

**A Benign Initiating System for Cationic
Polymerization of Vinyl Ethers and Styrene
Derivatives: Silver Salt/Aryl Methyl
Halide/Lewis Base**

環境に優しいビニルエーテルとスチレン誘導
体のカチオン重合反応開始系：銀塩/アリー
ルハロゲン化メチル/ルイス塩基

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埼玉大学 大学院 理工学研究科
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主指導教員 廣瀬 卓司

林 麗

Abstract

A combination of aryl methyl halides and silver salts was studied as an environmentally benign initiating system for cationic polymerization of vinyl ethers (VEs) and styrene derivatives (Sts). The reaction of aryl methyl halide and silver salt readily generates a benzyl cation, which induces the cationic polymerization. The reactivity of the benzyl cations and growing carbocations could be effectively controlled by sulfides, especially dimethyl sulfide (Me_2S), which exerts a strong effect as an additive on the rate of polymerization, resulting in a narrower MWD range than the system without it. Diethyl ether was important as reaction solvent in the initiation step.

Various EVs, isobutyl vinyl ether (IBVE), ethyl vinyl ether (EVE) and isopropyl vinyl ether (IPVE), were employed for cationic polymerization. The living nature of poly(IBVE) synthesized using the $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{Me}_2\text{S}$ system was examined by a successful chain extension experiment. Detailed study of the effects of Me_2S , various benzyl cations and the addition order of the reagents revealed that the reaction was controlled by the electronic and steric features of aryl methyl halides, LBs, and IBVE, and a plausible reaction mechanism was presented. Differences in the modes of coordination of added bases to benzyl cations were clearly demonstrated by ^1H NMR.

Cationic polymerizations of EVE and IPVE, also proceeded in a controlled fashion using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{Me}_2\text{S}$ system. The effects of tetrahydrothiophene (THT) and diethyl sulfide (Et_2S) were further investigated. Choosing a sulfide with suitable nucleophilicity was important for achievement of controlled polymerization. In addition, depending on monomer reactivity, selecting the reaction temperature was also essential for suppressing side reactions. The copolymerization of IBVE and EVE by the $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ system with Me_2S proceeded smoothly in CH_2Cl_2 at $-23\text{ }^\circ\text{C}$.

For polymerization of Sts, it was found that the polymerization of less reactive monomers (styrene, *p*-methoxymethylstyrene and *p*-butoxymethylstyrene) proceeded in an uncontrolled fashion, even in the presence of added base or ammonium salt. The polymerization of highly reactive *p*-methoxystyrene (pMOS) was effectively controlled by using sulfides (Me_2S , Et_2S and THT), which were shown to be effective Lewis bases. This polymerization behavior was dramatically influenced by the electronic and steric features of aryl methyl halides and LBs and the difference of modes of coordination between benzyl cations and the added bases were also demonstrated by ^1H NMR.

Keywords: cationic polymerization; controlled polymerization; copolymerization; poly(vinyl ether)s; polystyrene; aryl methyl halide; additives; alkyl sulfide

Abbreviations

AcO	Acetate
Bn	Benzyl
Bu	Butyl
CPME	Cyclopentyl methyl ether
DCM	Dichloromethane
DO	Dioxane
DMSO	Dimethylsulfoxide
E	Electrophile
EA	Ethyl acetate
Et	Ethyl
EVE	Ethyl vinyl ether
IBVE	Isobutyl vinyl ether
IPVE	Isopropyl vinyl ether
LB	Lewis base
Me	Methyl
M_n	Number average molecular weight
M_w	Weight average molecular weight
MWD	Molecular weight distribution
Nu	Nucleophile
<i>p</i>	Para
Ph	Phenyl
pMOS	<i>p</i> -methoxystyrene
Pr	Propyl
St	Styrene
Sts	Styrene derivatives
TfO	Trifluoromethanesulfonate, triflate
THF	Tetrahydrofuran
THT	Tetrahydrothiophene
VE	Vinyl ether

Publication List

This thesis based on the paper below and is also related to the following paper. The published articles are reproduced here with the permission of the publishers.

A Benign Initiating System for Cationic Polymerization of Isobutyl Vinyl Ether: Silver Salt/Aryl(Alkyl) Halide/Lewis Base

Li Lin, Guangyou Zhang, Koichi Kodama, Mikio Yasutake, Takuji Hirose

J. Polym. Sci., Part A: Polym. Chem. **2015**, Doi: 10.1002/pola.27656.

Related Published Paper

Synthesis of Cyclic Carbonates from CO₂ and Epoxides Catalyzed by Low Loadings of Benzyl Bromide/DMF at Ambient Pressure

Lin Wang, Li Lin, Guangyou Zhang, Koichi Kodama, Mikio Yasutake, Takuji Hirose

Chem. Commun. **2014**, 50, 14813–14816.

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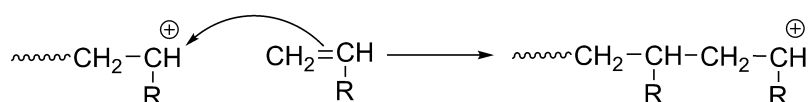
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Chapter 1 Introduction

1.1 Cationic Polymerization

Cationic polymerizations are chain polymerizations in which the kinetic chain carriers (active centers) are positively charged or electrophilic. These active species from the growing chain ends can be divided into two main types: carbenium ions in the “vinyl” polymerization and onium ions in the ring-opening polymerization (Scheme 1.1).

