text{OEt})_3$ in the presence of 200 equiv of $\text{CF}_3\text{CO}_2\text{H}$. After confirming the quantitative monomer conversion, the polymerization mixture was kept stirring another 24 h. Then the same amount of monomer was recharged into the mixture to conduct the post polymerization. The GPC elution peak of finally obtained poly δ -VL completely shifted into a higher M_n region keeping a narrow M_w/M_n ratio. The formation of cyclic oligomer was negligible as shown in Figure 5 even after the complete consumption of the monomer. This result indicated that the active center was enough stable even in the absence of the monomer, proceeding of *living* polymerization.

Scheme 8

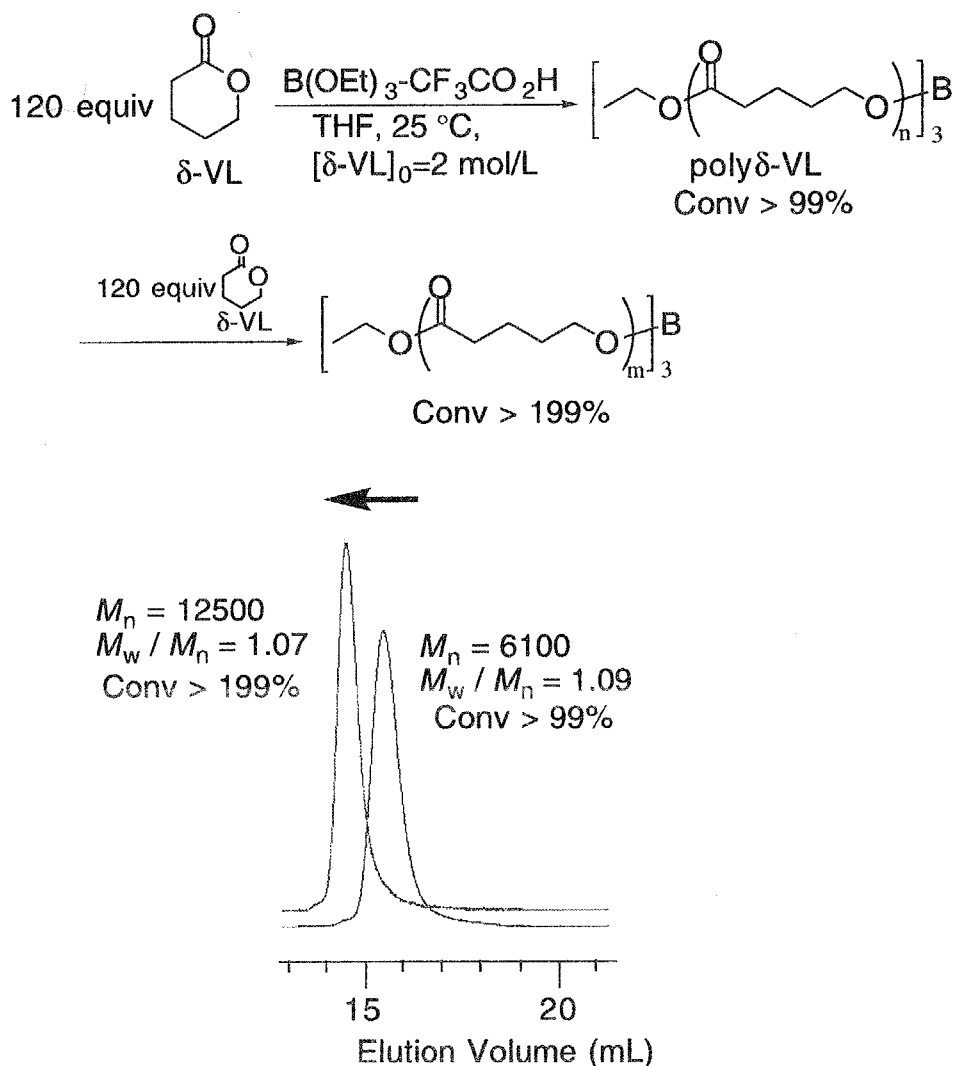


Figure 5. GPC traces of homo poly δ -VL obtained by the polymerization of δ -VL (120 equiv) with B(OEt)_3 in the presence of $\text{CF}_3\text{CO}_2\text{H}$ (200 equiv) in THF at 25 °C ($[\delta\text{-VL}]_0 = 2 \text{ mol/L}$), and the post polymer obtained by charging the same amount of monomer.

