# Ring-Expansion Cationic Polymerization:

# A New Precision Polymerization

# for Cyclic Polymers

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# CONTENTS

# GENERAL INTRODUCTION

## Background

### Cyclic Polymer: Unique Endless Topology

Polymer, a giant molecule consisting of repeating units, is generally illustrated as a long chain.[1] The long chains are entangled or interact with each other, which leads to applications as bulk materials, such as plastics, rubber, and fiber. Various functional groups can be introduced for use as functional materials in bio-related and electronic applications. Herein, some primary structural factors, such as molecular weight and tacticity, could affect properties or functions, but terminal groups existing at chain ends are also an essential factor determining chain behaviors, as clarified in long history of polymer science.[2] At the same time, "cyclic polymer" has also attracted attentions, especially among polymer physicists,[3–5] due to the "endless" topology clearly different from linear strands. Contrary to their interests, however, efficient and quantitative syntheses of cyclic polymers did not progress as expected, and unfortunately some researches were ended with prediction of ring-driven properties from simulation study.[3,4]

A conventional methodology to construct cyclic polymers is macrocyclization in which terminals of linear chain are connected with each other under high dilution conditions (Figure 1).[6,7] Indeed, cyclic polymers were prepared via the macrocyclization methodology

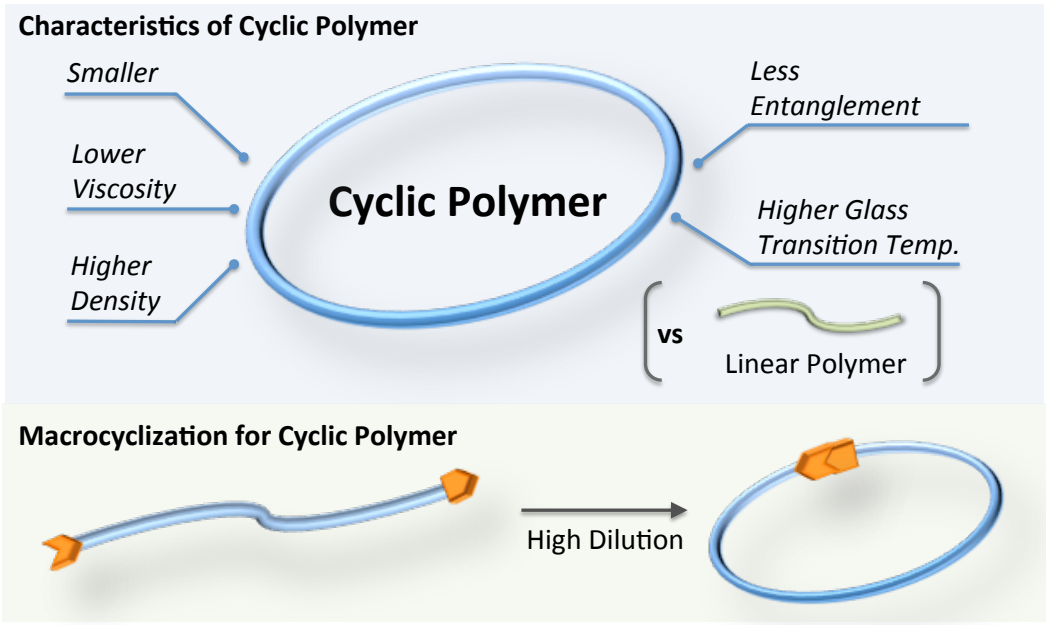



**Figure 1.** Characteristics and synthesis of cyclic polymers.

and thus obtained samples showed different properties from linear counterparts, such as less entanglement, lower viscosity, and more compact, and higher glass transition temperature (Figure 1).[3, 4] However, the macrocyclization approach relying on dilution condition is totally inefficient, and thus there are limits on purity and molecular weight of resultant cyclic polymers.[8] In addition, although ring-based polymer architectures, such as cyclic block copolymer and ring-linear hybrid polymer (e.g., ring-linear graft copolymer), are interesting toward functions based on the ring-oriented assembly, construction of these well-defined structures is not so straightforward by using the macrocyclization methodology.

**Ring-Expansion Polymerization: Expansion from Living Polymerization**

Most of living polymerizations are realized by introduction of dormant species capped with dissociative leaving groups (Figure 2).[9] Herein, some stimulus triggers reversible activation of the dormant to generate active species, i.e., ionic[10–16] and radical,[17–23] for initiation and propagation. The reversible feature allows suppression of unfavorable side reactions such as termination and chain transfer under control of instant concentration of active species, which leads to control of molecular weight. In most cases, the leaving group inevitably exists at terminals of growing polymers during the polymerization. Sequential addition of another monomer or design of monomers allows syntheses of well-defined architectures, such as block copolymers[26] and graft copolymers.[27]

Herein, if the leaving group can be embedded into cyclic structure while controlling the reversible activation for living polymerization, cyclic polymers will be synthesized: this type of polymerization has been called as "ring-expansion polymerization". The first example is ring opening living polymerization of ε-caprolactone with cyclic acetal-type tin alkoxide, which was designed from the corresponding living polymerization with "acyclic" initiator

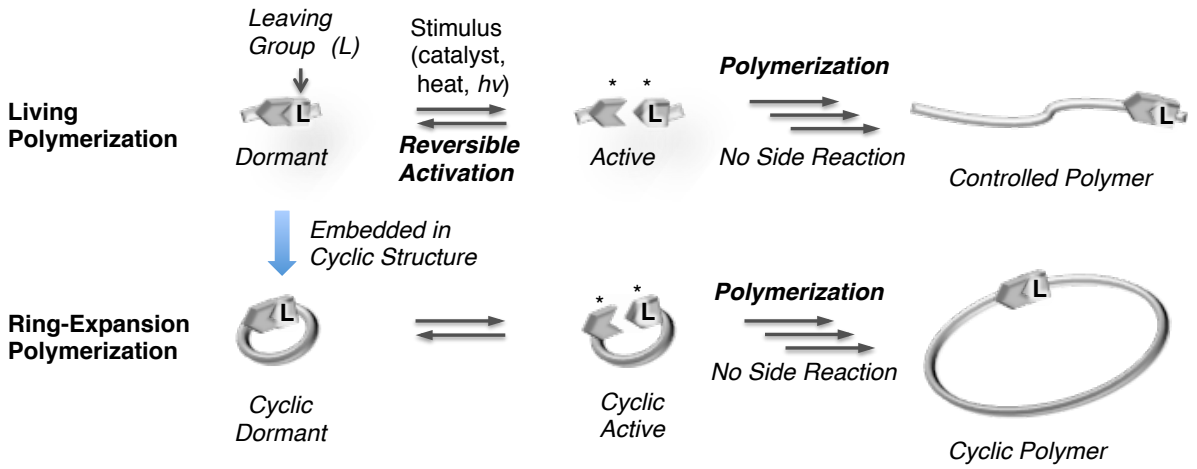



**Figure 2.** Living polymerization and ring-expansion polymerization.

(i.e., dibutyldimethoxystannane) giving linear polymers (Figure 3).[28] The next important breakthrough for ring-expansion polymerization was made with ring opening metathesis polymerization (ROMP) of cyclic olefin.[29] Central to this approach is design of cyclic ruthenium carbene catalyst where one side of *N*-heterocyclic carbene ligand was connected to ruthenium center though carbene. The cyclic olefin monomer undergoes metathesis reaction with the cyclic ruthenium carbene and repetition of the reaction leads to cyclic polymer. These pioneering researches are on the basis of ring opening polymerization of cyclic monomer, but it is more challenging to realize ring-expansion polymerization of vinyl compound, that is an acyclic monomer. However, development of living radical polymerization systems provided design of ring-expansion polymerization even for vinyl monomer. For example, leaving groups for reversible addition fragmentation chain transfer (RAFT) polymerization[30] and nitroxide mediated living radical polymerization (NMP)[31] were

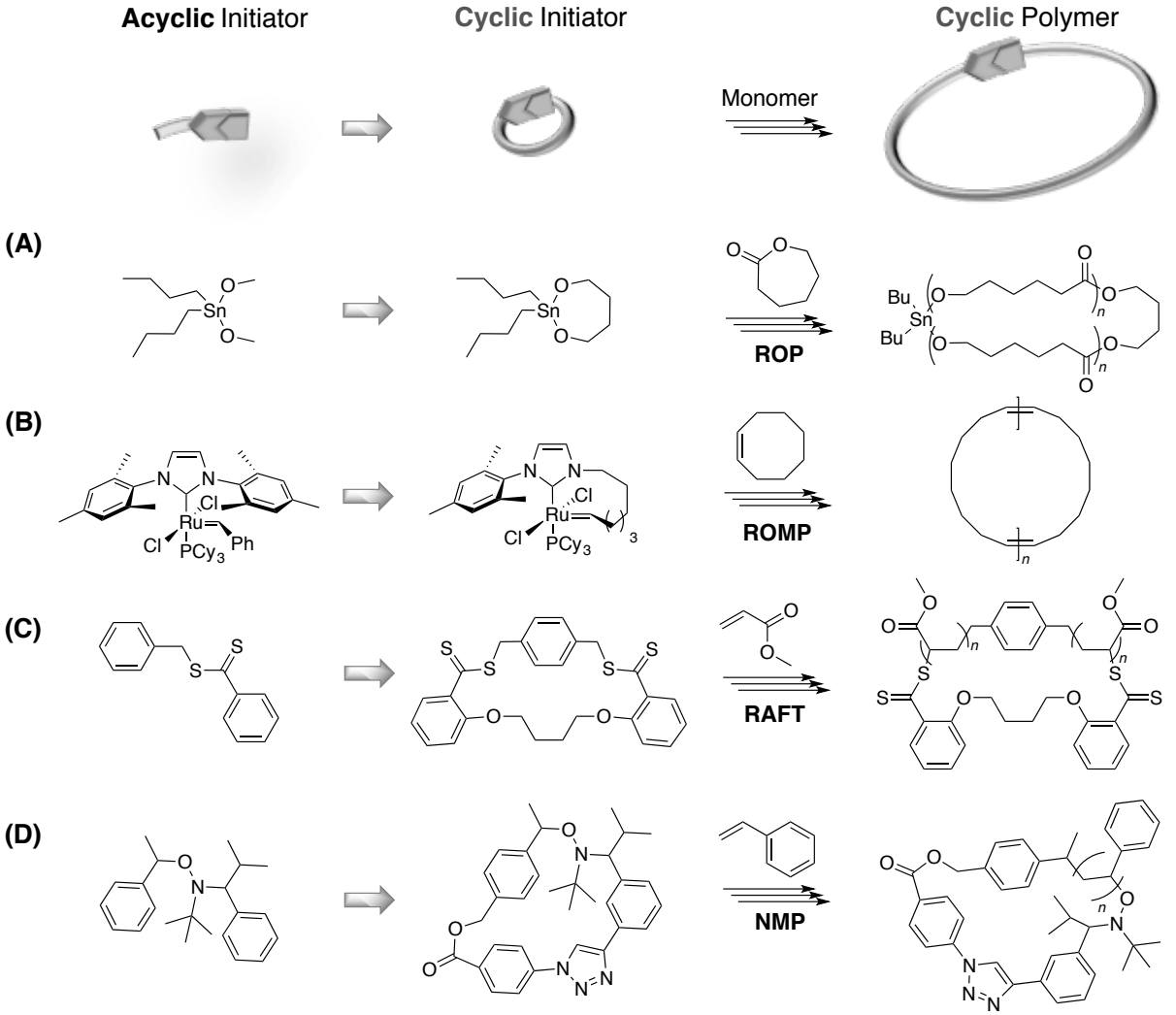



**Figure 3.** Design of cyclic initiators for ring-expansion polymerizations based on acyclic counterparts for living polymerization.

incorporated in cyclic molecules for ring expansion polymerizations. Upon stimulus (γ-ray or heat), the cyclic chain-transfer agent or the initiator bonds gave carbon radical together with sulfur radical or nitroxide. Vinyl monomer added to the carbon radical, which is electrostatically neutral species, and realized using cyclic; however, high dilution is required same as macrocyclization approach since growing species are far away from leaving group.

**Issues in Ring-Expansion Polymerization**

As mentioned above, some systems for ring-expansion polymerization have been developed for efficient syntheses of cyclic polymers.[28, 29, 32–36] However, most of examples on ring-expansion polymerization are mainly based on ring opening polymerization of cyclic monomers, probably because cyclic intermediate generate more advantageously than addition polymerization. Thus, number of examples is still limited on ring-expansion polymerization of vinyl monomer, which is an acyclic monomer. As already established, there are many systems for living "addition" polymerization, and now precise syntheses of well-defined polymers are easily reached. If ring-expansion polymerization can be controlled like conventional living polymerizations, what have been achieved with the living polymerizations, such as control of molecular weight and syntheses of block/graft copolymers, would be realized even for cyclic polymers. In this way, the advent of well-controlled ring-expansion addition polymerization would open the door to new polymer science as well as development of polymeric materials on the basis of macromolecular ring topology.

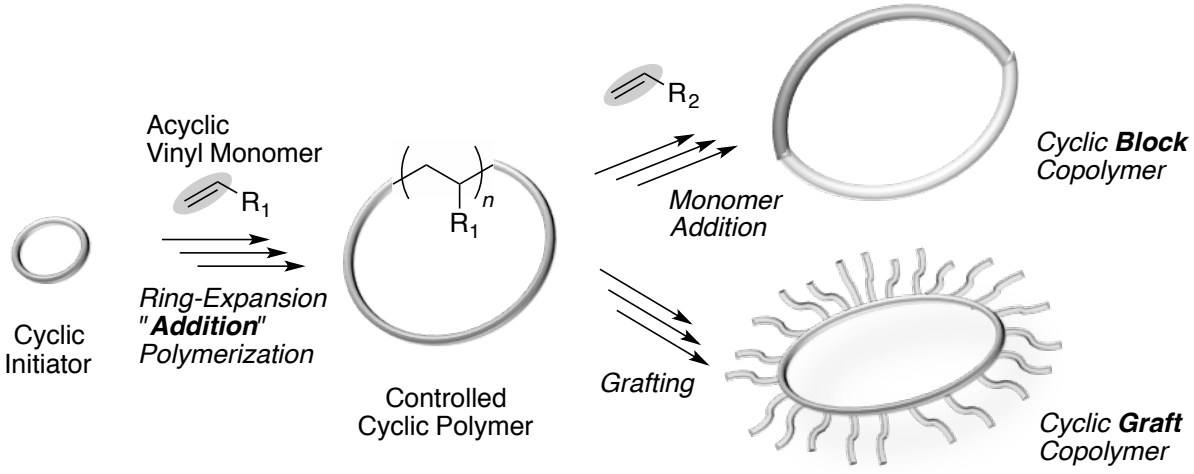



**Figure 4.** Issues in ring-expansion polymerization

## Objectives

As described in the background section, "ring" has been an intriguing topology for polymer design, but examples on ring-expansion polymerization, which is the methodology for the efficient synthesis, are limited. In particular, for addition polymerization of vinyl compounds, there are a few examples on ring-expansion polymerization that enable precision syntheses of cyclic polymers. In this thesis, the author determined to develop a versatile ring-expansion addition polymerization that accomplishes following goals:

(1) Control of molecular weight and molecular weight distribution
(2) Precision synthesis of cyclic polymer-based architecture
(3) Characterization of ring-driven properties

To this end, the author generalized the requirement for ring-expansion polymerization as follows.

(1) Dissociative leaving group should be organic to be embedded in cyclic structure
(2) No side reaction during polymerization not to produce linear polymer
(3) Leaving group (L) should be intact even after polymerization

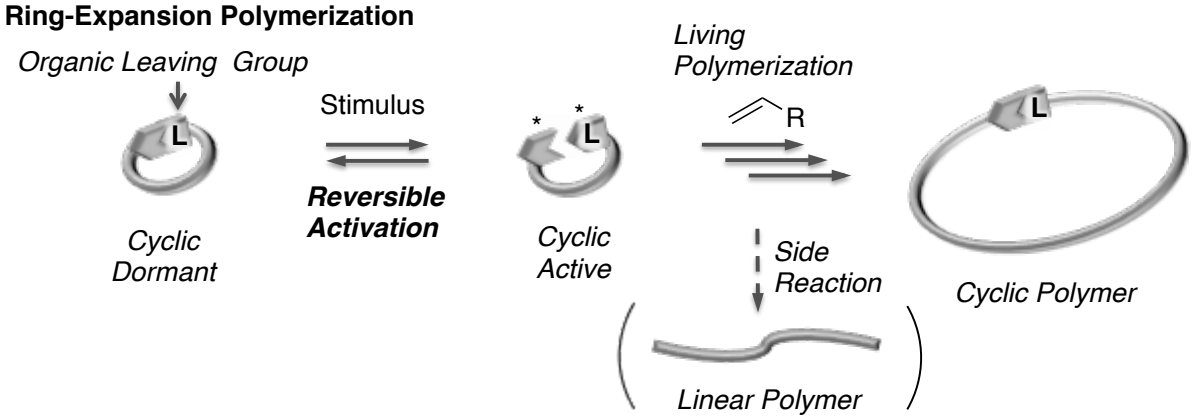



**Figure 5.** Schematic illustration of ring-expansion polymerization.

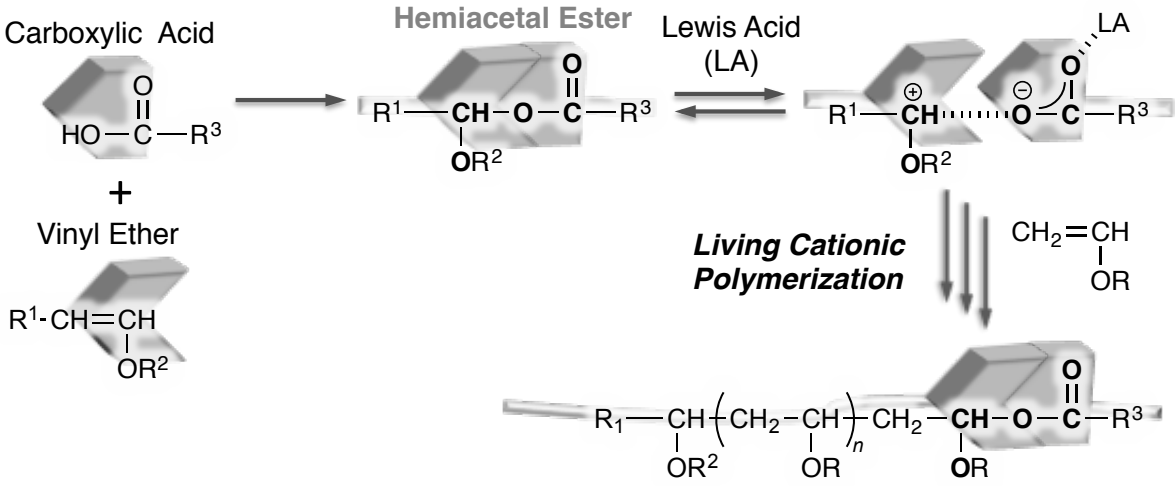



**Figure 6.** Chemistry of hemiacetal ester bond: synthesis and living cationic polymerization of vinyl ethers.

For requirement (1), a key is to find a "multivalent" leaving group that can be built-in into a cyclic initiator and a cyclic dormant species therefrom; this immediately excludes halogens (for radical and cationic species), alkali metals (for anionic species), and other monovalent leaving groups.

The author focused on cationic polymerization of vinyl ethers initiated from acetic acid adduct of vinyl ether.[37–41] Addition of acetic acid to vinyl ether forms hemiacetal ester (HAE) bond, and Lewis acid coordinates to the carbonyl group to generate ion pair of carbocation and carboxylate anion, and thus to living cationic polymerization of vinyl ethers proceed. If hemiacetal ester bond are embedded cyclically to endocyclically produce carbocation and carboxylate anion, and subsequent cationic polymerization is controlled while keeping hemiacetal ester bond, cyclic poly(vinyl ether) is expected. These characteristics satisfy both requirements (2) and (3).

### (1) Ring-expansion polymerization for cyclic polymers

In the first part of this thesis, the author developed ring-expansion cationic polymerization by using a hemiacetal ester bond. The author expected that connection of $R^1$, $R^2$, $R^3$ (in Figure 6) to introduce HAE bond in cyclic structure and choice of Lewis acid for activation HAE bond while maintaining HAE bond during and end of polymerization can realize ring-expansion living cationic polymerization. Furthermore, polymerization condition such as Lewis acid catalyst and reagent concentration were optimized to realize high molecular weight polymer and block polymerization. Moreover, the author thought that cyclic initiator

affected polymerization behavior, thus the relationship between cyclic structure of initiator and efficacy as the initiator was scrutinized.

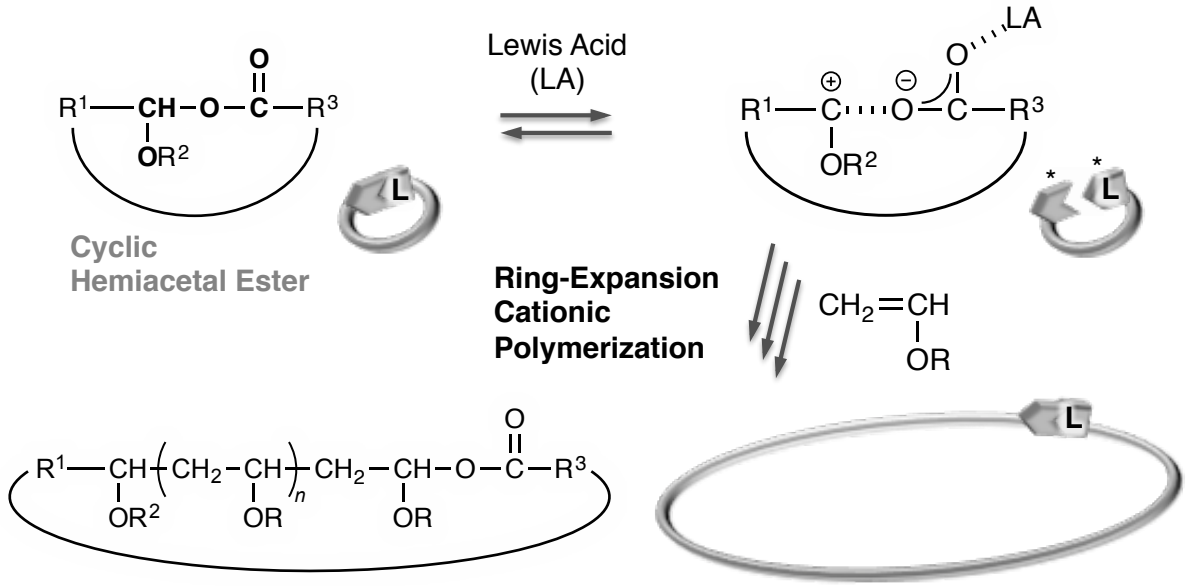



**Figure 7.** Ring-expansion living cationic polymerization using cyclic hemiacetal ester bond.

**(2) Precision synthesis of cyclic polymer-based architecture and ring-driven properties**

The author extended ring-expansion cationic polymerization to versatile ring-expansion polymerization that allowed control of molecular weight, molecular weight distribution, variety of pendant functionality, and branched structure. For pendant functionality and branched structures, he focused on designability of vinyl ether pendant for introducing functional group and for diversifying cyclic polymer-based architectures. Next, for controlled molecular weight and molecular weight distribution, the author exploited the reversible activation of HAE bond even in the absence of monomer. Although obtained polymer was broad because of intermolecular counter-anion exchange reaction during polymerization, the author elegantly switched the counter-anion exchange reaction to "intra"molecular at the final stage of polymerization without deactivation of Lewis acid catalyst. This method is extended to construct cyclic diblock copolymers. Finally, for evaluating ring-driven characteristics, the author designed vinyl ethers that give high glass transition temperature and thermo-sensitivity in solution, and these vinyl ethers were polymerized from cyclic and acyclic initiators. The cyclic and linear polymers therefrom were compared at same condition in the measurement of thermal analysis and turbidity measurement.

## Outline of This Study

The present thesis consists of two parts: **Part I** (Chapter 1–3) deals with the early development of ring-expansion cationic polymerization for cyclic polymers, where vinyl ethers sequentially inserted into cyclic hemiacetal ester, leading to macrocyclic polymer. **Part II** (chapter 4–6) focused on application of ring expansion cationic polymerization for more versatile use and elucidating the ring-driven physical properties.

**Chapter 1** describes the first report on ring expansion cationic polymerization by using cyclic hemiacetal ester as an initiator (Figure 8). The choice of a Lewis acid catalyst ($SnBr_4$) is crucial to retain the cyclic structure via the reversibly dissociable but relatively strong ester bond not only during propagation but also even after quenching. The formation of cyclic polymers was proved by irreversibly cleaving the hemiacetal ester linkage of the product via acidic hydrolysis into an open-chain structure, *i.e.*, an increase of peak top molecular weight (hydrodynamic radius) in size exclusion chromatography (SEC), along with the clean transformation of the endocyclic hemiacetal ester into an α-carboxylic acid and ω-aldehyde terminals (by $^1$H NMR). In addition, absolute mass of the polymer chain agreed calculated value assuming that the polymer has no chain-end group. The propagating species found to have long lifetime as demonstrated by successful monomer-addition experiments and a linear increase in molecular weight with conversion.

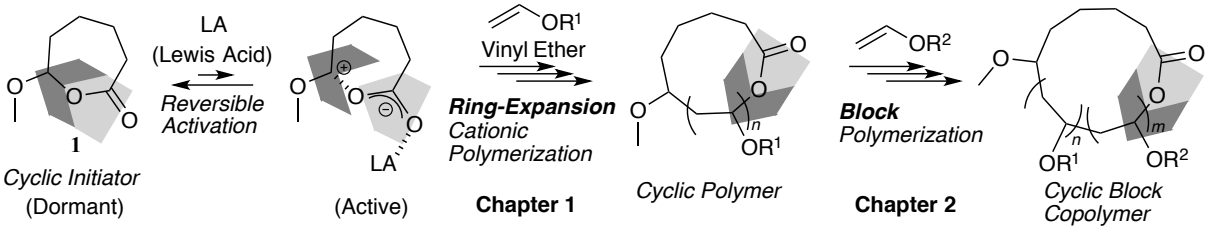



**Figure 8.** Ring-expansion cationic polymerization of vinyl ether with cyclic hemiacetal ester compound (Chapter 1) and the optimization of polymerization condition for block copolymerization (Chapter 2).

**Chapter 2** deals with optimization of reaction conditions (Lewis acid catalysts/activators, solvents, temperature, and reagent concentration) on the selectivity and controllability for construction of ring chains (Figure 8). For example, the choice of the Lewis acid catalysts turned out crucial. Specifically, tin tetrabromide ($SnBr_4$) was suitable for selective propagation in ring expansion manner, whereas other Lewis acids ($ElAlCl_2$, $SnCl_4$) gave less controlled polymer or linear polymer chain via unfavorable and irreversible side reactions.

Multimodal curves were obtained by "ring fusion", however, this could be relatively suppressed by decreasing concentration of the initiator from the beginning. Under these optimized conditions, the propagation is controlled enough to allow sequential addition of monomers to give either chain-extended homopolymers or block copolymers.

**Chapter 3** discusses effects of cyclic hemiacetal ester compound in ring-expansion cationic polymerization of vinyl ethers (Figure 9). 7-membered cyclic hemiacetal ester bond is strained enough to facilitate faster initiation reaction than propagation reaction, whereas 6-membered and linear counterparts are less strained and its propagation is not well controlled. This high strain in 7-membered hemiacetal ester allowed homo-oligomerization in ring-expansion manner to yield cyclic oligomer. Furthermore, concurrent cationic copolymerization of hemiacetal ester and isobutyl vinyl ether was also realized.

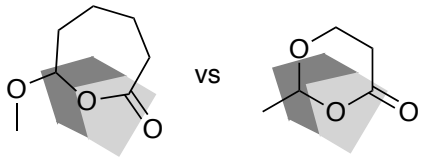



**Figure 9.** Comparison of cyclic hemiacetal ester in ring-expansion cationic polymerization (Chapter 3).

In **Chapter 4**, the author clarified the ring-expansion cationic polymerization with a cyclic hemiacetal ester (HAE)-based initiator were versatile in terms of applicable vinyl ether (VE) monomers toward ring-based polymers (Figure 10). Although there was a risk that higher reactive VEs may incur β-H elimination of the HAE-based cyclic dormant species to irreversibly give linear chains, the ring-expansion polymerizations of various alkyl vinyl ethers such as ethyl, cyclohexyl, tricyclodecane, and dodecyl vinyl ethers were controlled to give corresponding cyclic polymers. Functional vinyl ether monomers were also available, and for instance vinyl ether carrying an initiator moiety for metal-catalyzed living radical polymerization in the pendant allowed construction of ring-linear graft copolymers through the grafting-from approach. Furthermore, ring-based gel was prepared via the addition of divinyl ether, because multi HAE bonds cyclic polymers or fused rings were formed during the polymerization.

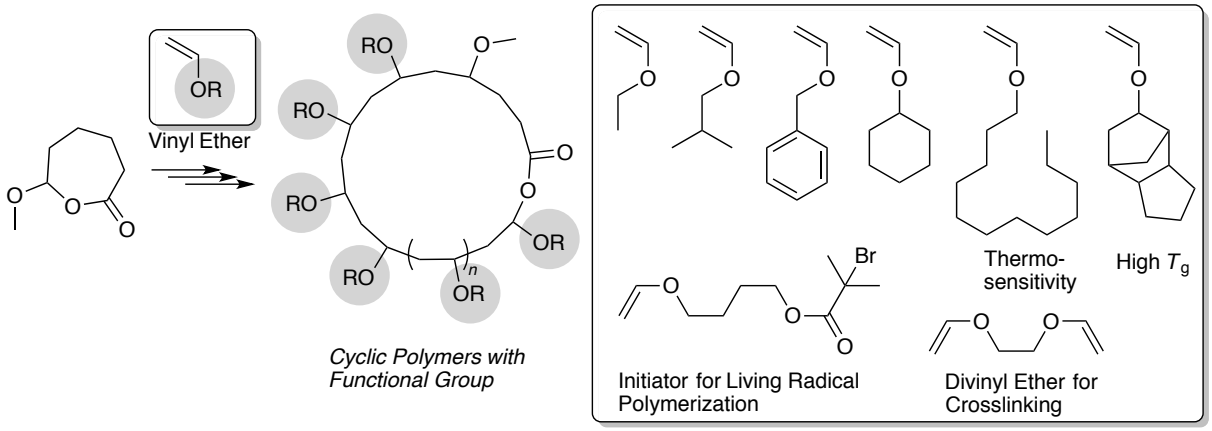



**Figure 10.** Applicable vinyl ethers in ring-expansion cationic polymerization for topologically designed polymers with functional groups (Chapter 4).

In **Chapter 5**, the author demonstrate a convergent approach to convert "fused" ring chains obtained via ring-expansion cationic polymerization of vinyl ether with a hemiacetal ester (HAE)-based cyclic initiator (1) into "sing" ring ones of narrow molecular weight distributions (Figure 11). In the ring-expansion propagation process, the propagation can be controlled without any side reactions but an intermolecular counteranion exchange reaction between hemiacetal ester bonds between propagating ring polymers ineluctably occurs resulting in broad molecular weight distributions composed of "fused" ring chains with multiple hemiacetal ester bonds as well as a "sing" ring chain with one HAE bond. Hence, after monomer conversion reached over 95%, the polymerization solution was diluted (*i.e.*, post dilution) without deactivation of an employed Lewis acid activator (*i.e.*, $SnBr_4$) to induce intramolecular counteranion exchange in the fused ring chain. SEC curves of the product eventually became almost unimodal, though a small shoulder peak from the fused ring

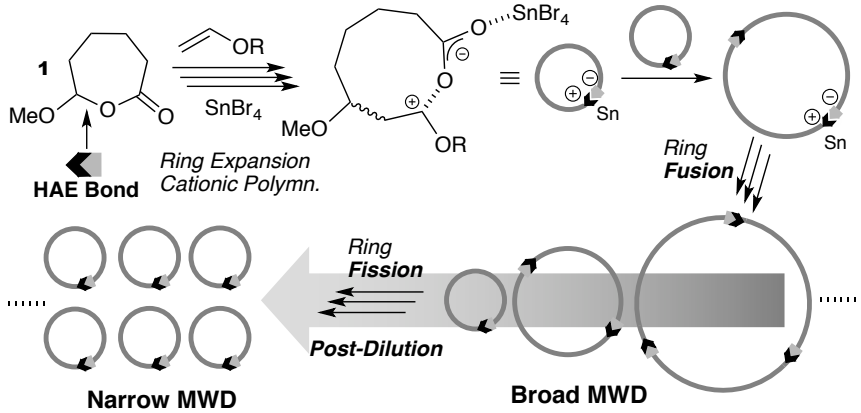



**Figure 11.** Convergent approach for cyclic polymers with narrow molecular weight distribution in ring-expansion cationic polymerization.

remained. Importantly, the HAE bond in ring chains still survived even after the post dilution process, which was confirmed by $^1$H NMR, and the retention of the ring structure was also supported by an acidolysis experiment where the apparent peak top molecular weight ($M_p$) was increased in SEC due to topology conversion from a ring to linear one. The approach was proved to be effective even for higher molecular weight ring polymers that were prepared with a higher [monomer]/[**1**] ratio as well as ring block copolymers

In **Chapter 6**, ring-driven physical properties of cyclic poly(vinyl ether)s were studied, such as thermal sensitivity in solution and glass transition temperature ($T_g$). The samples were precisely synthesized via ring-expansion cationic polymerization with a hemiacetal ester (HAE)-based cyclic compound as the initiator. To clarify the topology effects, linear polymers with similar molecular weights were also prepared via a conventional living cationic polymerization with the HAE-based acyclic initiator (i.e., an adduct of vinyl ether with acetic acid) for comparison. Cyclic poly(vinyl ether)s carrying bulky tricyclic alkane pendant exhibited higher $T_g$s than the linear counterparts of similar molecular weights. Interestingly, the $T_g$ was not so decreased even as the molecular weight was lower, which was clearly different from linear polymers. The thermo-sensitivity of cyclic polymer was also studied with ethyl acetate solution of poly(dodecyl vinyl ether) showing upper critical solution temperature (UCST) at around 45°C. The UCST behavior on cooling process was clearly different from for the linear counterpart, and the cyclic polymer showed duller sensitivity to temperature than the linear. These unique properties of cyclic polymers are likely attributed to the endless structures free from the terminal groups.

In summary, this thesis comprehensively presents developments of ring-expansion cationic polymerization, extensions of this ring-expansion polymerization to construction of various architecture based on cyclic topology, and evaluations of ring-driven physical properties of cyclic polymers. The author hopes that the researches in this thesis not only contribute to development of precision polymerization for efficient and presice synthesis of cyclic polymer but also impart the new possibility for conventional linear polymer-based polymer science and material researches.

## References


(1) Heimenz, P. C.; Lodge, T. P. *Polymer Chemstry, 2nd ed*.; CRC Press, 2007.

(2) Morawetz , H. *History of Polymer Science. Encyclopedia of Polymer Science and Technology*. 1–30. Wiley, 2014.

(3) Semlyen, J. A. *Cyclic Polymers, 2nd ed*.; Kluwer Academic: Dordrecht, The Netherlands, 2000.

(4) Tezuka, Y. *Topological Polymer Chemistry: Progress of Cyclic Polymers in Syntheses, Properties and Functions*. World Scientific Publishing Co. Pte. Ltd, 2013.

(5) H. R. Kricheldorf, *J. Polym. Sci., Part A: Polym. Chem.* **2010,** *48,* 251–284.

(6) Z. Jia and M. J. Monteiro, *J. Polym. Sci., Part A: Polym. Chem.* **2012,** *50,* 2085–2097.

(7) B. A. Laurent; S. M. Grayson, *Chem. Soc. Rev.* **2009,** *38,* 2202–2213.

(8) Geiser, D.; H. Hocker, K. *Macromolecules* **1980,** *13,* 653–656.

(9) Webster, O. W. *Science* **1991,** *251,* 887–893.

(10) Szwarc, M. *Nature* **1956,** *178,* 1168–1169.

(11) Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc*. 1956, 78, 2656–2657.

(12) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984,** *17,* 265–268.

(13) Sawamoto, M. *Prog. Polym. Sci*. **1991,** *16,* 111–172.

(14) Matyjaszewski, K.; Ed.; *Cationic Polymerizations*; Marcel Dekker: New York, 1996.

(15) Aoshima, S.; Kanaoka, S. *Chem. Rev*. **2009,** *109,* 5245–5287.

(16) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995,** *28,* 1721–1723.

(17) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev*. **2001,** *101,* 3689–3745.

(18) Ouchi, M.; Terashima, T.; Sawamoto, M. *Chem. Rev*. **2009,** *109,* 4963–5050.

(19) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc*. **1995,** *117,* 5614–5615.

(20) Matyjaszewski, K.; Xia, J. *Chem. Rev*. **2001,** *101,* 2921–2990.

(21) Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev*. **2007,** *107,* 2270–2299.

(22) B. M. Rosen; Percec, V. *Chem. Rev*. **2009,** *109,* 5069–5119.

(23) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem*. **2005,** *58,* 379–410.

(24) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev*. **2001,** *101,* 3661–3688.

(25) Yamago, S. *J. Polym. Sci., Part A: Polym. Chem*. **2006,** *44,* 1–12.

(26) Bates, F. S. *Annu. Rev. Phys. Chem*. **1990,** *41,* 525-557.

(27) Verduzco, R.; Li, X.; Peseka, S. L.; Steinc, G. E. *Chem. Soc. Rev*. **2015,** *44,* 2405–2420.

(28) Kricheldorf, H.; Lee, S. –R.; Schittenhelm, N. *Macromol. Chem. Phys*. **1998,** *199*,

273–282.

(29) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041–2044.

(30) He, T.; Zheng, G.–H.; Pan, C. *Macromolecules* **2003,** *36,* 5960–5966.

(31) Narumi, A.; Zeidler, S.; Barqawi, H.; Enders, C.; Binder, W. H. *J. Polym. Sci., Part A: Polym. Chem.* **2010,** *48,* 3402–3416.

(32) Takeuchi, D.; Inoue, A.; Osakada, K.; Kobayashi, M.; Yamaguchi, K. *Organometallics* **2006**, *25,* 4062–4064.

(33) Kudo, H.; Makino, S.; Kameyama, A.; Nishikubo, T. *Macromolecules* **2005,** *38,* 5964–5969.

(34) Kudo, H.; Sato, M.; Wakai, R.; Iwamoto, T.; .; Nishikubo, T. *Macromolecules* **2008,** *41,* 521–523.

(35) Endo, K.; Shiroi, T.; Murata, N.; Kojima, G.; Yamanaka, T. *Macromolecules* **2004,** *37,* 3143–3150.

(36) Imada, Y.; Okita, C.; Maeda, H.; Kishimoto, M.; Sugano, Y.; Kaneshiro, H.; Nishida, Y.; Kawamorita, S.; Komiya, N.; Naota, T. *Eur. J. Org. Chem.* **2014,** *26,* 5670–5674.

(37) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991,** *24,* 3988–3992.

(38) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992,** *25,* 2587–2591.

(39) Hashimoto, T.; Iwata, T.; Minami, A.; Kodaira, T. *J. Polym. Sci. Part A: Polym. Chem.* **1998,** *36,* 3173–3185.

(40) Hashimoto, T.; Iwata, T.; Uchiyama, N.; Kodaira, T. *J. Polym. Sci. Part A: Polym. Chem.* **1999,** *37,* 2923–2932.

(41) Hashimoto, T.; Takahashi, T.; Kodaira, T. *J. Polym. Sci. Part A: Polym. Chem.* **2000,** *38,* 781–784.

# PART I

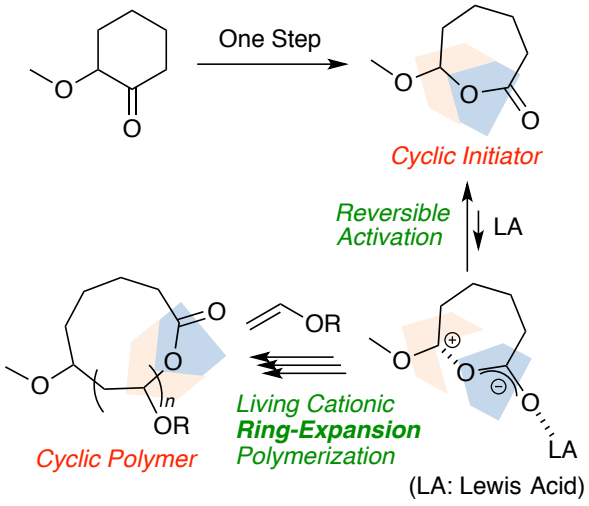
# Ring-Expansion Cationic Polymerization For Cyclic Polymers

# *Chapter 1*

## Ring–Expansion Living Cationic Polymerization via Reversible Activation of a Hemiacetal Ester Bond


### Abstract

In this chapter, the author provides an effective route to cyclic polymers via the Lewis acid-assisted "ring-expansion" living cationic polymerization of vinyl ethers, directly from a simple "cyclic initiator" designed with a hemiacetal ester for dynamic and reversible initiation and propagation. The built-in hemiacetal ester, or a carboxylic acid–vinyl ether adduct, is a key to control the polymerization: as the leaving group, the activated carboxylate is well-suited for designing the cyclic structure, differing from monovalent halogens often employed in carbocationic initiation. The choice of a Lewis acid catalyst ($SnBr_4$) is equally crucial to retain the cyclic structure via the reversibly dissociable but relatively strong ester bond not only during propagation but also even after quenching. The formation of cyclic polymers was proved by irreversibly cleaving the hemiacetal ester linkage of the product via acidic hydrolysis into an open-chain structure, i.e., an increase in size exclusion chromatography (SEC) molecular weight (hydrodynamic radius), along with the clean transformation of the endocyclic hemiacetal ester into an α-carboxylic acid and ω-aldehyde terminals (by NMR). The polymerization was really "living" polymerization via ring-expansion, as demonstrated by successful monomer-addition experiments and a linear increase in molecular weight with conversion. This ring-expansion living polymerization would open a door to well-defined cyclic polymers free from terminus (end groups) and to hybrid macromolecules with combinations of cyclic and linear architectures.

## Introduction

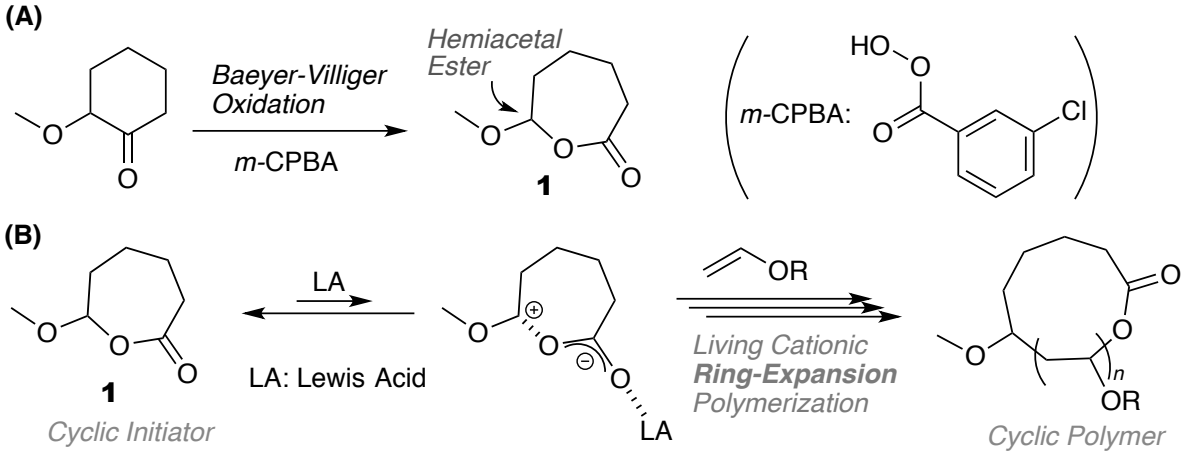
Linear polymers are so common that most polymer chemists would picture linear chains in their mind when discussing polymer design. In contrast, "cyclic" polymers belong to an atypical category in terms of topology[1] since they carry no end groups, by which they are accordingly expected to hold the promise of specific functions and physical properties. For example, polymer physicists have been interested in properties or functions derived from the cyclic structures in solution, in bulk, or on surface, most typically lower viscosity than linear counterparts, though still poorly understood. The paucity of detailed knowledge about cyclic polymers is primarily due to the limited availability of synthetic methods for cyclic polymers,[2,3] in sharp contrast to that a wide variety of well-defined linear polymers have been constructed by living and controlled polymerizations. Obviously, precision synthesis of cyclic polymers will open the door toward new polymer design and functions.[4]

A possible way to cyclic polymers is to connect both end groups of a linear chain, i.e., by intramolecular chain-end coupling.[5–7] In this case, diluted conditions are often required to prevent intermolecular coupling or chain extension, and quantitative single-chain cyclization is not so easy, which would have hindered extensive research and application of cyclic polymers.

Another methodology is a "ring-expansion" polymerization[8–18] from a cyclic initiator, which is in principle independent of the concentration and possibly quantitative in cyclization. Though rather limited in scope, successful examples include ring-opening metathesis polymerization (ROMP)[8] and nitroxide-mediated radical polymerization (NMP) [16,17]. The leaving or capping group in these cyclic initiators should be endocyclic, a carbene in ROMP or a nitroxide in NMP as designed for a "reversibly activatable" bond to which monomers successively insert to expand a cyclic architecture. However, the reported syntheses are apparently not so straightforward, and polymerization control is less perfect than with the corresponding linear initiator. Indeed, there have been little examples of well-defined ring-expansion block copolymerization.

In this research, the author provide an effective system for "ring-expansion living cationic polymerization", a precisely controlled ring-expansion via a carbocationic growing species (Scheme 1). Crucial is the use of a cyclic hemiacetal ester, or a carboxylic acid−vinyl ether adduct,[19] as an initiator where, upon coupling with a Lewis acid, the endocyclic activated carboxylate reversibly generates a growing carbocation associated with a nucleophilic ester anion within a single molecule. The initiator can readily be synthesized in

one step from a common compound, and the polymerization is really "living" polymerization, as demonstrated by a monomer addition experiment.




**Scheme 1.** (A) Synthesis of Cyclic Initiator (**1**) and (B) Ring-Expansion Living Cationic Polymerization of Vinyl Ethers with 1 (*m*-CPBA: *m*-Chloroperoxybenzoic Acid)

## Experimental

### Materials.

**For Synthesis of 1:** Dichrolomethane (Wako, >99.5%), tetrahydrofuran (THF) (Wako; >99.5%), *m*-chroloperbenzoic acid (Wako; >69%, with water), and sodium hydrogen carbonate (Wako; >99.5%) were used as received without further purification. 2-methoxycyclohexan-1-one (TCI; >95.0%) was purified by column chromatography (silica gel) before use.

**For Polymerization and Hydrolytic Cleavage**: Isobutyl vinyl ether (IBVE) (Tokyo Kasei; >99%) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide, and distilled twice from calcium hydride before use. 1,4-Dioxane (DO) was dried overnight over calcium chloride and distilled from sodium benzophenone ketyl. Toluene (Kishida Kagaku, Osaka; 99.5%), dichromethane (Kishida Kagaku, Osaka; 99.5%) and hexane (Kishida Kagaku, Osaka; 96%) were dried and purified by passing through purification columns (Solvent Dispensing System, SG Water USA, Nashua, NH; Glass Contour), kept over molecular sieves 4A for more than one day. $SnBr_4$ (Aldrich; >99%), 2,6-di-*tert*-butyl-4-methylpyridine (Aldrich; >99%) trifluoroacetic acid (Wako; >98%) were used as received.

**Synthesis of cyclic initiator 1 via Baeyer-Villiger oxidation.**

To a dichloromethane solution of 2-methoxycyclohexan-1-one were added sodium hydrogen carbonate (1.3 equiv) and *m*-chloroperbenzoic acid (*m*-CPBA, 1.5 equiv). The resulting mixture was stirred at 0 ˚C to room temperature for 1 hour. Excess *m*-CPBA was quenched with aqueous sodium sulfite solution, and the resulting mixture was extracted with chloroform. The organic layer was separated, washed with aqueous sodium hydrogen carbonate, and then with aqueous sodium chloride. Finally, it was concentrated with toluene under reduced pressure to remove water by azeotrope.

**Living cationic polymerization of IBVE with 1.**

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example is given below. The reaction was initiated by adding solutions of $SnBr_4$ (5.0 mM in $CH_2Cl_2$: 0.5 mL) via a dry syringe into a mixture (4.5 mL) containing IBVE (0.25 mL), 1.4-dioxane (0.13 mL), hexane (0.10 mL), cyclic initiator **1** and 2,6-di-*tert*-butyl-4-methylpyridine in $CH_2Cl_2$ at 0 ˚C. After a predetermined interval, the polymerization was terminated with prechilled methanol. Monomer conversion was determined from its residual concentration measured by gas chromatography with hexane as an internal standard. The quenched reaction mixture was washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(IBVE).

**Hydrolytic cleavage of hemiacetal ester in cyclic Poly(IBVE)**

A typical example of hydrolysis of hemiacetal ester linkage in cyclic poly(IBVE) is given below. In a round-bottom flask (50 mL) was placed “as-obtained” (i.e., cyclic) poly(IBVE) (0.15 g) and it was dissolved into THF (4 mL) and trifluoroacetic acid (1.0 mL). To the resultant solution was added $H_2O$ (0.2 mL) and it was stirred at room temperature for 12 hours. The solution was washed with water and hexane to remove trifluoroacetic acid and the organic layer was evaporated under vacuum to obtain linear-poly(IBVE).

## Result and Discussion

The cyclic hemiacetal initiator (**1**) was synthesized by Baeyer−Villiger oxidation from a cyclohexanone with a vicinal methoxy group (Scheme 1, A);[20] note that, with the six-membered precursor, **1** was designed to have a weakly strained seven-membered ring to facilitate initiation via transient ring-opening. As demonstrated in living cationic propagation of vinyl ethers,[21,22] the hemiacetal ester can be "reversibly" activated and dissociates into a carbocation with a Lewis acid (LA) as a catalyst, and proper choice of LA would allow retention of the intramolecular (endocyclic) hemiacetal ester bond not only in initiation/propagation but also even upon quenching the polymerization with methanol.[23] In this regard, the author found that tin tetrabromide ($SnBr_4$) is suitable as the LA catalyst for

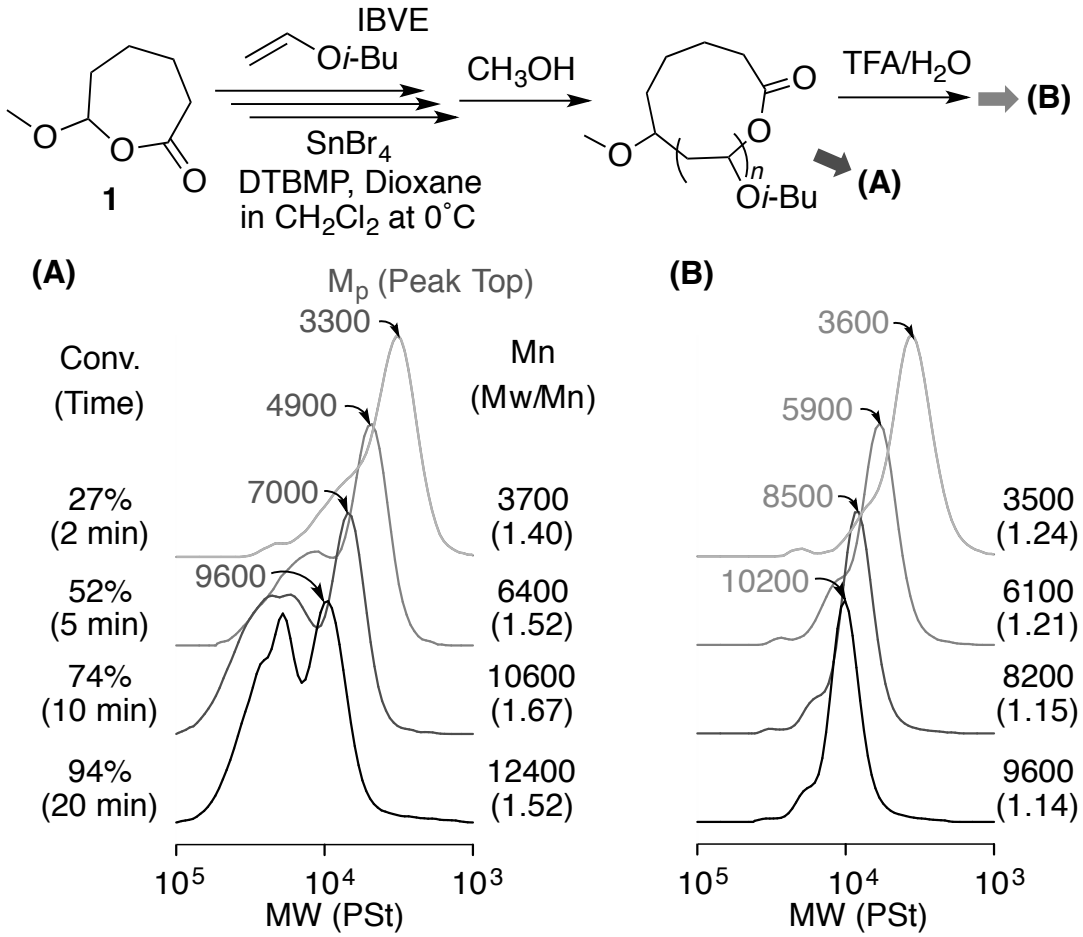



**Figure 1.** SEC curves of polymers in the polymerization of IBVE with **1** (A) and after hydrolysis of the products with aqueous trifluoroacetic acid (TFA) (B). Polymerization: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5.0/0.50/0.15 mM in $CH_2Cl_2$ with 2.5 vol % dioxane at 0 °C. Hydrolysis: TFA (1.40 mL) and $H_2O$ (0.20 mL) for polymer (0.157 g) in THF (4.0 mL) at rt for 12 h.

this purpose, as the author's group has already achieved, with this particular LA, precise syntheses of "cleavable" block copolymers in which two segments are connected by a hemiacetal ester connection.[24,25]

Given these initiator/catalyst design criteria, isobutyl vinyl ether (IBVE) was polymerized with **1** and $SnBr_4$ in the presence of dioxane and 2,6-di-tert-butyl-4-methylpyridine (DTBMP) in $CH_2Cl_2$ at 0 °C (Figure 1); the cyclic ether is a mild Lewis base for reaction control,[26] and the pyridine for sequestration of a proton is possibly generated from adventitious protogen and/or β-proton elimination (chain transfer) from the growing vinyl ether cation.[27] The polymerization was quenched by an addition of methanol in predetermined time. The monomer was smoothly consumed, and the conversion reached 94% in 20 min. Size exclusion chromatography (SEC) curves of the obtained polymers turned out multimodal, but the main population was very sharp and shifted to higher molecular weight with increasing conversion without any tailing (Figure 1A). From these results, any irreversible chain transfer reaction (typically β-hydrogen elimination) did not occur during the polymerization.

The obtained polymers were mixed with aqueous $CF_3COOH$ (TFA) to convert the expected cyclic form into a linear open-chain form via the hydrolysis of the hemiacetal ester linkage. As shown in Figure 1B, the SEC curve turned almost unimodal and narrower, and most importantly, the peak top shifted to higher molecular weight, as typical in the trans-formation of a cyclic polymer into a linear counterpart due to an increase in hydrodynamic volume.[6]

The product structures were further analyzed in detail by $^1$H NMR spectroscopy before and after the hydrolysis. For the as-obtained polymer before hydrolysis (Figure 2A), a peak (*i*) characteristic of the methine in the hemiacetal ester was clearly observed around 6.0 ppm, in addition to another distinct signal (*a*) at 2.4 ppm from the neighboring methylene. Note that virtually no peak was detected for the methine of a methoxy-capped terminal [$\sim\sim$CH(O*i*-Bu)$OCH_3$; around 4.6 ppm], though the polymerization was quenched with methanol.[21] The apparent number-average molecular weight ($M_{n,NMR}$) was 5300, as calculated from the integrated intensity of signal a relative to the main-chain peaks (0.7−1.1 ppm), which was much lower than $M_{n,SEC}$ (8600) by SEC but agreed well with $M_{n,conv}$ (4900) by conversion (at 63%). All these observations indicate the expected cyclic structure. The cyclic structure was also supported by MALDI-TOF-MS analysis (Figure 3).

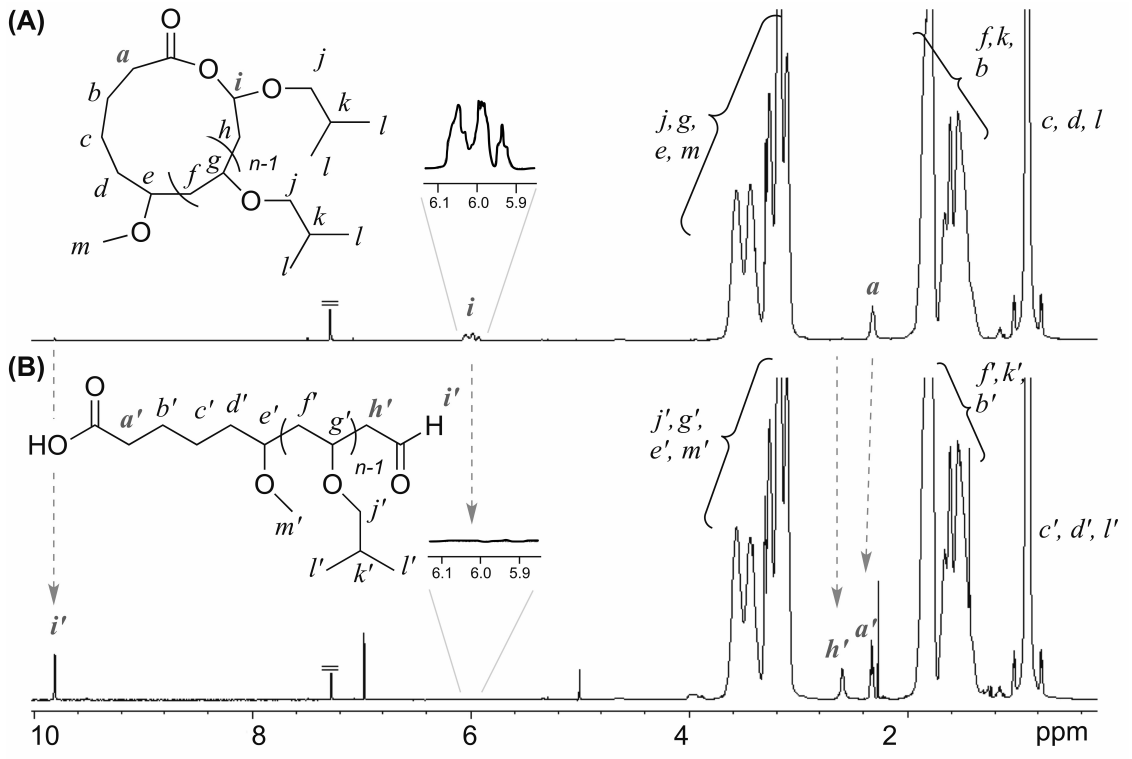



**Figure 2.** $^{1}$H NMR spectra of the obtained poly(IBVE)s before (A) and after (B) hydrolytic cleavage of hemiacetal ester.

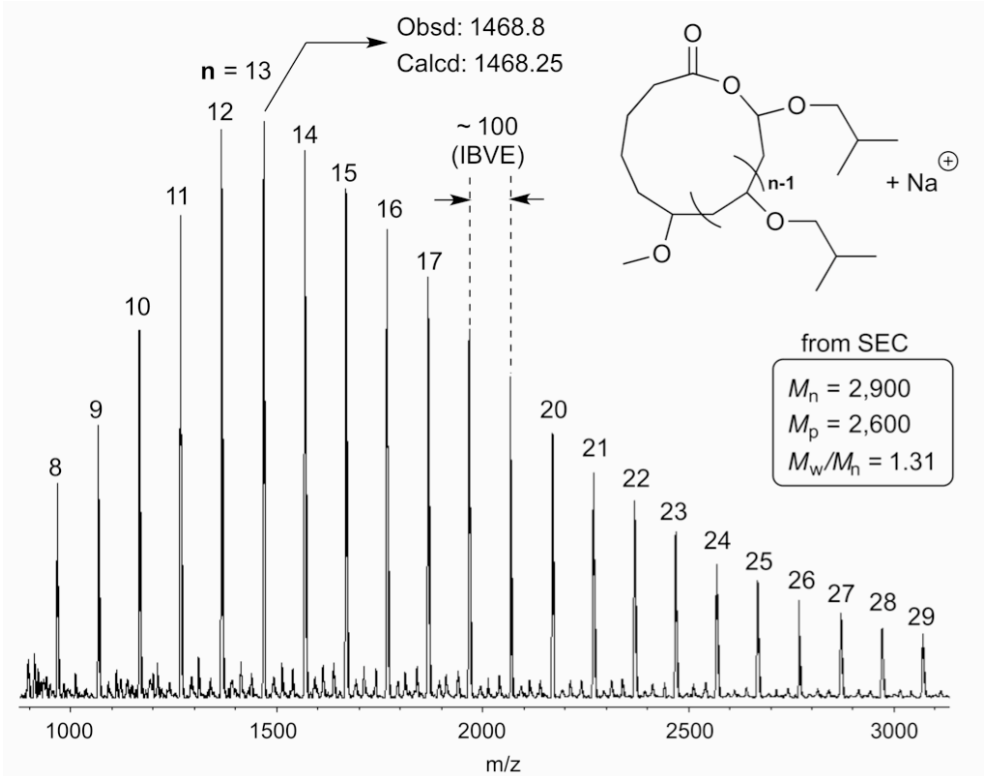
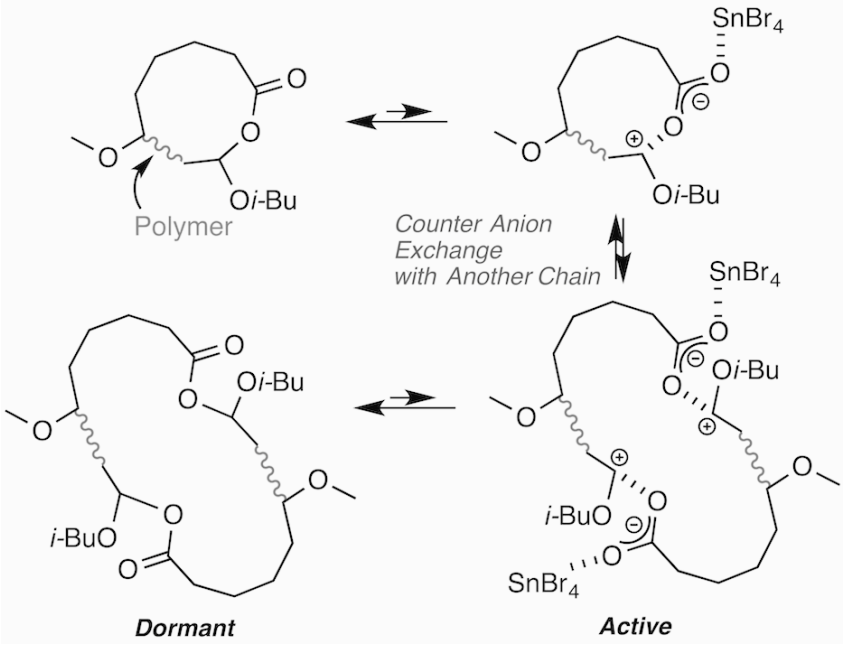



**Figure 3.** MALDI-TOF-MS spectrum of poly(IBVE) obtained with cyclic initiator **1**: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5.0/0.50/0.15mM in $CH_2Cl_2$ with 2.5 vol% dioxane at 0℃.

After the hydrolysis, the methine peak from the hemiacetal ester disappeared, and instead a new peak (*i'*) assignable to an aldehyde was observed at 9.8 ppm. The aldehyde/main chain signal ratio gave $M_{n,NMR}$ = 4600, reasonably close to $M_{n,conv}$ = 4900. From these results, the ring-expansion polymerization of IBVE was well controlled to give cyclic polymers.

The multimodal SEC profile of the pristine polymers (before cleavage), with a minor fraction of higher molecular weights, suggests that a larger cyclic polymer consisting of several segments (and thus of multiple hemiacetal linkages) was generated by occasional "fusion" of two or more cyclic living polymers via counteranion exchange, particularly at higher conversion (Scheme 2).[18,28] The near disappearance of these minor products upon hydrolytic cleavage supports this proposition, where the multiple hemiacetal linkages have all been cleaved to give a set of linear chains of similar molecular weights.




**Scheme 2.** Proposed Mechanism for Generation of Larger Cyclic Polymers

The living or precision-controlled nature of the polymerization was further demonstrated by sequential monomer-addition (chain-extension) experiments (Figure 4): When the polymerization was almost completed (conversion = 95%), a fresh feed of IBVE monomer was added to the reaction mixture. The added monomer was smoothly consumed up to a high conversion above 90% (Figure 4A), to give second-stage products with SEC distributions overall shifting to higher molecular weight along with conversion, though somewhat multimodal (Figure 4C, left).

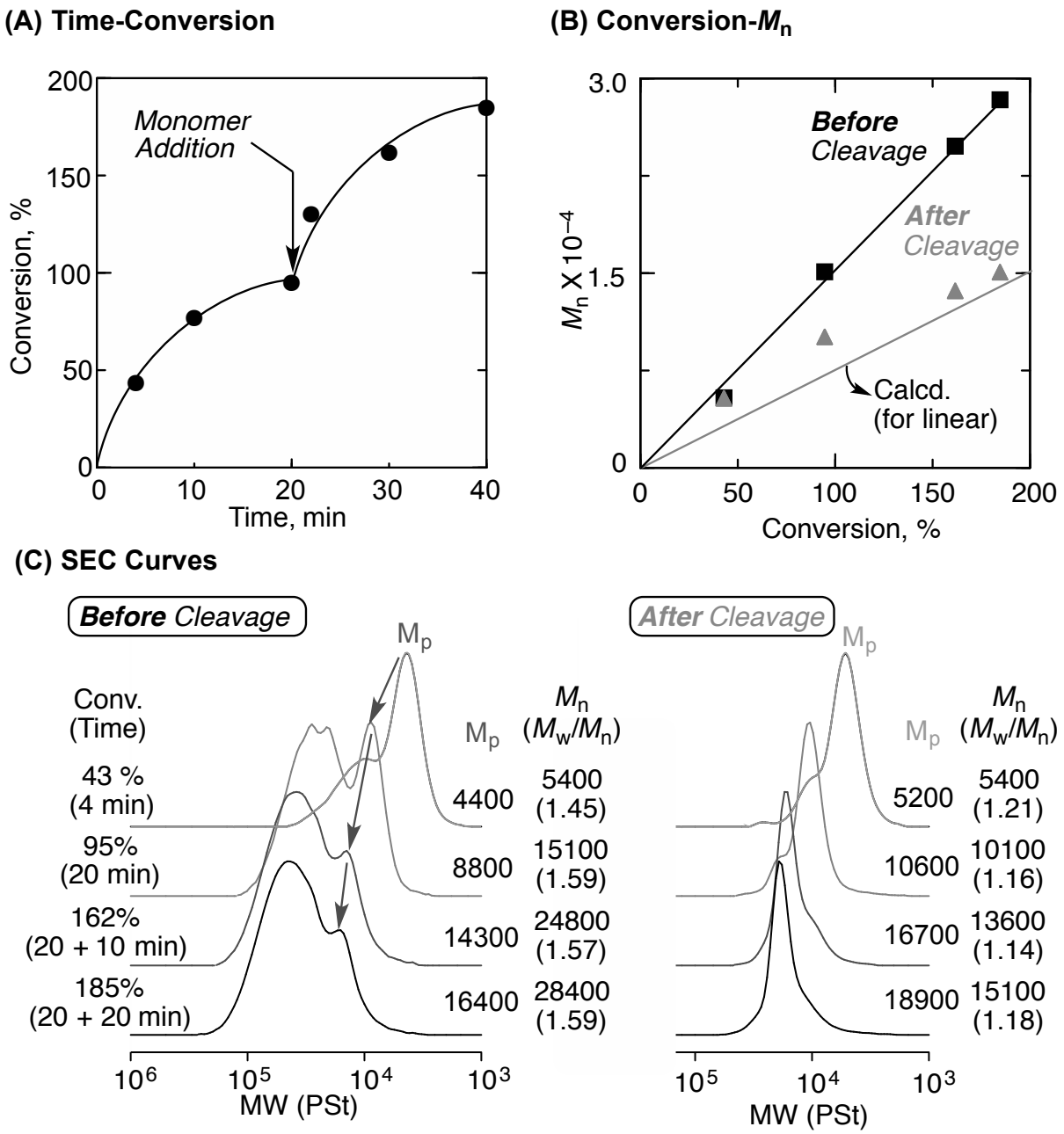



**Figure 4.** Sequential monomer-addition experiment in the ring-expansion living cationic polymerization of IBVE and hydrolysis (ring-cleavage) of the polymers with aqueous TFA: (A) Time−conversion curve; (B) conversion−$M_n$ plots before and after hydrolysis; and (C) SEC curves of the products. Polymerization: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0//[DTBMP]_0$ = 380/5.0/0.50/0.15 mM in $CH_2Cl_2$ with 2.5 vol % dioxane at 0 °C; $[IBVE]_{add}$ = 380 mM. Hydrolysis: see Figure 1 (caption).

After hemiacetal cleavage, much narrower and virtually monomodal SEC curves emerged (Figure 4C, right), with a clear molecular weight increase. The conversion−$M_{n,SEC}$ plots (Figure 4B) are linear and passing through the origin, both before and after the ring cleavage (squares and triangles, respectively), and the slope was reduced into half upon the cycle-to-linear transformation, all consistent with living nature of the polymers as well as the cyclic structures maintained throughout the two-stage polymerization processes. In addition, as also seen in Figure 3B, $M_{n,SEC}$ (triangles) after the cleavage agreed well with the calculated values ($M_{n,conv}$) for linear polymers (the straight line in gray).

From these results, the system is essentially "living" polymerization via the proposed ring-expansion mechanism. This feature further implies the possibility of ring-expansion "block" copolymerization by sequential addition of different monomers, and this will be presented in our forthcoming publication.

## Conclusion

In conclusion, the author has achieved a ring-expansion living cationic polymerization with a hemiacetal ester-based cyclic initiator **1** and an LA catalyst $SnBr_4$. The polymerization was well controlled without any unfavorable reactions to the ring-expansion event, such as β-hydrogen elimination and a bromide capping of the cationic intermediate with $SnBr_4$ [e.g., ~~C(OR)−OCO~~ + $SnBr_4$ → ~~C(OR)−Br + ($SnBr_3$)- OCO~~]. The polymerization control even after the fresh monomer would involve the potential of ring-expansion block copolymerizations. Block copolymers of cyclic structures would interest us for material applications of the ring-oriented self-assembly.[29] Larger cycles were in fact generated apparently via counteranion exchange between two hemiacetal linkages, but in our viewpoint, contriving polymerization conditions (solvent, temperature, and reagent concentrations) would suppress this process. In another extreme, the promotion of this cyclic fusion via counteranion exchange would in turn be interesting in that it would lead to another synthetic possibilty of cyclic "multiblock copolymers", which is also among our future research targets.

## References


(1) Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **2010,** *48,* 251–284.

(2) Laurent, B. A.; Grayson, S. M. *Chem. Soc. Rev.* **2009,** *38,* 2202– 2213.

(3) Tezuka, Y. *Polym. J.* **2012,** *44,* 1159–1169.

(4) Yamamoto, T. *Polym. J.* **2013,** *45,* 711–717.

(5) Hild, G.; Kohler, A.; Rempp, P. *Eur. Polym. J.* **1980,** *16,* 525–527.

(6) Lepoittevin, B.; Dourges, M. A.; Masure, M.; Hemery, P.; Baran, K.; Cramail, H. *Macromolecules* **2000,** *33,* 8218–8224.

(7) Schappacher, M.; Deffieux, A. *Macromolecules* **2001,** *34,* 5827–5832.

(8) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002,** *297,* 2041–2044.

(9) He, T.; Zheng, G. H.; Pan, C. Y. *Macromolecules* **2003,** *36,* 5960–5966.

(10) Kudo, H.; Makino, S.; Kameyama, A.; Nishikubo, T. *Macromolecules* **2005,** *38,* 5964–5969.

(11) Li, H.; Debuigne, A.; Jerome, R.; Lecomte, P. *Angew. Chem., Int. Ed.* **2006,** *45,* 2264–2267.

(12) Takeuchi, D.; Inoue, A.; Osakada, K.; Kobayashi, M.; Yamaguchi, K. *Organometallics* **2006,** *25,* 4062–4064.

(13) Culkin, D. A.; Jeong, W. H.; Csihony, S.; Gomez, E. D.; Balsara, N. R.; Hedrick, J. L.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **2007,** *46,* 2627–2630.

(14) Jeong, W.; Shin, E. J.; Culkin, D. A.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2009,** *131,* 4884–4891.

(15) Jeong, W.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2007,** *129,* 8414–8415.

(16) Narumi, A.; Zeidler, S.; Barqawi, H.; Enders, C.; Binder, W. H. *J. Polym. Sci., Part A: Polym. Chem.* **2010,** *48,* 3402–3416.

(17) Nicolay, R.; Matyjaszewski, K. *Macromolecules* **2011,** *44,* 240–247.

(18) Schuetz, J.-H.; Vana, P. *Macromol. Chem. Phys.* **2011,** *212,* 1263–1275.

(19) Aoshima, S.; Higashimura, T. *Macromolecules* **1989,** *22,* 1009–1013.

(20) Matsutani, H.; Ichikawa, S.; Yaruva, J.; Kusumoto, T.; Hiyama, T. *J. Am. Chem. Soc.* **1997,** *119,* 4541–4542.

(21) Sawamoto, M. *Prog. Polym. Sci.* **1991,** *16,* 111–172.

(22) Aoshima, S.; Kanaoka, S. *Chem. Rev.* **2009,** *109,* 5245–5287.

(23) Usually methoxy-capped (acetal-end) polymers are formed upon methanol quench

in living cationic polymerization of vinyl ethers, which is unfavorable in this work. See: Katayama, H.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001,** *39,* 1249–1257.

(24) Ouchi, M.; Konishi, A.; Takenaka, M.; Sawamoto, M. *Polym. Chem.* **2012,** *3,* 2193–2199.

(25) Hashimoto, T.; Iwata, T.; Minami, A.; Kodaira, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998,** *36,* 3173–3185.

(26) Higashimura, T.; Kishimoto, Y.; Aoshima, S. *Polym. Bull.* **1987,** *18,* 111–115.

(27) Gyor, M.; Wang, H. C.; Faust, R. *J. Macromol. Sci. Pure* **1992,** *29,* 639–653.

(28) Di Stefano, S. *J. Phys. Org. Chem.* **2010,** *23,* 797–805.

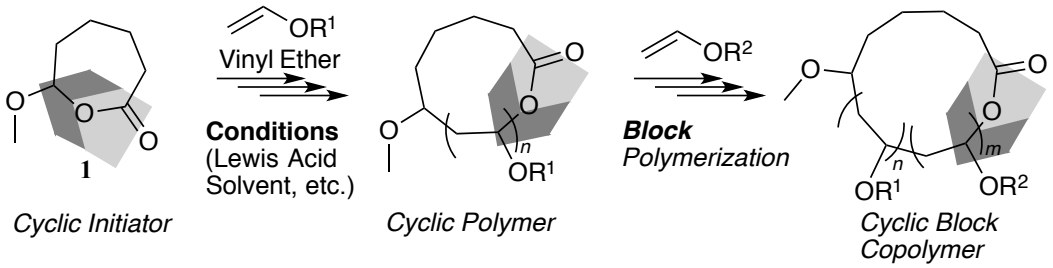
(29) Poelma, J. E.; Ono, K.; Miyajima, D.; Aida, T.; Satoh, K.; Hawker, C. J. *ACS Nano* **2012,** *6,* 10845–10854.

# *Chapter 2*

## Ring-Expansion Living Cationic Polymerization of Vinyl Ethers: Optimized Ring Propagation


### Abstract

For the "ring-expansion" living cationic polymerization of vinyl ethers that has been achieved in *Chapter 1* with a hemiacetal ester-embedded cyclic initiator (**1**), the author investigated the effects of reaction conditions (Lewis acid catalysts/activators, solvents, temperature, and reagent concentration) on the selectivity and controllability for construction of cyclic chains. For example, the choice of the Lewis acid catalysts turned out crucial. Specifically, tin tetrabrommide ($SnBr_4$) was suitable, with which an undisturbed ring-expansion propagation proceeded without irreversible side reactions, to selectively construct the cyclic topology, though accompanied by ″ring fusion″ into fused cyclic polymers of higher molelcular weights. The fusion event, however, could be suppressed by decreasing concentration of the initiator, namely, polymers to be formed therefrom. Under these optimized conditions, the propagation is controlled enough to allow sequential addition of monomers to give either chain-extended homopolymers or block copolymers. Thus, the ring-expansion cationic polymerization is potentially a powerful tool to construct cyclic polymer architectures with precision control similar to that for linear living polymers.

## Introduction

*Topology* of polymers and macromolecules would affect their physical properties, chemical functions, and aggregation behaviors, among others, in solid, melt, and solution. The polymer topology implies not the conformational but the configurational shapes of single molecules that include linear, ring (or cyclic), star, eight-shaped, catenane, and numerous others.[1–6] Nevertheless, only *linear* topology has been employed for synthetic polymers, except for some limited examples of cyclic and other configurations. *Ring* should be the simplest but interesting topology other than linear, and indeed cyclic polymers, free from terminals by definition, are known to possess different structural features and physical properties[7, 8]: lower excluded volume in solution; lower solution and melt viscosity stemming from reduced entanglement; and perhaps unique aggregation states in solution as well as phase separation in solid.[9–11] This fact also suggests that, in addition to cyclic homopolymers, well-defined cyclopolymers, such as cyclic block copolymers and cyclic pendent-functionalized polymers, could offer novel functions and physical properties derived from the endocyclic topologies, as amply found for those of linear block copolymers often strikingly different from linear homopolymers or polymer blends.

Despite this expectation, there has been paucity in synthetic methodologies for cyclic polymers in regard to efficiency, generality, and versatility (*i.e.*, the range of applicable monomers and backbone structures therefrom). The simplest approach thus far reported is the intramolecular end-to-end coupling of a linear polymer, which, however, generally requires highly diluted conditions[12–14] and/or a special end-group interaction[15–17] to prevent intermolecular chain-extension or multiple coupling.

A potentially more efficient and general approach is "ring-expansion" polymerization, where an endocyclic small molecule (a cyclic initiator) successively propagates with monomers into a cyclic macromolecule while retaining its cyclic shape. For example, the ring-expansion metathesis polymerization of cycloolefins has been developed with cyclic ruthenium alkylidene catalysts.[18] Another example is the *N*-heterocyclic carbene-catalyzed polymerization of lactone monomers, where propagation takes place via a zwitterionic intermediate.[19, 20] Note that most of these previous examples involve ring-opening polymerizations, because the endocyclic monomers therein potentially tend to form cyclic chains upon propagation.

On the other hand, limited examples have been available for ring-expansion *addition* polymerization of vinyl monomers ($CH_2$=CH–R).[21] Given that most of recent living

polymerizations, such as metal-catalyzed living radical polymerization,[22] involve a covalent "dormant" species (P–L) derived from a growing species (P*) and a “intramolecularly” associating leaving group (L), ring-expansion addition polymerization would be designed with an endocyclic initiator that would in turn generate a endocyclic dormant species. For this a key is to find a "multivalent" leaving group that can be built-in into a cyclic initiator and a cyclic dormant species therefrom; this requirement immediately excludes halogens (for radical and cationic species), alkali metals (for anionic species), and other monovalent leaving groups.

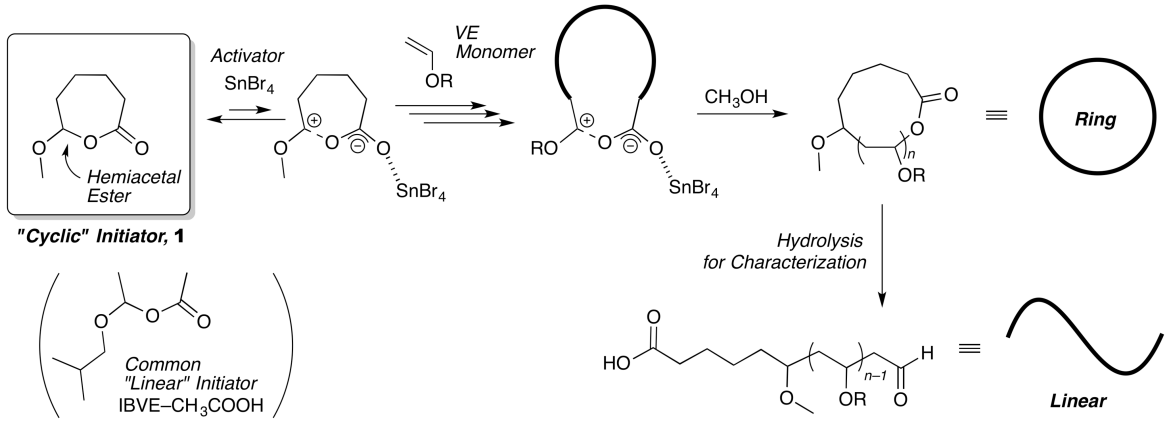
The author recently reported that a cyclic hemiacetal ester (**1**) initiates ring-expansion living cationic polymerization of vinyl ethers in conjunction with tin tetrabromide ($SnBr_4$) as a catalyst (Scheme 1).[23] Similar to linear hemiacetal esters, *e.g.*, the acetic acid adduct of isobutyl vinyl ether [$CH_3CH(O\mathit{i}Bu)OCOCH_3$; IBVE–$CH_3COOH$],[24] the embedded hemiacetal ester in **1** is reversibly activated by $SnBr_4$ to cleave the cyclic structure into an open-chain carbocation to which a carboxylate anion intramolecularly associates. More accurately, the dissociated growing species should not be a completely open chained but a temporarily opened pseudo-ring topology involving a highly associative ionic interaction at the cation-counteranion junction (with an associating Lewis acid catalyst on the carboxylate), and thus propagation may proceed by "insertion" of a monomer (IBVE) between the carbocation and the carboxylate counteranion by disrupting their coulombic interaction, realizing a ring-expansion propagation into a cyclic or ring polymer. Note that this basically ionic mechanism differs from the coordination–insertion pathway in the ring-expansion metathesis polymerization,[18] which is a more or less concerted process and is by definition able to consistently retain the cyclic intermediate topology throughout propagation. The temporary dissociation in the cationic counterpart might suffer from a more enhanced totally open-chain, completely dissociated propagation into a linear polymers, but our experience in the Lewis acid-catalyzed linear living cationic polymerization[25, 26] tells that the problem might be contained by a judicious choice of Lewis acid catalysts and reaction parameters (solvents, temperature, etc.) that in turn could effectively dictates the ionic dissociation of the in-ring hemiacetal ester.

In accordance with the proposed mechanism, acidolysis of the products selectively cleaved the hemiacetal ester to give the corresponding linear polymers [poly(IBVE) with a carboxyl and an aldehyde terminals], demonstrating a ring topology of the pristine products. Equally important, SEC and NMR analysis of the products showed that the polymerization is

controlled, akin to the Lewis-acid-catalyzed living cationic polymerization with an open-chain (linear) initiator such as IBVE–$CH_3COOH$.

However, it has turned out that, as indicated by multimodal SEC profiles,[23] a portion of the products contain larger rings, or "fused rings", with multiple hemiacetal esters, apparently by the intermolecular counteranion exchange between two or more cyclic polymers. Thus, finer control of the ring-expansion process is needed.

In this work, therefore, we further examined reaction parameters of the ring-expansion cationic polymerization of IBVE with initiator **1**, such as temperature, Lewis acid catalysts, solvents, and reagent concentrations, to see their effects on ring formation efficiency, the ring fusion, and the control of polymer molecular weight. Optimized conditions led to not only higher yield of non-fused ring polymers but also ring block copolymers by the first ring-expansion cationic block copolymerization.




**Scheme 1.** Ring-Expansion Living Cationic Polymerization of Vinyl Ether with **1**

## Experimental

### Materials

For Synthesis of **1**: Dichrolomethane (Wako, >99.5%), tetrahydrofuran (THF) (Wako; >99.5%), *m*-chroloperbenzoic acid (Wako; >69%, with water), and sodium hydrogen carbonate (Wako; >99.5%) were used as received without further purification. 2-Methoxycyclohexan-1-one (TCI; >95.0%) was purified by column chromatography (silica gel) before use.