Figure 4 illustrates the ^1H NMR spectrum of poly ϵ -CL obtained by the polymerization of ϵ -CL in run 7 in Table 4. In addition to signals $c \sim f$ assignable to α - \sim δ -methylene protons of the ester carbonyl moiety at 2.34, 1.68, 1.68, and 4.08 ppm, signals a and g assignable to terminal methyl and α -methylene protons of a hydroxyl group were observed at 1.26 and 3.65 ppm, respectively. The integration ratio of signals a to g was about 3 / 2, which agreed well with the expected value. The average unit number of the obtained polymer estimated by the integrated ratio of a and c showed good agreement

with one-third of the feed ratio of $[\delta\text{-VL}]_0 / [\text{B}(\text{OEt})_3]_0$, which also indicated all of the ethoxide groups of $\text{B}(\text{OEt})_3$ initiated the polymerization.

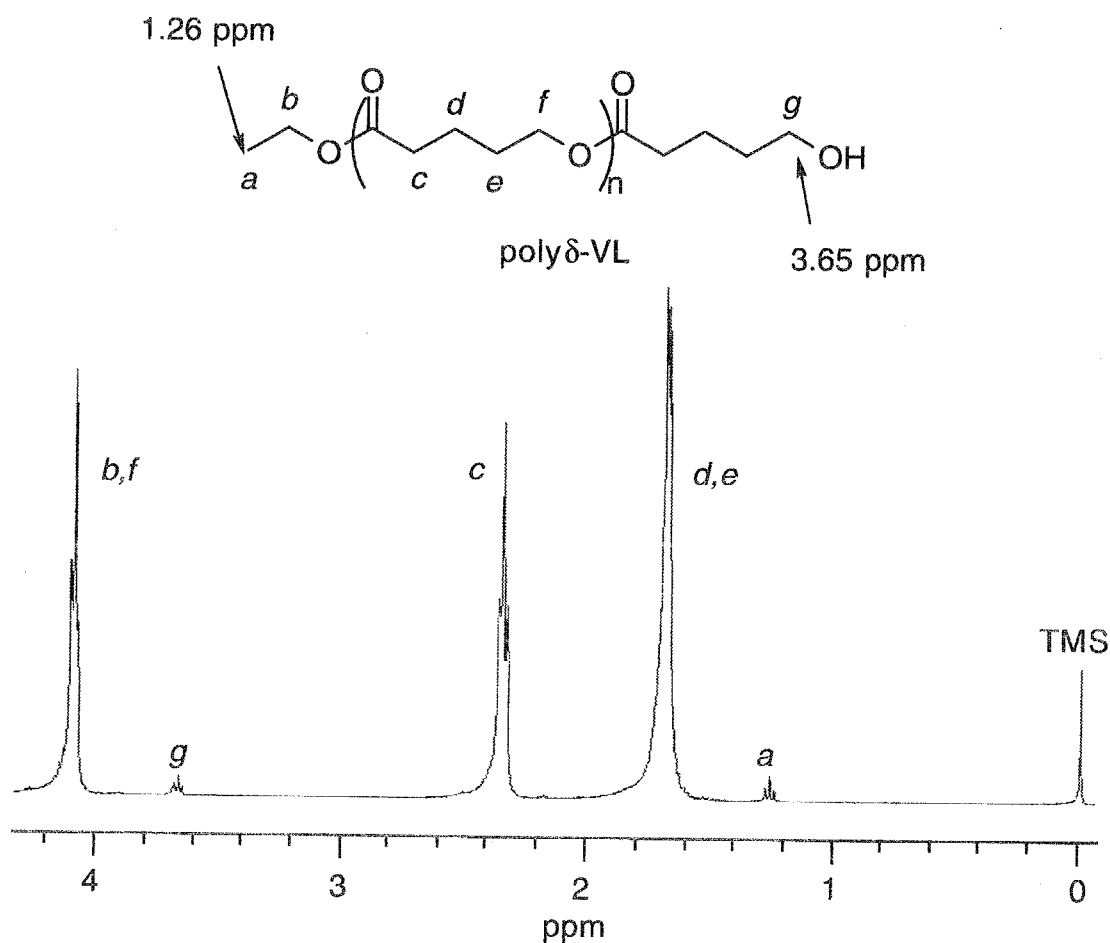


Figure 5. ^1H NMR spectrum (300 MHz, CDCl_3) of poly δ -VL obtained by the polymerization in run 7 in Table 4.