For Polymerization and Hydrolytic Cleavage: Isobutyl vinyl ether (IBVE) (Tokyo Kasei; >99%) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide, and distilled twice from calcium hydride before use. 1,4-Dioxane (DO) was dried overnight over calcium chloride and distilled from sodium benzophenone

ketyl. Toluene (Kishida Kagaku; 99.5%), dichromethane (Kishida Kagaku; 99.5%) and hexane (Kishida Kagaku; 96%) were dried and purified by passing through purification columns (Solvent Dispensing System, SG Water USA, Nashua, NH; Glass Contour), kept over molecular sieves 4A for more than one day. $SnBr_4$ (Aldrich; >99%), $SnCl_4$ (Aldrich, 1 M in $CH_2Cl_2$) 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, Aldrich; >99%) trifluoroacetic acid (Wako; >98%), and $EtAlCl_2$ (Kanto Kagaku, 1.04 M Solution in hexane) were used as received.

**Measurements (SEC and $^1$H NMR)**

Number-averaged molecular weight ($M_n$), and its distribution ($M_w/M_n$) of polymers were measured by size exclusion chromatography (SEC) at 40˚C in THF as an eluent on three polystyrene-gel columns (Shodex KF-803; pore size, 20–1000 Å; 8.0 mm i.d. x 30 cm; flow rate, 1.0 mL min$^{-1}$) connected to a DU-H2000 pump, a 74S-RI refractive-index detector, and a 41-UV ultraviolet detector (all from Shodex). The columns were calibrated against 13 standard poly(St) samples (Polymer Laboratories; $M_n$ = 500–3840000; $M_w/M_n$ = 1.01–1.14). $^1$H NMR spectra of the obtained polymers were recorded in $CDCl_3$ at 25 ˚C on a JEOL JNM-ECA500 spectrometer, operating at 500.16 MHz. Polymer purification was performed by preparative SEC in $CHCl_3$ at room temperature (flow rate: 10 mL min$^{-1}$) on a polystyrene gel fractional column (K-5003: exclusion limit = 7 x $10^4$; particle size = 15 mm; 5.0 cm i.d. x 30 cm) that was connected to a Jasco PU-2086 precision pump, a Jasco RI-2031 refractive index detector, and a Jasco UV-2075 UV/vis detector set at 250 nm.

**Synthesis of cyclic initiator 1 via Baeyer-Villiger oxidation.**

To a dichloromethane solution of 2-methoxycyclohexan-1-one were added sodium hydrogen carbonate (1.3 equiv) and *m*-chloroperbenzoic acid (*m*-CPBA, 1.5 equiv) at 0 ˚C. The resulting mixture was stirred at room temperature for 1 hour. Excess *m*-CPBA was quenched with aqueous sodium sulfite solution, and the resulting mixture was extracted with dichloromethane. The organic layer was separated, washed with aqueous sodium hydrogen carbonate, and then with aqueous sodium chloride. Finally, it was distilled from calcium hydride under reduced pressure to give pure cyclic initiator **1**.

**Living cationic polymerization of IBVE with 1**.

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a

three-way stopcock. A typical example is given below. The reaction was initiated by adding solutions of $SnBr_4$ (5.0 mM in $CH_2Cl_2$: 0.5 mL) *via* a dry syringe into a mixture (4.5 mL) containing IBVE (0.25 mL), 1.4-dioxane (0.13 mL), hexane (0.10 mL), cyclic initiator **1** and DTBMP in $CH_2Cl_2$ at 0 ˚C. After a predetermined interval, the polymerization was terminated with prechilled methanol. Monomer conversion was determined from its residual concentration measured by gas chromatography with hexane or tetrachloromethane as an internal standard. The quenched reaction mixture was washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(IBVE).

**Block copolymerization of IBVE with EVE**

Living cationic polymerization of IBVE was first performed in toluene (with 2.5vol% of 1.4-dioxane) at 0˚C with **1**/$SnBr_4$/DTBMP. When the conversion of IBVE was reached 97% in 25 hours, the second monomer EVE (neat) was directly added into glass tube of the polymerization solution. Other procedures were same as those in the homopolymerization of IBVE (see above).

**Hydrolytic cleavage of hemiacetal ester in cyclic poly(IBVE)**

A typical example of hydrolysis of hemiacetal ester linkage in cyclic poly(IBVE) is given below. In a round-bottom flask (50 mL) was placed "as-obtained" (*i.e.*, cyclic) poly(IBVE) (0.15 g) and it was dissolved into THF (4 mL) and trifluoroacetic acid (1.0 mL). To the resultant solution was added $H_2O$ (0.2 mL) and it was stirred at room temperature for 12 hours. The solution was washed with water and hexane to remove trifluoroacetic acid and the organic layer was evaporated under vacuum to obtain linear poly(IBVE).

## Results and Discussion

**Effects of Lewis Acids (Catalysts/Activators)**

To realize ring-expansion cationic polymerization, chain transfer *via* proton elimination should be avoided, because it incurs generation of olefin-terminated linear polymers as well as proton-initiated new growing chains. The counteranion exchange with a halogen (X in $MX_n$) within the Lewis acid catalyst should be also suppressed, which results in halogen-capped "linear" growing species and polymers. Thus, choice of Lewis acid activator is very important.

Thus, in addition to $SnBr_4$, two Lewis acids ($EtAlCl_2$ and $SnCl_4$) were employed in the

polymerization of isobutyl vinyl ether (IBVE) with **1** in toluene or hexane at 0 ˚C. For $EtAlCl_2$ catalyst, dioxane was additionally used as a Lewis base additive, as with the living linear polymerization with the same catalyst and a linear hemiacetal ester initiator (IBVE–$CH_3COOH$).[24] For $SnCl_4$, the conditions were identical to those with $SnBr_4$ for the previously reported ring-expansion polymerization:[23] 2.5vol% dioxane, a base additive, and a small amount of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), a proton trap. Polymerization was quenched with methanol, followed by washing with water to remove the Lewis acid residues, to obtain "products before acidolysis". A portion of the obtained polymers was treated with TFA/water to cleave the in-chain hemiacetal ester, giving "products after acidolysis".

As described above, with $SnBr_4$, the as-obtained products before acidolysis exhibited multimodal SEC profiles consisting of a major and narrow peak of lower MW and a minor and broader peak of higher MW. Acidolysis led to a single peaked product of a narrow distribution where the peak MW was clearly higher than that of the major peak for the pristine

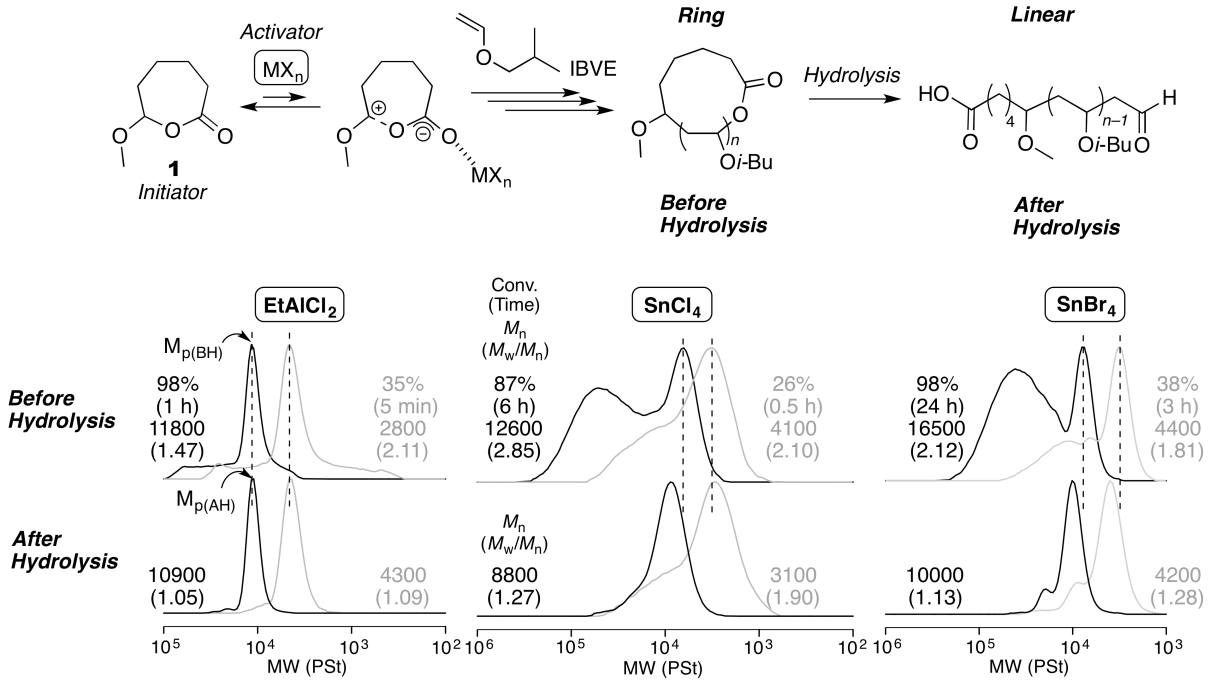



**Figure 1.** SEC curves of poly(IBVE)s with $EtAlCl_2$, $SnCl_4$, and $SnBr_4$ as an activator for cationic polymerization of IBVE with **1** as an initiator: $[IBVE]_0/[\mathbf{1}]_0$ = 380/5 mM in *n*-hexane ($EtAlCl_2$) or toluene [$SnX_4$ (X = Cl, Br)] at 0˚C. Polymerization with $EtAlCl_2$: $[EtAlCl_2]_0$ = 10 mM with 10 vol% dioxane; those with $SnX_4$: $[SnX_4]_0$ = 0.50 mM, $[DTBMP]_0$ = 0.15 mM with 2.5 vol% dioxane.

products. Such a phenomena would indicate that ring-expansion occurs in controlled fashion in parallel with a concurrent ring fusion.

The newly employed two Lewis acids ($EtAlCl_2$ and $SnCl_4$) also smoothly promoted polymerization with IBVE monomer. In Figure 1, SEC curves of the poly(IBVE)s were compared as a function of activators. With $EtAlCl_2$ the SEC profiles remarkably differ from those with $SnBr_4$, primarily with a sharper and predominant peak alone but with a minor shoulder of higher MW. Upon hydrolysis, the distribution narrowed and nearly without shoulders ($M_w/M_n < 1.1$), but the peak-top molecular weight ($M_{p(AH)}$) remained the same as that before hydrolysis ($M_{p(BH)}$), indicating the absence of ring-expansion propagation. Probably, a counteranion exchange would have occurred between the acetate from **1** and the chlorine in $EtAlCl_2$, to give chlorine-capped open-chain linear growing species.

With $SnCl_4$, overall the polymerization and the products were more or less similar to those with $SnBr_4$, but the molecular weight distributions after hydrolysis were broader, without notable peak shift at low IBVE conversion. From these results, $SnBr_4$ was found suitable for the ring-expansion polymerization with **1**.

**Effects of Temperature**

Effects of polymerization temperature were then studied. The $SnBr_4$-catalyzed polymerization of IBVE with **1** was performed in toluene in a range from –78 to +70 ˚C (Figure 2). As expected, the higher the temperature, the faster the polymerization; little monomer was consumed at –78 ˚C (Figure 2A). As seen in the SEC profiles in Figure 2D, the as-obtained products invariably consisted of single cyclic polymers and fused rings, where the latter progressively decreased in proportion as well as peak MW at higher temperature (see also Figure 2B). Acidolysis converted the products distributions virtually single-peaked, but the extent of the MW increase expected for cyclic polymers was less at higher temperature, and MW did decrease at 70 ˚C. The conversion–$M_n$ plots (Figure 2C) conform with these changes, where linear increase in $M_n$, indicative of controlled propagation, occurred at 0 and 40 ˚C but was absent at 70 ˚C, probably because of the β-proton elimination (conventional chain transfer for carbocations) from the hemiacetal ester cyclic growing end into an open-chain olefin terminal. These temperature effects indicate that, at 40 ˚C, ring-expansion cationic polymerization can be fairly controlled in regard to maintaining cyclic growing end, while minimizing not only chain transfer but the concurrent ring fusion.

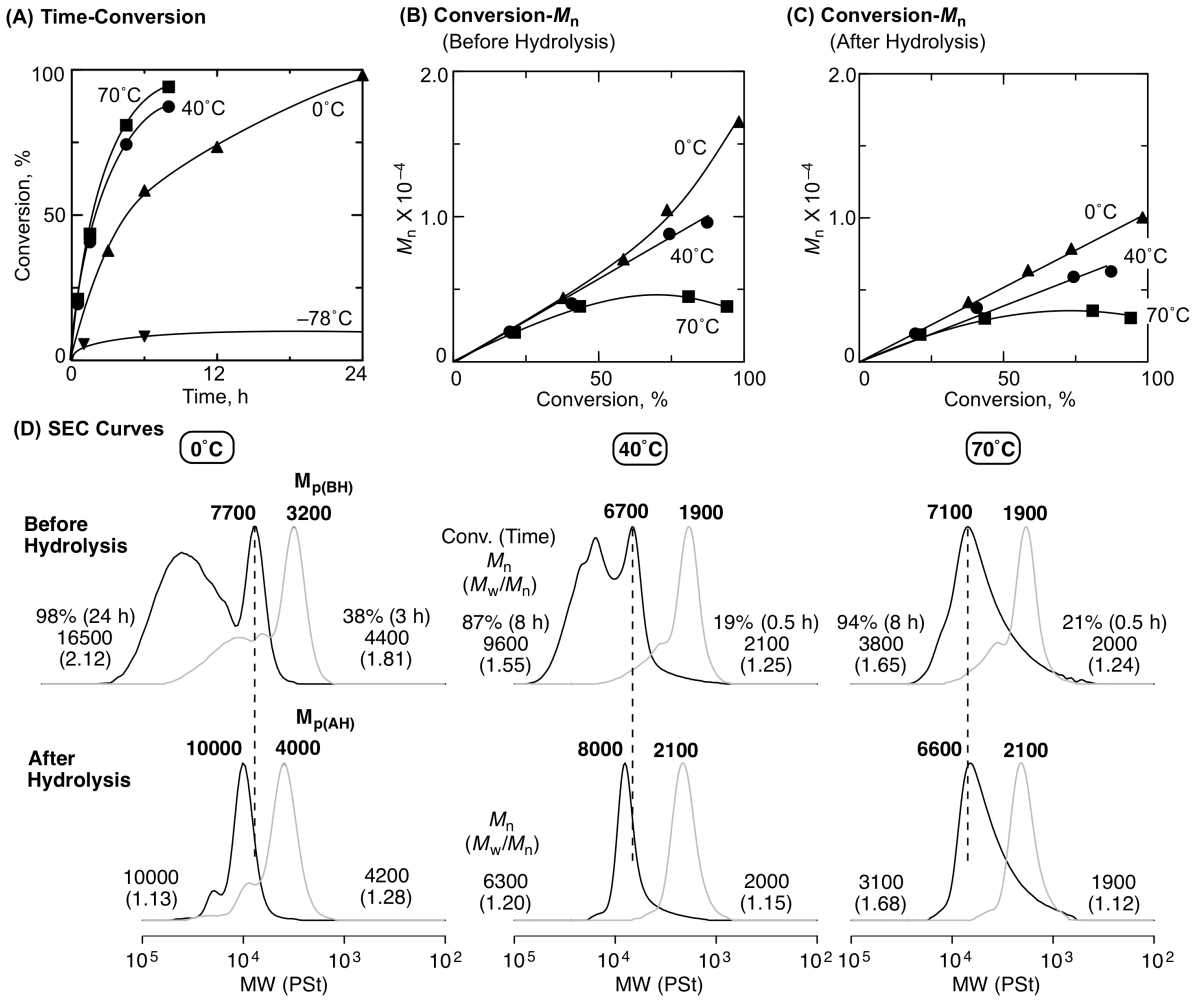



**Figure 2.** Effects of polymerization temperature (70, 40, 0, and –78 ˚C) in ring-expansion cationic polymerization of IBVE with **1** and $SnBr_4$ in toluene: (A) Time-conversion plots; (B) conversion-$M_n$ plots before hydrolysis; (C) conversion-$M_n$ plots after hydrolysis; (D) SEC curves of obtained poly(IBVE) before and after hydrolysis: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/0.50/0.15 mM in toluene. Dioxane of 2.5 vol% was added as a base additive.

## Effects of Solvents

In cationic polymerization, solvent polarity greatly affects the ionic dissociation of growing carbocations and counteranions and thereby the cationic propagation relative to chain transfer and termination. This point is more specifically critical in the ring-expansion cationic polymerization in that the enhanced growing-end dissociation would disrupt the preferred cyclic propagation while promoting the ring fusion via ester exchange or the

open-chain propagation into linear polymers.

The author thus examined the polymerization of IBVE with the **1**/$SnBr_4$ system at 0 ˚C in solvents of increasing polarity, toluene, dichloromethane ($CH_2Cl_2$), and their 1:1 mixture (tol/$CH_2Cl_2$) (Figure 3). As with conventional linear cationic polymerization, the ring-initiated reactions proceeded faster in more polar solvents. The SEC curves of the obtained polymers, however, were independent of solvent polarity, all bimodal and consisting of a narrow main peak (single rings) and a higher MW broad peak (fused rings). Subsequent acidolysis invariably led to narrow, near single-peaked products with increased MW expected for the conversion from cyclic to linear polymers. Before and after the acidolysis, conversion–$M_n$ profiles were independent of solvents polarity, giving nearly overlapping straight lines through the origin indicative of controlled propagation.

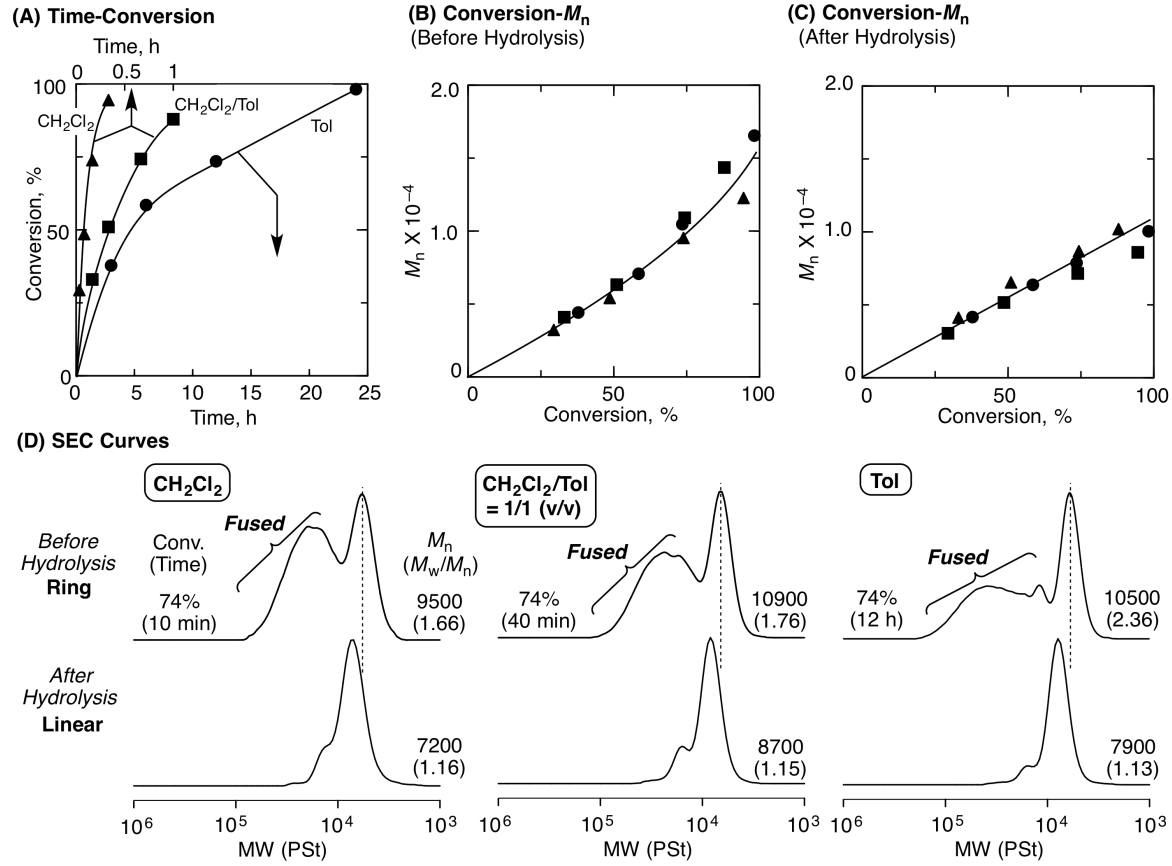



**Figure 3**. Effects of solvent polarity [$CH_2Cl_2$, $CH_2Cl_2$/toluene (1/1 vol%), toluene] in ring-expansion cationic polymerization of IBVE with **1** and $SnBr_4$ at 0˚C: (A) Time-conversion plots; (B) conversion-$M_n$ plots before hydroloysis; (C) conversion-$M_n$ plots after hydroloysis; (D) SEC curves of obtained poly(IBVE) before and after hydroloysis: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/0.5/0.15 mM. Dioxane of 2.5 vol% was added a base additive.

Importantly, however, the apparent MW of fused cyclic polymers (higher MW portions) increased in more polar solvents (toluene < tol/$CH_2Cl_2$ < $CH_2Cl_2$), whereas their proportion relative to single rings remained nearly the same (toluene, 60 %; tol/$CH_2Cl_2$, 58 %; $CH_2Cl_2$, 57 %; roughly estimated from deconvoluted and integrated SEC peaks). Given the MW of fused rings proportional to the degree of ring-fusion (the number of hemiacetal units) per polymer, the trend indicates that less polar solvents suppresses ring-fusion into larger rings, though its frequency or selectivity over single ring-propagation remains unaffected by solvent polarity.

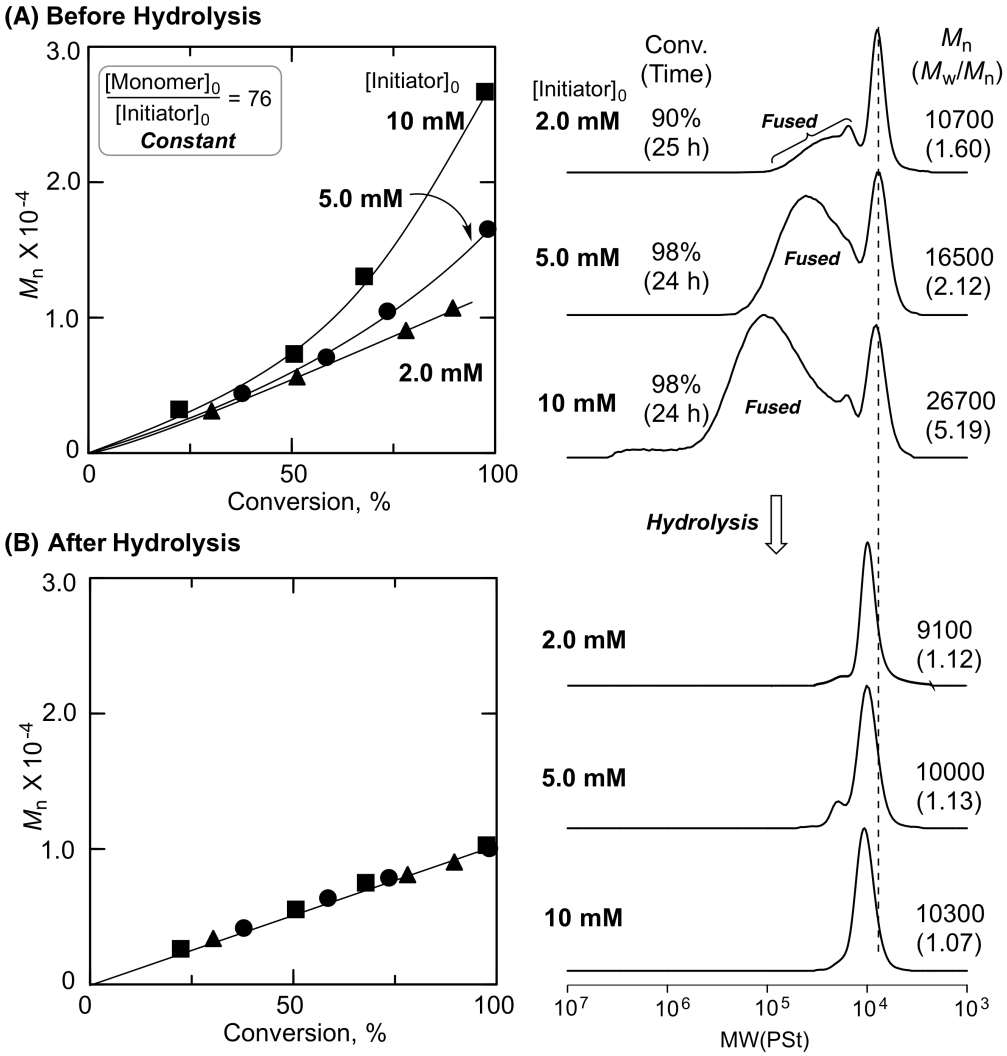
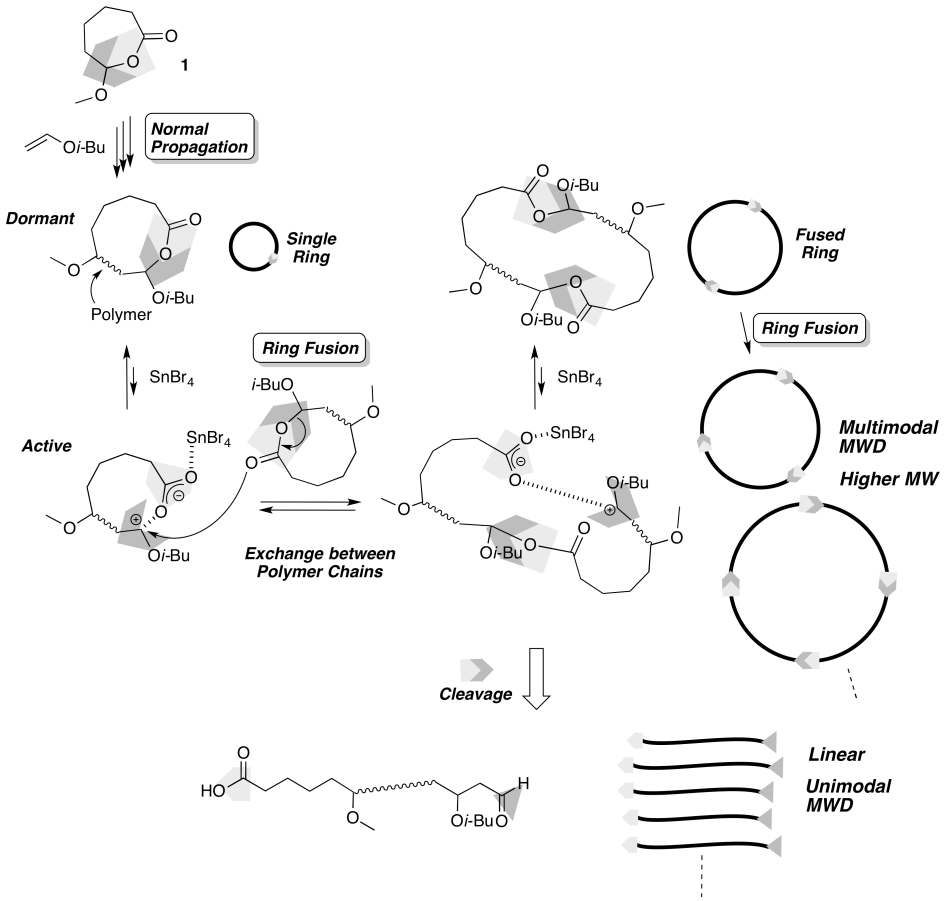



**Figure 4.** Effects of initiator concentration in ring-expansion cationic polymerization of IBVE with **1** and $SnBr_4$ in toluene at 0˚C: (A) conversion-$M_n$ plots and SEC curves for obtained poly(IBVE)s before hydrolysis; (B) conversion-$M_n$ plots and SEC curves for obtained poly(IBVE)s after hydrolysis: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/0.50/0.15 mM. Dioxane of 2.5 vol% was

**Effects of Initiator Concentration**

The ring fusion would intermolecularly occur between single-ring polymers, most likely via ester exchange (counteranion reshuffling) between their in-ring hemiacetal ester units, thus to be suppressed at lower polymer concentration. The author thus studied effects of the in-situ concentration of polymer chains (i.e., the initiator) on the selectivity for single-rings relative to the fused products (Figure 4). Thus, the initial concentration of **1** was changed ($[\mathbf{1}]_0$ = 2.0, 5.0, and 10 mM), while the initiator/monomer feed mole ratio was kept unchanged ($[\mathbf{1}]_0/[\text{IBVE}]_0$= 1/76). In accordance with the assumption, fused rings remarkably decreased at lower initiator concentration (see SEC curves). As seen in the conversion–$M_n$ plots, the overall molecular weight of fused rings is also reduced, indicating that not only the ring-fusion/expansion selectivity but also the fusion frequency per polymer are suppressed. Equally important, the ring-to-linear topological change by acidolysis gave near unimodal SEC curves with narrow MWDs and $M_n$'s fairly close to the calculated values assuming that one initiator molecule gives one "linear" polymer with a single hemiacetal terminal. All




**Scheme 2.** Ring Fusion in Ring-Expansion Living Cationic Polymerization of IBVE from **1** and Topology Change into Linear

these results conform with the ring fusion occurs between pristine single-ring polymers via ester/counteranion exchange concurrently with ring-expansion propagation (Scheme 2). However, the propagation is basically free from chain transfer and other side reactions, as supported by the unimodal MWDs after acidolysis and by the linear increase in products MW.

**Control of Molecular Weight**

The long-lived ring-expansion propagation was supported by the molecular weight control by the monomer/initiator feed ratio ($[IBVE]_0/[\mathbf{1}]_0$) (Figure 5). Though the as-obtained products contained an increased portion of fused rings at higher monomer feed, the $M_n$'s for the acidolysis products was directly proportional to the ratio and close to the calculated values (one linear or single-ringed polymer per **1**). It should be noted in particular

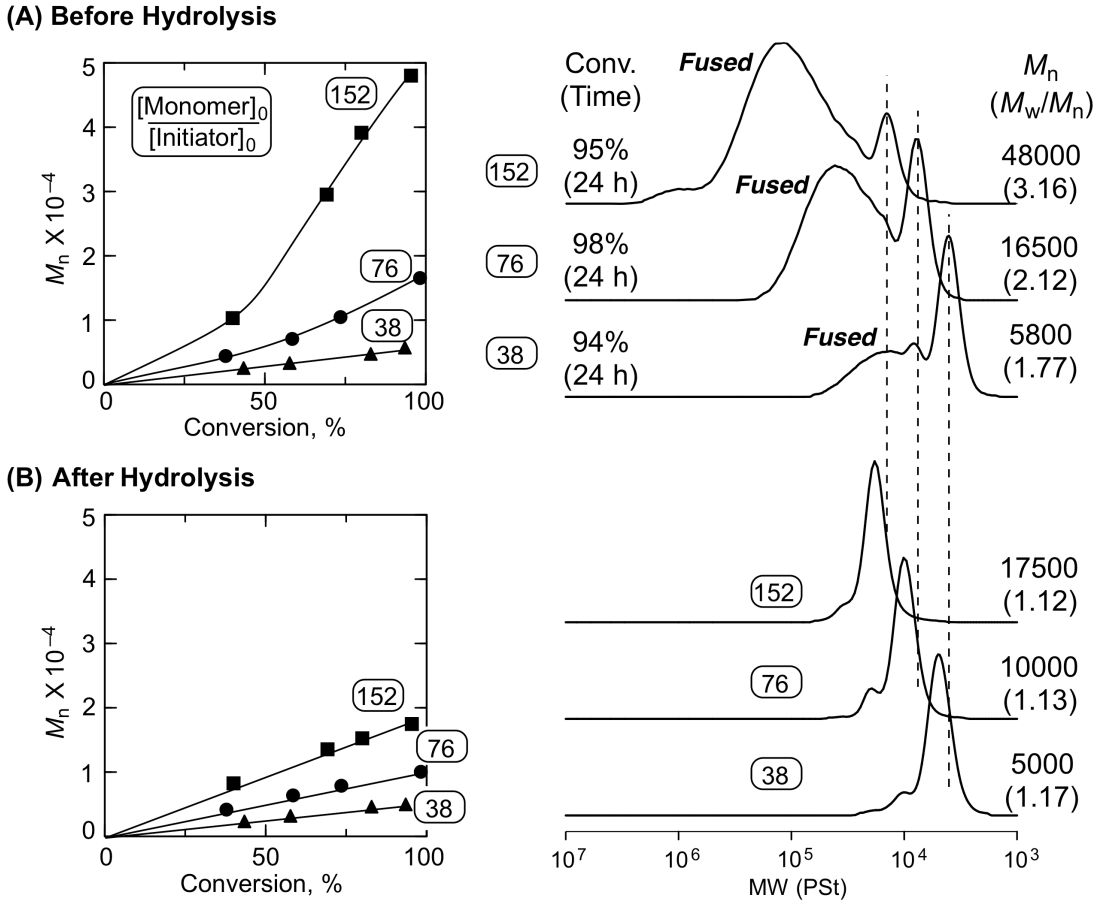



**Figure 5**. Molecular weight control in ring-expansion cationic polymerization of IBVE with **1** and $SnBr_4$ in toluene at 0 ˚C: (A) conversion–$M_n$ plots and SEC curves for obtained poly(IBVE)s before hydrolysis; (B) conversion–$M_n$ plots and SEC curves for obtained poly(IBVE)s after hydrolysis: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 760 or 380 or 190/5.0/0.50/0.15 mM. Dioxane of 2.5 vol% was added as a base additive.

that all the three ring-cleaved polymers have a narrow MWD with a peak MW clearly higher than that of the lower MW peak in the corresponding pristine products; acidolysis cleaves all hemiacetal ester units, in either single-ringed or fused ring polymers, thus let them converge into a single peaked linear polymers with a single carboxylate terminal.

## Block Copolymerization

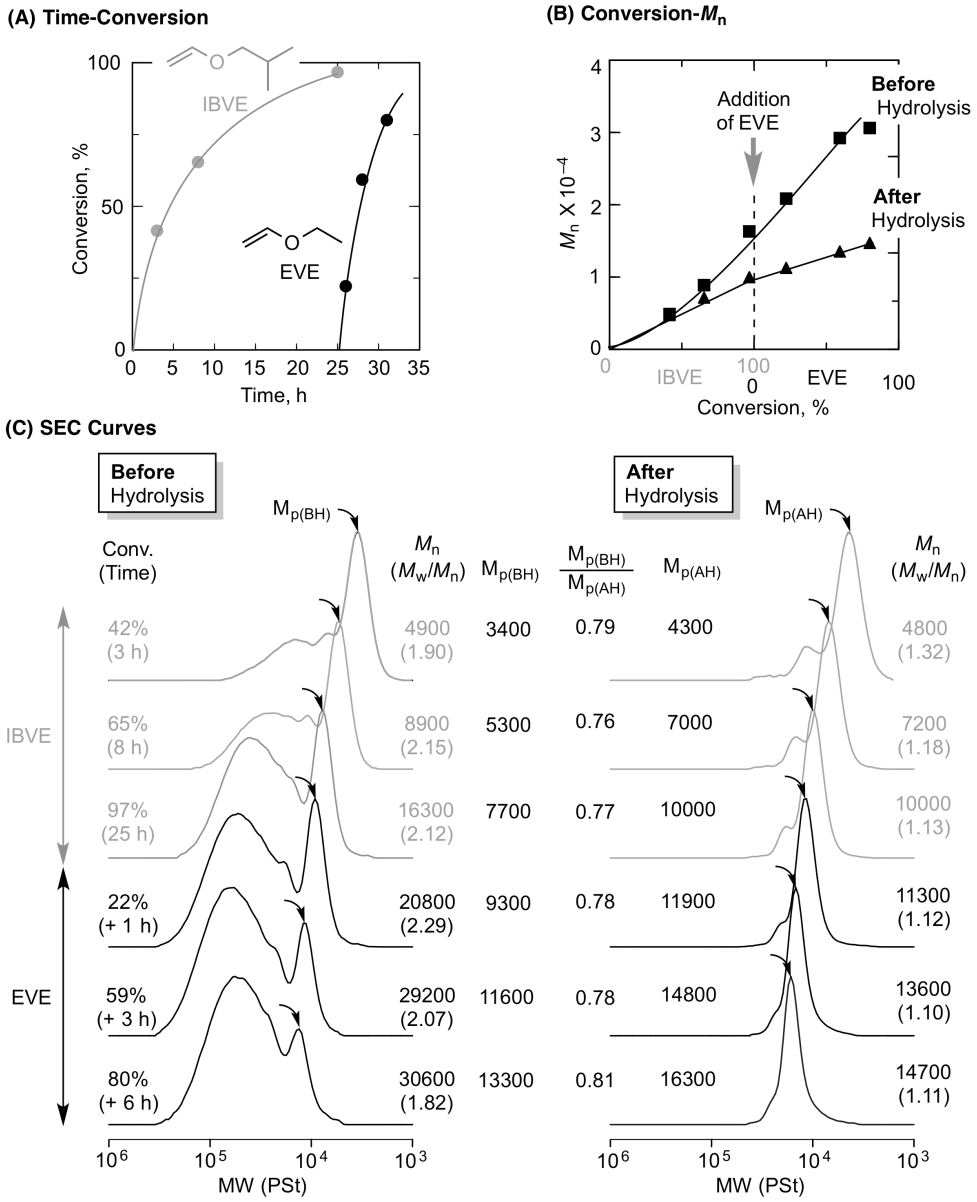
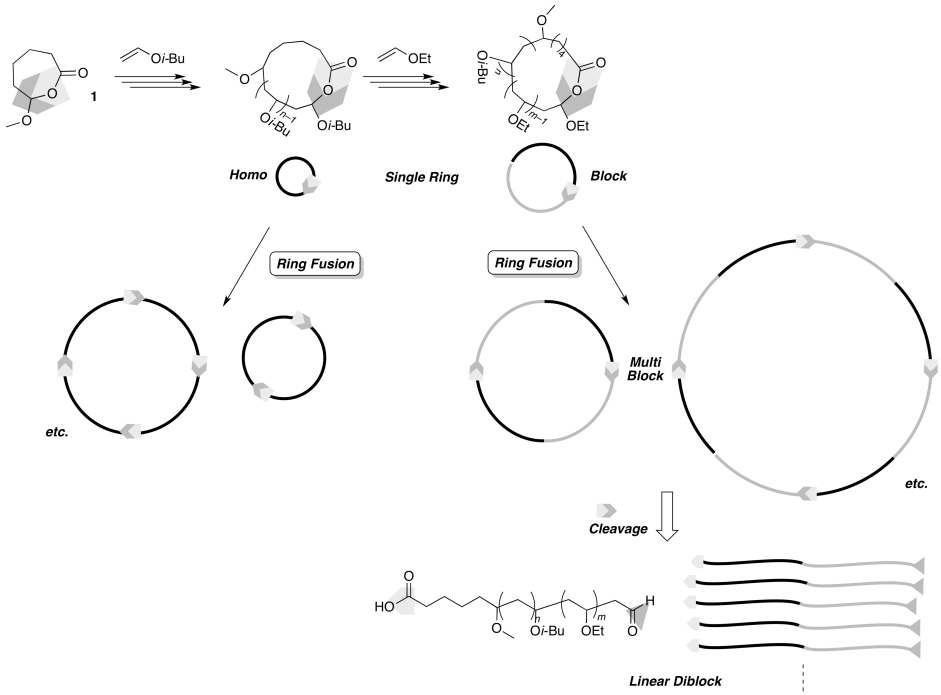



**Figure 6.** Ring-expansion block copolymerization of IBVE and EVE with **1** and $SnBr_4$ in toluene at 0˚C: (A) Time–conversion plots; (B) conversion–$M_n$ plots before and after hydrolysis; (C) SEC curves for obtained polymers before and after hydrolysis: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0/[EVE]_{add}$ = 380/5/0.50/0.15/380 mM. Dioxane of 2.5 vol% was added as a base additive.

The undisturbed ring-expansion propagation, demonstrated as above, was extended to the block copolymerization to synthesize cyclic block copolymers in the IBVE polymerization by the **1**/$SnBr_4$ system in toluene (Figure 6), perhaps for the first time to our knowledge. Thus, when IBVE conversion reached near 100 %, a bulk portion of ethyl vinyl ether (EVE) was injected to the unquenched reaction mixtures. The second monomer was smoothly consumed to high conversion, and SEC curves all shifted to higher MW without altering the double-peaked shape. Acidolysis gave almost unimodal products with SEC peak molecular weights [$M_{p(AH)}$] higher than those [$M_{p(BH)}$] beforehand, while the $M_{p(BH)}$/ $M_{p(AH)}$ ratio remained nearly unchanged (~ 0.8). Inclusion of EVE repeat units has been confirmed by NMR analysis on the pristine products before and after the sequential monomer addition along with those after acidolysis. All these indicate that both single ringed and fused ring "cyclic block" copolymers formed; the former is therefore an interesting cyclic AB diblock copolymers, whereas the latter rather unusual segmented multiblock copolymers (Scheme 3). These cyclic block polymers will be subject to detailed characterization in regard of primary structure, physical and thermal properties, and, above all, possible microphase separation.




**Scheme 3.** Ring Fusion in Ring-Expansion Block Copolymerization of IBVE and EVE from **1** and Topology Change into Linear Diblock Copolymer

## References


(1) T. Yamamoto, Y. Tezuka, *Polym. Chem.* **2011**, *2*, 1930–1941.

(2) Y. Tezuka, *Polym. J.* **2012**, *44*, 1159–1169.

(3) T. Yamamoto, *Polym. J.* **2013,** *45,* 711–717.

(4) B. A. Laurent, S. M. Grayson, *Chem. Soc. Rev.* **2009**, *38*, 2202–2213.

(5) H. R. Kricheldorf, *J. Polym. Sci. Part A. Polym. Chem.* **2010**, *48*, 251–284.

(6) B. Schmidt, N. Fechler, J. Falkenhagen, J. F. Lutz, *Nat. Chem.* **2011**, *3*, 234–238.

(7) K. Dodgson, J. A. Semlyen, *Polymer* **1977**, *18*, 1265–1268.

(8) A. Takano, Y. Ohta, K. Masuoka, K. Matsubara, T. Nakano, A. Hieno, M. Itakura, K. Takahashi, S. Kinugasa, D. Kawaguchi, Y. Takahashi, Y. Matsushita, *Macromolecules* **2012**, *45*, 369–373.

(9) M. Schappacher, A. Deffieux, *Science* **2008**, *319*, 1512–1515.