Table 5 summarizes the ^{13}C NMR chemical shifts of the carbonyl carbon signals of δ -VL (a), $\text{CF}_3\text{CO}_2\text{H}$ (b), and methylene carbon of $\text{B}(\text{OEt})_3$ in the presence and absence of $\text{CF}_3\text{CO}_2\text{H}$. The carbonyl carbon signal of δ -VL shifted 4.69 ppm to the lower field by the addition of $\text{CF}_3\text{CO}_2\text{H}$ indicating the activation of δ -VL with $\text{CF}_3\text{CO}_2\text{H}$ (runs 2 and 3). Correspondingly, the carbonyl carbon signal b of $\text{CF}_3\text{CO}_2\text{H}$ shifted to the higher field and the coupling constant got smaller compared with $\text{CF}_3\text{CO}_2\text{H}$ alone (runs 1 and 3). When $\text{B}(\text{OEt})_3$ and $\text{CF}_3\text{CO}_2\text{H}$ were mixed, signal c assignable to the methylene carbon of $\text{B}(\text{OEt})_3$ was observed at 58.81 ppm, higher than that of $\text{B}(\text{OEt})_3$

alone (runs 4 and 5). At the same time, signal *b* of $\text{CF}_3\text{CO}_2\text{H}$ was observed at 158.67 ppm, lower than that of $\text{CF}_3\text{CO}_2\text{H}$ alone (runs 1 and 5). These observations suggested that the polymerization proceeded via monomer insertion mechanism between the B-O bond, where the monomer was activated and the B-O bond was somewhat weakened by $\text{CF}_3\text{CO}_2\text{H}$ enough to undergo living polymerization.

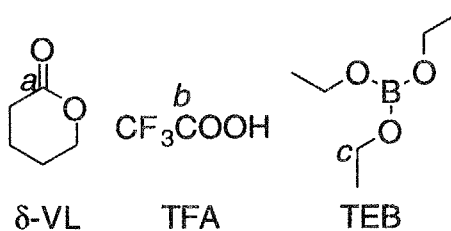


Table 5. Chemical shifts in ^{13}C NMR^a

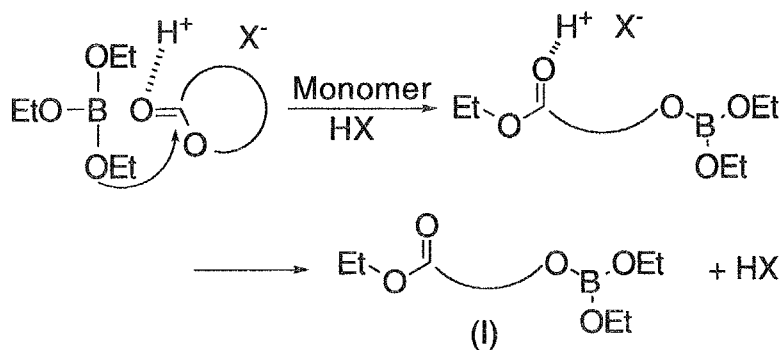
run	reagents	<i>a</i> (ppm)	<i>b</i> (ppm)	<i>c</i> (ppm)
1	TFA	—	162.36 (44.0 Hz) ^b	—
2	$\delta\text{-VL}$	171.03	—	—
3	$\delta\text{-VL} + \text{TFA}$	175.72	158.07 (41.0 Hz) ^b	—
4	TEB	—	—	59.55
5	TEB + TFA	—	158.67 (42.3 Hz) ^b	58.81

^a $[\text{TFA}]_0 = [\delta\text{-VL}]_0 = [\text{TEB}]_0 = 0.5 \text{ mol/L}$ in CDCl_3 at 25 °C (75 MHz). ^b $J_{\text{C-F}}$ value.

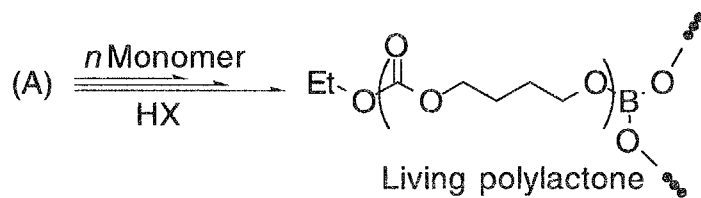
Scheme 9 depicts a plausible mechanism of the lactone polymerization with $\text{B}(\text{OEt})_3$ promoted with protonic acid. The monomer carbonyl group activated with the acid is nucleophilically attacked by the ethoxide of $\text{B}(\text{OEt})_3$, reproducing borate compound (I). The propagation is the monomer insertion into the B-O bond. Consequently, the polymer hydrolyzed by HCl has ethyl carbonate and hydroxyl groups at the initial and terminal units, respectively.