(10) B. A. Laurent, S. M. Grayson, *Polym. Chem.* **2012**, *3*, 1846–1855.

(11) J. E. Poelma, K. Ono, D. Miyajima, T. Aida, K. Satoh, C. J. Hawker, *ACS Nano* **2012**, *6*, 10845–10854.

(12) D. Geiser, H. Hocker, *Macromolecules* **1980**, *13*, 653–656.

(13) J. Roovers, P. M. Toporowski, *Macromolecules* **1983**, *16*, 843–849.

(14) M. Schappacher, A. Deffieux, *Makromol. Chem., Rapid Commun.* **1991**, *12*, 447–453.

(15) M. Kubo, T. Hayashi, H. Kobayashi, K. Tsuboi, T. Itoh, *Macromolecules* **1997,** *30,* 2805–2807.

(16) H. Oike, H. Imaizumi, T. Mouri, Y. Yoshioka, A. Uchibori, Y. Tezuka, *J. Am. Chem. Soc.* **2000**, *122*, 9592–9599.

(17) B. Lepoittevin, X. Perrot, M. Masure, P. Hemery, *Macromolecules* **2001**, *34*, 425–459.

(18) C. W. Bielawski, D. Benitez, R. H. Grubbs, *Science* **2002**, *297*, 2041–2044.

(19) D. A. Culkin, W. H. Jeong, S. Csihony, E. D. Gomez, N. R. Balsara, J. L. Hedrick, R. M. Waymouth, *Angew. Chem. Int. Ed.* **2007**, *46*, 2627–2630.

(20) W. Jeong, E. J. Shin, D. A. Culkin, J. L. Hedrick, R. M. Waymouth, *J. Am. Chem. Soc.* **2009**, *131*, 4884–4891.

(21) A. Narumi, S. Zeidler, H. Barqawi, C. Enders, W. H. Binder, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 3402–3416.

(22) M. Ouchi, T. Terashima, M. Sawamoto, *Chem. Rev.* **2009**, *109*, 4963–5050.

(23) H. Kammiyada, A. Konishi, M. Ouchi, M. Sawamoto, *ACS Macro Lett.* **2013**, *2*, 531–534.

(24) S. Aoshima, T. Higashimura, *Macromolecules* **1989**, *22*, 1009–1013.

(25) M. Sawamoto, *Prog. Polym. Sci.* **1991**, *16*, 111–172.

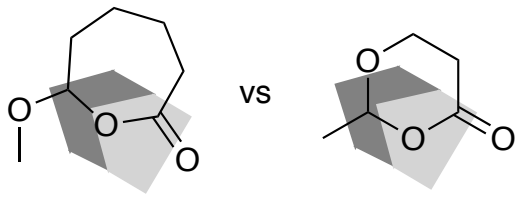
(26) S. Aoshima, S. Kanaoka, *Chem. Rev.* **2009**, *109*, 5245–5287.

# *Chapter 3*

## Effects of Initiator Structure on Propagation in Ring-Expansion Cationic Polymerization: Dual Role of Cyclic Hemiacetal Ester as an Initiator and a Monomer


### Abstract

In this chapter, relationship between cyclic structure and efficacy of cyclic hemiacetal ester compounds as the initiator in ring expansion cationic polymerization of vinyl ethers were studied. 7-membered cyclic hemiacetal ester initiated more efficiently cationic polymerization of isobutyl vinyl ether than 6-membered one due to high ring strain, which was also confirmed by in-situ $^{1}$H NMR spectroscopy measurement in the presence of Lewis acid catalyst and by homo-polymerization of cyclic hemiacetal esters. The highly strained cyclic hemiacetal esters also worked as monomers for ring-expansion cationic polymerization, and furthermore, unprecedented copolymerization with vinyl ether was also realized.

## Introduction

Cyclic polymers are of great curiosity because the endless structure renders them unique properties compared with linear analogue such as lower viscosities, smaller hydrodynamic values, and higher glass transition temperature.[1,2] Ring-expansion polymerization is one of the most effective approaches for the cyclic polymer synthesis because the process can take place under relatively high monomer concentration.[3–5] Also, ring-expansion polymerization is intriguing target in terms of polymerization chemistry because the circular connectivity during polymerization ineluctably affects polymerization behavior. The most known instance is Grubbs' ring-expansion metathesis polymerization using cyclic ruthenium alkylidene catalyst.[6] In the case, ring number of cyclic initiator dictates the initiation, propagation and reversible chain transfer reactions, thus polymerization speed and molecular weight of obtained polymer are dependent on catalyst design.[7]

The author has developed ring-expansion cationic polymerization of vinyl ethers as an efficient method to construct cyclic polymers.[8–10] In ring-expansion cationic polymerization, 7-membered cyclic hemiacetal ester compound is employed as the initiator, and Lewis acid activates hemiacetal ester bond through coordination of metal to carbonyl oxygen, forming carbocation accompanied by tin carboxylate-type anion. Vinyl ether molecules added to the cation to insert and expand cycles to form (*2n+7*) membered ring. Besides, ring "fusion" and the reverse reaction ring "fission" event concurrently occurs along with polymerization through counter-anion exchange reaction, gives fused rings periodically connected with hemiacetal ester junction. It is thought that initiator structure affects these processes;

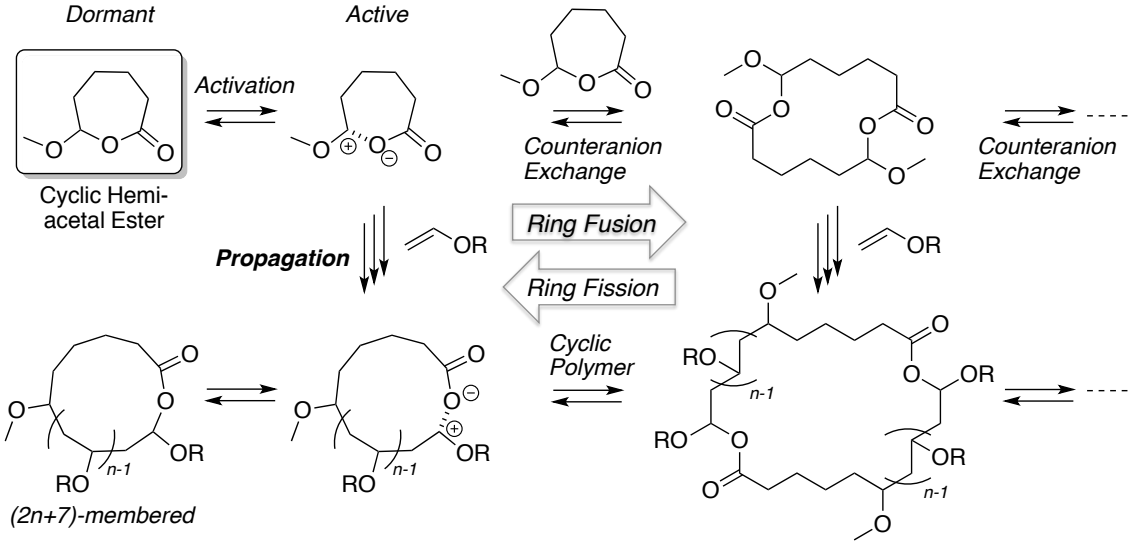



**Figure 1.** Ring expansion cationic polymerization of vinyl ethers from cyclic hemiacetal ester, ring fusion and ring fission.

however, detailed discussion on cyclic initiator is still not unexplored. Therefore scrutinizing initiator structure is crucial for pushing forward the utility of ring-expansion cationic polymerization.

In this chapter, the author evaluated that relation between structure of cyclic hemiacetal ester and effectiveness as the initiator in ring expansion cationic polymerization. 6-membered hemiacetal ester was designed and compared with 7-membered one in cationic polymerization of isobutyl vinyl ether. Besides, ring strain was evaluated by activation under high hemiacetal ester concentration and in situ $^{1}$H NMR measurement in the presence of Lewis activator. Furthermore, the author successfully utilized cyclic hemiacetal ester compound as the "monomer" in ring-expansion polymerization with isobutyl vinyl ether, allowing concurrent ring opening and vinyl-addition cationic polymerization of hemiacetal ester and vinyl ether.

## Experimental

### Materials.

Isobutyl vinyl ether (IBVE) (Tokyo Kasei; >99%) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide, and distilled twice from calcium hydride before use. Carbon tetrachloride was distilled from calcium hydride once before use. Toluene (Kishida Kagaku, Osaka; 99.5%) was dried and purified by passing through purification columns (Solvent Dispensing System, SG Water USA, Nashua, NH; Glass Contour), kept over molecular sieves 4A for more than one day. $SnBr_4$ (Aldrich; >99%), 2,6-di-tert-butyl-4-methylpyridine (DTBMP, Aldrich; >99%), and trifluoroacetic acid (TFA, Wako; >98%) were used as received. The 7-membered cyclic hemiacetal ester (**1**) was synthesized according to our previous paper.[7]

### Synthesis of 6-membered cyclic hemiacetal ester

To a dichloromethane solution of 2-methyltetrahydrofuran-3-one were added sodium hydrogen carbonate (1.3 equiv) and *m*-chloroperbenzoic acid (*m*-CPBA, 1.5 equiv) at 0 °C. The resulting mixture was stirred at room temperature for 1 hour. Excess *m*-CPBA was quenched with aqueous sodium sulfite solution, and the resulting mixture was extracted with dichloromethane. The organic layer was separated, washed with aqueous sodium hydrogen carbonate, and then with aqueous sodium chloride. Finally, it was distilled from calcium hydride under reduced pressure to give pure 6-membered cyclic hemiacetal ester.

**Ring-expansion cationic polymerization of IBVE with hemiacetal ester.**

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical procedure is given below: the polymerization was initiated by adding solutions of $SnBr_4$ (50 mM in toluene: 0.5 mL) via a dry syringe into a mixture (4.5 mL) containing IBVE (0.25 mL), $CCl_4$ (internal standard, 0.10 mL), hemiacetal ester, and 2,6-di-tert-butyl-4-methylpyridine (DTBMP) in toluene at –40˚C: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/5/0.15 mM. After a predetermined interval, the polymerization was terminated with prechilled ammoniacal methanol. Monomer conversion was determined from its residual concentration measured by gas chromatography with $CCl_4$ as an internal standard. The quenched reaction mixture was washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(IBVE).

**Activation of cyclic hemiacetal ester in the absence or presence of IBVE**

Reaction was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical procedure is given below: the reaction was initiated by adding solutions of $SnBr_4$ (50 mM in toluene: 0.5 mL) via a dry syringe into a mixture (4.5 mL) containing hemiacetal ester, 2,6-di-tert-butyl-4-methylpyridine (DTBMP), and IBVE in toluene at –40˚C: $[IBVE]_0/[\text{Hemiacetal ester}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/100/5/0.15 mM. After a predetermined interval, the polymerization was terminated with prechilled ammoniacal methanol. The quenched reaction mixture was washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give the product.

**In-situ $^1$H NMR measurement of hemiacetal esters with $SnBr_4$**

The reaction was started by adding a solution of $SnBr_4$ (in toluene-$d_8$; 0.07mL) to a prechilled solution of hemiacetal ester (in toluene-$d_8$; 0.54 mL) in a septum-capped NMR tube (5 mm o.d.) under dry nitrogen via dry syringes at –78 ˚C ($[HAE]_0/[SnBr_4l_0$ = 5/0.5 mM]). The tube was vigorously shaken at-78 ˚C and immediately placed in the thermostated probe. The chemical shifts were determined with reference to the methyl group of toluene-$d_8$ (2.09 ppm).

**HAE cleavage of cyclic poly(IBVE) via Acidolysis**

A typical procedure for cleavage of HAE bond in cyclic poly(IBVE) is given below. In a vial (2 mL) was placed 1.0 mL of cyclic poly(IBVE) solution (1wt% in THF) and added 5 drops of $H_2O$/THF (1/2 v/v) solution was added. The resultant solution was kept at ambient

temperature for 12 hours, and the resultant solution was vacuum dried to remove THF, water and trifluoroacetic acid to obtain linear poly(IBVE).

### Measurements

The molecular weight distribution, $M_n$, and $M_w/M_n$ values of polymers were measured by size exclusion chromatography (SEC) at 40 °C in THF as an eluent on three polystyrene-gel columns (Shodex KF-803; pore size, 20–1000 A; 8.0 mm i.d. x 30 cm; flow rate, 1.0 mL $min^{-1}$) connected to a DU-H2000 pump, a 74S-RI refractive-index detector, and a 41-UV ultraviolet detector (all from Shodex). The columns were calibrated against 13 standard poly(St) samples (Polymer Laboratories; $M_n$= 500–3840000; $M_w/M_n$ = 1.01–1.14). $^1$H NMR spectra of the obtained polymers were recorded in benzene-$d_6$ at 25 °C on a JEOL JNM-ECA500 spectrometer, operating at 500.16 MHz.

## Result and Discussion

### Comparison of cyclic hemiacetal esters in cationic polymerization of vinyl ether

The author selected 6-membered hemiacetal ester compound for comparison because Hillmyer and co-workers revealed that 6-membered cyclic hemiacetal ester can be polymerized as the monomer in either ring opening anionic or cationic polymerization to form linear poly(hemiacetal ester)s by using an acyclic initiator.[11, 12]

Polymerizations of isobutyl vinyl ether were commenced with 7-membered, 6-membered

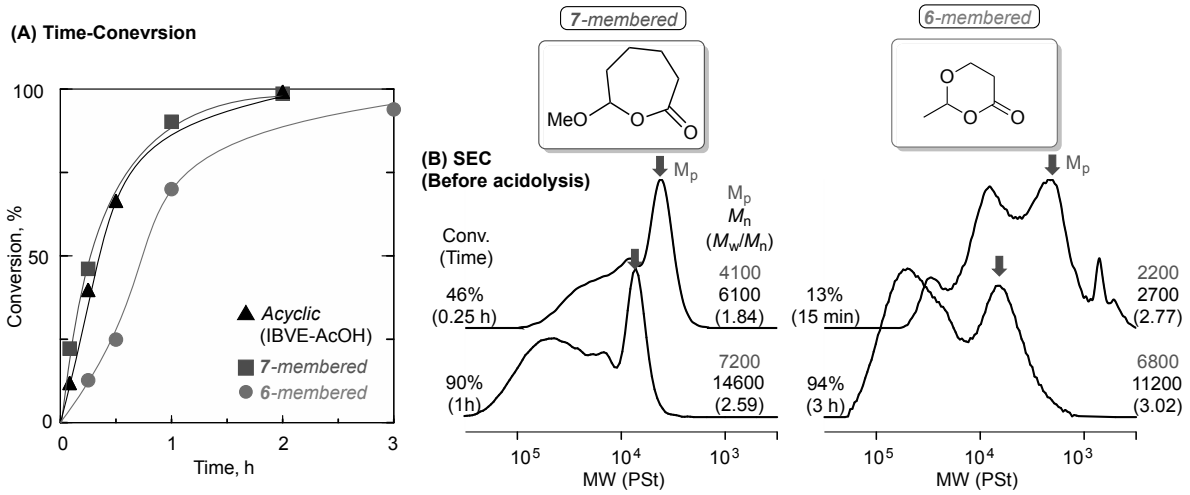



**Figure 2.** Comparison of cyclic hemiacetal ester bond as the initiator in ring expansion cationic polymerization: $[IBVE]_0/[hemiacetal\ ester]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/5/0.15 mM in toluene at –40°C.

cyclic hemiacetal ester as well as acyclic one (IBVE-AcOH) in toluene at –40˚C. Polymerization proceeded smoothly from all initiators (Figure 2A), although there seems induction period in the case from 6-HAE at the very beginning of polymerization. In sharp contrast, 7-membered cyclic HAE and acyclic HAE initiated polymerization of IBVE quicker than 6-membered one. This implies that structure of 6-membered HAE bond is so stable that initiation reaction becomes slower than propagation. Interestingly, fused rings were also observed from both cyclic initiators in SEC curves (Figure 2B), giving broad molecular weight distribution. Since the cause of ring fusion is counter-anion exchange reaction of HAE bond in cyclic polymer, introduction of HAE bond in obtained polymer is implied.

To confirm the hypothesis, acidolysis experiment of hemiacetal ester bond in obtained polymers was performed with trifluoroacetic acid and water (Figure 3). Polymers from 7-membered cyclic HAE gave monomodal SEC curve with narrow molecular weight distribution ($M_w/M_n$ = 1.08), and the peak top ratio before and after hydrolysis was 0.8, which means smaller hydrodynamic radii of cyclic polymer than that of linear one. Role of ring strain was also confirmed by comparing 7-membered cyclic HAE and acyclic HAE as the initiator. Conversion of IBVE by 7-membered HAE was larger than that of acyclic one, particularly at lower conversion. This means faster initiation than that of acyclic one. Smaller molecular weight distribution was also supports faster initiation. On the other hand, polymers from 6-membered one gave multimodal curves even though the peak top ratio was 0.8. This is considered that the reason of multimodal curve is probably initiation from trace amount of water in glass tube because 6-membered cyclic HAE was not so effective to initiate

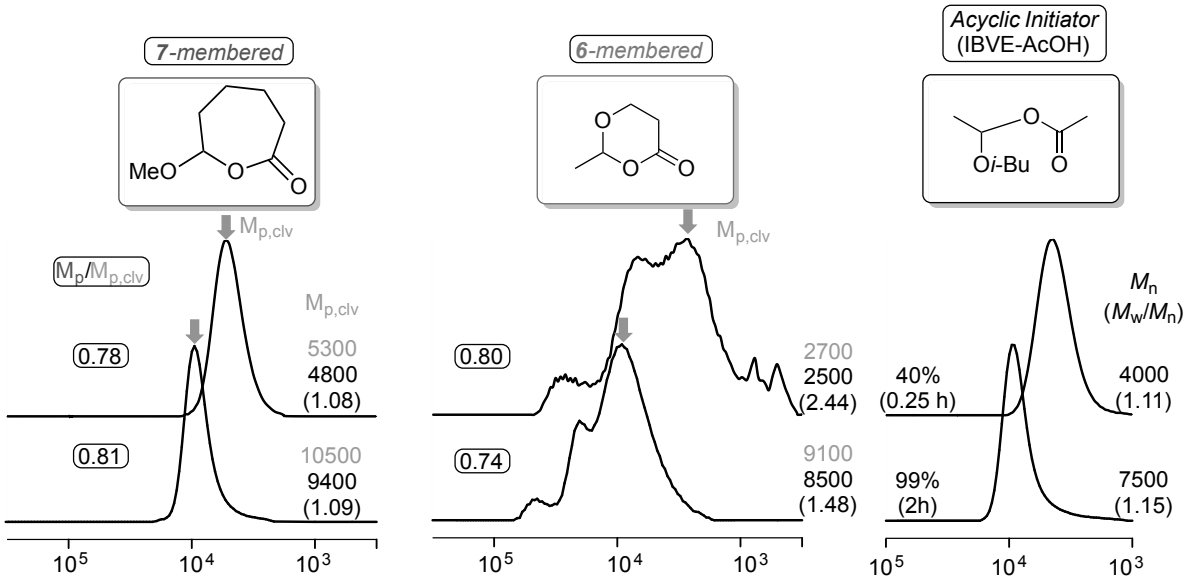



**Figure 3.** SEC curves of cleaved form in figure 1 and polymer from acyclic initiator.

polymerization, and these propagating species grew independently of each other.

Furthermore, $^1$H NMR of polymer initiated from 6-HAE was performed (Figure 4). Methine proton of HAE bond (*a*) was observed, which is consistent with acidolysis experiment, and aldehydes and carboxylic acid protons caused by decomposition of hemiacetal ester were not seen in this polymer. Protons by side reactions, however, clearly observed; terminal enol ethers (*i, j*) by β-hydrogen elimination, internal olefins (*g, h*) by de-alcohol of side chain, and acetals (*k*) were observed. Taking these observations into account, it can be presumed that a portion of hemiacetal ester bond underwent exchange reaction with bromine atom on Lewis acid to form carbon-bromine bond. This bond is labile toward methanol and at the end of polymerization the bromide was substituted by alcohol. Furthermore, Lewis acid also reacts with ether oxygen atom in pendant, leading to abstraction of alcohol to form internal olefin. Produced alcohol might react with propagating cation/hemiacetal ester/carbon-bromine bond to make terminal acetal. The acetal also potentially can be activated by Lewis acid. These bonds have different reactivity toward

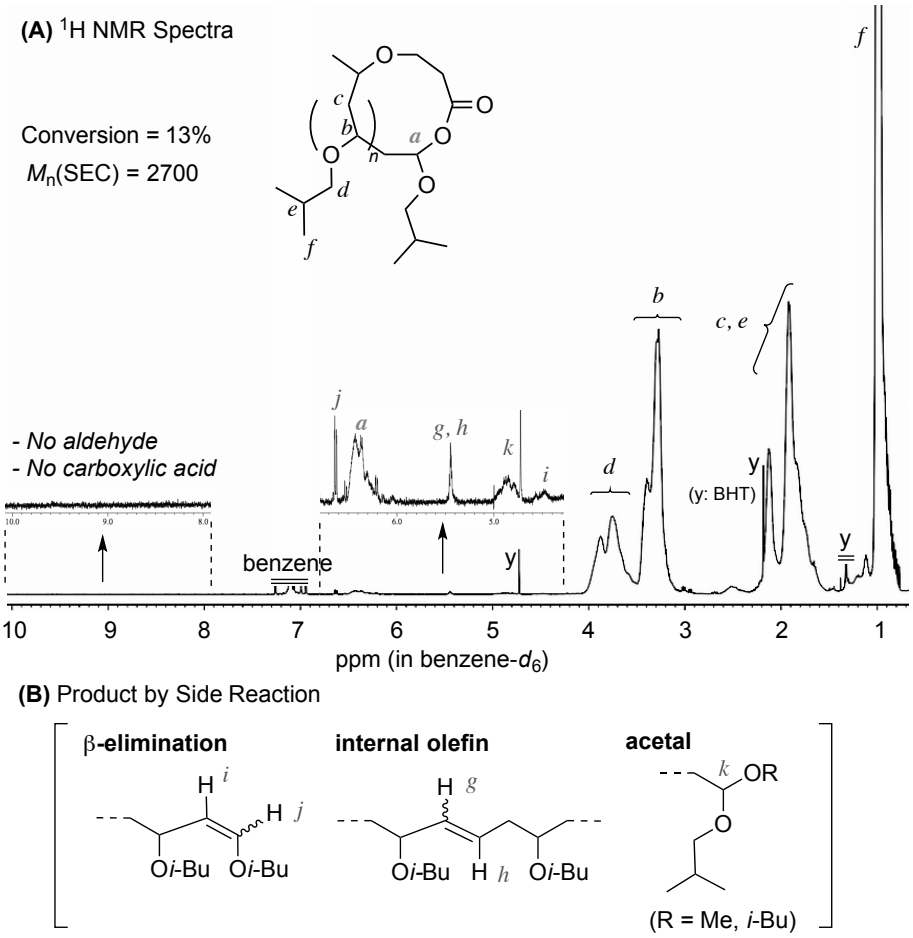



**Figure 4.** $^1$H NMR spectra of obtained polymer from 6-membered cyclic HAE.

activation process, resulting several types of propagating species and multimodal SEC curves.

**Evaluation of the Stability of Cyclic HAE by $^1$H NMR**

Next, to further confirm ring strain of the cycles, in-situ $^1$H NMR measurements of 7-membered and 6-membered hemiacetal ester (5 mM) bonds were conducted in the absence and presence of $SnBr_4$ in toluene-$d_8$ at 0°C, respectively. For 7-membered cyclic HAE (Figure 5), hemiacetal ester methine proton (*a*) and methyl proton (*b*) were observed before activation. To the solution of 7-membered HAE, solution of $SnBr_4$ was added and then the resultant mixture was stirred at –78°C for 30 minutes and then temperature was switched to 0°C for measurement. Original methine proton (*a*) disappeared and methin proton in fused ring (*a1*) and halogen terminal (*a2*) were alternatively observed. Additionally, aldehyde (*a3*) and carboxylic acid (*c*) protons were observed, which came from hydrolysis of cyclic hemiacetal ester by trace amount of adventitious water.

In sharp contrast to 7-membered HAE, spectra of 6-membered HAE was not changed after the activation by $SnBr_4$ (Figure 6); hemiacetal ester methine (*a*) and methyl (*b*) protons are not shifted during activation. This is due to 6-membered HAE was too stable to undergo ring opening reaction at this condition.

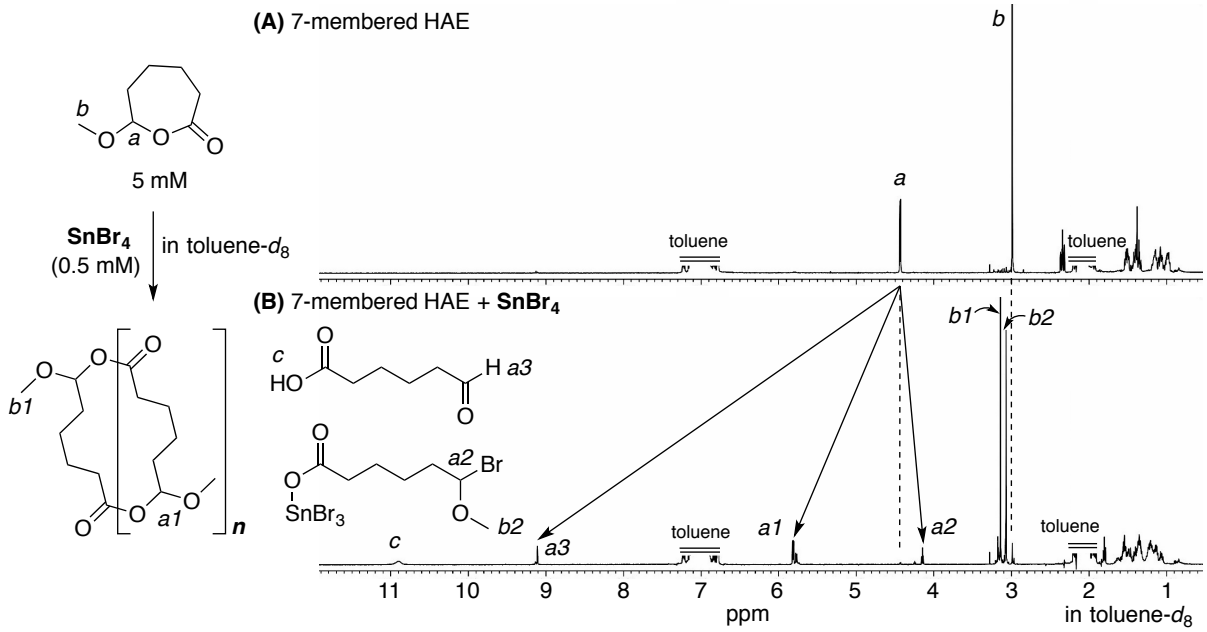



**Figure 5.** In-situ NMR spectra of 7-membered HAE in the (A) absence and (B) presence of $SnBr_4$. Condition: [HAE]/[$SnBr_4$] = 5/0.5 mM in toluene-$d_8$ at 0°C.

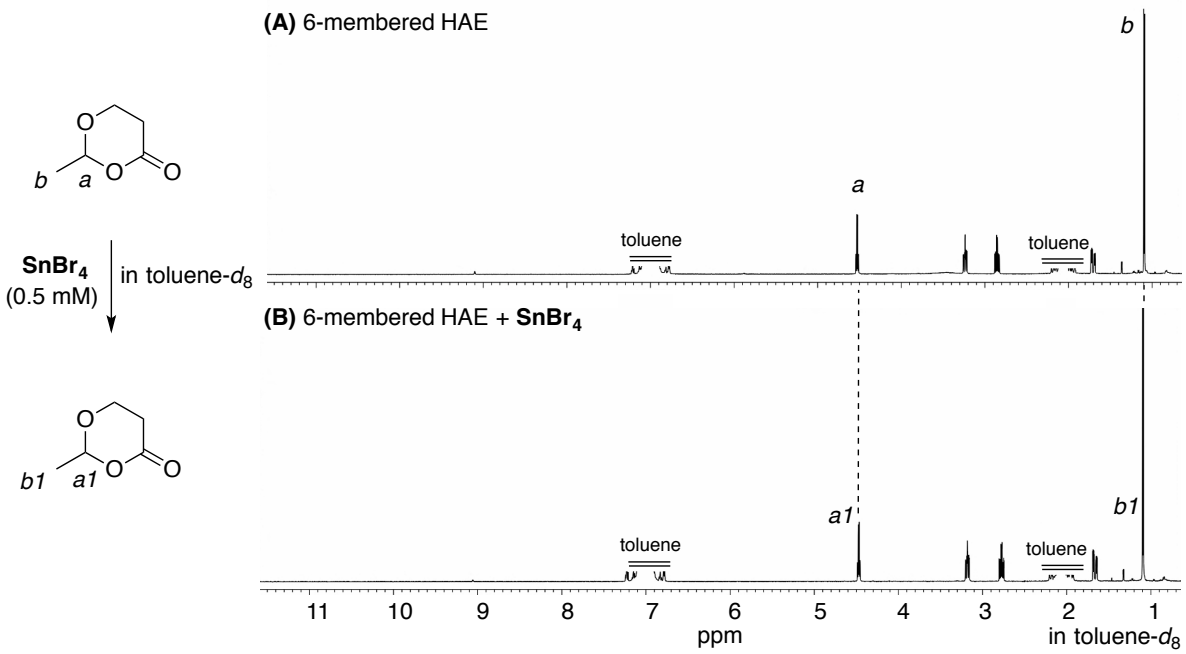



**Figure 6.** in-situ NMR spectra of 6-membered HAE in the absence (A) and presence (B) of $SnBr_4$. Condition: [HAE]/[$SnBr_4$] = 5/0.5 mM in toluene-$d_8$ at 0°C.

**Evaluation of the Stability of Cyclic HAE by Polymerization of Itself**

If above-mentioned hypothesis was clear, the author thought that ring strain in cyclic HAEs can work as the driving force to undergo ring-opening homo-polymerization of cyclic HAE itself. In the absence of exogenous initiator, cyclic HAE bond are expected to generate cation assisted by $SnBr_4$. Toward the cation, hemiacetal esters might react to be inserted and finally form oligo/poly(hemiacetal ester)s. Thus, cyclic HAEs were activated by $SnBr_4$ at relatively high HAE concentration (200 mM) (Figure 7).

In case of 7-membered cycles, cyclic hemiacetal esters completely disappeared within 30 minutes, giving distinct SEC curves oligomeric products. After 2 hours, the SEC curves didn't change, meaning that the solution was thermodynamically stable state. On the other hand, 6-membered cycles also disappeared upon addition of $SnBr_4$ catalyst; however, the product was unimodal peak, which is probably dimer, even after 2 hours activation. This difference between these cycles also supports the stronger ring strain in 7-membered cyclic HAE bond than 6-membered, which leads to homopolymerization of cycles. That is, energy release from highly strained 7-membered ring allowed polymerization of the ring, whereas relatively stable 6-membered compound didn't induce polymerization. This agrees that an equilibrium concentration of 6-membered hemiacetal ester is reported 4.53 M at room

temperature;[12] in 200 mM concentration, 6-membered one would not be polymerized.

Matrix-assisted laser desorption-ionization time of flight mass spectroscopy (MALDI-TOF-MS) analysis of the product from 7-membered cyclic HAE revealed that these multiple SEC curves were proved to have integer molecular weight of the 7-membered cyclic HAE compounds (Figure 8). For instance, calculated m/z of tetramer of 7-HAE was 599.3 (+Na) and observed m/z was 600.6 (+Na). An interval of peak was 144 that correspond to mass of 7-HAE. Furthermore, there are no peaks derived from side reactions such as halogen exchange, methanol substitution, and initiation from adventitious water. This

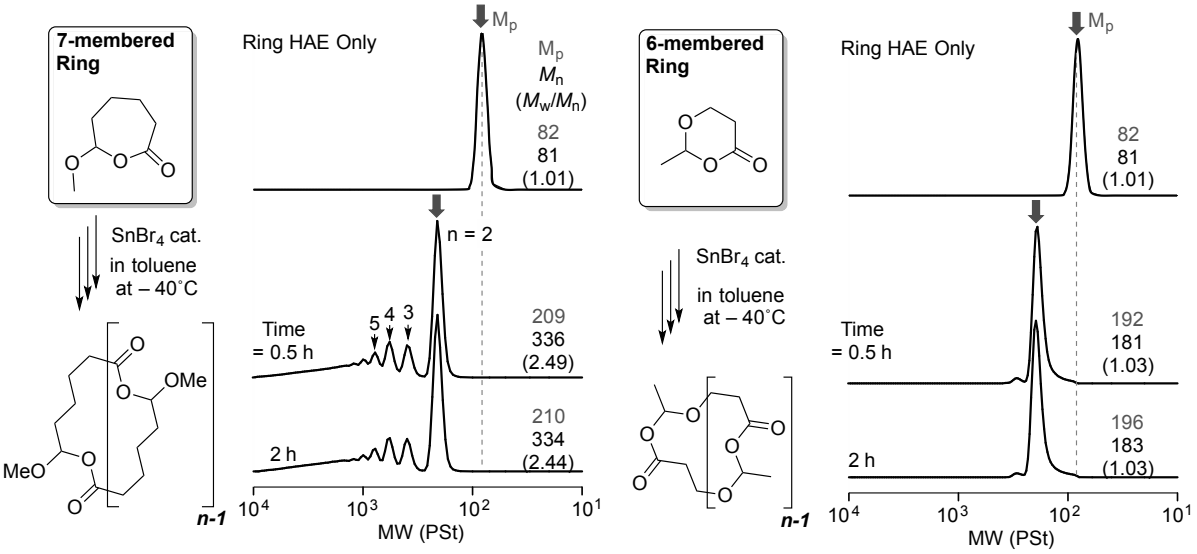



**Figure 7.** Activation of 7- and 6-membered ring hemiacetal esters in conjunction with tin tetrabromide as a catalyst and their SEC analysis; Condition: [cyclic hemiacetal ester]$_0$/[$SnBr_4$]$_0$/[DTBMP]$_0$ = 200/5/0.15 mM in toluene at –40˚C.

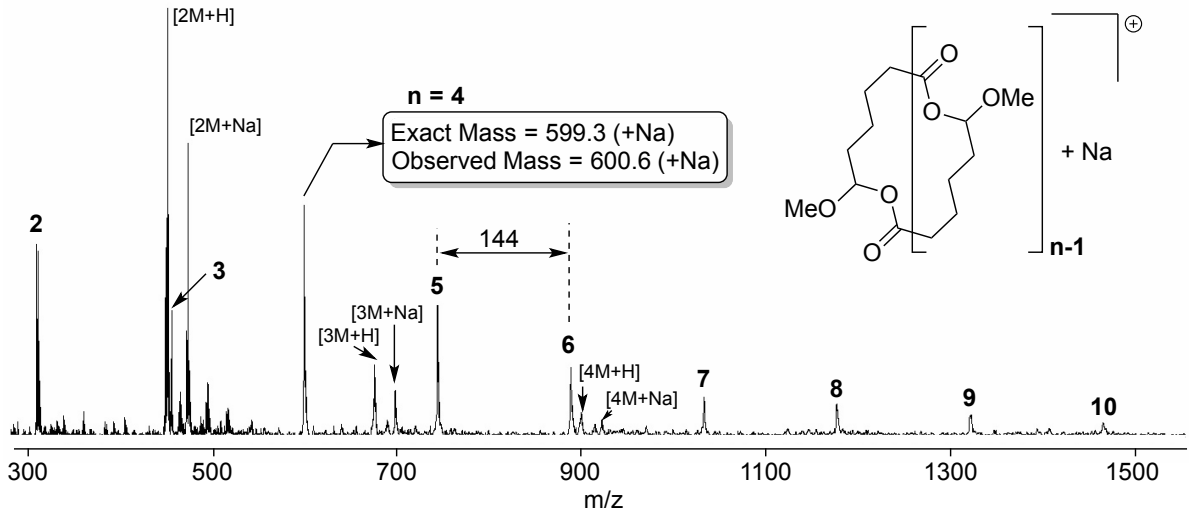



**Figure 8.** MALDI-TOF MS spectra of poly/oligo 7-membered HAE (M: Matrix (Dithranol)).

analysis revealed that also supports that ring opening polymerization of 7-membered cycles underwent in ring-expansion manner.

**Copolymerization of HAE with Vinyl Ether**

Encouraged by incidental finding of ring-expansion cationic polymerization of cyclic hemiacetal ester, the author assumed that if vinyl ether is employed together with large amount of HAE, concurrent vinyl addition-ring opening copolymerization of vinyl ether and cyclic HAE will be realized.

Therefore, activation of hemiacetal ester was conducted under HAE concentration 5, 10, 20, 50, and 100 mM, keeping concentration of IBVE 380 mM in toluene at –40˚C for 30

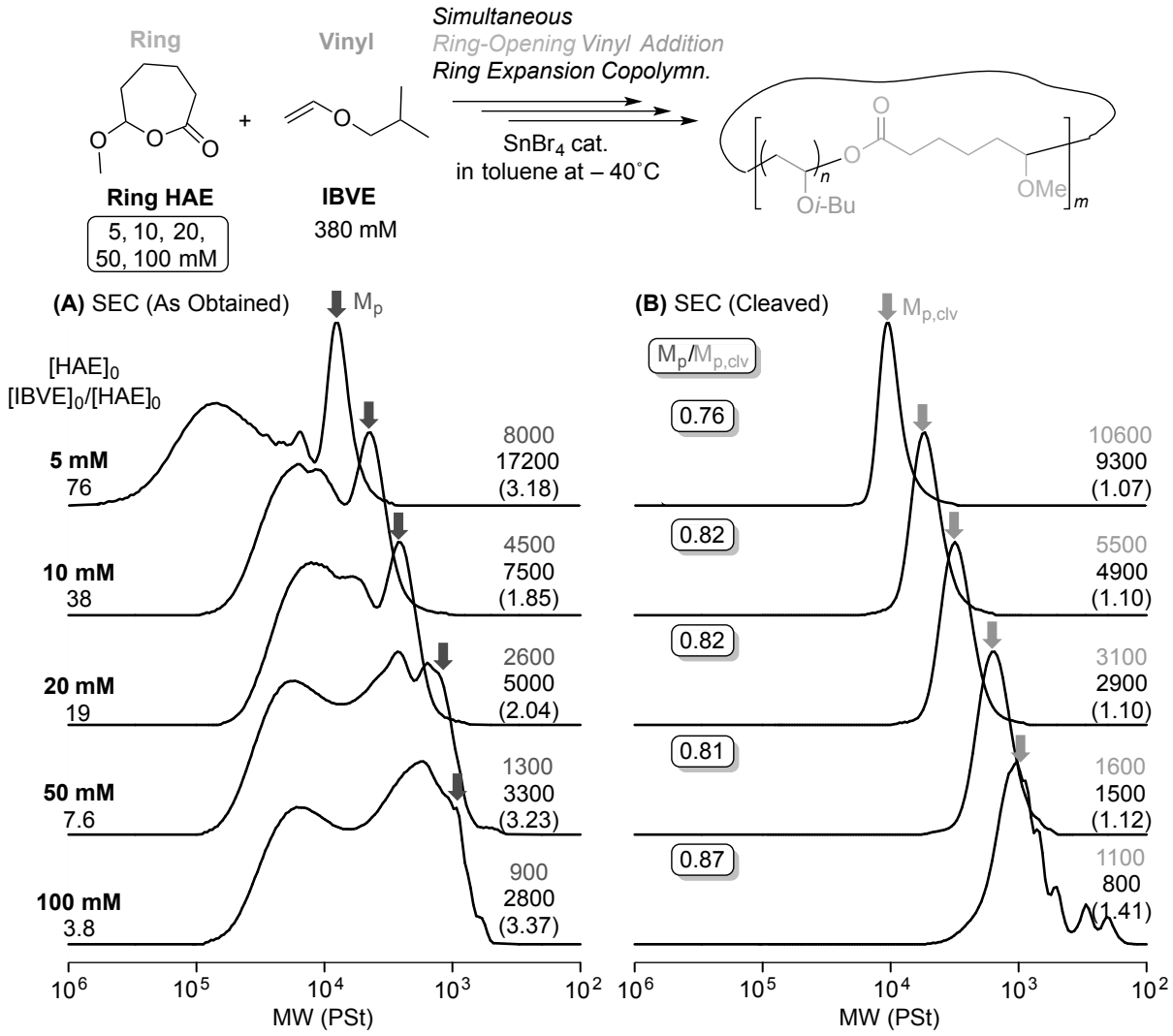



**Figure 9.** Effects of hemiacetal ester concentration on simultaneous ring-opening vinyl-addition polymerization: $[IBVE]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/0.15 mM, [7-membered cyclic HAE]$_0$ = 5, 10, 20, 50, 100 mM in toluene at –40˚C.

minutes. SEC curves of as-obtained polymer and after cleavage were shown in Figure 9. As the HAE concentration increased, $M_p$s and $M_n$s of as-obtained polymer became smaller because ratio of IBVE and HAE ($[IBVE]_0/[HAE]_0$) also become smaller; however, there are sufficient portion of polymeric product in SEC curves even under small $[IBVE]_0/[HAE]_0$ value (= 3.8). This is realized by frequent ring fusion reaction during the experiment. Acidolysis experiment gave monomodal SEC curves in all cases, where peak top molecular weight shifted higher molecular weight region, giving reasonable $M_p/M_{p,clv}$ values for ring polymers. $M_n$s of the cleaved polymer were plotted against $[IBVE]_0/[HAE]_0$ in Figure 10. $M_n$ increased along with $[IBVE]_0/[HAE]_0$, indicating that ring HAE acted as pseudo-initiator for polymerization of IBVE. From these results, unprecedented concurrent vinyl addition-ring opening copolymerization of vinyl ether and cyclic HAE was supported.

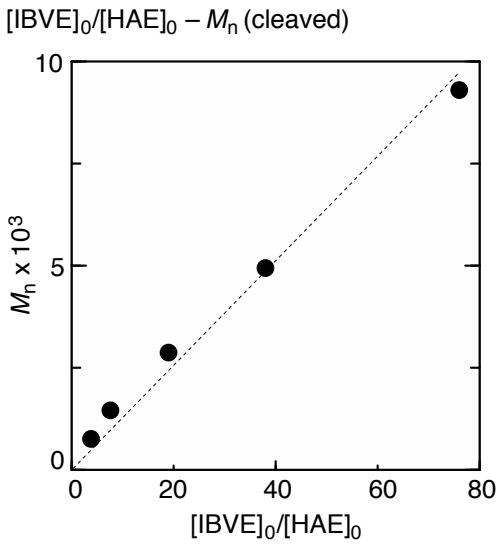



**Figure 10.** Correlation between $[IBVE]_0/[HAE]_0$ and $M_n$ (cleaved).

## Conclusion

In conclusion, 7-membered cyclic hemiacetal ester is proved to have stronger ring strain than 6-membered counterparts, and therefore it worked as an efficient initiator in ring expansion cationic polymerization. Furthermore, 7-membered cycles underwent homo-oligomerization only by itself, whereas 6-membred one only produced dimer. Using the strong ring strain, concurrent ring opening of cyclic hemiacetal ester and vinyl addition of vinyl ether polymerization was also succeeded.