Scheme 9

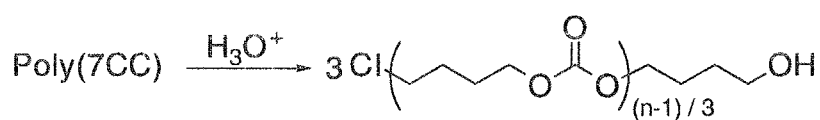
Initiation



Propagation



Quenching



7-5 Summary:

In this chapter, I demonstrated the controlled ring-opening polymerization of ϵ -caprolactone (ϵ -CL) and δ -valerolactone (δ -VL) with $B(OEt)_3$ promoted by $HCl \cdot Et_2O$ and CF_3CO_2H , respectively. The M_n values of the obtained polymers were controlled with the feed ratio of the monomer to $B(OEt)_3$, where the M_w/M_n ratios kept small. The protonic acids promoted the monomer insertion into the B-O bond to produce the corresponding polymers with controlled M_n and narrow M_w / M_n ratio.

7-6 Experimental Section

Materials. CH_2Cl_2 and CDCl_3 were distilled sequentially over P_2O_5 and CaH_2 under nitrogen. Monomers, ϵ -caprolactone and δ -valerolactone were purchased from Aldrich, and distilled over CaH_2 prior to use. Triethylborate [$\text{B}(\text{OEt})_3$] was purchased from Aldrich, distilled under nitrogen, diluted with dry CH_2Cl_2 so to use as a 0.5 mol/L solution. A 2.0 mol/L HCl solution in diethyl ether (Et_2O) was purchased from Aldrich and used without further purification. 2-Mercaptobenzoxazole, fumaric, malonic, nicotinic, and maleic acids were recrystallized from ethyl acetate, THF, diethyl ether/toluene, THF, and THF, respectively. Acetic acid, trichloroacetic acid, trifluoroacetic acid were distilled under nitrogen atmosphere.

Measurements. ^1H and ^{13}C NMR spectra were recorded with a JEOL Lambda-300 spectrometer. Number- and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Tosoh HLC-8120 system equipped with two consecutive polystyrene gel columns eluted with tetrahydrofuran (THF) at a flow rate of $1.0 \text{ mL}\cdot\text{min}^{-1}$ calibrated by standard polystyrenes.

Polymerization. All manipulations were carried out under dry nitrogen. Typical procedure was following: Into a 30 mL baked glass flask equipped with a three-way stopcock were placed 0.46 g (4 mmol) of trifluoroacetic acid, 4 mL of CH_2Cl_2 , and 42 μL (0.042 mmol) of $\text{B}(\text{OEt})_3$ solution (0.5 mol/L) in CH_2Cl_2 . The polymerization was initiated by the addition of δ -VL (0.50 g, 5.0 mmol) at 25°C . After a set time the reaction mixture was poured into 100 mL of *n*-hexane to precipitate a polymer. The precipitate was filtered, washed with *n*-hexane (10 mL), and dried in vacuo at 25°C for 5 h to give 0.392 g of white powdery polymer (yield 80%).

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Chapter 8

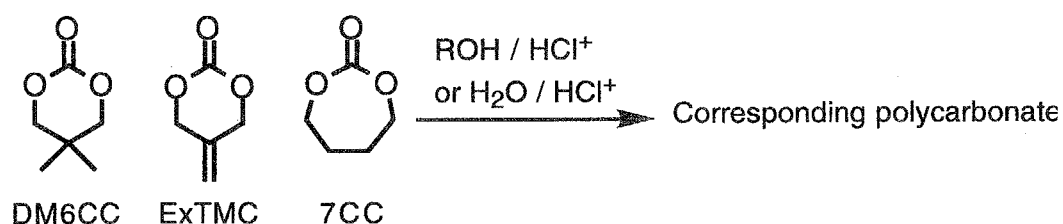
Summary

Chapter 8.
Summary

In this thesis, the author described the development of cationic ring-opening polymerization of cyclic carbonates and lactones with controlled M_n s and narrow M_w/M_n ratios via activated monomer mechanism, and novel acid promoted living cationic ring-opening polymerization of those monomers with boron compounds.