## References

(1) Semlyen, J. A. Cyclic Polymers, 2nd ed.; Kluwer Academic: Dordrecht, The Netherlands, 2000.

(2) Tezuka, Y. Topological Polymer Chemistry: Progress of Cyclic Polymers in Syntheses, Properties and Functions, World Scientific Publishing Co. Pte. Ltd, 2013.

(3) Laurent, B. A.; Grayson, S. M. *Chem. Soc. Rev.* **2009,** *38,* 2202–2213.

(4) Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **2010,** *48,* 251–284.

(5) Jia, Z. Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2012,** *50,* 2085–2097.

(6) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science,* **2002**, *297*, 2041–2044.

(7) Xia, Y.; Boydston, A. J.; Yao, Y.; Kornfield, J. A.; Gorodetskaya, I. A. Spiess, H. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009,** *131,* 2670–2677.

(8) Kammiyada, H.; Konishi, A.; Ouchi, M.; Sawamoto, M. *ACS Macro Lett.* **2013,** *2,* 531–534.

(9) Kammiyada, H.; Ouchi, M.; Sawamoto, M. *Macromol. Symp.* **2015,** *350,* 105-116.

(10) Kammiyada, H.; Ouchi, M.; Sawamoto, M. *Polym. Chem.* **2016,** *7,* 6911–6917.

(11) Neitzel, A. E.; Peterson, M. A.; Kokkoli, E.; Hillmyer, M. A. *ACS Macro Lett.* **2014,** *3,* 1156–1160.

(12) Neitzel, A. E.; Haversang, T. J.; Hillmyer, M. A. *Ind. Eng. Chem. Res.,* **2016,** *55,* 11747–11755.

# PART II

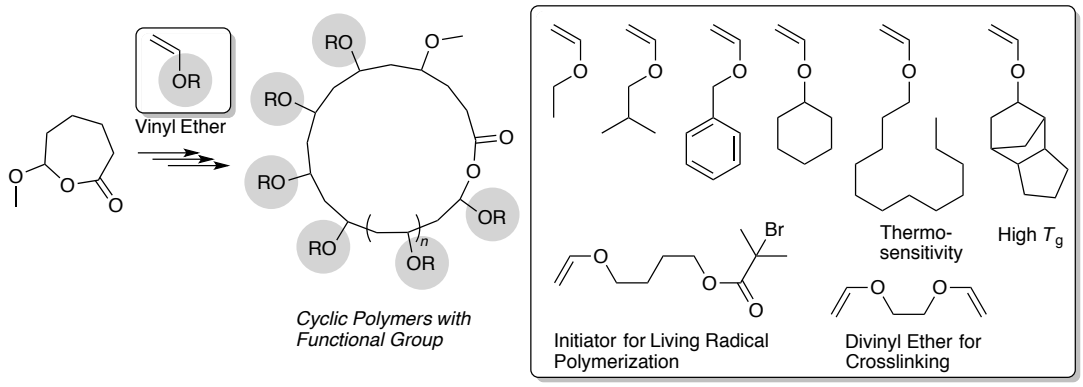
# Ring-Based Polymers:
# Precision Synthesis and Ring-Driven Properties

# *Chapter 4*

## Expanding Vinyl Ether Monomer Repertoire for Ring-Expansion Cationic Polymerization: Various Cyclic Polymers with Tailored Pendant Groups


### Abstract

Herein, the author clarified the ring-expansion cationic polymerization with a cyclic hemiacetal ester (HAE)-based initiator were versatile in terms of applicable vinyl ether (VE) monomers. Although there was a risk that higher reactive VEs may incur β-H elimination of the HAE-based cyclic dormant species to irreversibly give linear chains, the ring-expansion polymerizations of various alkyl vinyl ethers such as ethyl, cyclohexyl, tricyclodecane, and dodecyl vinyl ethers were controlled to give corresponding cyclic polymers. Functional vinyl ether monomers were also available, and for instance vinyl ether carrying an initiator moiety for metal-catalyzed living radical polymerization in the pendant allowed construction of ring-linear graft copolymers through the grafting-from approach. Furthermore, ring-based gel was prepared via the addition of divinyl ether at the end of the ring-expansion polymerization, where multi HAE bonds cyclic polymers or fused rings were cross-linked with each other.

## Introduction

"Cyclic polymer" has a simple but interesting topology different from linear polymer, endless and more compact structure. The structural factors as the chain can lead to unique behaviors and properties,[1] such as smaller dimension in solution, unique diffusion behavior, different thermo-sensitive property,[2–4] etc. The synthesis in early reports on cyclic polymers mainly relied on end-to-end coupling reaction of precursory linear polymer, where the terminal groups intramolecularly react with each other under highly diluted condition to avoid intermolecular reaction.[5] The approach is definitely less efficient especially for higher molecular weight polymer.

On the other hand, "ring-expansion polymerization (REP)" has attracted attentions as the efficient methodology to synthesize cyclic polymers. Herein, a ring initiator is designed for leaving or dissociative group of living polymerization to be embedded into the cyclic structure, and a suitable monomer is polymerized from the initiator keeping the cyclic topology, as balloon is blew up. For instance, Grubbs precisely designed a cyclic ruthenium carbene for ring-opening metathesis polymerization to realize REP of cycloolefin monomer.[6]

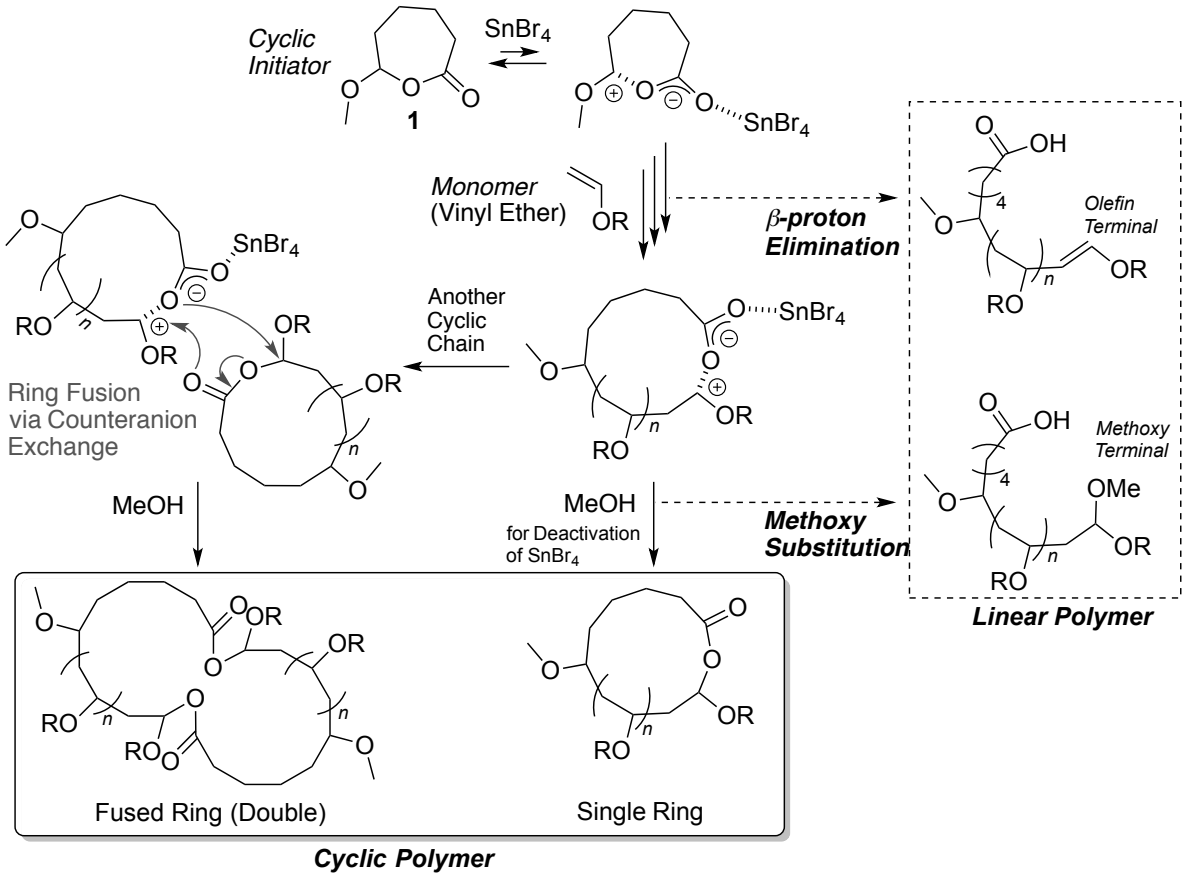



**Figure 1.** Ring-expansion cationic polymerization, ring fusion, and plausible side reactions during polymerization.

Since the pioneering research, REP has been studied for some polymerizations. However, most examples on REP were limited to ring-opening polymerization of cyclic monomers:[7] REP of ethylene derivatives, i.e., acyclic monomers, has been more challenging.[8]

Our group has developed a ring-expansion cationic polymerization (RECP) of vinyl ethers with a hemiacetal ester-embedded cyclic initiator (**1**) in conjunction with $SnBr_4$ (Figure 1).[9–11] In this polymerization, $SnBr_4$ reversibly activates the hemiacetal ester in **1** to give inherently cyclic propagating species, and propagation of the vinyl ether monomer takes place along with reversible activation of the cyclic hemiacetal ester dormant species. The polymerization can be terminated by the addition of methanol for deactivation of $SnBr_4$, eventually giving cyclic poly(vinyl ether). Herein, there are some points that must be kept in mind to realize REP with this system. First, once β-proton elimination, which is a typical side reaction in cationic polymerization, occurs, olefin-terminated linear polymer could be formed. Second, there is a possibilty that methanol for the termination may incur substitution reaction for growing terminal to convert into the methoxy-capped linear chains. The two reactions must be avoided to obtain cyclic polymer.

In our previous study, we have found that vinyl ether is applicable for the monomer of the REP, due to formation of hemiacetal ester dormant species. As for vinyl ether, design of the pendant is easily accessed through several approaches;[12] addition of alcohol into acetylene,[13] substitution reaction to 2-chloroethyl vinyl ether,[14] esterification of hydroxyl substituted vinyl ethers,[15] and transvinylation to alcohol from commercially available vinyl ether.[16,17] Toward study on ring-driven functions as well as construction of ring-based architectures with the RECP, it is important to expand applicable monomers. Extensive studies on conventional cationic polymerization of vinyl ethers have revealed that the pendant group affects the reactivity in cationic polymerization as well as the side reactions depending on the electron donation ability and interaction with cationic species and/or Lewis acid.[18,19,20] Even for RECP, investigation of the polymerization behaviors with various monomers is required toward more convenient system leading to not only study on ring-driven properties but also construction of advanced ring-based architectures.

## Experimental

### Materials

Dodecyl vinyl ether (DDVE) (Aldrich; >98%), 8-vinyloxytricyclo[5.2.1.$0^{2,6}$]decane (TCDVE) (Maruzen Petrochemical; >99.8% ), cyclohexyl vinyl ether (TCI; >98%), Benzyl vinyl ether (Maruzen Petrochemical; >99.8%) and tetralin (TCI; >97%) were distilled from calcium hydride under reduced pressure once before use. Ethyl vinyl ether (TCI; >98%) and ethyleneglycol divinyl ether were distilled from calcium hydride twice before use. Triethylamine (TCI; >99%) was distilled from calcium hydride once before use. Toluene (Kishida Kagaku, Osaka; 99.5%) was dried and purified by passing through purification columns (Solvent Dispensing System, SG Water USA, Nashua, NH; Glass Contour), kept over molecular sieves 4A for more than one day. $SnBr_4$ (Aldrich; >99%), 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, Aldrich; >99%) trifluoroacetic acid (TFA, Wako; >98%), 2-bromoisobutyryl bromide (TCI; >98%),. tetramethylene glycol monovinyl ether (TCI; >97%) and dichloromethane (Wako; >99.5%) were used as received. The cyclic initiator (1) was synthesized according to our previous paper.[9]

### Measurements (SEC and $^1$H NMR)

Number-averaged molecular weight ($M_n$), and its distribution ($M_w/M_n$) of polymers were measured by size exclusion chromatography (SEC) at 40˚C in THF as an eluent on three polystyrene-gel columns (Shodex KF-803; pore size, 20–1000 Å; 8.0 mm i.d. x 30 cm; flow rate, 1.0 mL min$^{-1}$) connected to a DU-H2000 pump, a 74S-RI refractive-index detector, and a 41-UV ultraviolet detector (all from Shodex). The columns were calibrated against 13 standard poly(St) samples (Polymer Laboratories; $M_n$ = 500–3840000; $M_w/M_n$ = 1.01–1.14). $^1$H NMR spectra of the obtained polymers were recorded in $CDCl_3$ at 25 ˚C on a JEOL JNM-ECA500 spectrometer, operating at 500.16 MHz. Polymer purification was performed by preparative SEC in $CHCl_3$ at room temperature (flow rate: 10 mL min$^{-1}$) on a polystyrene gel fractional column (K-5003: exclusion limit = 7 x $10^4$; particle size = 15 mm; 5.0 cm i.d. x 30 cm) that was connected to a Jasco PU-2086 precision pump, a Jasco RI-2031 refractive index detector, and a Jasco UV-2075 UV/vis detector set at 250 nm.

### Ring-Expansion Cationic Polymerization of Vinyl Ethers with 1.

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical procedure is given below: the polymerization was initiated by

adding solutions of $SnBr_4$ (50 mM in toluene: 0.5 mL) via a dry syringe into a mixture (4.5 mL) containing DDVE (0.49 mL), tetralin (internal standard, 0.10 mL), cyclic initiator **1**, and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) in toluene at –40˚C: $[DDVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/5/0.15 mM. After a predetermined interval, the polymerization was terminated with prechilled ammonical methanol. Monomer conversion was determined from its residual concentration measured by gas chromatography with tetralin as an internal standard. The quenched reaction mixture was washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(DDVE).

**HAE Cleavage of Cyclic Poly Vinyl Ethers via Acidolysis**

A typical procedure for cleavage of HAE bond in cyclic poly(DDVE) is given below. In a vial (2 mL) was placed 1.0 mL of ring poly(DDVE) solution (1wt% in THF) and added 5 drops of $H_2O$/THF (1/2 v/v) solution was added. The resultant solution was kept at ambient temperature for 12 hours, and the resultant solution was vacuum dried to remove THF, water and trifluoroacetic acid to obtain linear poly(DDVE).

**Synthesis of vinyl ethers with initiator moiety for living radical polymerization**

To a solution of tetramethylene glycol monovinyl ether (6.4 g, 55 mmol) and triethylamine (6.0 g, 60 mmol) in dichloromethane ($CH_2Cl_2$; 50 mL) was added 2-bromoisobutyryl bromide (11.5 g, 50 mmol) slowly at 0 ˚C. The resulting mixture was warmed to room temperature and stirred for 3 hours. The reaction was quenched with large portion of $H_2O$ and the resultant solution was partitioned between $CH_2Cl_2$ and $H_2O$. The aqueous layer was extracted with $CH_2Cl_2$ three times. The combined $CH_2Cl_2$ solution was washed with aqueous solution of ammonium chloride, dried on $Na_2SO_4$. The crude product was purified by silica-gel chromatography ($CH_2Cl_2$ as the eluent) to afford (4-(vinyloxy)butyl 2-bromo-2-methylpropanoate) as an oil in 83% yield (11.0 g). $^1$H NMR (500 MHz, $CDCl_3$, δ) 6.45 (dd, 1H), 4.21 (t, 2H), 4.17 (dd, 1H), 3.71 (t, 2H), 1.92 (s, 6H), 1.78 (m, 4H).

## Results and Discussion

**Scope of Monomers: Alkyl-Based Vinyl Ethers and Designer Vinyl Ethers**

In this chapter, In this paper, we studied some allyl vinyl ethers of different relativities and functions to construct various cyclic architectures toward ring-based properties and functions. For example, the cyclohexyl derivative (CHVE), which is one of highly reactive

monomers for cationic polymerization, is likely to cause side reactions than other monomers during ring-expansion propagation. The Benzyl ether pendant monomer (BnVE) is interesting in that the polymer could be converted into poly(vinyl alcohol). The bicyclic monomer (TCDVE) gives the rigid polymer of higher glass transition temperature ($T_g$ ~ 100˚C), whereas the long alkyl pendant monomer (DDVE) does the soft polymer with no observable $T_g$ and low melting temperature ($T_m$ ~ 30 ˚C). The alkyl-bromide of BrVE can serve as an initiator for metal-catalyzed living radical polymerization and thus graft copolymer is expected through the graft-from approach. The divinyl monomer, EGDVE, is interesting as the crosslinking monomer toward ring-based gels..

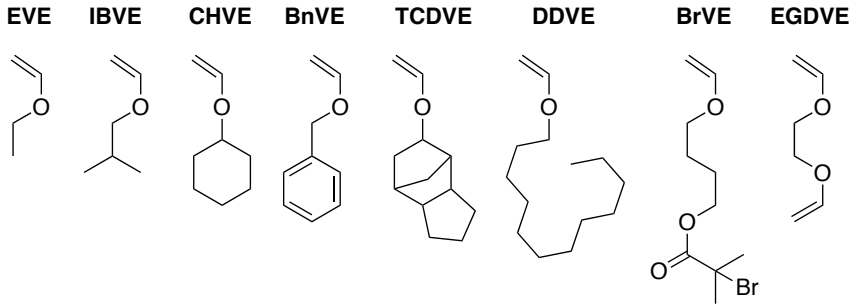



**Figure 2.** Vinyl ethers used in this chapter.

**Ring-Expansion Cationic Polymerization of Various Alkyl Vinyl Ethers**

Polymerizations of the alkyl pendant vinyl ethers (EVE, CHVE, BnVE, TCDVE, and DDVE) with **1** as the initiator were performed under the condition, which was established for RECP of IBVE: $[monomer]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/5/0.15 mM in toluene at –40˚C (Figure 2A). The five monomers were smoothly consumed similar to IBVE. The polymerization rates varied depending on the pendant group (Figure 2B), and the tendency almost agreed with results in literatures. [18,19,20]

In SEC curves of as-obtained polymers (Figure 3C), fused rings were observed for all monomers. The fused rings were formed through counteranion exchange reaction during polymerization, resulting large rings with multiple hemiacetal ester bond at regular intervals. As criteria to evaluate the percentage of single ring, the author introduced a parameter as peak area of single rings. Interestingly, there is no correlation between the percentage of single ring and monomer reactivity (percentage of single: DDVE> TCDVE> CHVE> (IBVE>) EVE> BnVE); that is, monomer reactivity affected both inter- and intra- molecular counteranion exchange reaction and the balance was independent of the monomer. In SEC curves after acidolysis experiment, all polymers gave monomodal curves with relatively narrow molecular

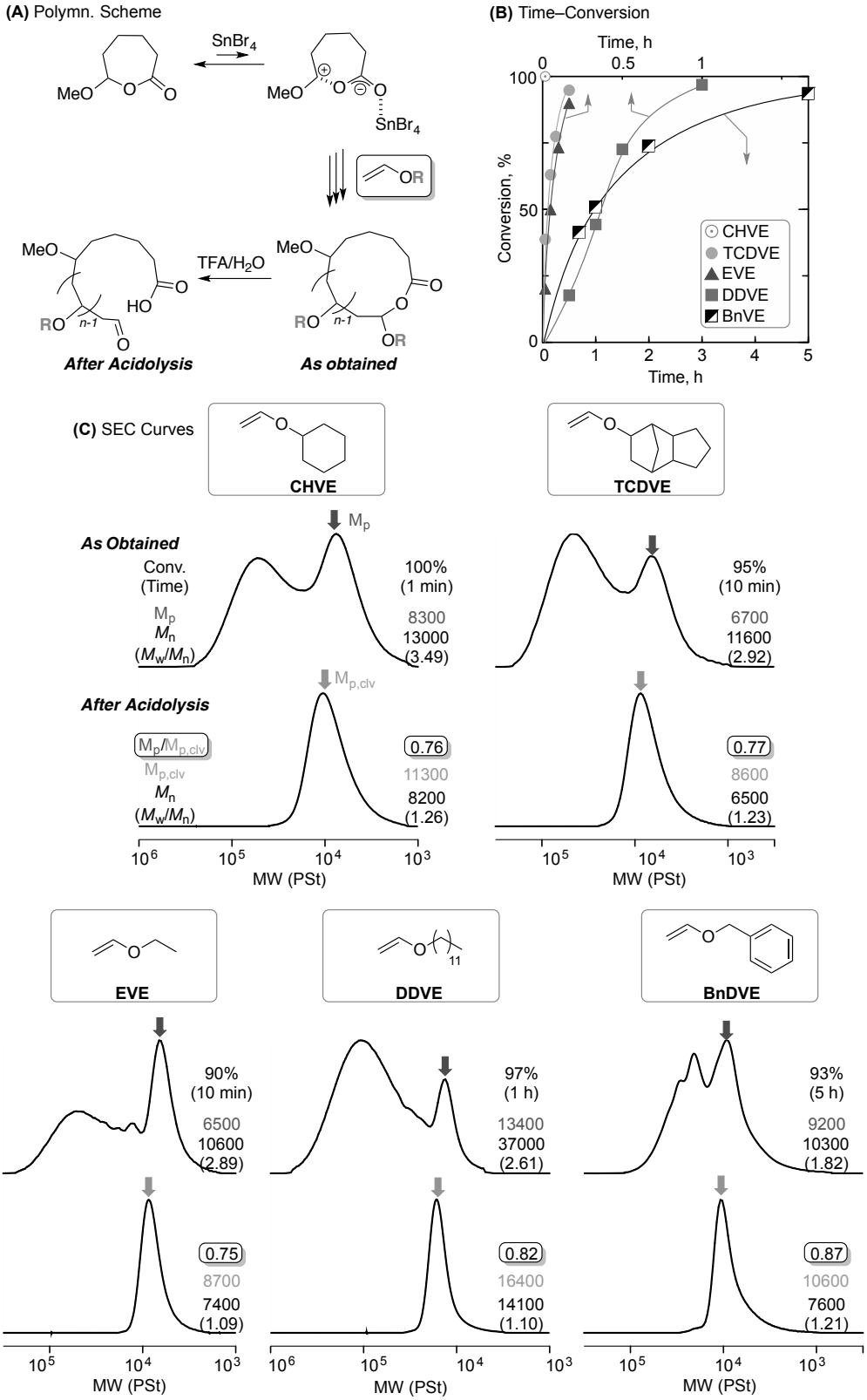



**Figure 3.** Ring-expansion cationic polymerization of various vinyl ethers with cyclic initiator **1**. $[\text{Vinyl Ether}]_0/[\mathbf{1}]_0/[SnBr_4]_0/[\text{DTBMP}]_0$ = 380/5/5/0.15 mM in toluene at –40˚C.

weight and higher peak top molecular weight ($M_{p,clv}$) than that of precursors ($M_p$). Herein hemiacetal ester bonds were cleaved by acidolysis, and fused ring connected with hemiacetal ester bond were converted into linear polymers with smaller molecular weight. The ratios of $M_p$ and $M_{p,clv}$ ($M_p/M_{p,clv}$) were in range of 0.75–0.87. These values agree to smaller dimension of cyclic polymer than linear analogue. These values, however, were different among monomer structure; for example, 0.75 for EVE while 0.82 for DDVE and 0.87 for PBnVE. This is likely because monomer unit was released upon acidolysis experiment and molecular weight in SEC was underestimated, and thus polymer with longer alkyl side chain (PDDVE) gives slightly higher $M_p/M_{p,clv}$ value than that of shorter alkyl side chain (PEVE). In case of BnVE, the value probably meant that the as-obtained polymer contained small amount of linear poly(BnVE), because the SEC curve after acidolysis had a shoulder in low molecular weight region that came from side reaction. The cause of this side reaction is sigmatropic rearrangement of benzyl vinyl ether catalyzed by tin tetrabromide, which is known as claisen rearrangement, giving aldehyde in polymerization solution.[21] The resultant aldehyde reacted with cationic species/tin catalyst to incur cyclic polymer to produce linear byproduct.

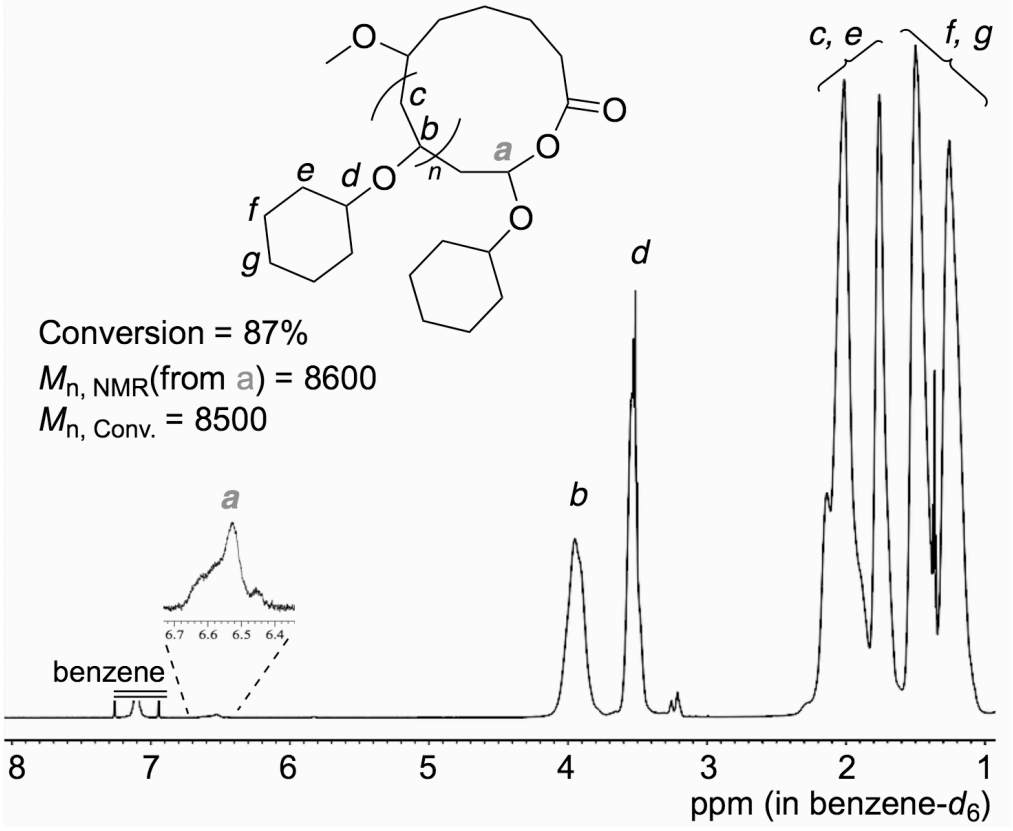



**Figure 4.** $^1$H NMR analysis of PCHVE in benzene-$d_6$ at 25°C.

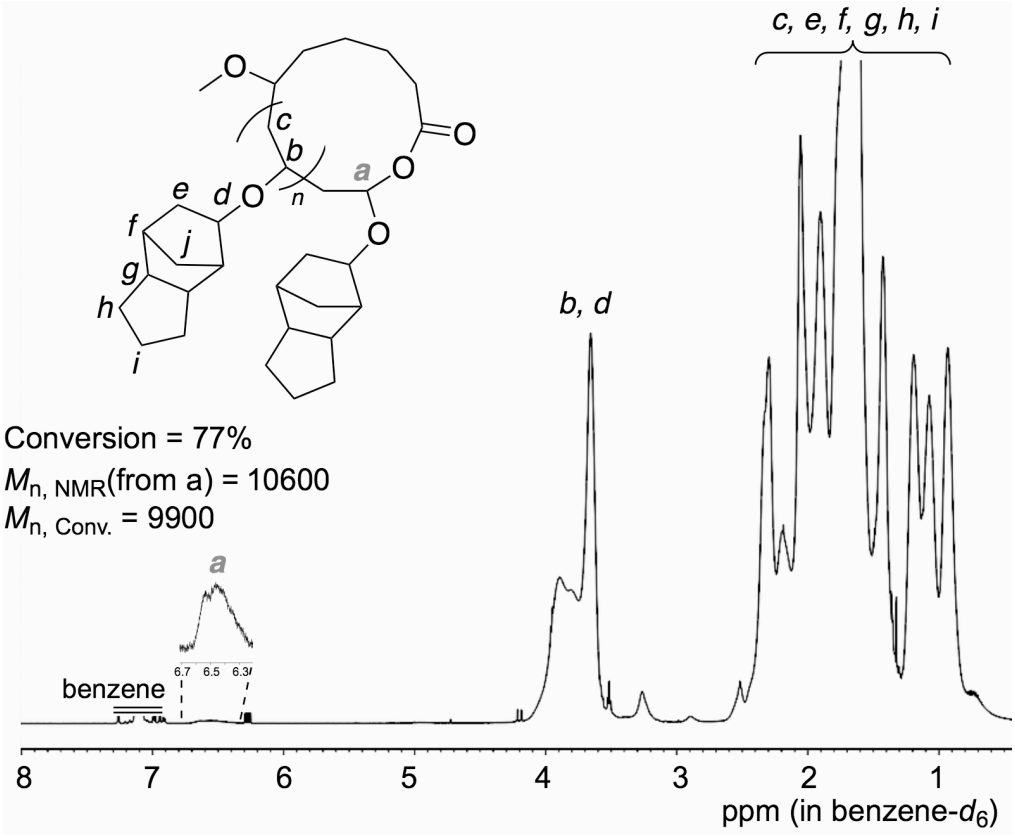



**Figure 5.** $^1$H NMR analysis of PTCDVE in benzene-$d_6$ at 25˚C.

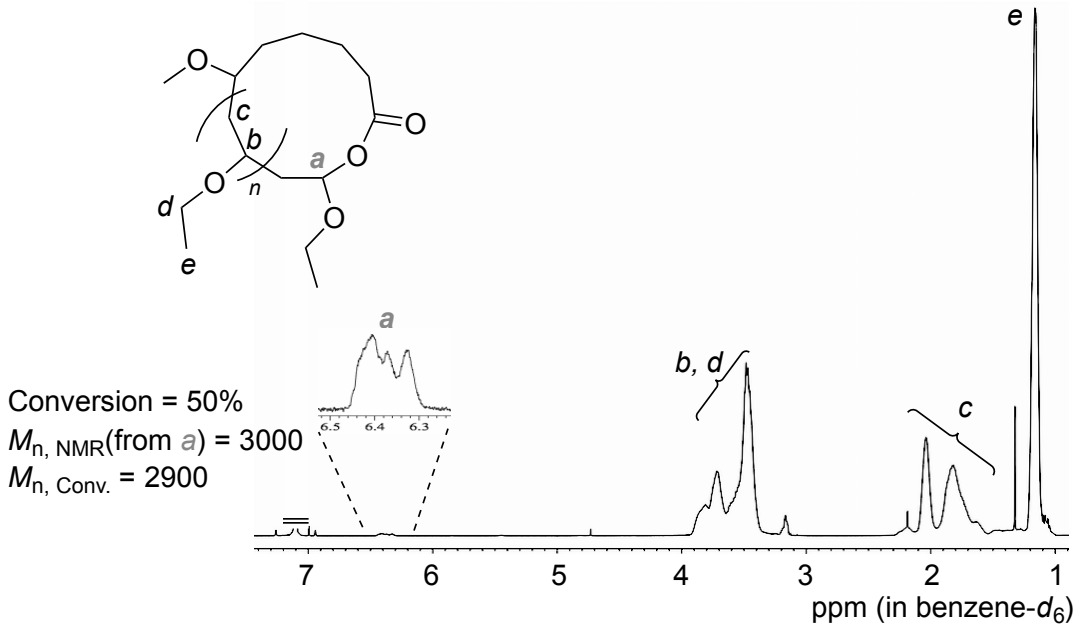



**Figure 6.** $^1$H NMR analysis of PEVE in benzene-$d_6$ at 25˚C.

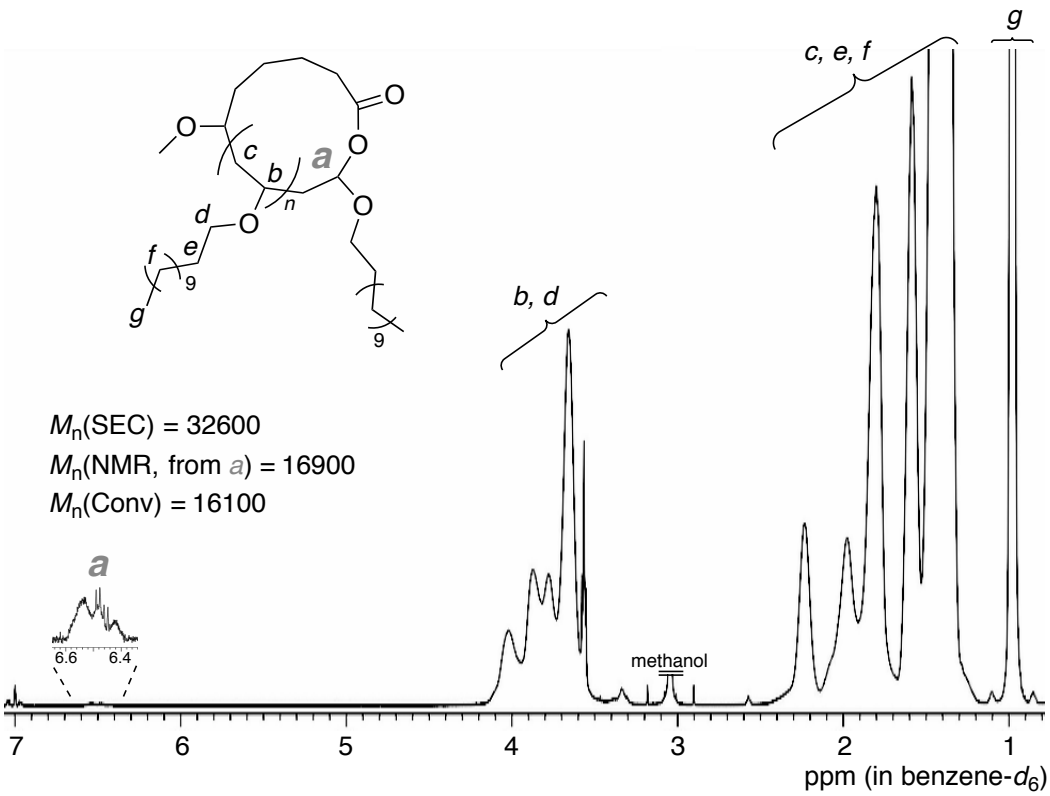



**Figure 7.** $^1$H NMR analysis of PDDVE in benzene-$d_6$ at 25˚C.

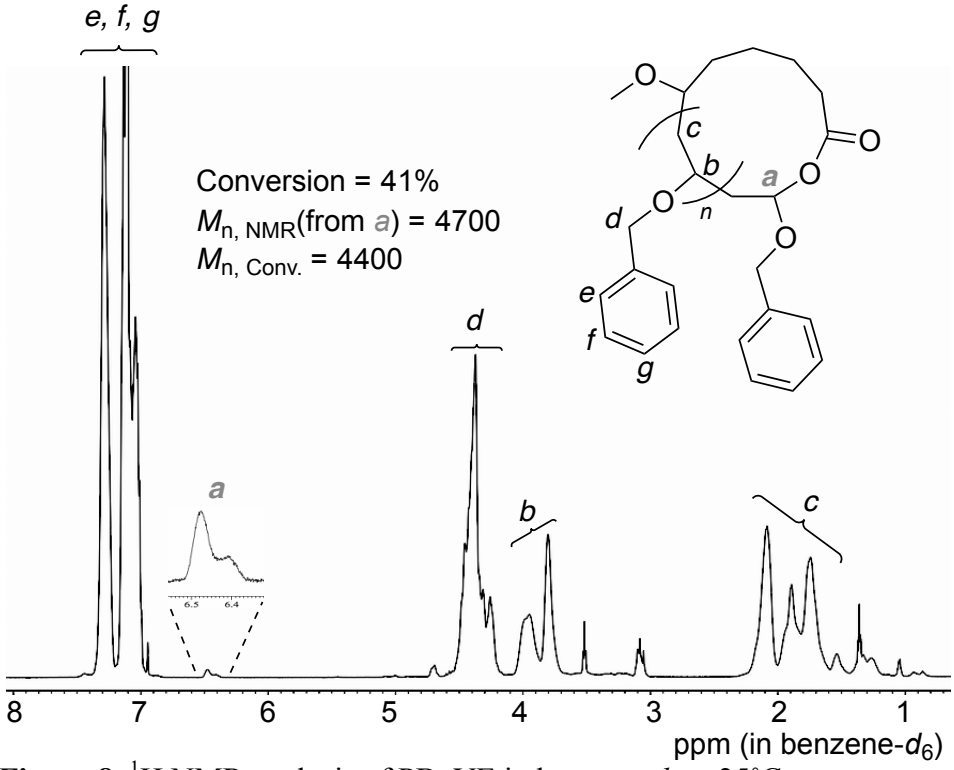



**Figure 8.** $^1$H NMR analysis of PBnVE in benzene-$d_6$ at 25˚C.

$^1$H NMR analyses were conducted for all polymers and $^1$H NMR spectra of PCHVE was shown as follows (Figure 4). Methine proton (*a*) characteristic to hemiacetal ester bond was clearly observed along with main-chain (*b, c*) and side chain (*d, e, f, g*). Molecular weight calculated from peak area of (*a*) and (*d*) was 8600. On the other hand, molecular weight from monomer conversion and injection ratio of initiator and monomer was 8500. These values were nicely consistent to each other, showing almost quantitative introduction of hemiacetal ester bond in the polymer after polymerization. $^1$H NMR analyses for other polymers were shown in Figure 5–8.

In short summary, alkyl-based vinyl ethers were proved to undergo ring-expansion cationic polymerization without unfavorable side reactions except for BnVE. The reduction of side reaction in polymerization of BnVE is underway.

**Ring-based Advanced Polymer Architecture: Cyclic Graft Copolymer**

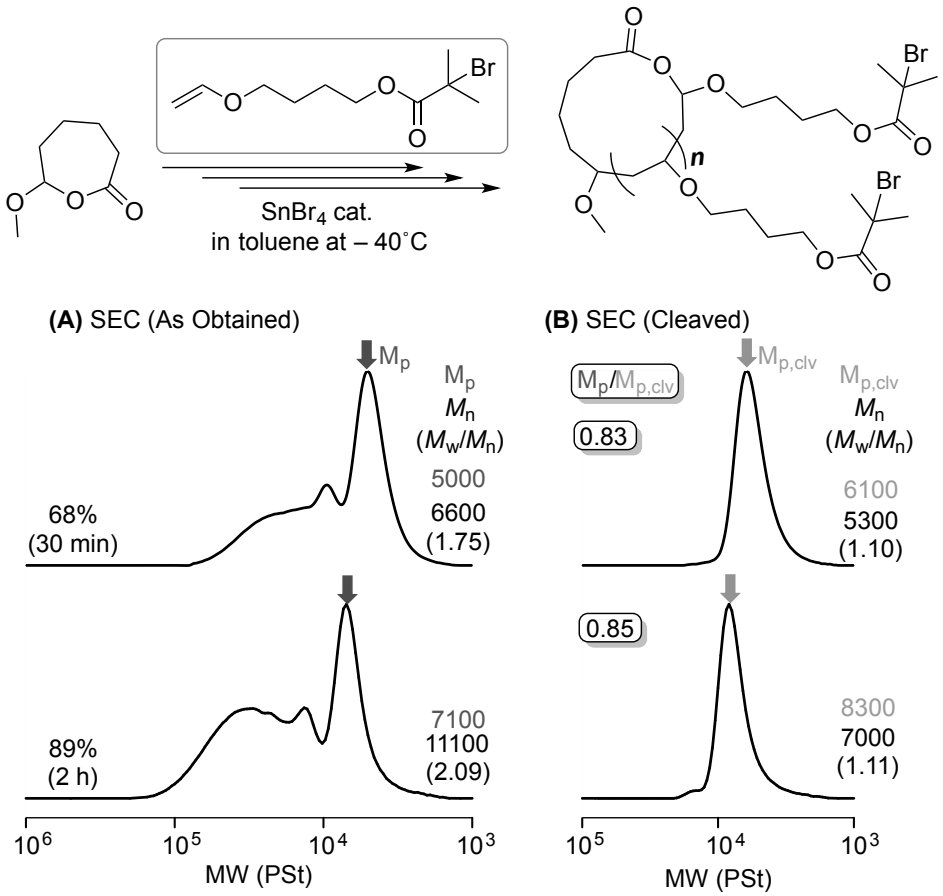



**Figure 9.** Ring expansion cationic polymerization of vinyl ether having initiator moiety for living radical polymerization: $[\text{Vinyl ether}]_0/[\text{Ring initiator}]_0/[SnBr_4]_0/[\text{DTBMP}]_0$ = 200/5/5/0.15 mM in toluene at –40˚C.

Graft polymers have attracted many attentions in many fields including drug delivery,[22] stimuli-responsive coating,[23] photonics,[24] and lithographic patterning.[25] Introducing cyclic structure in graft polymer in main chain can expand the possible applications. Synthetic pathways of graft copolymer are categorized in three parts: i) graft-through, ii) graft-onto and iii) graft-from approach. Among them, the author employed graft-from approach for easy handling. For this purpose, initiator moiety should be embedded in the pendant of monomer. In cationic polymerization, polar groups such as hydroxyl group are known to retard or inhibit polymerization. Thus, the author introduced a halo-ester moiety into pendant of vinyl ether so as to act as an initiator of living radical polymerization. Carbon-bromine bond adjacent to ester group reversibly generates radical species by catalyst to induce living radical polymerization. Note that carbon-bromine bond presumably wouldn't dissociate ionically during cationic polymerization, thanks to electron-withdrawing nature of halo-ester.