Chapter 2 dealt with ring-opening polymerization of cyclic carbonates, 5,5-dimethyl-1,3-dioxan-2-one (DM6CC), 5-exomethylene-1,3-dioxan-2-one (Ex6CC), and 1,3-dioxepan-2-one (7CC) with alcohol / acid and H_2O / acid initiator systems. $HCl \cdot Et_2O$ was quite effective to obtain the corresponding polymers quantitatively. The molecular weights (M_n s) of the polymers could be varied with the amount of alcohol or water in the range of $10^2 \sim 10^4$ keeping narrow polydispersity ratios (M_w/M_n s 1.11 \sim 1.17). The second portion of the monomer after completion of the first polymerization was converted quantitatively to give the corresponding polymer with a narrow M_w/M_n . The kinetic and 1H NMR spectroscopic studies suggested that the nucleophilic attack of water to the monomer activated with hydrogen chloride afforded an α -hydroxyl- ω -carboxylic acid, followed by decarboxylation reaction to give an α, ω -dihydroxyl compound. It was suggested that the chain growth in this system was the attack of the terminal hydroxyl group to the monomer activated with hydrogen chloride.

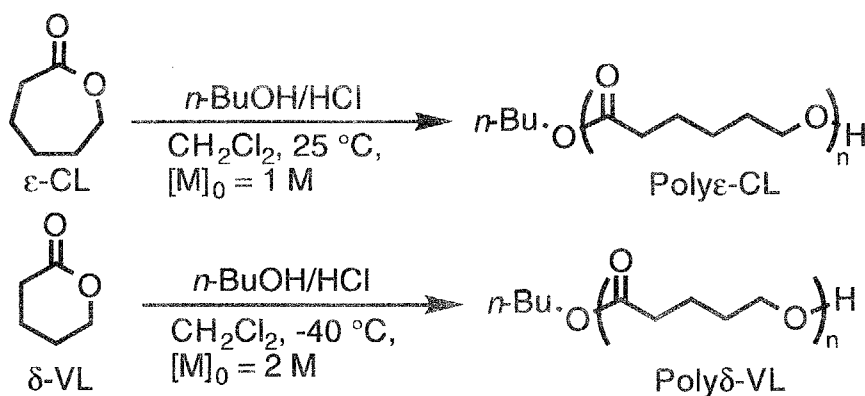
Cationic controlled polymerization of cyclic carbonates



- Controlled M_n by $[M]_0/[I]_0$; M_n 2000 \sim 12000
- Narrow polydispersity; M_w/M_n 1.09 \sim 1.19
- Free from cyclic oligomers
- No decarboxylation during the polymerization

Chapter 3 dealt with activated monomer cationic ring-opening polymerization of ϵ -caprolactone (ϵ -CL) and δ -valerolactone (δ -VL) with *n*-butyl alcohol / HCl•Et₂O initiator system. Poly ϵ -CL with small polydispersity (M_w/M_n) ratios was obtained at 25°C quantitatively. The polymerization of δ -VL showed typical equilibrium polymerization behavior between the monomer and polymer. Poly δ -VL with controlled M_n s and small M_w/M_n values was obtained by the polymerization at -40 °C. The molecular weights of the polymers could be controlled with the feed ratio of the monomer and initiator. The post polymerization was successfully achieved, keeping small M_w/M_n s to indicate that the polymerization proceeded in living fashion.

Cationic controlled polymerization of lactones

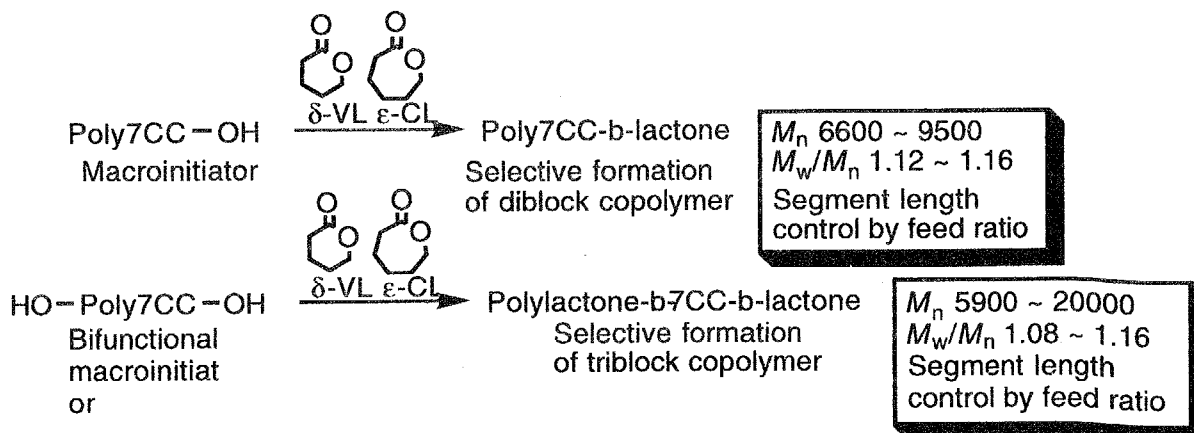


- Controlled M_n by $[\text{M}]_0/[\text{I}]_0$; M_n 2000 ~ 11000
- Narrow polydispersity; M_w/M_n 1.08 ~ 1.17
- Free from cyclic oligomers