Cationic polymerization of BrVE was conducted in toluene at –40 ˚C in conjunction with $SnBr_4$ as an activator. BrVE was smoothly consumed and conversion was reached at 89% in 2 hours. Same as seen as other monomers, BrVE also gave multimodal SEC curves consisting of fused rings and single rings, yielding poly(BrVE) ($M_n$ = 11100, $M_w/M_n$ = 2.09) (Figure 9A). To remove residual monomers from the mixture, poly(BrVE)s were re-precipitated into cold

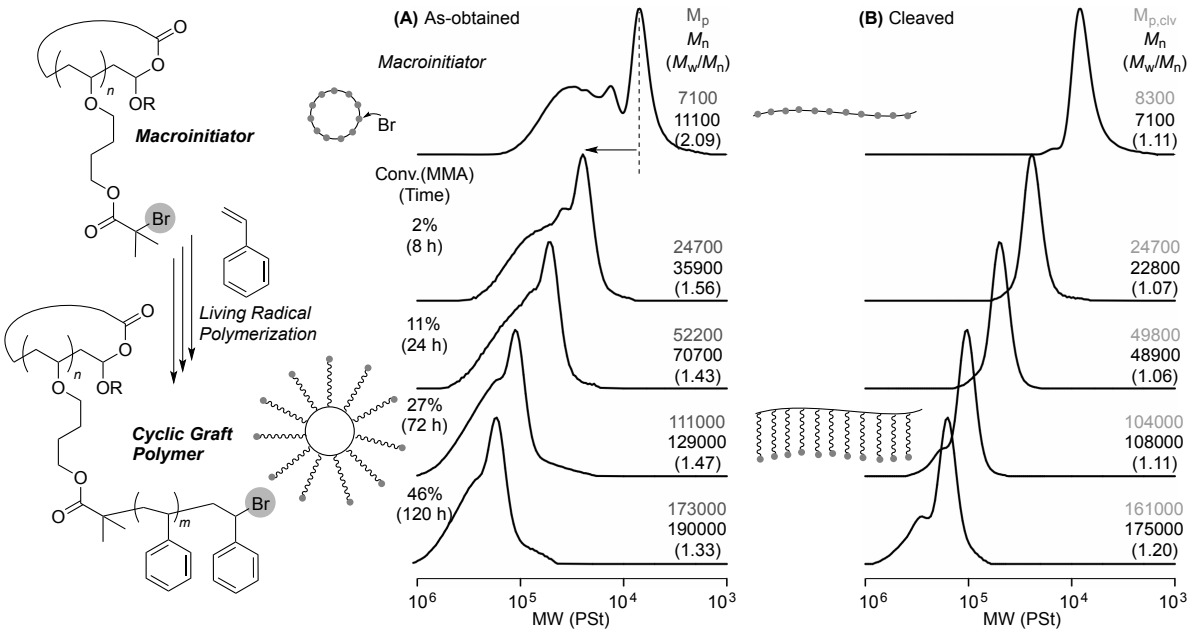



**Figure 10.** Synthesis of graft polymer through living radical polymerization of styrene using cyclic macro-initiator in conjunction with a ruthenium catalyst: $[St]_0/[$ring multifunctional macro initiator$]_0/[Ru(Ind)Cl(PPh_3)_2]_0/[n Bu_3N]_0$ = 2000/10/0.5/20 mM in toluene at 80˚C.

methanol three times and the polymer was isolated as sediment and then dried and degassed in vacuo. By $^1$H NMR measurement, incorporation of hemiacetal ester was estimated as 92% (Figure 11A). Surely peak area of methyl group kept constant based on methylene proton on main chain, which agrees that carbon-bromine bond was not affected throughout the course of cationic polymerization. Upon acidolysis experiment, peak top molecular weight shifted higher molecular weight region, implying compact cyclic structure (Figure 9B).

Using the cyclic polymer as a macroinitiator, living radical polymerization of styrene (St) was carried out in conjunction with ruthenium catalyst (Figure 10).[26] At monomer conversion reached to 2%, SEC peak significantly shifted to the higher molecular weight. Since initiator moieties are attached to each monomeric unit of macro-initiator, increment of apparent molecular weight seem large. As monomer conversion increased, $M_p$ and $M_n$ increased in direct proportion to monomer conversion. Shape of SEC curves gradually changed and amount of fused rings looks smaller and molecular weight distribution became

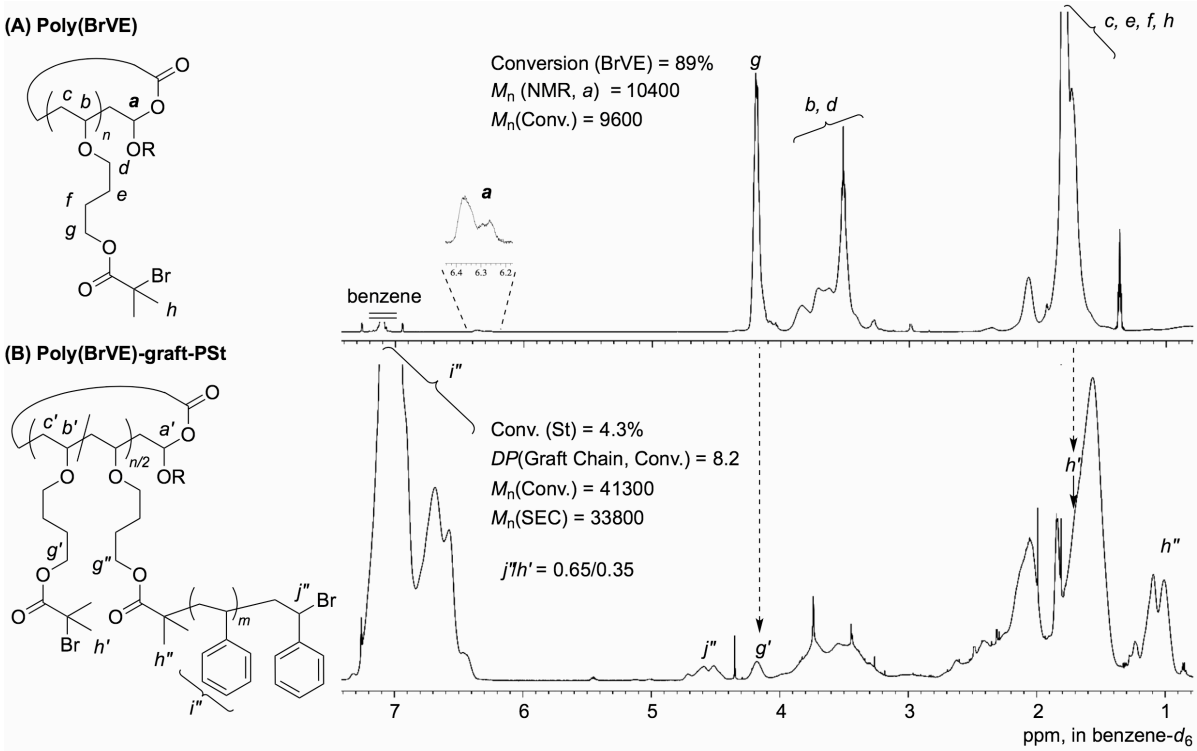



**Figure 11.** $^1$H NMR spectra of poly(BrVE)(A) and polystyrene therefrom (B). Polymerization condition: (A) $[\text{Vinyl ether}]_0/[\text{Ring initiator}]_0/[SnBr_4]_0/[\text{DTBMP}]_0$ = 200/5/5/0.15 mM in toluene at –40˚C. (B) $[St]_0/[\text{ring multifunctionalmacroinitiator}]_0$ $/[Ru(Ind)Cl(PPh_3)_2]_0/[n\text{Bu}_3\text{N}]_0$ = 2000/10/0.5/20 mM in toluene at 80˚C, Conversion = 4.3%.

smaller. This is explained as follows: difference of hydrodynamic volume between fused rings and single rings diminished because of compact graft structure.

In $^{1}$H NMR spectra of the obtained polymer (Figure 11B), hemiacetal ester methane proton was not observed due to high molecular weight of graft polymer. Peak integration of proton adjacent to halo-ester (*g*) decreased, and protons of bromine-capped styrene terminal were alternatively observed. Initiation efficiency was calculated to be 80% from integration ratio of these peaks. Monomer units in its pendant were 8.2 on average calculate from *j"* + *g'* and *i"*, which is consistent to pendant unit calculated from monomer conversion and monomer/initiator ratio (8.6). The relatively low initiation efficiency in radical polymerization step was likely due to low accessibility of catalyst around crowded carbon-halogen bond. Molecular weight by SEC was 33800, which is smaller than that from monomer conversion (= 43100). This observation also supported that graft polymer has compact structure.

**Ring-based Advanced Polymer Architecture: Cyclic Polymer-Based Gel**

It is well known that structural flaws in network polymer, such as dangling chain ends and loops, significantly weaken gel properties because these defects do not serve as network chain. If cyclic polymers are employed as the building block alternatively to linear polymers, resultant network is expected to have defect-less network without dangling chain when cyclic polymers were crosslinked by more than two points. Tew and coworkers reported that gel

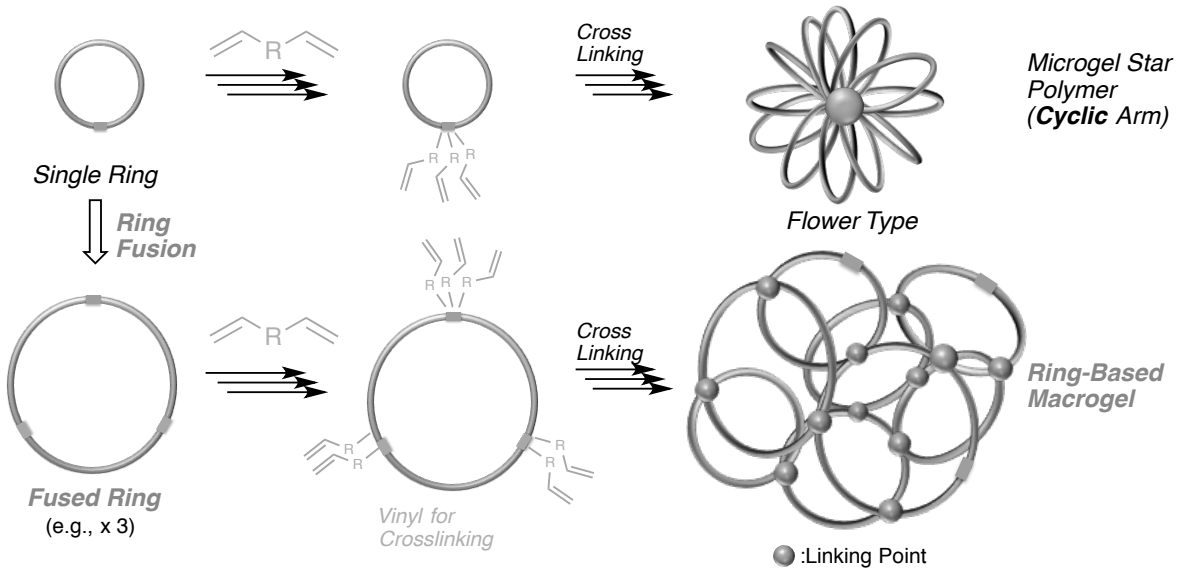



**Figure 12.** Concept for cyclic polymer–based Gel: Crosslinking of cyclic polymers by divinyl ether with or without ring-fusion.

based on cyclc polymers significantly affected the gel fraction, modulus, and swelling ratio comapred with linear polymer-based gels.[27] Thus, the author applied ring-expansion cationic polymerization of vinyl ether to realize cyclic polymer-based gel formation.

The procedure for cyclic polymer-based gel is as follows: to a solution of ring-expansion cationic polymerization of isobutyl vinyl ether was added divinyl ether to form short segment of vinyl ether, and pendant vinyl ether reacted to other cyclic polymer to crosslink (Figure 12). Herein, if single rings were cross-linked by divinyl ether, product would be flower type microgel star polymer with cyclic arms. However, if fused rings are employed as the precursor, vinyl groups are introduced at regular interval, and then crosslinked cyclic polymers, giving cyclic polymer-based macrogel. Therefore, high concentration of cyclic initiator in ring expansion polymerization is desirable.

First, ring-expansion cationic polymerization of IBVE was commenced with high initiator concentration (10 mM) to promote ring fusion for more crosslinking points (Figure 13, left). At 100% IBVE conversion, the polymerization mixture was fluid with liquidity. Then ethylene glycol divinyl ether (EGDVE) was directly injected to the polymerization mixture, targeting 10 times of EGDVE against a hemiacetal ester bond to ensure efficient crosslinking. $M_p$ was shifted higher molecular weight region with low molecular weight distribution, which means precursory polymers had cyclic structure before crosslinking. After 15 minutes, 72% of EGDVE was consumed and the polymerization mixture was still

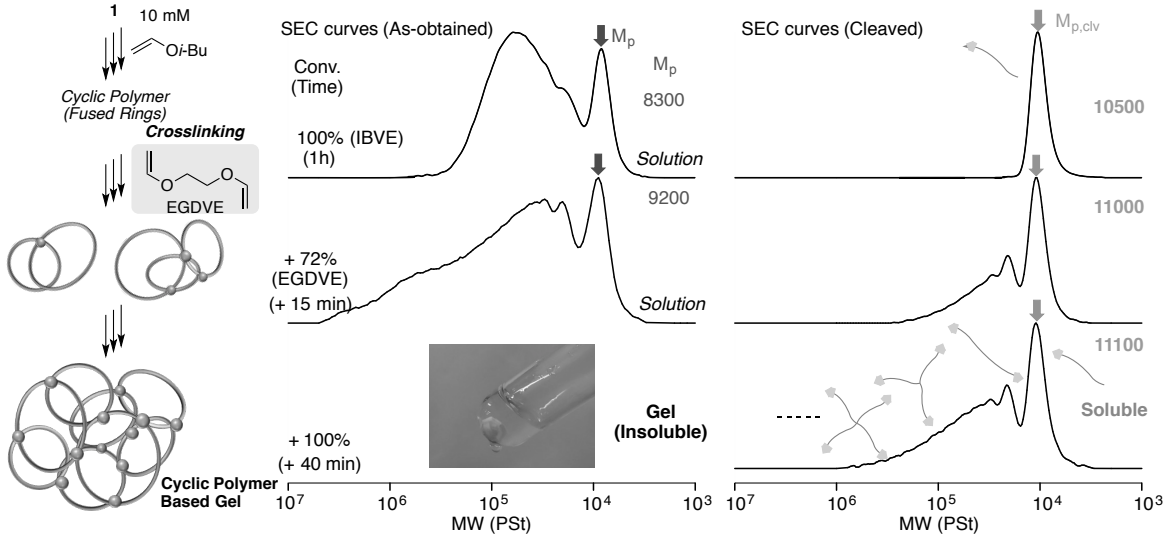



**Figure 13.** Synthesis of cyclic polymer-based gels via ring-expansion cationic polymerization followed by crosslinking reaction with ethylene glycol divinyl ether. Polymerization: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 760/10/5/0.15 mM in toluene at 0˚C. Crosslinking: $[EGDVE]_{add}$ = 50 mM at 0˚C.

fluid. On SEC analysis, $M_p$ shifted slightly higher molecular weight region, meaning several EGDVE were added to form short-segmented block copolymer. Interestingly, population of high molecular weight region increased, meaning some part of the cyclic polymers are connected each other. The polymerization mixture was gradually lost fluidity as the time passed. In 40 minutes after monomer addition, conversion of EGDVE reached to 100% and the solution lost its fluidity, giving gel that is constituted by cyclic polymers. Upon addition of excess amount of toluene to the mixture, the gel would not dissolve. A part of the mixture was dispersed in THF, and TFA and $H_2O$ were added to cleave HAE bonds for all of the samples (Figure 13, right). $M_p/M_{p.clv}$ of precursor polymer was 0.8, meaning cyclic structure. At monomer conversion was 72% and more, SEC traces became multimodal, which also supports crosslinking by divinyl ether. Interestingly, the dispersion of insoluble gel became homogenious solution, giving multimodal polymer consisted of star polymers.

## Conclusion

Versatility of ring-expansion cationic polymerization for synthesizing cyclic polymer-based architectures was shown in this chapter. Various alkyl pendants could be applied in vinyl ether without side reactions that may lead to linear polymer formation except BnVE. Furthermore, a combination of ring-expansion cationic polymerization and subsequent living radical polymerization realized easy preparation of cyclic graft polymer. Additionally, the fused rings were crosslinked by divinyl ether at hemiacetal ester junction, yielding gels based on cyclic polymers.

## References

(1) Semlyen, J. A. *Cyclic Polymers, 2nd ed*.; Kluwer Academic: Dordrecht, The Netherlands, **2000**.

(2) Jian, X.; Jing, Y.; Shiyong, L. *Macromolecules* **2007,** *40,* 9103–9110.

(3) Qiu, X.- P.; Tanaka, F.; Winnik, F. M. *Macromolecules* **2007,** *40,* 7069–7071

(4) *Chapter 6* of this thesis

(5) Geiser, D.; H. Hocker, K. *Macromolecules* **1980,** *13,* 653–656.

(6) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041–2044.

(7) Brown, H. A.; Waymouth, R. M. *Acc. Chem. Res.* **2013,** *46,* 2585–2596.

(8) Quite recently, REP of acetylene has been reported: Roland, C. D.; Li, H.; Abboud, K. A.; Wagener, K. B.; Veige, A. S. *Nature Chem.* **2016,** *8,* 791–796.

(9) Kammiyada, H.; Konishi, A.; Ouchi, M.; Sawamoto, M. *ACS Macro Lett*. **2013,** *2,* 531–534.

(10) Kammiyada, H.; Ouchi, M.; Sawamoto, M. *Macromol. Symp*. **2015,** *350,* 105-116.

(11) Kammiyada, H.; Ouchi, M.; Sawamoto, M. *Polym. Chem*. **2016,** *7,* 6911–6917.

(12) Winternheimer, D. J.; Shade, R. E.; Merlic, C. A. *Synthesis,* **2010,** *15,* 2497–2511.

(13) J. W. Cnpenhaver, M. H. Rigelow. *Acetylene and Carbon monoxide Chemistry:* Reinhold Publishing Corp., New York, N. Y., **1949.**

(14) Higashimura, T.; Aoshima, S.; Sawamoto, M. *Makromol. Chem., Macromol. Symp*. **1986,** *3,* 99–111.

(15) Seno, K.; Date, A.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci. Part A: Polym. Chem*. **2008,** *46,* 4392–4406.

(16) Dujardin, G.; Rossignol, S.; Brown, E. *Tetrahedron Letters* **1995,** *36,* 1653–1656.

(17) Okimoto, Y.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc*. **2002,** *124,* 1590–1591.

(18) Yuki, H.; Hatada, K.; Takeshita, M. *J. Polym. Sci. Part A-1: Polym. Chem*. **1969,** *7,* 667–678.

(19) Ledwith, A.; Lockett, E. *Polymer,* **1975,** *16,* 31-37.

(20) Aoshima, S.; Kanaoka, S. *Chem. Rev*. **2009,** *109,* 5245–5287.

(21) Nelson, J. A.; Czarny, M. R.; Spencer, T. A. *J. Am. Chem. Soc.,* **1978,** *100,* 4902–4903.

(22) Johnson, J. A.; Lu, Y. Y.; Burts, A. O.; Lim, Y.-H.; Finn, M. G.; Koberstein, J. T.; Turro, N. J.; Tirrell, D. A.; Grubbs, R. H. *J. Am. Chem. Soc*. **2010,** *133,* 559–566.

(23) Li, X.; Prukop, S. L.; Biswal, S. L.; Verduzco, R. *Macromolecules* **2012,** *45,* 7118–7127.

(24) Miyake, G. M.; Piunova, V. A.; Weitekamp, R. A.; Grubbs, R. H. *Angew. Chem., Int. Ed*. **2012,** *51,* 11246–11248.

(25) Sun, G.; Cho, S.; Clark, C. Verkhoturov, S. V. ; Eller, M. J.; Li, A.; Pavia-Jimenez, A. Schweikert, E. A.; Thackeray, J. W.; Trefonas, P.; Wooley, K. L. *J. Am. Chem. Soc*. **2013,** *135,* 4203–4206.

(26) Miura, Y.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *Polym. J*. **2006**, *38*, 930-939.

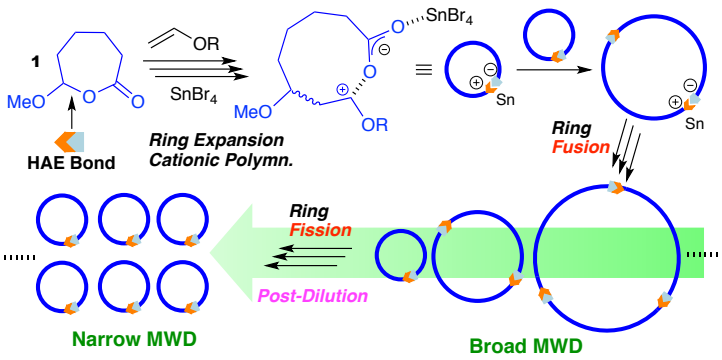
(27) Zhang, K.; Lackey, M. A.; Cui, J.; Tew, G. N. *J. Am. Chem. Soc*. **2011,** *133,* 4140–4148.

# *Chapter 5*

## A convergent Approach to Ring Polymer with Narrow Molecular Weight Distribution through Post-Dilution in Ring-Expansion Cationic Polymerization


### Abstract

In this chapter, the author demonstrate a convergent approach to convert "fused" ring chains obtained *via* ring-expansion cationic polymerization of vinyl ether with a hemiacetal ester (HAE)-based ring initiator (**1**) into "sing" ring ones of narrow MWDs. In the ring-expansion propagation process, the propagation can be controlled without any side reactions but an intermolecular counteranion exchange reaction between HAE bonds between propagating ring polymers ineluctably occurs resulting in broad molecular weight distributions (MWDs) composed of "fused" ring chains with multiple HAE bonds as well as a "sing" ring chain with one HAE bond. Hence, after monomer conversion reached over 95%, the polymerization solution was diluted (*i.e.,* post dilution) without deactivation of an employed Lewis acid activator (*i.e.,* $SnBr_4$) to induce intramolecular counteranion exchange in the fused ring chain. Size exclusion chromatography (SEC) curves of the product eventually became almost unimodal, though a small shoulder peak from the fused ring remained. Importantly, the HAE bond in ring chains still survived even after the post dilution process, which was confirmed by $^1$H NMR, and the retention of the ring structure was also supported by an acidolysis experiment where the apparent peak top molecular weight ($M_p$) was increased in SEC due to topology conversion from a ring to linear. The approach was proved to be effective even for higher molecular weight ring polymers that were prepared with a higher [monomer]/ [**1**] ratio as well as cyclic block copolymers.

## Introduction

Cyclic polymers have attracted the attention of polymer scientists over the last several decades.[1–4] The only difference from their linear counterparts is the absence of terminal groups, nevertheless it is known that the closed chain topology can give unique features different from the corresponding linear counterparts, such as viscosity,[5,6] diffusion,[7] glass transition temperature,[8] self-assembly,[9–13] temperature sensitivity,[14] and swelling behavior.[15] Despite the continuing interest in ring polymers, the fundamental research studies on ring polymers as well as their applications have not progressed well, likely due to a difficulty in the synthesis. One well-known methodology is end-to-end macrocyclization *via* intramolecular coupling reactions of linear telechelic polymers. However, this is less efficient because a highly diluted condition is required to suppress intermolecular reactions giving longer linear chains, and thus the process causes limitation of molecular weight and yield of the obtained ring polymers.

Ring-expansion polymerization (REP) is another methodology to prepare ring polymers, and it is more useful than the macrocyclization approach in terms of efficiency in yield and structural expandability. Herein, a potentially active species or the generator is embedded in a ring topology to prepare a cyclic initiator, and monomer molecules are inserted for initiation and propagation step by step while the ring topology is maintained throughout the polymerization. Some examples have been reported on REP: metathesis of cyclic olefins with cyclic Ru-alkylidene catalysts,[16] Pd-mediated polymerization of methylidenecyclopropanes with cyclic Pd-complexes,[17] and zwitterionic polymerization of heterocyclic monomers (e.g., lactide, *N*-substituted *N*-carboxyanhydride) with *N*-heterocyclic carbene.[18–20] It should be noted that most of the previous examples of REP are restricted almost exclusively to ring-opening polymerization of cyclic monomers. This is likely due to that cyclic monomers could be inherently transformed into cyclic polymers. On the other hand, controlled REP of vinyl monomers *via* addition polymerization is still challenging in polymer science. If REP of vinyl monomers can be controlled likewise in a common living polymerization process, various ring-based architectures could be constructed and the advanced applications also could be expected.

Given these backgrounds, the author have reported a controlled ring-expansion cationic polymerization of vinyl ethers (VEs).[21,22] Crucial is the design of a cyclic initiator in which a hemiacetal ester (HAE) bond is embedded into the ring topology and control of the reversible activation of the embedded HAE bond to give cyclic ion pairs with a suitable Lewis

acid activator. To synthesize ring polymers with this approach, side-reactions resulting in generation of linear polymers should be strictly inhibited, such as β-hydrogen elimination and counteranion exchange with halogens of the Lewis acid catalyst. After studying in some combinations of HAE-embedded cyclic initiators with Lewis acid catalysts, a 7-membered HAE compound (**1**: Figure. 1) in conjunction with $SnBr_4$ was proved to allow control of ring-expansion polymerizations of vinyl ethers: SEC curves shifted to higher molecular weight without tailing at the lower molecular weight region along with monomer conversion; the HAE bond is almost quantitatively introduced into the obtained polymer; block copolymerization is possible by sequential addition of a second monomer after the first polymerization.[22] However, as seen in other ring-expansion polymerizations with ROMP[16] and NMP,[23,24] exchange reactions between ring polymer chains likely take place during polymerization, resulting in multimodal SEC curves of the obtained polymers. Interestingly, trifluoroacetic acid (TFA) treatment to cleave the HAE bond in the obtained polymers gave very narrow SEC curves and higher peak top molecular weights ($M_p$s). From these results, unfavorable side reactions are suppressed in the REP to give ring polymers quantitatively, however, molecular weight distribution becomes broad due to the ring fusion event from the controlled sing ring chains. Thus, inhibition of the ring fusion is highly required to construct well-defined ring polymers of narrow molecular weight distributions as well as ring block copolymers.

The author's effort in this research is directed to suppression of the fused ring generation, and herein careful attention was paid that the ring fusion would "intermolecularly" occur between ring chains via reversible activation of the HAE bond. It was thus hypothesized that "intramolecular" counteranion exchange for the fused ring could be promoted *via* post-dilution at the final stage of polymerization to lead to a non-fused or single ring. The author termed the process "ring fission", imitating the terminology of nuclear fusion/fission, and studied the effects of dilution conditions after the ring-expansion cationic polymerization on behaviors of "ring fission". The key point is how to promote selective and reversible activation of HAE bonds in fused ring chains under diluted conditions while suppressing the irreversible side reactions (*i.e.,* β-hydrogen elimination) that might result in contamination by linear chains.

## Experimental

### Materials.

Isobutyl vinyl ether (IBVE) (Tokyo Kasei; >99%) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide, and distilled twice from calcium hydride before use. 2-Chloroethyl vinyl ether (CEVE) (Tokyo Kasei; >97%) was dried overnight over calcium chloride, and distilled once before use. Carbon tetrachloride was distilled from calcium hydride once before use. Toluene (Kishida Kagaku, Osaka; 99.5%) and *n*-hexane (Kishida Kagaku, Osaka; 96%) were dried and purified by passing through purification columns (Solvent Dispensing System, SG Water USA, Nashua, NH; Glass Contour), kept over molecular sieves 4A for more than one day. $SnBr_4$ (Aldrich; >99%), 2,6-di-tert-butyl-4-methylpyridine (DTBMP, Aldrich; >99%), and trifluoroacetic acid (TFA, Wako; >98%) were used as received. The cyclic initiator (**1**) was synthesized according to the author's previous paper.[21]

### Ring-Expansion Cationic Polymerization of IBVE with 1.

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical procedure is given below: the polymerization was initiated by adding solutions of $SnBr_4$ (50 mM in toluene: 0.5 mL) via a dry syringe into a mixture (4.5 mL) containing IBVE (0.25 mL), $CCl_4$ (internal standard, 0.10 mL), cyclic initiator **1**, and 2,6-di-tert-butyl-4-methylpyridine (DTBMP) in toluene at –40˚C: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/5/0.15 mM. After a predetermined interval, the polymerization was terminated with prechilled ammoniacal methanol. Monomer conversion was determined from its residual concentration measured by gas chromatography with $CCl_4$ as an internal standard. The quenched reaction mixture was washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(IBVE).

### Ring fission via post-dilution of polymerization solution

When IBVE was almost consumed (Conv. > 98%) for the cationic polymerization with **1**/$SnBr_4$, predetermined amount of dried *n*-hexane was added to the solution under dry nitrogen, followed by stirring. A typical procedure is given below: when the monomer conversion reached 100% for the ring expansion cationic polymerization, *n*-hexane (45 mL) was added to the polymerization solution. At predetermined interval, prechilled ammoniacal methanol was added to deactivate Lewis acid catalyst. The quenched reaction mixture was

washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(IBVE).

**HAE cleavage of cyclic poly(IBVE) via Acidolysis**

A typical procedure for cleavage of HAE bond in cyclic poly(IBVE) is given below. In a vial (2 mL) was placed 1.0 mL of cyclic poly(IBVE) solution (1wt% in THF) and added 5 drops of $H_2O$/THF (1/2 v/v) solution was added. The resultant solution was kept at ambient temperature for 12 hours, and the resultant solution was vacuum dried to remove THF, water and trifluoroacetic acid to obtain linear poly(IBVE).

**Measurements**

The molecular weight distribution, $M_n$, and $M_w/M_n$ values of polymers were measured by size exclusion chromatography (SEC) at 40 ˚C in THF as an eluent on three polystyrene-gel columns (Shodex KF-803; pore size, 20–1000 Å; 8.0 mm i.d. x 30 cm; flow rate, 1.0 mL $min^{-1}$) connected to a DU-H2000 pump, a 74S-RI refractive-index detector, and a 41-UV ultraviolet detector (all from Shodex). The columns were calibrated against 13 standard poly(St) samples (Polymer Laboratories; $M_n$= 500–3840000; $M_w/M_n$ = 1.01–1.14). $^1$H NMR spectra of the obtained polymers were recorded in benzene-$d_6$ at 25 ˚C on a JEOL JNM-ECA500 spectrometer, operating at 500.16 MHz.

## Result and Discussion

**Ring-expansion cationic polymerization of IBVE**

Figure 2 shows cationic polymerization of isobutyl vinyl ether (IBVE) with **1** as the initiator in conjunction with $SnBr_4$ (in toluene at −40 °C). The SEC curves of the obtained polymers were unique consisting of a monomodal main peak and multimodal ones of higher molecular weight: herein the former is likely from a “single” ring and the latter from the “fused” ring as described above. The whole peaks gradually shifted to higher molecular weight (MW) without tailing on the lower MW region, indicating propagation was fairly controlled without chain transfer reactions and termination. Importantly, once the HAE bonds embedded into ring polymers were irreversibly cleaved with a strong protic acid (trifluoroacetic acid: TFA), the SEC curves turned into very narrow peaks ($M_w/M_n$ < 1.1). More importantly, the peak top slightly shifted to higher MW, likely due to a larger hydrodynamic volume of the linear polymer than the ring one.

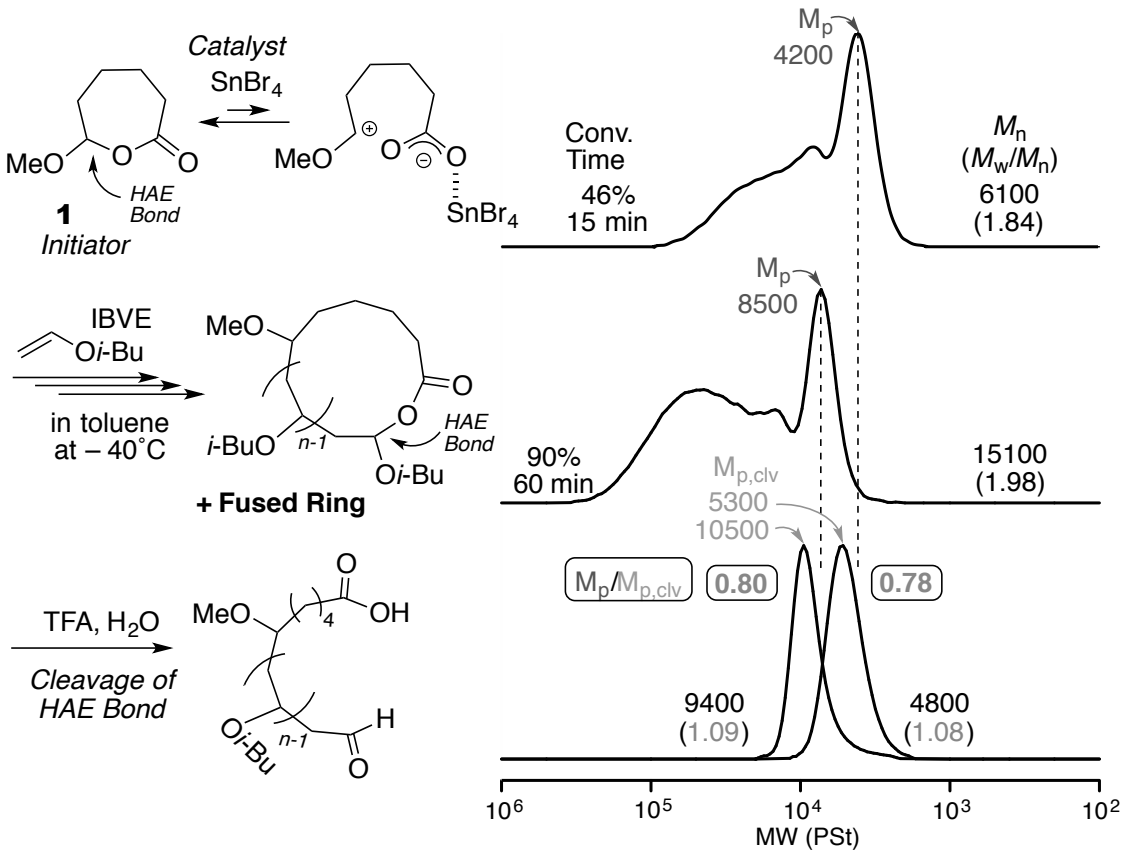



**Figure 2.** Ring-expansion cationic polymerization of IBVE and cleavage of the HAE bond in the resultant ring polymer. Polymerization: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/5/0.15 mM in toluene at –40 ˚C.

The ratio of a peak top molecular weight for the obtained polymers to the HAE cleaved samples ($M_p/M_{p,clv}$) was around 0.8, which is consistent with the literature describing the ratio of apparent molecular weight in SEC for a ring to a linear polymer.[25,26] In this paper, the ratio (often called as "g-factor") is used as an index to judge generation of the ring polymer. It should be noted that $^1$H NMR and MALDI-TOF-MS could characterize quantitative incorporation of the HAE bond.[21]

**Post-dilution after ring expansion cationic polymerization**

When the monomer conversion reached over 95% for the ring-expansion cationic polymerization of IBVE (in toluene at −40 °C), a large amount of *n*-hexane was directly added to the solution for 20-time dilution, followed by stirring at −40 °C for an additional 20 hours.[27] Herein, $SnBr_4$ would be still active in the diluted solution and thus it can be

expected to promote the intramolecular counteranion exchange or "ring fission". Finally, methanol as a quencher was added to deactivate $SnBr_4$ for the work up process as usual.

Before the dilution, the SEC trace of the obtained polymer was clearly multimodal of broad molecular weight distribution (MWD: $M_w/M_n$ = 3.43, Figure. 3) due to the ring fusion reaction during polymerization. In this work, the percentage of the single ring (*Single*) is roughly estimated from the ratio of the unimodal peak area (shaded) to the whole peak area and single of the obtained ring polymer could be estimated as 31%. On the other hand, the SEC curve of the polymer after the dilution process exhibited much narrower MWD ($M_w/M_n$ = 1.21) and much higher single value (90%) than the polymer before the dilution treatment, though a small peak with high MW still remained. Most importantly, the acidolysis process with trifluoroacetic acid gave higher MW of the peak top and 0.80 of the index ratio ($M_p/M_{p,clv}$) that was comparable to before the dilution ($M_p/M_{p,clv}$ = 0.78), supporting that the ring structure was retained during the dilution process. Thus, these analyses with $^1$H NMR

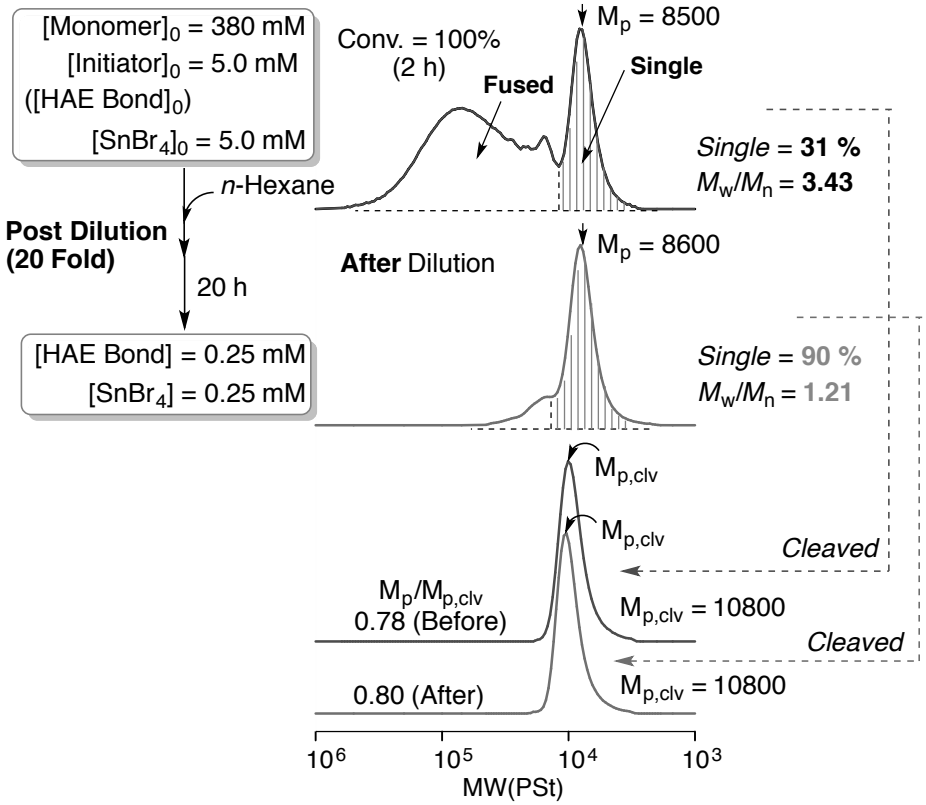



**Figure 3.** SEC analyses of the obtained polymers for the ring fission process through post-dilution. (Upper) SEC curves of the as-obtained polymer, (Lower) SEC curves after cleavage. Post-dilution: *n*-hexane was added for the concentration of the HAE bond in chains to be 0.50 mM (20-fold dilution), and the solution was stirred at −40 °C for an additional 20 hours.

and SEC indicated that the dilution process after monomer consumption was effective to convert the "fused ring" into a "single ring" without irreversible damage to the linear chain.

The polymer structures were further analyzed by $^1$H NMR. For the polymer before the dilution (*i.e.,* as polymerized), the minor peak derived from the methine proton of the HAE bond (a) can be detected in addition to the main peaks from the repeating IBVE unit (b–f), and the "apparent" number-average degree of polymerization ($DP_n$) for the HAE bond can be calculated as 80 from the integration ratio (upper, Figure. 4). The value was consistent with that calculated by the injection ratio ($[IBVE]_0/[\mathbf{1}]_0$ = 76) and monomer conversion (100%) ($DP_{n,Conv.}$ = 76), indicating that the HAE bond was almost quantitatively introduced in the polymer. Importantly, the spectrum after the dilution (lower, Figure 4) was almost the same as before and a similar "apparent" $DP_n$ value ($DP_n$ = 79) was obtained. Thus, the relative ratio of the HAE bond to the IBVE repeating unit was not changed before and after the dilution, though the SEC curve or molecular weight was dramatically changed. Furthermore, due to the formation of a single-rich ring polymer, the $M_n$ by $^1$H NMR ($M_{n,NMR}$ = 8000) was close to $M_n$ by SEC ($M_{n,SEC}$ = 8800).

Based on the analyses, it can be interpreted that hemiacetal ester bonds were

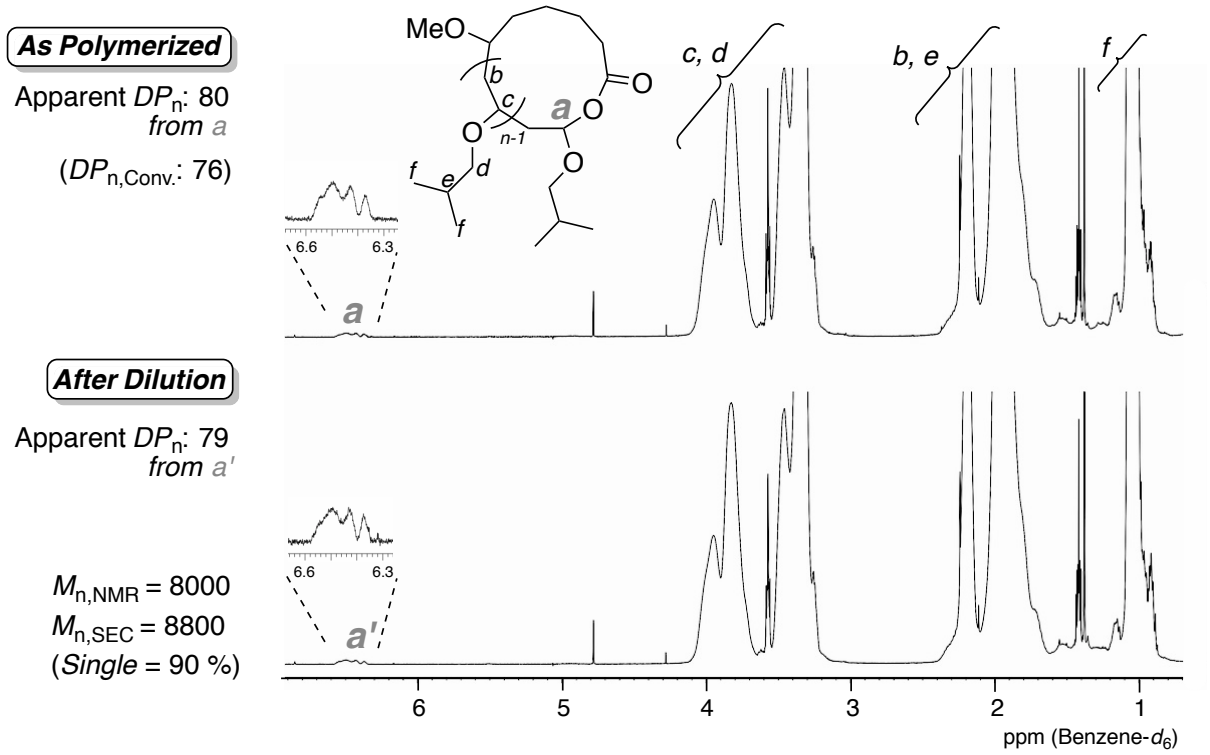



**Figure 4.** $^1$H NMR spectra of (upper) the as-obtained polymer and (lower) the transformed polymer in benzene-$d_6$.

intramolecularly shuttled in a fused ring chain under diluted conditions to give a single ring, as shown in Figure 5. As the solution is diluted, the relative distance between HAE bonds in the fused ring would be shorter than that between ring chains to promote formation of a single ring via intramolecular HAE bond exchange.