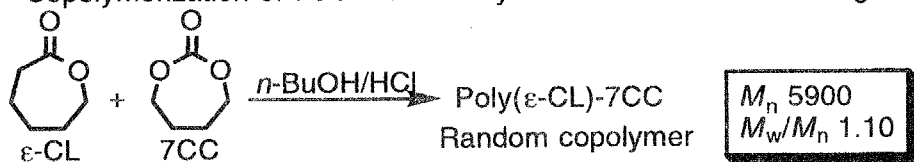
Chapter 4 dealt with syntheses of di-, triblock, and random copolymers of a seven-membered cyclic carbonate (7CC) and lactones (ϵ -caprolactone and δ -valerolactone) with *n*-butyl alcohol / HCl•Et₂O and H₂O / HCl•Et₂O initiator systems. The corresponding di- and triblock copolymers with small polydispersity ratios (1.08 ~ 1.16) were obtained quantitatively in one pot. The molecular weights and composition of the block copolymers could be controlled with varying the feed ratio of the monomer to initiator, and the first monomer to second one, respectively.

Controlled copolymerization of lactones with a cyclic carbonate

Copolymerization of lactones with poly7CC macroinitiator

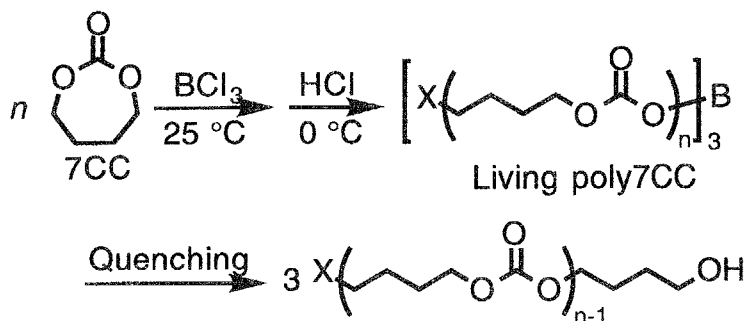


Copolymerization of 7CC with ϵ -CL by one-shot monomer feeding



Chapter 5 dealt with ring-opening polymerization of a seven-membered cyclic carbonate, 1,3-dioxepan-2-one (7CC) with a novel initiator system, $BX_3 \cdot HCl \cdot Et_2O$ ($X = Cl$ and Br). After treatment of 7CC with BCl_3 in CH_2Cl_2 for 24 h, the addition of $HCl \cdot Et_2O$ promoted the controlled polymerization to give a corresponding polycarbonate quantitatively with a relatively narrow polydispersity (~ 1.15) at $0^\circ C$. The molecular weights of the obtained polymers showed good agreement with the values calculated from one-third of the feed ratio of the monomer to initiator, indicating that all the chlorine groups of BCl_3 initiated and propagated the polymerization of 7CC.

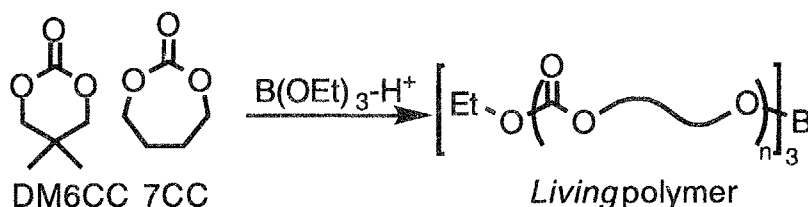
Investigation of ring-opening
polymerization of 7CC with $\text{BCl}_3\text{-HCl}$



- M_n control 2000 ~ 12000
- Narrow M_w/M_n 1.14 ~ 1.19
- Telechelic polymer having -Cl and -OH moieties

Chapter 6 dealt with ring-opening polymerization of cyclic carbonates (1,3-dioxepan-2-one and 5,5-dimethyl-1,3-dioxan-2-one) with triethyl- and triisopropylborates as initiators promoted by hydrogen chloride. The molecular weights of the obtained polymers could be controlled by the amount of alkylborates, and their polydispersity ratios were narrow (~ 1.15). The polymerization obeyed good first order kinetics throughout the reaction. After the monomers were completely consumed, the polymerization took place again when the same amount of monomers were introduced into the polymerization mixtures. ^1H and ^{13}C NMR spectroscopic studies confirmed that the polymerization proceeded in a living manner via insertion of the monomer to the boron-oxygen bond.

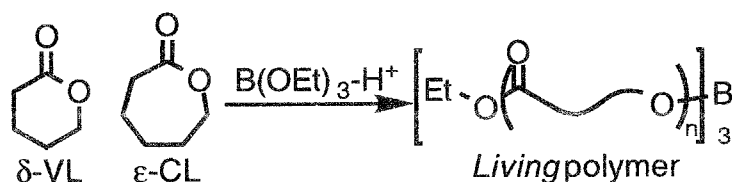
Development of living ring-opening
polymerization of cyclic carbonates



- M_n control 2000 ~ 6500
- Narrow M_w/M_n 1.11 ~ 1.19
- Free from cyclic oligomers

Chapter 7 dealt with acid promoted ring-opening polymerization of ϵ -caprolactone (ϵ -CL) and δ -valerolactone (δ -VL) with triethylborate $[B(OEt)_3]$. Poly ϵ -CL and poly δ -VL with controlled molecular weights (~ 12000) and small polydispersity ratios ($1.05 \sim 1.20$) were obtained quantitatively when the polymerizations were conducted in CH_2Cl_2 with $B(OEt)_3/HCl$ and in tetrahydrofuran with $B(OEt)_3/CF_3CO_2H$, respectively. The post polymerizations after quantitative monomer conversion successfully proceeded keeping narrow polydispersities, which suggested that these polymerizations proceeded via living fashion.

Development of living ring-opening polymerization of lactones



- M_n control 1300 ~ 14000
- Narrow M_w/M_n 1.06 ~ 1.19
- Free from cyclic oligomers

As summarized above, this thesis developed cationic ring-opening polymerization of cyclic carbonates and lactones with a controlled M_n and narrow M_w/M_n ratio via activated monomer mechanism, and novel acid promoted living cationic ring-opening polymerization of those monomers with boron compounds. The cationic activated monomer ring-opening polymerization is one of the most versatile methods to obtain monodisperse polymers like polycarbonates, polyesters, and their copolymers. The initiator system consists of a protonic acid and an alcohol (or H_2O), which are convenient and low toxic reagents. Acid promoted cationic polymerization utilizing boron compounds enables living polymerization of cyclic carbonates and lactones. Especially in the polymerization of δ -VL, the corresponding monodisperse polymer samples could be obtained even at $25^\circ C$ indicating the formation of stable boron species preferable than activated cationic

polymerization. Because the present system can be tolerant of various monomers, numerous designs of macromolecules will be realized without any difficulties. The author hopes the study described in this thesis will be applied and matured in the future.

List of publications

Chapter 2

Yuji Shibasaki, Fumio Sanda, Takeshi Endo, : Activated monomer cationic polymerization of 1,3-dioxepan-2-one initiated by water-hydrogen chloride; *Macromol. Rapid Commun.*, **20**, 532 (1999)

Yuji Shibasaki, Fumio Sanda, Takeshi Endo, : Cationic precise polymerization of seven-membered cyclic carbonate with water-hydrogen chloride through activated monomer process; *Macromolecules in press*

Chapter 4

Yuji Shibasaki, Hidetsugu Sanada, Makiko Yokoi, Fumio Sanda, Takeshi Endo, : Activated monomer cationic polymerization of lactones and the application of block copolymer synthesis with a seven-membered cyclic carbonate; *Macromolecules in revision*

Chapter 5

Yuji Shibasaki, Fumio Sanda, Takeshi Endo, : A novel acid promoted ring-opening polymerization of a seven-membered cyclic carbonate initiated with BCl_3 ; *Macromol. Chem. Rapid Commun. in press*

Yuji Shibasaki, Fumio Sanda, Takeshi Endo, : A novel acid promoted ring-opening polymerization of a seven-membered cyclic carbonate

initiated with BCl_3 . Mechanistic aspect of the polymerization; *in preparation*

Chapter 6

Yuji Shibasaki, Fumio Sanda, Takeshi Endo, : Acid promoted living ring-opening polymerization of cyclic carbonates with B(OR)_3 ; *Macromolecules in press*

Chapter 7

Yuji Shibasaki, Fumio Sanda, Takeshi Endo, : Living Ring-Opening Polymerization of δ -valerolactone with B(OEt)_3 promoted by protonic acid; *in preparation*