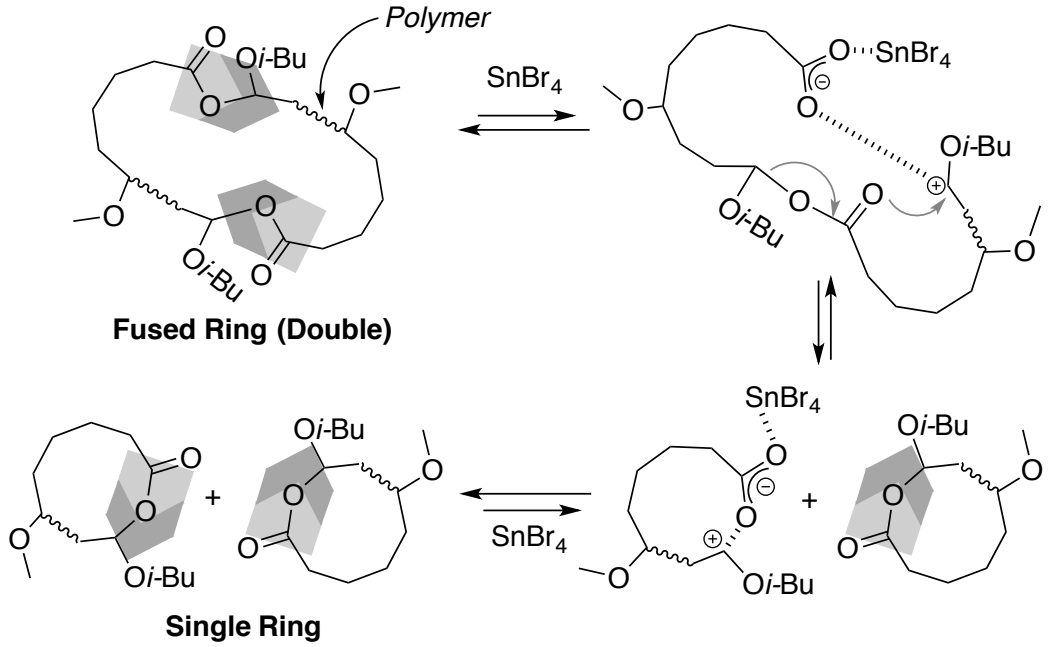



**Figure 5.** Proposed Mechanism of the ring fission process under diluted conditions.

As a preliminary control experiment, the pre-dilution methodology, that is, the polymerization under diluted conditions, was also attempted: $[\text{monomer}]_0/[\text{initiator}]_0$ = 19/0.25 mM, 20-fold diluted. The population of the fused ring was likely decreased, however, the polymerization proceeded very slowly resulting in limited conversion (conversion = 42% in 24 hours, $M_n$ = 2900, $M_w/M_n$ = 1.18, $M_p/M_{p,clv}$ = 0.82). The two methodologies (*i.e.,* post- and pre-dilution) can be used appropriately, according the synthetic purpose.

**Effects of concentration**

The author investigated various conditions for the dilution process on the ring fission behavior. Most probably, as far as $SnBr_4$ can reversibly activate HAE bonds in ring polymers, there would be equilibrium between intermolecular (*i.e.,* ring-fusion) and intramolecular (*i.e.,* ring-fission) exchange reactions, and these events would depend on the concentration of the HAE bond. Thus, he studied the effects of dilution degree or concentration of the HAE bond

on the ring fission process. For the polymerization of IBVE using 5.0 mM of **1**, the amount of added *n*-hexane at the end of polymerization was changed to make 2, 5, 10 and 20-fold diluted solution (2.5, 1.0, 0.5, and 0.25 mM of the HAE bond, respectively). After the addition, the solution was stirred for an additional 20 hours at the same temperature as the polymerization (−40 °C), followed by work up procedures.

As seen in the SEC curves of the obtained polymers (Figure 6A), the relative intensity of the peak from the single ring was clearly increased and MWD of the whole peak became narrower according to the degree of dilution. Herein the SEC curves are standardized as the height of the narrow main peak derived from the single ring. Indeed, the value of *Single* was increased depending on the degree of dilution (Figure 6C), eventually reaching 90% for 20-fold dilution. However, it seemed to be difficult to approach 100% *Single* with the post dilution process. In all cases, the TFA treatment gave perfectly monomodal SEC curves and peak top MWs were increased to give around 0.8 values of $M_p/M_{p,clv}$ (Figure 6D), indicating

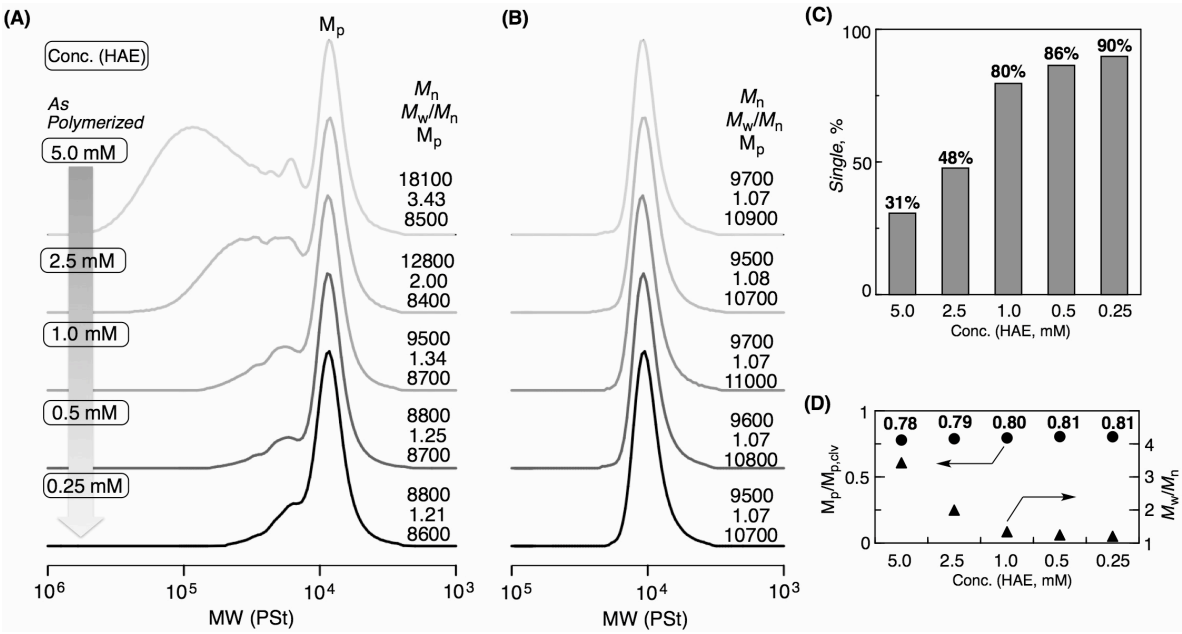



**Figure 6.** Effects of HAE concentration for the post-dilution process on ring fission: (A) SEC curves of the obtained polymers after the post-dilution process and (B) those after HAE cleavage; (C) weight percentage of single rings in SEC; (D) peak top ratio before and after HAE cleavage ($M_p/M_{p,clv.}$) and $M_w/M_n$ before HAE cleavage. Polymerization conditions: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5.0/5.0/0.15 mM in toluene at −40 °C. Post-dilution: *n*-hexane was added for the concentration of the HAE bond in chains to be 2.5, 1.0, 0.50, and 0.25 mM (2, 5, 10, and 20-fold dilution, respectively), and the solution was stirred at −40 °C for an additional 20 hours.

that the ring structures were sustained.

**Time-dependence**

For the 20-fold dilution after polymerization ([HAE bond] = 0.25 mM), the change in SEC curves over time was observed to clarify how the ring fission event proceeded (Figure 7). After 1 hour, the broad peak at higher MW (>$10^5$ or 100 K) was clearly decreased. Instead, three peaks appeared on the lower MW region from 15 K to 30 K, in addition to the main peak of narrow MWD having $M_p$ of 8 K, likely from the single ring. After 2 hours, the peak split became clear and the intensity of the second lowest MW peak around 16 K was relatively increased. In 5 hours, the SEC curve turned into an almost bimodal peak. As the time increased further, SEC traces grew close to the monomodal peak to eventually give

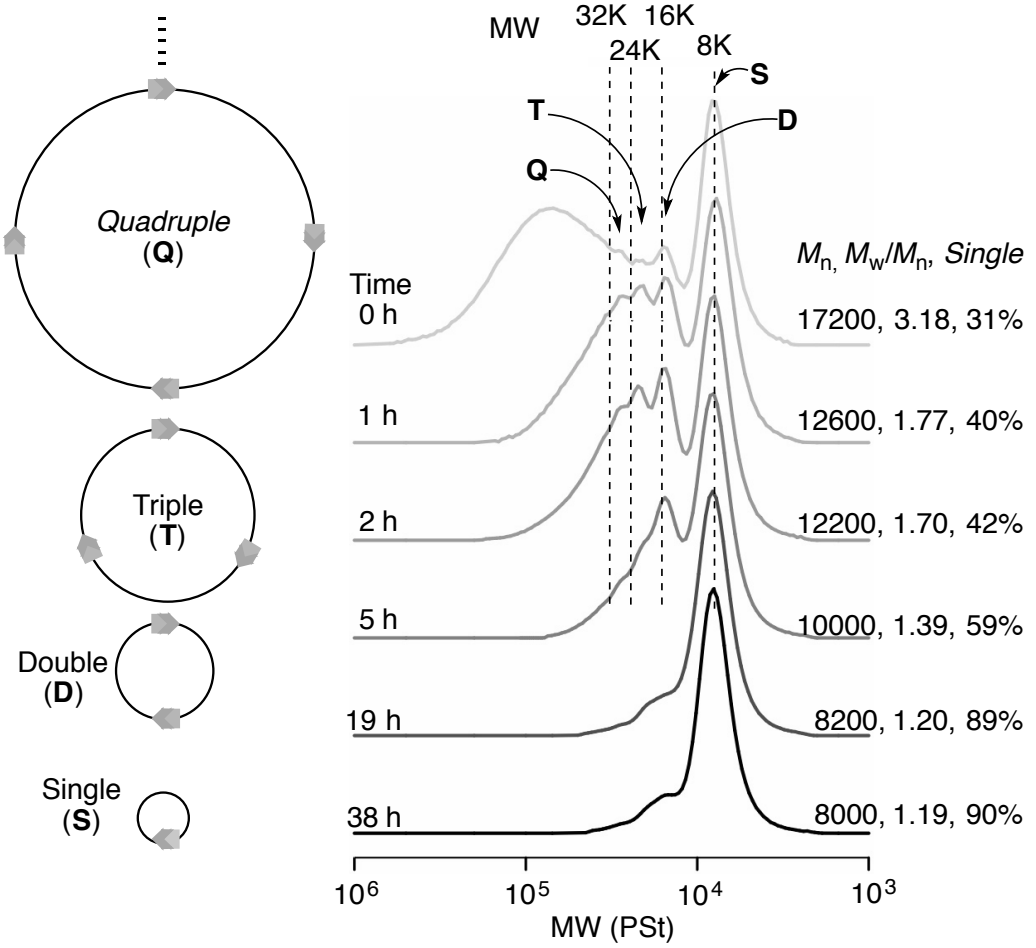



**Figure 7.** SEC curves of obtained poly(IBVE)s during ring fission. Polymerization conditions: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5.0/ 5.0/0.15 mM in toluene at −40 °C. Post-dilution: *n*-hexane was added for the concentration of the HAE bond in chains to be 0.25 mM (20-fold dilution), and the solution was stirred at −40 °C.

narrow MWD ($M_w/M_n$ = 1.19) and a higher percentage of the single ring (*single* = 90%). The observed peaks during the dilution process are probably derived from fused rings consisting of double (D), triple (T), and quadruple (Q) chains. Herein, each $M_p$ did not perfectly correspond to the integer multiple values of that from the single peak (8 K), which is likely due to that multiple HAE bonds could affect main chain conformation in solution. The ring formations for all the samples were confirmed through the acidolysis experiments giving narrow MWDs ($M_w/M_n$ < 1.1) and around 0.8 values of $M_p/M_{p,clv.}$ Note that the feature of controlled propagation in this ring expansion polymerization allows such observations of the ring fission process with SEC curves because the chain length between HAE bonds in fused rings shows narrow distribution.

**Effects of temperature**

The effect of temperature on the ring fission process was also studied. When the conversion reached around 100% (in 2 hours) in the ring-expansion cationic polymerization of IBVE at −40 °C, a large amount of n-hexane was directly added to make 20-fold dilution and the solution was stirred for an additional 2 hours at different temperatures (−78, 40, and 60 °C, Figure 8).

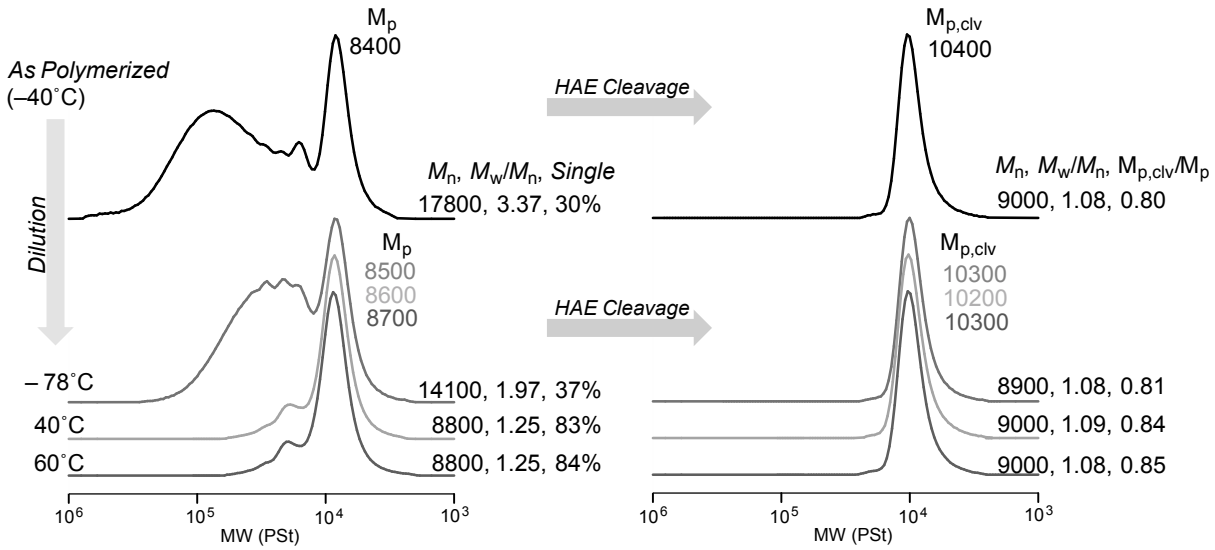



**Figure 8.** Effects of temperature on ring fission. SEC curves of the obtained polymers as polymerized and after post dilution (left), and those after acidolysis treatment for HAE cleavage (right). Polymerization conditions: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/5/0.15 mM in toluene at −40 °C. Post-dilution: *n*-hexane was added to make the con- centration of the HAE bond in chains of 0.5 mM (10-fold dilution), and the solution was stirred at −78, 40 and 60 °C for an additional 2 hours.

When the diluted solution was kept at −78 °C, the ring fission progressed slowly to give a lower *Single* value (37%). On the other hand, when the temperature for the post dilution was increased (40 and 60 °C), narrower MWDs ($M_w/M_n$ = 1.25) and higher *Single* values (>80%) were obtained. These ring fissions progressed faster than that at −40 °C giving 1.70 of $M_w/M_n$ and 42% of *Single* in the same standing time (2 hours). Despite such accelerations in ring fission, the ring topology seemed to be maintained, supported by the acidolysis experiments. However, as the temperature was increased, the value of $M_p/M_{p,clv}$ seemed to be slightly higher. There is some possibility that a very small part of the HAE bond could be decomposed at higher temperature, though the post-dilution at higher temperature is useful to accelerate ring fission. The author is further studying to approach a more efficient ring fission process without damage of the ring topology.

**Post dilution for higher MW ring polymers**

Precise control of molecular weight and MWD for ring polymers is highly required for understanding the properties of ring polymers. Particularly, syntheses of higher molecular weight ring polymers are limited with the classical methodology relying on intramolecular coupling of linear telechelic polymers. The author thus performed ring-expansion cationic polymerization with a higher ratio of monomer (IBVE) to initiator (1) ($[IBVE]_0/[\mathbf{1}]_0$ = 152: $[IBVE]_0$ = 760 mM, $[\mathbf{1}]_0$ = 5 mM; $[IBVE]_0/[\mathbf{1}]_0$ = 304: $[IBVE]_0$ = 760 mM, $[\mathbf{1}]_0$ = 2.5 mM) than that in the above polymerizations ($[IBVE]_0/[\mathbf{1}]_0$ = 76) and the post- dilution to synthesize ring polymers fulfilling higher molecular weight and narrower MWD (Figure 9).

The monomer was quantitatively consumed even under these conditions. The SEC curves of polymers were quite broad (>97% conversions, $M_w/M_n$ = 3.21 and 2.45) and the ratio of the single ring seemed to be quite low. n-Hexane was added at −40 °C to make a diluted solution with 0.05 mM of the HAE bond (50 and 100 fold, respectively) and then the diluted solution was stirred at a higher temperature (40 °C) for an additional 5 hours to effectively promote the ring fission. Consequently, the MWDs of the obtained polymers were narrow ($M_w/M_n$ = 1.22 and 1.37) and higher ratios of the single ring were obtained (*Single* = 89 and 85%).

The acidolysis experiments gave controlled linear polymers of narrow MWDs ($M_w/M_n$ = 1.15 and 1.20) and the reasonable peak top MW ratios ($M_p/M_{p,clv}$ = 0.83 and 0.82) for the formation of ring polymers. Thus, the post-dilution approach was effective to obtain sing ring polymers even with higher molecular weights.

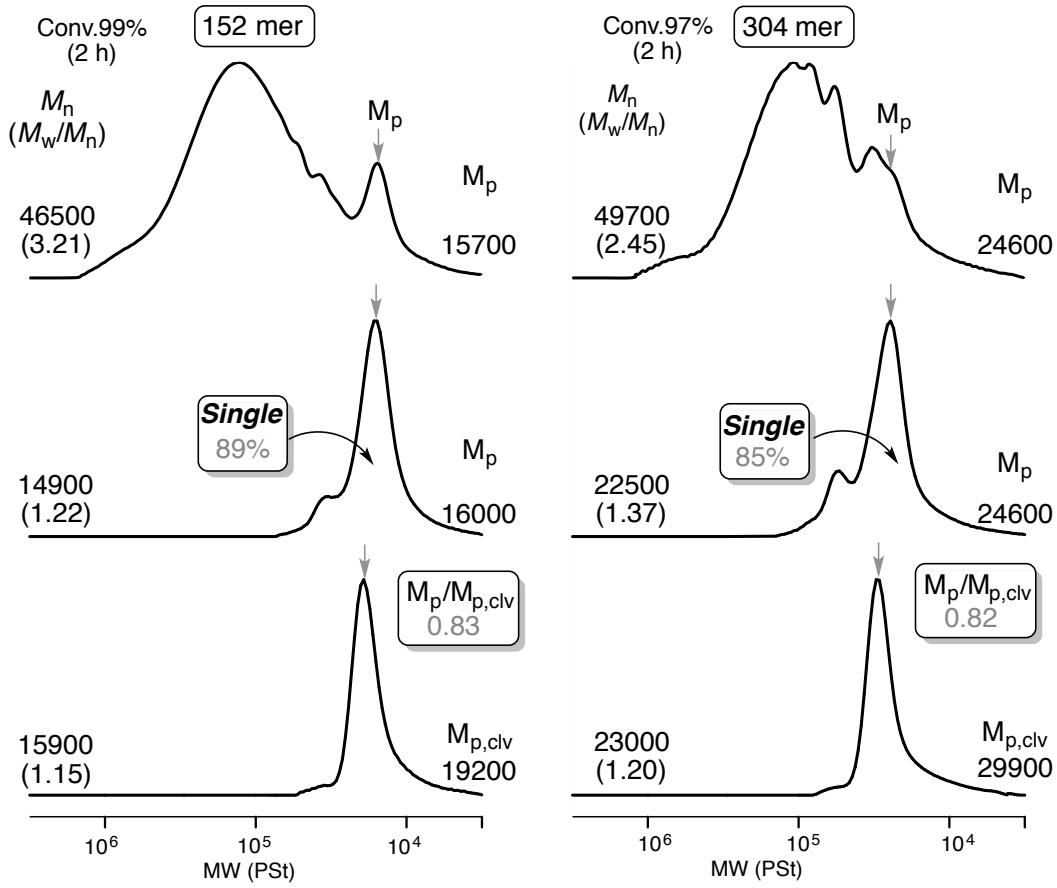



**Figure 9.** Syntheses of high molecular weight ring polymers through ring-expansion polymerization, followed by ring fission. Polymerization conditions: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 760/5.0/5.0/0.15 mM (for 152 mer) or 760/2.5/5.0/0.15 mM (for 304 mer) in toluene at −40 °C. Post-dilution: *n*-hexane was added for the concentration of the HAE bond in chains to be 0.05 mM (50- and 100-fold dilution, respectively), and the solution was stirred at 40 °C for an additional 5 hours.

**Post dilution for ring block copolymers**

Block copolymerization using the cationic polymerization with **1** is of great interest, since the propagation is well controlled without irreversible side reactions. However, the ring fusion phenomena would result in the generation of multiblock copolymers together with diblock copolymers. Thus, the post dilution methodology was finally applied for block copolymerization to synthesize well-defined ring block copolymers of narrow molecular weight distribution.

When the conversion of IBVE reached 90% (1 h), a bulk portion of 2-chloroethyl vinyl ether (CEVE) was directly injected into the solution, and then the set temperature was increased from −40 °C to 0 °C because of the lower reactivity of CEVE (Figure 10). The added CEVE monomer was also consumed slowly but smoothly (92%, 48 h), and the SEC curve of the product shifted to higher MW though the MWD became much broader ($M_n$ = 11 100, $M_w/M_n$ = 1.88). The *Single* value of this block copolymer was estimated as 39%, and the acidolysis experiment supported the formation of the ring polymer ($M_p/M_{p,clv}$ = 0.81). On the other hand, the post dilution with a large portion of toluene28 (20 fold in an additional 24 hours) gave narrower MWD and higher single value ($M_w/M_n$ = 1.22, *Single* = 90%), and importantly the index ratio ($M_p/M_{p,clv}$ = 0.83) indicated retaining the ring topology during the

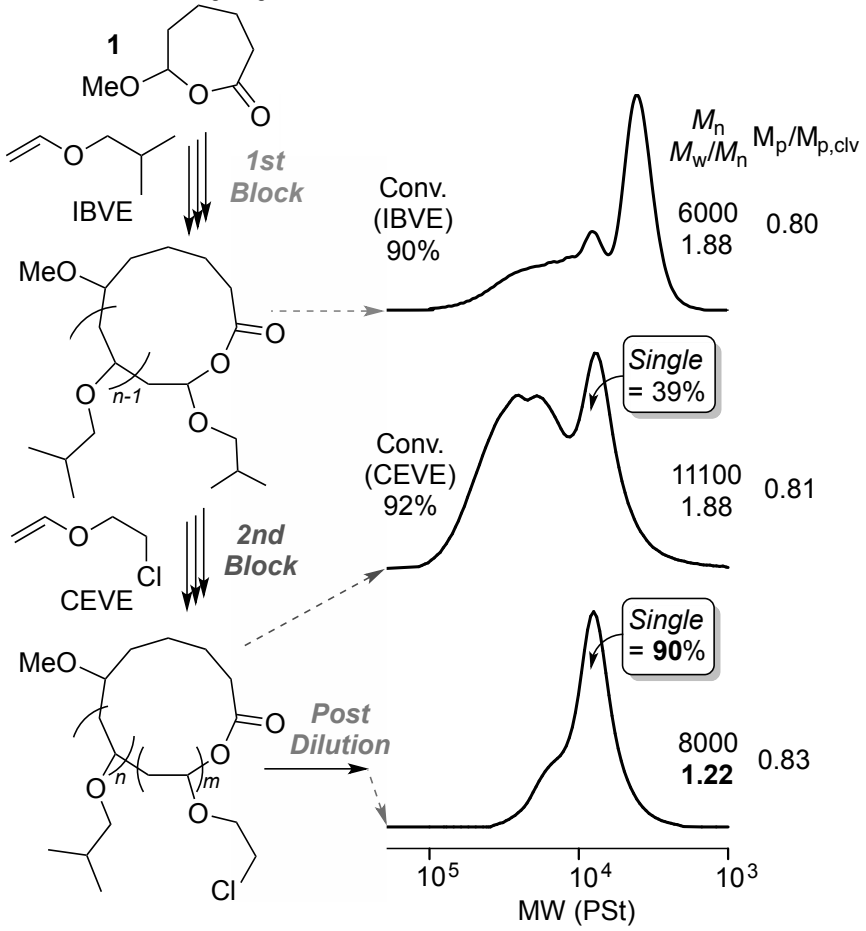



**Figure 10.** Block copolymerization of IBVE and CEVE through ring-expansion cationic polymerization with **1**, followed by post dilution. Polymerization: $[IBVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 190/5/5/0.15 mM in toluene at −40 °C; $[CEVE]_{add}$ = 190 mM in toluene at 0 °C. Post-dilution: toluene was added to make the concentration of the HAE bond in chains of 0.25 mM (20-fold dilution), and the solution was stirred at 0 °C for an additional 24 hours.

dilution process. Thus, it was demonstrated that the post dilution was effective even for block copolymerization.

## Conclusion

In the ring-expansion cationic polymerization of vinyl ether with the HAE-based cyclic initiator (**1**), the counteranion exchange resulting in generation of fused ring polymers with broad MWDs is unavoidable, however, the propagation is highly controlled without irreversible side reactions to maintain the HAE bond in fused ring chains under the reversible activation by a Lewis acid activator (*i.e.*, $SnBr_4$). This feature allowed conversion of fused ring polymers into non-fused or single ring polymers of narrow MWDs via post dilution. The author thus demonstrated the "ring fission" process by changing conditions, leading to syntheses of higher molecular weight ring polymers of narrow MWDs. The approach opened the door to construct well-defined ring-based polymers, such as ring block copolymers of narrow MWDs.

## References

(1) Tezuka, Y. Topological Polymer Chemistry: Progress of Cyclic Polymers in Syntheses, Properties and Functions, World Scientific Publishing Company, 2012.
(2) Jia, Z.; Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2012,** *50,* 2085–2097.
(3) Tezuka, Y. *Polym. J,* **2012,** *44,* 1159–1169.
(4) Laurant, B. A.; Grayson, S. M. *Chem. Soc. Rev.* **2009,** *38,* 2202–2213.
(5) Schäler, K.; Ostas, E.; Schröter, K.; Thurn-Albrecht, T.; Binder, W. H. Saalwächter, K. *Macromolecules* **2011,** *44,* 2743–2754.
(6) Roovers, J. *Macromolecules* **1988,** *21,* 1517–1521.
(7) Tead, S. F.; Kramer, E. J.; Hadziioannou, G.; Antonietti, M.; Sillescu, H.; Lutz, P. Strazielle, C. *Macromolecules* **1992,** *25,* 3942–3947.
(8) McLeish, T. *Science* **2002,** *297,* 2005–2006.
(9) Williams, R. J.; Dove, A. P.; O'Reilly, R. K. *Polym. Chem.* **2015,** *6,* 2998–3008.
(10) Yamamoto, T.; Tezuka, Y. *Soft Matter* **2015,** *11,* 7458–7468.
(11) Poelma, J. E.; Ono, K.; Miyajima, D.; Aida, T.; Satoh, K.; Hawker, C. J. *ACS Nano* **2012,** *6,* 10845–10854.
(12) Coulembier, O.; Deshayes, G.; Surin, M.; Winter, J. D.; Boon, F.; Delcourt, C.; Leclère, P.; Lazzaroni, R.; Gerbaux, P.; Dubois, P. *Polym. Chem.* **2013,** *4,* 237–241.

(13) Honda, S.; Yamamoto, T.; Tezuka, Y. *J. Am. Chem. Soc.* **2010,** *132,* 10251–10253.

(14) Xu, J.; Liu, S. *Macromolecules* **2007,** *40,* 9103–9110.

(15) Jang, S. S.; Çagin T.; Goddard III, W. A. *J. Chem. Phys.* **2003,** *119,* 1843–1854.

(16) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002,** *297,* 2041–2044.

(17) Takeuchi, D.; Inoue, A.; Osakada, K.; Kobayashi M.; Yamaguchi, K. *Organometallics* **2006,** *25,* 4062–4064.

(18) Culkin, D. A.; Jeong, W.; Csihony, S.; Gomez, E. D.; Balsara, N. P.; Hedrick, J. L.; Waymouth, R. M. *Angew. Chem. Int. Ed.* **2007,** *46,* 2627–2630.

(19) Jeong, W.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2007,** *129,* 8414–8415.

(20) Guo, L.; Zhang, D. *J. Am. Chem. Soc.* **2009,** *131,* 18072– 18074.

(21) Kammiyada, H.; Konishi, A.; Ouchi, M.; Sawamoto, M. *ACS Macro Lett.* **2013,** *2,* 531–534.

(22) Kammiyada, H.; Ouchi, M.; Sawamoto, M. *Macromol. Symp.* **2015,** *350,* 105–116.

(23) Narumi, A.; Hasegawa, S.; Yanagisawa, R.; Tomiyama, M.; Yamada, M.; Binder, W. H.; Kikuchi, M.; Kawaguchi, S. *React. Funct. Polym.* **2016,** *104,* 1–8.

(24) Narumi, A.; Zeidler, S.; Barqawi, H.; Enders, C.; Binder, W. H. *J. Polym. Sci., Part A: Polym. Chem.* **2010,** *48,* 3402–3416.

(25) Rique-Lurbet, I.; Schapper, M.; Deffieux, A. *Macromolecules* **1994,** *27,* 6318–6324.

(26) Oike, H.; Kobayashi, S.; Mouri, T. Tezuka, Y. *Macromolecules* **2001,** *34,* 2742–2744.

(27) We expected nonpolar solvents would be useful as the diluent to prevent irreversible cleavage of a hemiacetal ester bond in a ring polymer. We thus selected n-hexane as the dilution solvent because the polar is very low (zero). As shown in block copolymerization later, toluene was also available.

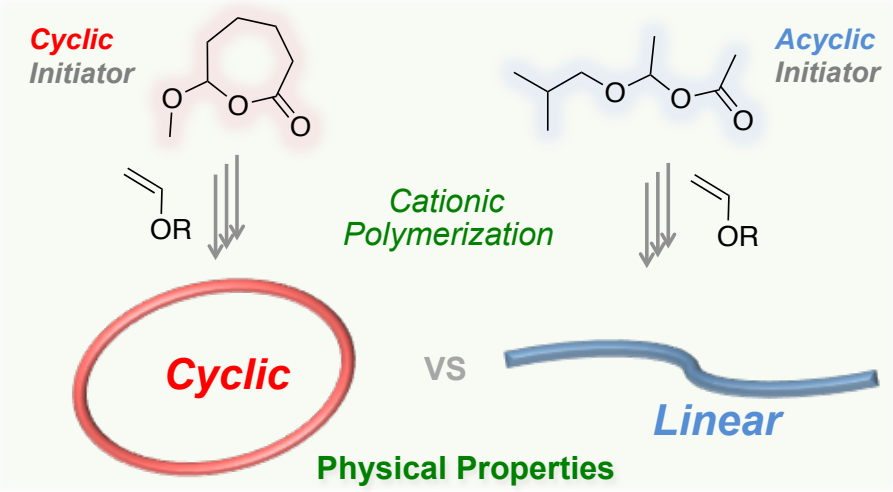
(28) The poly(CEVE) segment is insoluble in *n*-hexane, so toluene was used for the block copolymerization.

# *Chapter 6*

## A Study on Physical Properties of Cyclic Poly(Vinyl Ether)s Synthesized via Ring-Expansion Cationic Polymerization


### Abstract

In this work, ring-driven physical properties of cyclic poly(vinyl ether)s were studied, such as thermal sensitivity in solution and glass transition temperature ($T_g$). The samples were precisely synthesized via ring-expansion cationic polymerization with a hemiacetal ester (HAE)-based cyclic compound as the initiator. To clarify the topology effects, linear polymers with similar molecular weights were also prepared via a conventional living cationic polymerization with the HAE-based acyclic initiator (i.e., an adduct of vinyl ether with acetic acid) for comparison. Cyclic poly(vinyl ether)s carrying bulky tricyclic alkane pendant exhibited higher $T_g$s than the linear counterparts of similar molecular weights. Interestingly, the $T_g$ was not so decreased even as the molecular weight was lower, which was clearly different from linear polymers. The thermo-sensitivity of cyclic polymer was also studied with ethyl acetate solution of poly(dodecyl vinyl ether) showing upper critical solution temperature (UCST) at around 45°C. The UCST behavior on cooling process was clearly different from for the linear counterpart, and the cyclic polymer showed duller sensitivity to temperature than the linear. These unique properties of cyclic polymers are likely attributed to the endless structures free from the terminal groups.

## Introduction

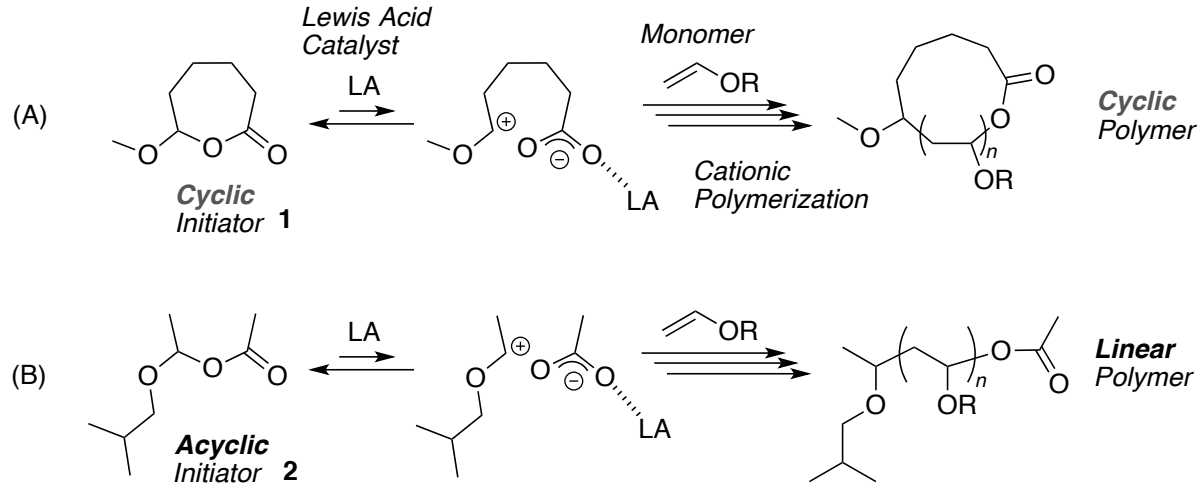
Terminal structures of polymer chain often influence the properties as well as the aggregation behaviors, unless the molecular weight is extremely high. This is the case of linear topology, and as compared to linear string, most of synthetic polymers are composed of linear chains. On the other hand, cyclic polymer is free of influence of terminal groups due to the endless loop structure. The topologically unique but fundamental structure has attracted attentions from polymer physicists for long time.[1–3] Indeed, it has been clarified that some fundamental properties of cyclic polymer are different from those of linear: lower intrinsic viscosity,[1] smaller hydrodynamic volume,[1] higher density,[1] higher glass transition temperature [1] and higher refractive index.[1] However, the study on the ring-driven properties has not progressed so steadily, likely because of difficulty in the synthesis. One conventional method to approach cyclic polymers is endocyclic reaction in which terminal groups of linear polymer are intramolecularly connected with each other.[4] Highly diluted condition is required to realize the intramolecular reaction without intermolecular one leading to chain extension, unless special interaction is used before the connection.[5, 6] Thus it is not so straightforward to prepare samples of pure cyclic polymers through the endocyclic methodology.

On the other hand, ring-expansion polymerization (REP) could be more useful to obtain cyclic polymers. In the typical process, a cyclic molecule as an initiator is activated to generate active species and monomer molecules are inserted for propagation while keeping the cyclic topology. Since the brilliant discovery of ring-opening metathesis-based REP by Grubbs,[7] some approaches have been attempted.[8–11] However, most of the pioneering researches rely on ring opening polymerization, namely syntheses of cyclic polymers from cyclic monomers. There have been limited examples on ring-expansion addition polymerization of "acyclic" vinyl monomer,[12–14] and particularly, it has been a challenging subject to develop the controlled REP system leading to precise construction of ring-based architectures.

The author has developed ring-expansion cationic polymerization of vinyl ether with a hemiacetal ester (HAE) bond-embedded cyclic initiator (**1**: Scheme 1A).[15–17] The initiation and propagation can be controlled under reversible activation of HAE bond by suitable Lewis acid catalyst (e.g., $SnBr_4$) and unfavorable side reactions such as β-proton elimination are suppressed like conventional living cationic polymerization. Structural analyses of resultant products with $^1H$ NMR and MALDI-TOF-MS support almost quantitative generation of

cyclic polymer. The cyclic topology can be also proved by acidolysis experiment where HAE bonds in resultant chains is irreversibly cleaved with strong protonic acid and water to convert ring to line for SEC analysis. In the case of successful generation of cyclic polymer, peak top molecular weight ($M_p$) is specifically increased via the acidolysis, and most typically the $M_p$ ratio before to after cleavage ($M_p/M_{p,clv}$) of around 0.8 is given. The propagation is fairly controlled to generate cyclic polymers but intermolecular counter-anion exchange reaction or "ring-fusion" is accompanied to result in broad molecular weight distribution of obtained polymer. However, he has recently developed post-dilution methodology to approach cyclic polymers of narrow molecular weight distributions (MWDs), in which the polymerization solution after monomer consumption is diluted while keeping the activity of $SnBr_4$ and thus intramolecular exchange in fused ring is promoted to give non-fused or single ring chain.[17]

Based on these backgrounds, in this chapter he studied properties of cyclic poly(vinyl ether)s that were synthesized via the ring-expansion cationic polymerization with **1**. Importantly, he can synthesize linear polymers of similar molecular weights from same monomer via living cationic polymerization with a HAE-based "acyclic" initiator (**2**: an acetic acid adduct of isobutyl vinyl ether, Scheme 1B),[18] which is helpful for discussion on effects of topology on properties. In particular, he employed a bulky substitute-pendant vinyl ether to synthesize the cyclic polymers of various molecular weights as well as the linear counterparts, and compared glass transition temperatures ($T_g$s) of the two types of polymers. The study would be valuable, since there have been a few studies on molecular weight




**Scheme 1.** (A) Ring-Expansion Cationic Polymerization of Vinyl Ether with Cyclic Initiator (**1**) and (B) Living Cationic Polymerization with Acyclic Initiator (**2**)

dependence on glass transition temperature of cyclic polymers (e.g., polydimethylsiloxane,[19] polystyrene,[20, 21] and polyvinyl pyridine.[22] Another interest in this study is thermo-sensitivity of cyclic polymer. It has been reported that aqueous solution of cyclic poly(*N*-isopropylacrylamide) showed different lower critical solution temperature (LCST) from that for the linear.[23, 24] He used a vinyl ether with dodecyl pendant whose polymer is known to show upper critical solution temperature (UCST) in ethyl acetate to clarify the difference in the thermo-sensitivity between cyclic and linear polymer.

## Experimental

### Materials

Dodecyl vinyl ether (DDVE) (Aldrich; > 98%), 8-vinyloxytricyclo-[5.2.1.$0^{2,6}$]decane (TCDVE) (Maruzen Petrochemical; > 99%) and tetralin (TCI; >97%) were distilled from calcium hydride under reduced pressure. Toluene (Kishida Kagaku, Osaka; 99.5%) were dried and purified by passing through purification columns (Solvent Dispensing System, SG Water USA, Nashua, NH; Glass Contour), kept over molecular sieves 4A for more than one day. $SnBr_4$ (Aldrich; >99%), 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, Aldrich; >99%) trifluoroacetic acid (TFA, Wako; >98%) were used as received. A cyclic initiator (**1**) and an acyclic initiator (**2**) were synthesized according to literature.[15, 25]

### Ring-Expansion Cationic Polymerization of Vinyl Ether with 1.

All polymerizations were carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical procedure of ring-expansion cationic polymerization of DDVE with **1** is given below: the polymerization was initiated by adding solutions of $SnBr_4$ (50 mM in toluene: 0.5 mL) via a dry syringe into a mixture (4.5 mL) containing DDVE (0.50 mL), tetralin (internal standard, 0.10 mL), cyclic initiator **1**, and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) in toluene at –40˚C: $[DDVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/5/0.15 mM. After a predetermined interval, the polymerization was terminated with prechilled ammoniacal methanol. Monomer conversion was determined from its residual concentration measured by gas chromatography with tetralin as an internal standard. The quenched reaction mixture was washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(DDVE).

**Post-Dilution for Synthesis of Cyclic Polymer with Narrow MWD**

When DDVE was almost consumed (conversion > 98%) in the cationic polymerization with **1**/$SnBr_4$, predetermined amount of dried solvent (e.g., toluene) was added to the solution under dry nitrogen, followed by stirring. A typical procedure is given below: when the monomer conversion reached 100% for the ring expansion cationic polymerization at –40˚C for 5 mL solution scale, 195 mL of dried toluene was directly added for 40-fold dilution, followed by stirring without changing the setting temperature (i.e., –40˚C). Three hours later after the dilution, prechilled ammoniacal methanol was added to deactivate Lewis acid catalyst. The quenched reaction mixture was washed with water, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(DDVE).