Yuji Shibasaki, Fumio Sanda, Takeshi Endo, : Living Ring-Opening Polymerization of ϵ -caprolactone with B(OEt)_3 promoted by protonic acid; *in preparation*

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Yuji Shibasaki, Ryoji Nomura, Takeshi Endo, : Reduction of the cationic growing center of polyisobutylene by activated magnesium. Block copolymerization of isobutylene with *tert*-butyl methacrylate ; *Macromol. Chem. Phys.*; **199** 2619 (1998)

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Yuji Shibasaki, Ryoji Nomura, Takeshi Endo, : Block Copolymerization of Tetrahydrofuran with δ -valerolactone by the Samarium Iodide-Induced Transformation; The 70th Annual Meeting of Chem. Society of Jpn., *Prepr.*, **II** 766 (TOKYO, Mar 1996)

Yuji Shibasaki, Ryoji Nomura, Takeshi Endo, : A Novel Transformation Reaction of a Cationic Propagating End into an Anionic One by Bis(pentamethylcyclopentadienyl)samarium and its Application to Block Copolymerization of Tetrahydrofuran with δ -valerolactone; The 45th Annual Meeting of Chem. Society Polym. Sci., Jpn., *Polym. Prepr.*, **45**, 153 (NAGOYA, May 1996)

Yuji Shibasaki, Ryoji Nomura, Takeshi Endo, : A Novel Transformation Reaction of a Cationic Propagating End into an Anionic One by Bis(pentamethylcyclopentadienyl)samarium and its Application to Block Copolymerization of Tetrahydrofuran with δ -valerolactone; The 45th Annual Meeting of Chem. Society Polym. Sci., Jpn., *Polym. Prepr.*, **45**, 153 (NAGOYA, May 1996)

Yuji Shibasaki, Ryoji Nomura, Takeshi Endo, : A Novel Transformation Reaction of a Cationic Propagating End into an Anionic One by Bis(pentamethylcyclopentadienyl)samarium and its application to Block

Copolymerization of Tetrahydrofuran with Methyl Methacrylate; The 45th Annual Meeting of Chem. Society Polym. Sci., Jpn., *Polym. Prepr.*, **45**, 153 (NAGOYA, May 1996)

Yuji Shibasaki, Ryoji Nomura, Takeshi Endo, : A Novel Transformation Reaction of a Cationic Propagating End of Polyisobutylene into an Anionic One by Activated Magnesium ; The 46th Annual Meeting of the Society of Polymer Science, Jpn, *Polym. Prepr.* **45**, 1155 (HIROSHIMA, Oct. 1996)

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Yuji Shibasaki, Fumio Sanda, Takeshi Endo, : Controlled Ring-Opening Polymerization of 1,3-Dioxepan-2-one by Protonic Acid-H₂O System ; IUPAC INTERNATIONAL SYMPOSIUM ON IONIC POLYMERIZATION 149 (Kyoto, July 1999)

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an Initiator; The 48th Polymer Symposium of the Society of Polymer
Science, Japan, *Polym. Prepr.* **48**, 1453 (NIIGATA, October 1999)

Acknowledgment

The studies described in this thesis have been carried out under the direction of Prof. Takeshi Endo at Research Laboratory of Resources Utilization, Tokyo Institute of Technology during 1997 - 2000. The studies are concerned with the novel acid promoted ring-opening polymerization of cyclic carbonates and lactones as well as the cationic activated monomer controlled ring opening polymerization of these monomers.

The author wishes to express his sincerest gratitude to Prof. Takeshi Endo for his constant guidance and valuable suggestions throughout this work. The author is deeply grateful to Assistant Prof. Fumio Sanda for their constant and helpful suggestions. The author wishes to express his gratitude to Assistant Prof. Ikuyoshi Tomita for his instructive advice during this study. The author wishes to express his gratitude to Dr. Daisuke Takeuchi for his educational advice during this study. The author wishes to express his gratitude to Dr. Atsushi Sudo and Hideyuki Otsuka for his instructional admonition during this study. The author is grateful to Mr. Hidetsugu Sanada for his kind help to write this thesis, and is thankful to his colleague for his active collaboration. The author appreciates the helps received from Dr. Yoshiyuki Nakamura with NMR measurements.

The author would like to thank to emeritus Prof. Yoshio Imai who led the author to chemistry before the works in this thesis. Finally, the author wishes to express his deep appreciation to his parents and brother, Masayasu Shibasaki, Kazuko Shibasaki, and Toshihiko Shibasaki, for their constant assistance encouragement.

Yuji Shibasaki

March, 2000