**Measurements**

The $M_n$, and $M_w/M_n$ values of polymers were measured by size exclusion chromatography (SEC) at 40˚C in THF as an eluent on three poly- styrene-gel columns (Shodex KF-803; pore size, 20–1000 Å; 8.0 mm i.d. x 30 cm; flow rate, 1.0 mL $min^{-1}$) connected to a DU-H2000 pump, a 74S-RI refractive-index detector, and a 41-UV ultraviolet detector (all from Shodex). The columns were calibrated against 13 standard poly(St) samples (Polymer Laboratories; $M_n$ = 500–3840000; $M_w/M_n$ = 1.01–1.14). $^1$H NMR spectra of the obtained polymers were recorded in benzene-$d_6$ at 25˚C on a JEOL JNM-ECA500 spectrometer, operating at 500.16 MHz. Differential scanning calorimetry of polymers (ca. 5.0 mg weighed into an aluminum pan) was performed on a DSC Q200 calorimeter (TA instruments) equipped with a RCS 90 electric freezing machine under dry nitrogen flow at a heating or cooling rate of 10 ˚C/min. Turbidity was measured in ethyl acetate (UV-1800, Shimadzu, optical path length = 1.0 cm). Wave length = 500 nm

## Results and Discussion

**Effects of Cyclic Structure on Glass Transition Temperature**

A vinyl ether with a bulky tricyclic alkane pendant, 8-vinyloxytricyclo-[5.2.1.$0^{2,6}$]decane (TCDVE), is known to provide the polymer of higher $T_g$ (~100˚C) unlike common alkyl vinyl ethers.[26, 27] For reasons of interest in thermal properties of cyclic polymer with such a rigid structure as well as easier preparation of measurement samples, the author selected the monomer to see effects of cyclic topology on $T_g$ measurement.

Ring-expansion cationic polymerization of TCDVE was performed with **1** as an initiator

in conjunction with $SnBr_4$ in toluene at –40˚C targeting 152 mer for 100% conversion under optimized condition: $[TCDVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 152/1/2/0.06 mM.

The polymerization smoothly proceeded without any induction period up to high conversion. The whole SEC curves of the resultant products shifted to higher MW, though they were broad especially at higher MW region (1A). This is likely due to generation of fused ring polymers via counter-anion exchange along with propagation, as seen in the ring-expansion cationic polymerizations of other alkyl vinyl ethers with **1**.[15, 16] The polymers were purified by precipitation in methanol three times to remove residual monomer for structural analyses with $^1$H NMR (Figure1B). The peak from methine proton (*a*) in HAE bond was observed with the reasonable integration ratio to protons of main chain (*b, c*), according to the monomer conversion. The molecular weights [$M_n$(NMR)s] that were calculated from the integration ratios showed good agreement with those from the

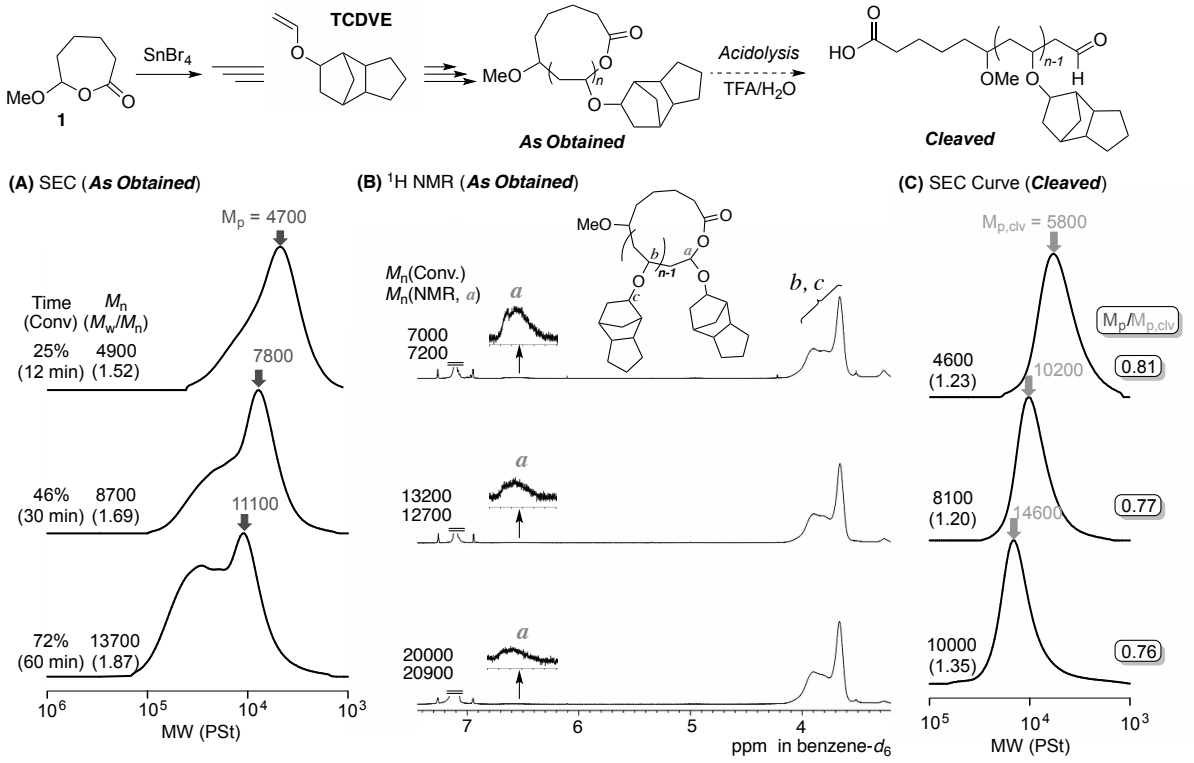



**Figure 1.** Synthesis of cyclic poly(TCDVE) through ring-expansion cationic polymerization: (A) SEC traces of as obtained polymer. (B) $^1$H NMR spectra of cyclic poly(TCDVE) (C1–C3) in benzene-$d_6$. (C) Cleaved form. Polymerization: $[TCDVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 152/1/2/0.06 mM in toluene at –40˚C. Acidolysis: several drops of $H_2O$/THF(1/2 v/v) solution was added to 1 wt% of THF solution of obtained polymer (1.0 mL) and the resultant solution was kept at ambient temperature for 12 hours.

conversions [$M_n$(Conv.)s], indicating almost quantitative formation of cyclic polymers. The generation of cyclic polymer was also supported by the acidolysis experiment, in which about 0.8 of $M_p/M_{p,clv}$ was obtained (Figure 1C). The three cyclic polymers in Figure 1 were used as samples of DSC measurement, as described below, along with another sample of higher molecular weight (Figure S1). Thus, four samples of cyclic poly(TCDVE)s of different molecular weights were prepared (**C1**–**4**: Table 1).[28] The linear poly(TCDVE)s (**L1**–**4**) were also synthesized via living cationic polymerization with the acyclic initiator (**2**) in conjunction with $SnBr_4$ catalyst in toluene at –40˚C.

**Table 1.** $M_n$, $M_w$, and $M_w/M_n$ of cyclic and linear poly(TCDVE)s for DSC measurement and their glass transition temperature ($T_g$)

| Sample | $M_n$[a] | $M_w$[a] | $M_w/M_n$[a] | $T_g$ |
|---|---|---|---|---|
| **C1** | 4,900 | 7,400 | 1.52 | 98 ˚C |
| **C2** | 8,700 | 14,600 | 1.69 | 101 ˚C |
| **C3** | 15,400 | 30,000 | 1.95 | 102 ˚C |
| **C4** | 21,400 | 39,400 | 1.83 | 102 ˚C |
| **L1** | 3,300 | 4,300 | 1.29 | 82 ˚C |
| **L2** | 6,200 | 8,000 | 1.29 | 93 ˚C |
| **L3** | 10,500 | 14,200 | 1.36 | 99 ˚C |
| **L4** | 16,700 | 18,500 | 1.11 | 101 ˚C |

[a] $M_n$, $M_w$, and $M_w/M_n$ were measured by size exclusion chromatography against polystyrene calibration

Figure 2A shows the DSC thermograms (2nd heating process at 10˚C/min) of the cyclic (**C1**–**4**) and linear PTCDVEs (**L1**–**4**). As reported in the literature,[26] all the samples showed endothermic peaks around 100˚C attributed to glass transition. Interestingly, the glass transition temperatures ($T_g$s) of the cyclic polymers were apparently different from those of the linear counterparts with similar molecular weights (Table 1). As shown in Figure 2B, $T_g$ of linear polymer was apparently decreased, as the $M_n$ was low, whereas $T_g$ of the cyclic one was not affected by molecular weight so much. To further study effects of the topology, $T_g$ dependence on molecular weight was analyzed with the Flory-Fox equation[29]: $T_g = T_{g,\infty} - A*M_n^{-1}$ , where $T_{g,\infty}$ is the maximum glass transition temperature that can be achieved at a

theoretical molecular weight and A is an empirical parameter that is related to the free volume present in the polymer sample. Thus, glass transition temperatures were plotted against inverse of molecular weight (Figure 2C). The plots were on straight line for the both topologies but the slope was clearly different: the slope for cyclic polymers was gentler. The difference indicates that free volume of cyclic polymers is smaller than that of linear counterpart. As shown in schematic illustration for cyclic and linear polymer (Figure 3), the free volume around terminals is larger than inside for linear chain, whereas it is almost

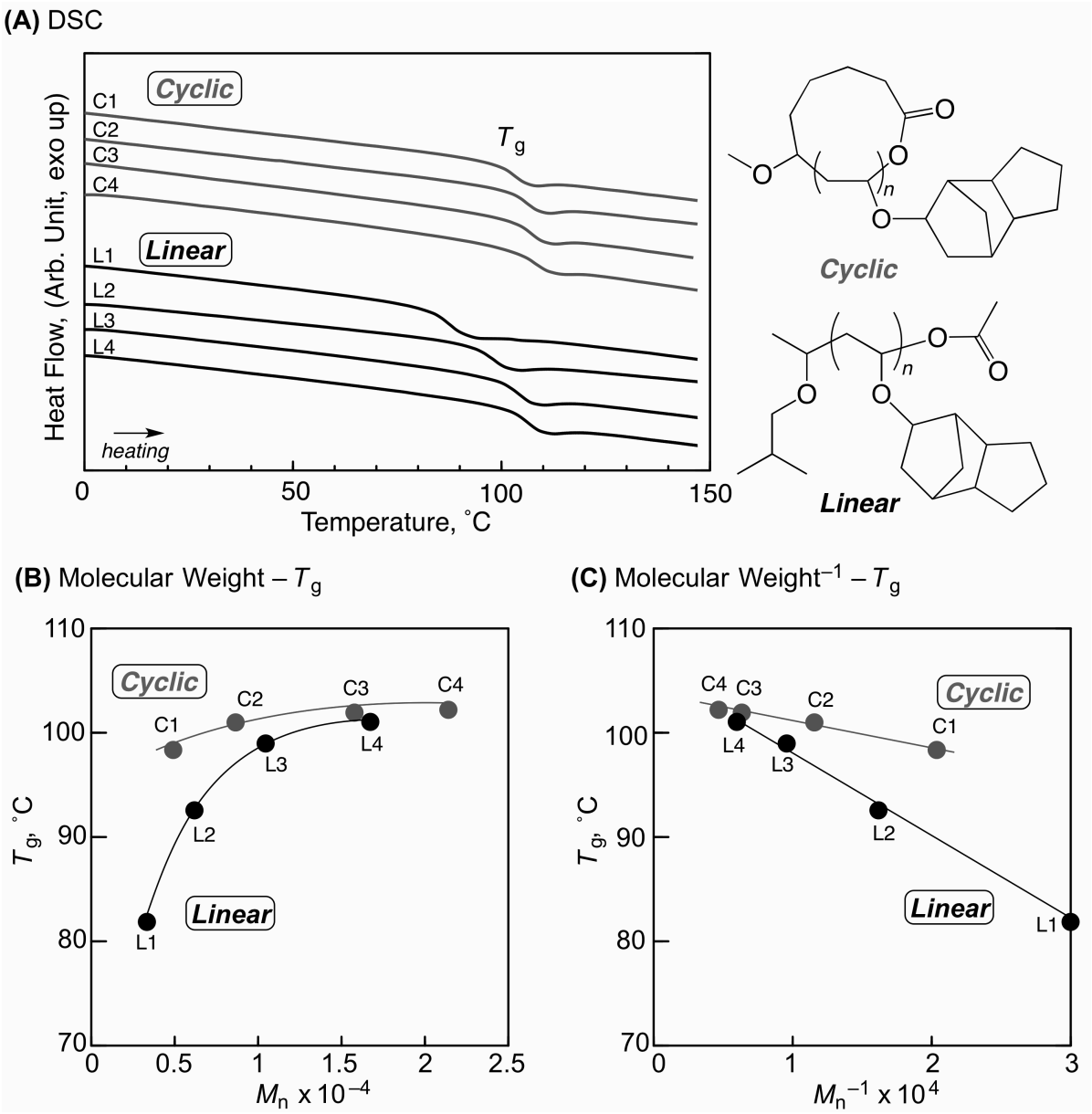



**Figure 2.** (A) DSC Thermograms of cyclic (**C1–4**) and linear (**L1–4**) polymers. (B) Molecular weight–glass transition temperature plot of cyclic and linear polymers. (C) Inverse of molecular weight–glass transition temperature of cyclic and linear polymers.

uniform along chain for the cyclic topology due to the terminal-free structure. This explanation fairly agrees to literatures describing difference between cyclic and linear polymers for molecular weight dependence of glass transition temperature.[19–22]

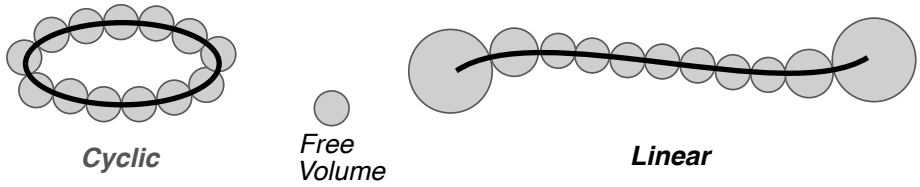



**Figure 3.** Schematic illustration of free volume for cyclic and linear polymer chain.

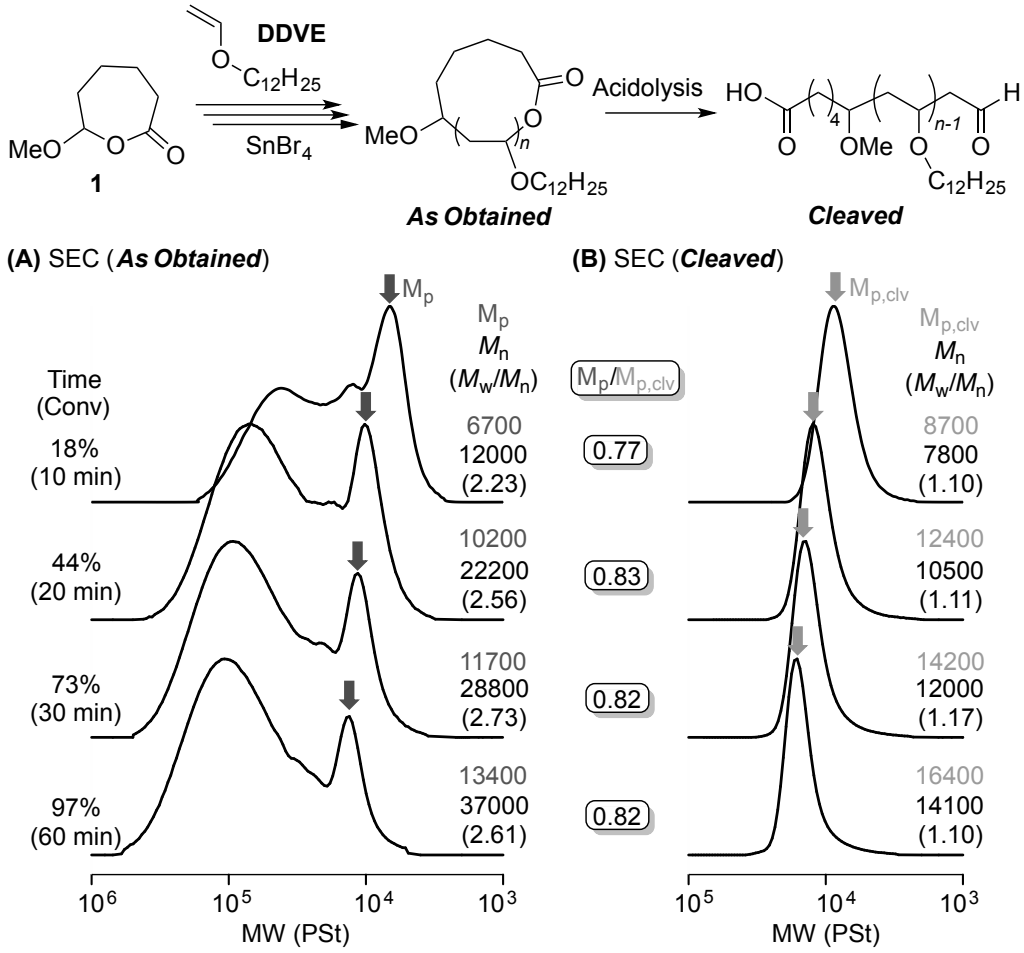



**Figure 4.** Ring-expansion cationic polymerization of DDVE: SEC traces of (A) as-obtained polymers and (B) those after acidolysis. Polymerization: $[DDVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/5/0.15 mM in toluene at –40˚C. Acidolysis was done in the manner described above (see caption of Figure 1).

**Effects of Cyclic Structure on Thermosensitive Behaviors**

Aoshima and coworkers reported that the ethyl acetate solution of poly(DDVE) showed UCST-type phase transition at around 45˚C.[30] The author focused on the thermo-sensitivity of poly(DDVE) to study difference in the behavior between cyclic and linear topologies.

Ring-expansion cationic polymerization of DDVE with the cyclic initiator (**1**) was performed in conjunction with $SnBr_4$ as an activator (Figure 4). Upon an addition of $SnBr_4$, DDVE was smoothly consumed to give 97% conversion in one hour. The product showed broad SEC curves particular to the ring-expansion polymerization with **1** (Figure 4A): propagation is controlled without forming dead chains but MWDs were broad due to formation of fused ring. As is the case with TCDVE, the acidolysis experiments gave monodispersed linear polymers with narrow molecular weight distributions and 0.77–0.83 of $M_p/M_{p,clv}$, indicating generation of cyclic polymers (Figure 4B).

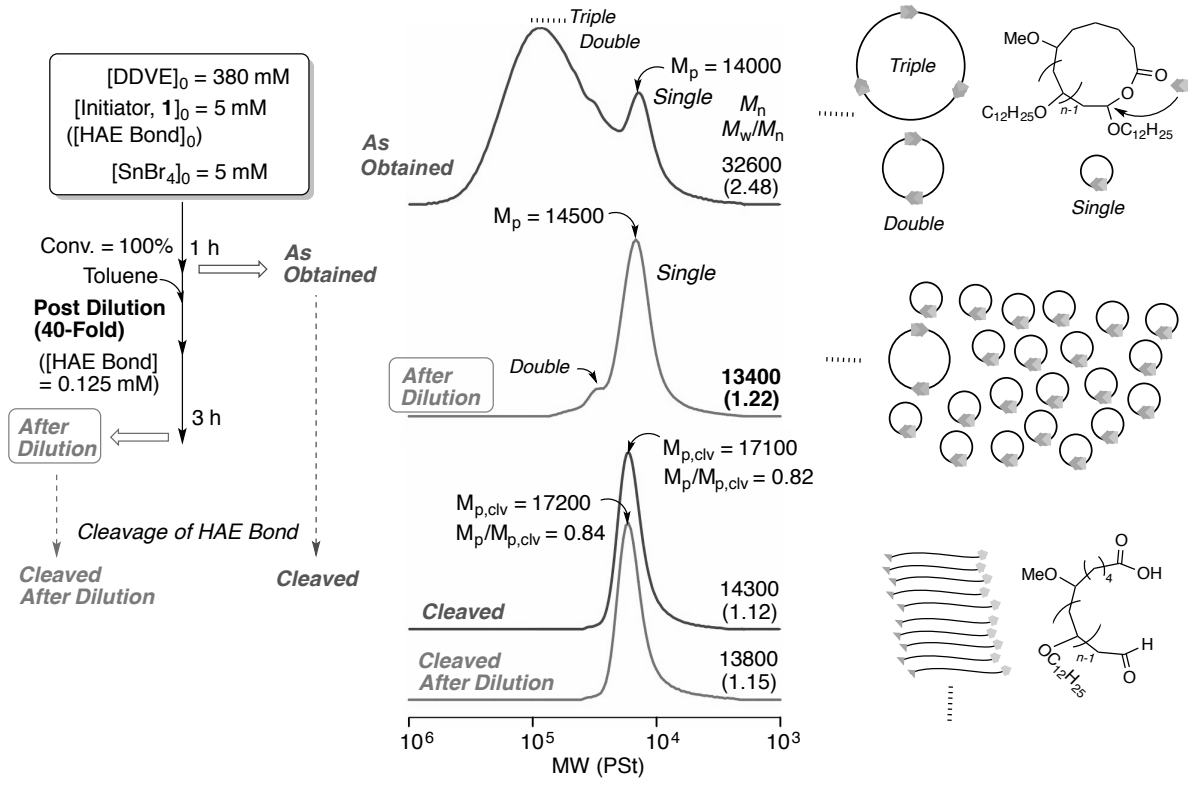



**Figure 5.** Post dilution toward synthesis of monodispersed cyclic poly(DDVE) via ring-expansion cationic polymerization. Polymerization: $[DDVE]_0/[\mathbf{1}]_0/[SnBr_4]_0/[DTBMP]_0$ = 380/5/5/0.15 mM in toluene at –40˚C; Post Dilution: Addition of toluene for 40-fold dilution ([HAE Bond] = 0.125 mM), followed by stirring the diluted solution for additional 3 hours at –40˚C. Acidolysis was done in the manner described above (see caption of Figure 1).

In chapter 5, the author have found a post-dilution to approach cyclic polymers of narrow MWDs, in which the polymerization solution is diluted under Lewis acid activation at almost 100% monomer conversion to induce intramolecular counter-anion exchange.[17] To strictly evaluate effects of chain topology on the UCST behavior, the post-dilution approach was applied to synthesize cyclic poly(DDVE)s of narrow MWDs. When the conversion of DDVE reached 100% (in one hour), the polymerization solution was diluted 40 times with toluene, followed by stirring for additional three hours and quenching with methanol (Figure 5). As seen in the SEC curve of the obtained polymer, the peaks at higher MW from fused rings (double, triple, etc.) almost vanished to give almost unimodal SEC curve. Importantly, position of the peak top likely from single ring was immobile even after the dilution to give almost same $M_p$, and the acidolysis experiment supported formation of cyclic polymer even after the dilution process ($M_p/M_{p,clv}$ = 0.84)

The cyclic structure was also analyzed with $^1$H NMR (Figure 6). In the spectrum of the "as-obtained" polymer, the calculated molecular weight from peak integration ratio of hemiacetal ester methine proton (*a*) to methyl pendant protons (*g*) in the repeating units group was 16,900, which showed a good agreement with the molecular weight calculated from

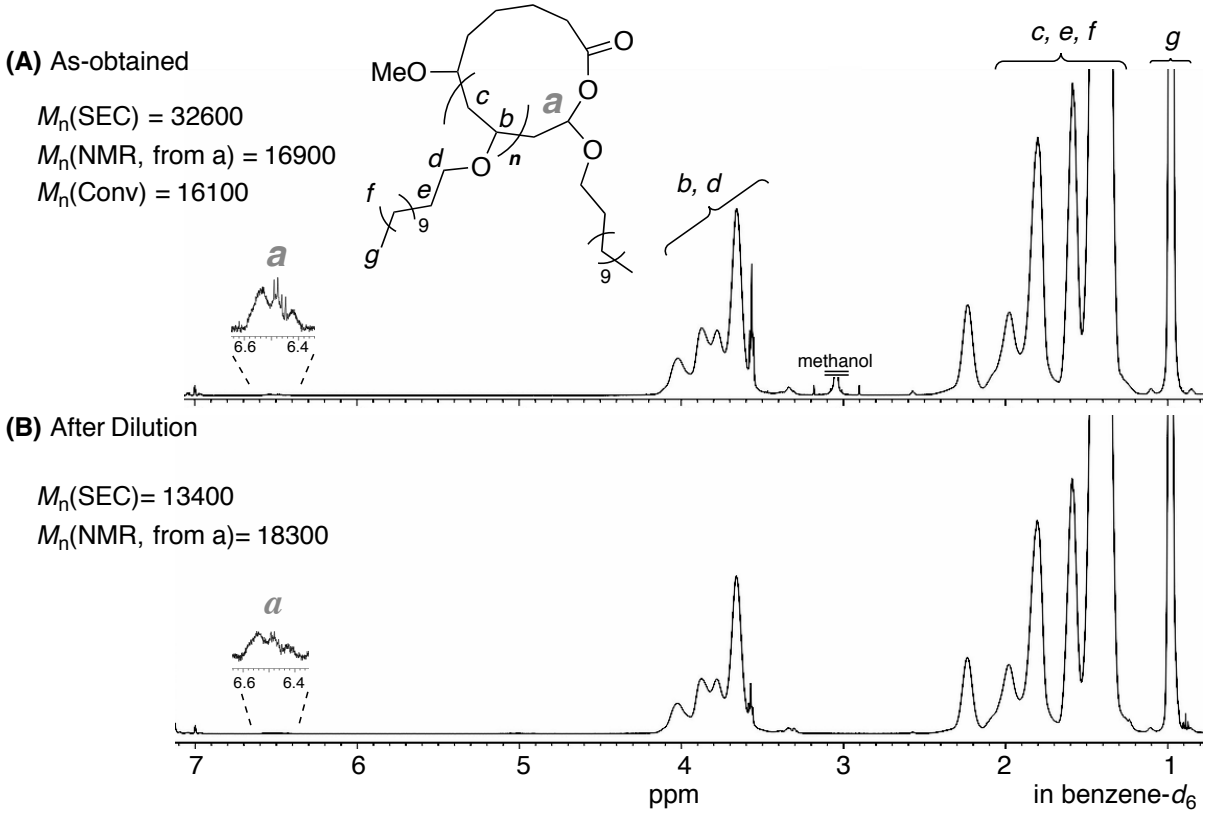



**Figure 6.** $^1$H NMR spectra of (A) as-obtained poly(DDVE) and (B) poly(DDVE) after dilution

injection ratio of the monomer to the initiator ($M_n$ = 16,100) (Figure 6A). After the dilution process, the peak from the hemiacetal ester methine proton was relatively decreased to give higher molecular weight than the calculated [$M_n$ (NMR) = 18,300] (Figure 6B).

There is a possibility that a small quantity of HAE bond was lost to contain linear chains. Anyhow, the polymer ($M_n$ = 13200, $M_w/M_n$ = 1.22) was used as the cyclic sample for the USCT study. The linear poly(DDVE) of almost the same molecular weight was also synthesized via living cationic polymerization with the acyclic initiator **2** ($M_n$ = 14300, $M_w/M_n$ = 1.18).

The thermo-sensitive property of the poly(DDVE) solution in ethyl acetate was evaluated through temperature-variable turbidity measurement with UV–vis spectrophotometer, and herein the temperatures at the solution transmittance of 99% (UCST) and 50% (cloud point)

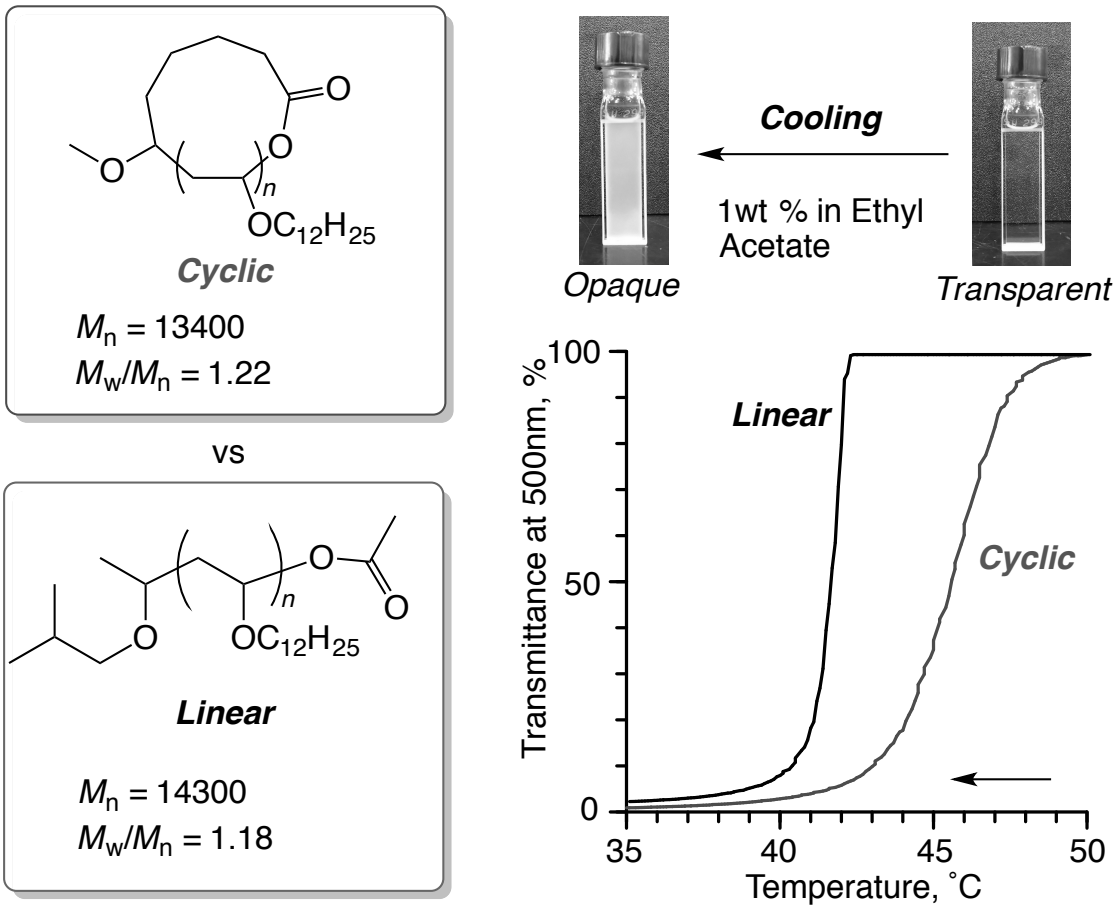



**Figure 7.** Evaluation of thermosensitivity for 1wt% ethyl acetate solutions of cyclic and linear poly(DDVE)s with temperature variable UV measurement (transmittance at 500 nm, cooling at 1˚C/min). Cyclic poly(DDVE): $M_n$ = 13400, $M_w/M_n$ = 1.22; linear poly(DDVE): $M_n$ = 14300, $M_w/M_n$ = 1.18.

were measured. Figure 7 shows the transmittance against temperature for 1wt% ethyl acetate solutions of cyclic and linear poly(DDVE). The solutions were heated at 70˚C before the measurement to make transparent solution, followed by sample setting for the UV–vis measurement on the cooling process. As for the linear poly(DDVE), the transition from transparent to opaque solution sharply occurred to give almost same temperature (~42˚C) of UCST and cloud point (CP), similar to results in the literature. On the other hand, the cyclic showed a dull transition: the transmittance commenced to decrease at higher temperature (~50˚C) and gradually attenuated giving CP at 46˚C. The higher UCST and CP mean poorer solubility of the cyclic polymer. This is probably due to that number of solvent molecules contributing to solvation is lower than for the linear chain because of the terminal free structure.

The difference in the transition behavior with 1 wt% solution encouraged the author to change the concentration for more detailed exploration. Figure 8A and B show the temperature-dependent transmittance of the ethyl acetate solution of cyclic and linear poly(DDVE)s at various concentration (from $6.25 \times 10^{-2}$ to 2.00 wt%). As the concentration was decreased, the transition became insensitive to temperature and UCST and cloud point shifted to lower in both cases. To further understand difference in the temperature sensitivity between the two topologies, the subtraction from UCST and CP, UCST–CP, was used as the parameter that describes the broadness of transition: the lower value is indicating the solution is more sensitive to temperature. The values were plotted against logarithm of polymer concentration (Figure 8C). As the solution was diluted, the difference between the

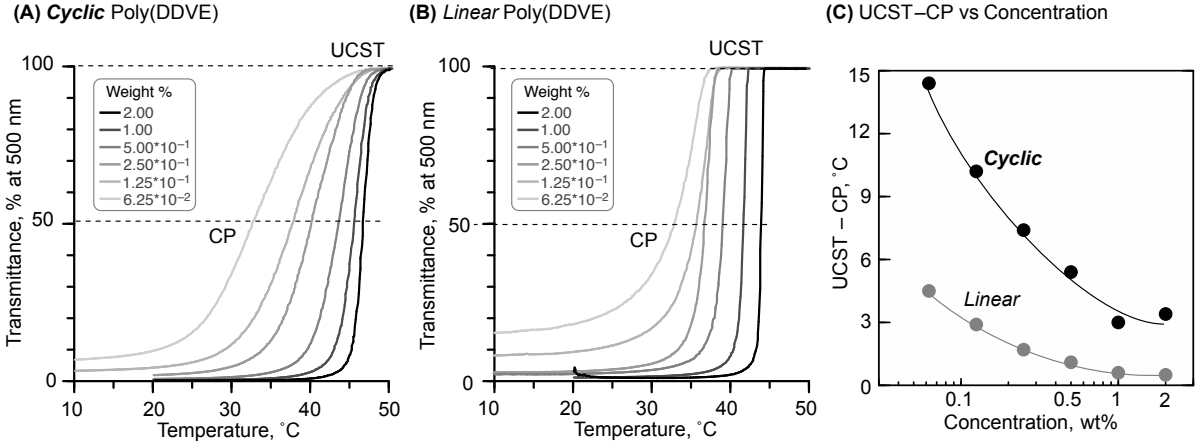



**Figure 8.** Transmittance of ethyl acetate solution of (A) cyclic and (B) linear polymers at 0.00625, 0.125, 0.25, 0.5, 1, 2 wt%; on cooling rate at 1˚C/min. (C) Relationship between UCST–CP and concentration. Cyclic poly(DDVE): $M_n$ = 13400, $M_w/M_n$ = 1.22; Linear poly(DDVE): $M_n$ = 14300, $M_w/M_n$ = 1.18.

two topologies was increased, and the solution of the cyclic polymer was more and more insensitive. The endless structure of the cyclic polymer would cause poor solubility and difficulty in aggregation upon cooling. One plausible explanation for the result of concentration dependence is that the transition from intramolecular aggregation to intermolecular one of the cyclic polymers was slower than that of the linear polymers and the difference became more pronounced as the concentration was lower.

## Conclusion

The author precisely synthesized cyclic poly(vinyl ether)s via ring-expansion cationic polymerization with the cyclic initiator **1** to study the ring-driven physical properties. Taking advantage of controlled feature of the system, linear polymers of similar molecular weights were also synthesized for the comparison. Consequently, the cyclic poly(TCDVE)s showed higher $T_g$ than the linear counterparts of similar molecular weights, and the $T_g$ was not so decreased even though the molecular weight was lower. These are likely owing to the relatively low free volume in contrast to linear analogues having large free volume around the chain terminals. Thermo-sensitivity of cyclic polymer was also examined for the UCST behavior of ethyl acetate solution of poly(DDVE). The thermo-sensitivity of the cyclic polymer was obviously duller than the linear analogue, which is probably caused by poorer segment packing from random-coil to globules. The difference became more remarkable as the concentration was lower. Thus, he clarified ring-driven properties by using the ring-expansion cationic polymerization. Other ring-driven properties and behaviors are also expected in the near future through design of side chain and/or development to block or random copolymerization.

## References

(1) Semlyen, J. A. Cyclic Polymers, 2nd ed.; Kluwer Academic: Dordrecht, The Netherlands, 2000.

(2) Tezuka, Y. Topological Polymer Chemistry: Progress of Cyclic Polymers in Syntheses, Properties and Functions, World Scientific Publishing Co. Pte. Ltd, 2013.

(3) Carothers, W. H. *J. Am. Chem. Soc.* **1929,** *31,* 2548–2559.

(4) Geiser, D.; H. Hocker, K. *Macromolecules* **1980,** *13,* 653–656.

(5) Oike, H.; Imaizumi, H.; Mouri, T.;Yoshioka, Y.; Uchibori, A. Tezuka, Y. *J. Am. Chem. Soc.* **2000,** *122,* 9592-9599.

(6) Tezuka, Y.; Oike, H. *Macromol. Rapid Commun.* **2001,** *22,* 1017–1029.

(7) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041–2044.

(8) Takeuchi, D.; Inoue, A.; Osakada, K.; Kobayashi, M.; Yamaguchi, K. *Organometallics* **2006**, *25,* 4062–4064.

(9) Shea, K. J.; Lee, S. Y.; Busch, B. B. *J. Org. Chem.* **1998,** *63,* 5746-5747.

(10) Brown, H. A.; Waymouth, R. M. *Acc. Chem. Res.* **2013,** *46,* 2585–2596.

(11) Kaitz, J. A.; Diesendruck, C. E.; Moore, J. S. *J. Am. Chem. Soc.* **2013,** *135,* 12755−12761.

(12) Narumi, A.; Zeidler, S.; Barqawi, H.; Enders, C.; Binder, W. H. *J. Polym. Sci., Part A: Polym. Chem.* **2010,** *48,* 3402–3416.

(13) Roland, C. D.; Li, H.; Abboud, K. A.; Wagener, K. B.; Veige, A. S. *Nature Chem.* **2016,** *8,* 791–796.

(14) He, T.; Zheng, G.–H.; Pan, C. *Macromolecules* **2003,** *36,* 5960–5966.

(15) Kammiyada, H.; Konishi, A.; Ouchi, M.; Sawamoto, M. *ACS Macro Lett.* **2013,** *2,* 531–534.

(16) Kammiyada, H.; Ouchi, M.; Sawamoto, M. *Macromol. Symp.* **2015,** *350,* 105-116.

(17) Kammiyada, H.; Ouchi, M.; Sawamoto, M. *Polym. Chem.* **2016,** *7,* 6911–6917.

(18) Hashimoto, T.; Iwata, T.; Minami, A.; Kodaira, T. *J. Polym. Sci. Part A: Polym. Chem.* **1998,** *36,* 3173–3185.

(19) Clarson, S. J.; Semlyen, J. A.; Dodgson, K. *Polymer* **1991,** *32,* 2823–2827.

(20) Liu, X.; Chen, D.; He, Z.; Zhang, H.; Hu, H. *Polym. Commun.* **1991,** *32,* 123–124.

(21) Rique-Lurbet, L.; Sshappacher, M.; Deffieux, A. *Macromolecules* **1994,** *27,* 6318–6324.

(22) Hogen-Esch, T. E.; Sundararajan, J.; Toreki, W. *Makromol. Chem., Macromol. Symp.* **1991,** *47,* 23–42.

(23) Jian, X.; Jing, Y.; Shiyong, L. *Macromolecules* **2007,** *40,* 9103–9110.

(24) Qiu, X.- P.; Tanaka, F.; Winnik, F. M. *Macromolecules* **2007,** *40,* 7069–7071.

(25) Higashimura, T.; Kishimoto, Y.; Aoshima, S. *Polym. Bull.* **1987,** *18,* 111–115.

(26) Namikoshi, T.; Hashimoto, T.; Kodaira, T. *J. Polym. Sci. Part A: Polym. Chem.* **2004,** *42,* 3649–3653.

(27) Lal, J.; Trick, G. S. *J. Polym. Sci. Part A: Polym. Chem.* **1964,** *2,* 4559–4572.

(28) They are purified via methanol precipitation three times to remove lower molecular weight compounds

(29) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950,** *21,* 581–591.

(30) Seno, K.; Date, A.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci. Part A: Polym. Chem.* **2008,** *46,* 4392–4406.

# LIST OF PUBLICATIONS

## Part I

### *Chapter 1*

"Ring-Expansion Living Cationic Polymerization via Reversible Activation of a Hemiacetal Ester Bond"

Hajime Kammiyada, Akito Konishi, Makoto Ouchi, and Mitsuo Sawamoto

*ACS Macro Lett*. **2013**, *2*, 531–534.



### *Chapter 2*

"Ring-Expansion Living Cationic Polymerization of Vinyl Ethers: Optimized Ring Propagation"

Hajime Kammiyada, Makoto Ouchi, and Mitsuo Sawamoto

*Macromol*. *Symp*. **2015,** *350,* 105-116.

*Kobunshi Ronbunshu,* **2015,** *72,* 468–479.



### *Chapter 3*

"Effects of Initiator Structure on Propagation in Ring-Expansion Cationic Polymerization: Dual Role of Cyclic Hemiacetal Ester as an Initiator and a Monomer"

Hajime Kammiyada, Makoto Ouchi, and Mitsuo Sawamoto

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(Chapter 3 is the Author's version of an Unsubmitted Work that will be submitted for publication.)

# Part II

## *Chapter 4*

"Expanding Vinyl Ether Monomer Repertoire for Ring-Expansion Cationic Polymerization: Various Cyclic Polymers with Tailored Pendant Group "

Hajime Kammiyada, Makoto Ouchi, and Mitsuo Sawamoto

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(Chapter 4 is the Author's version of an Unsubmitted Work that will be submitted for publication.)

## *Chapter 5*

"A Convergent Approach to Ring Polymers with Narrow Molecular Weight Distribution through Post Dilution in Ring-Expansion Cationic Polymerization"

Hajime Kammiyada, Makoto Ouchi, and Mitsuo Sawamoto

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## *Chapter 6*

"A Study on Physical Properties of Cyclic Poly(vinyl ether)s Synthesized via Ring-Expansion Cationic Polymerization"

Hajime Kammiyada, Makoto Ouchi, and Mitsuo Sawamoto

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## Other Publications

**1** "Precise Construction of Ring-Linear Block Copolymers via Ring-Expansion Cationic Polymerization and Metal-Catalyzed Living Radical Polymerization"
Taizo Yamamoto, Hajime Kammiyada, Makoto Ouchi, and Mitsuo Sawamoto
*to be submitted*.

**2** "Ring-Expansion Cationic Polymerization of Vinyl Ethers"
Makoto Ouchi, Hajime Kammiyada, and Mitsuo Sawamoto
*to be submitted*.

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