Carbenium ionic propagation



Cationic ring-opening propagation

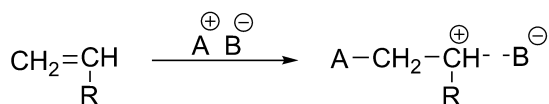
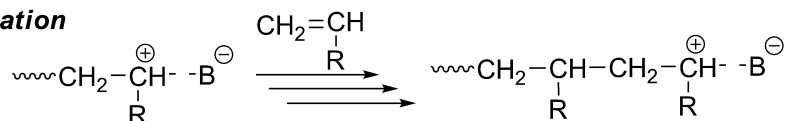
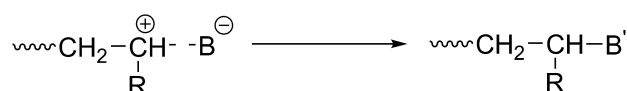
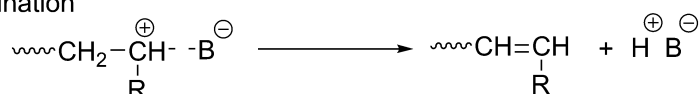
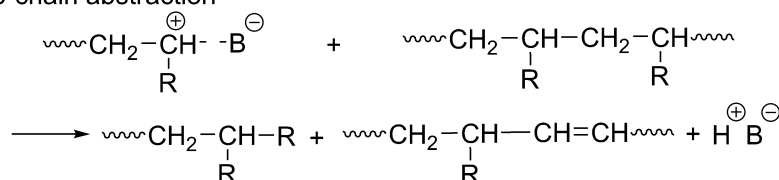


Scheme 1.1 Propagation Reaction in Cationic Polymerization of Olefin and Heterocyclic Monomer (counteranion omitted).

Cationic polymerization has attracted considerable attention in the academic research and industrial area for producing well-defined polymers or copolymers. Comparison with other types of polymerization, cationic polymerization exhibits some significant advantages. It proceeds faster than the other methods (sometimes just in several seconds). Various shapes polymers (star, block, random, etc.) can be synthesized without troublesome purification.^{1,2}

1.1.1 Historical Background of Cationic Polymerization

Cationic polymerization has a long history and the first cationic polymerization was first proposed in the late 18th century.³ Since then, a wide variety of catalysts from Brønsted acids to Lewis acids and numerous monomers were developed for cationic polymerization. Wislicenus in 1878 firstly reported the preparation of poly(vinyl ether)s which was recognized as a cationic polymerization initiated by I^+ and chain growth via carbenium ions.³ Until the 1960s, pioneering work on cationic polymerizations was performed from elucidation of the elementary steps of polymerization mechanisms by the kinetic studies, similar to the research on the living anionic polymerization firstly reported in the same period.⁴ However, it became soon clear that during the reactions highly active growing species caused various side reactions, such as β -proton elimination (Scheme 1.2), which were more complex and frequent than anionic systems.⁵

Initiation**Propagation****Termination****Side reactions** **β -Elimination****Side-chain abstraction****Scheme 1.2** Elementary Reactions for Cationic Polymerization.⁵

Pepper firstly reported the occurrence of a reversible termination involving the active growing chain terminal (active form) and a non-propagating chain end (dormant form) by the investigation of the kinetics of styrene polymerization conducted by perchloric acid.⁶ However, to get controlled cationic polymerization, until the late 1970s, it appeared a turning point because of the discovery of long lived species in the cationic polymerization of styrene derivatives.^{7,8} Following this result, long lived cationic species in polymerization of vinyl ethers were also demonstrated.⁹ Kennedy et al. reported the achievement of quasi-living polymerization of isobutylene involving a continuous equilibrium between a dormant and an active chain end in the early 1980s.¹⁰ Finally, the first living cationic polymerization was observed using alky vinyl ethers as monomers in 1984 by Higashimura's group.^{11,12} Subsequently, living polymerization of isobutene was also observed by Kennedy and Faust.^{13,14} Since then, a wide variety of initiating systems for living cationic polymerization were developed and different types of monomers were employed to satisfy the specific demands both in academia and industry. Living polymerization brought revolutionary change in polymer chemistry because of the significant advantages, narrow molecular weight distribution (MWD), predetermined molecular weight (MW) and controllable chain end group. Thus, various shaped (co)polymers (block, random, graft, star, et al.) with well-defined structures were prepared.^{1,2,15} The first synthesis of living block copolymer was reported by Higashimura's group in 1984.¹⁶ For example, the first living polymerization of IBVE was carried out with the HI/I₂ initiating

system in toluene at $-35\text{ }^{\circ}\text{C}$, and then adding the second monomer, pMOS. To accelerate the rate of polymerization, the reaction temperature was increased to $-15\text{ }^{\circ}\text{C}$ to produce the target copolymers with quantitative conversion. Since this discovery, a wide variety of copolymers with controlled architecture were developed.^{1,5} Until 1991, well-defined star-like polymers were successfully synthesized by living cationic polymerization.¹⁷ For example, Higashimura et al. reported the polymer-linking reactions of living polymers with bifunctional monomers, to generate star shaped polymers having hydrophilic segments including hydroxyl¹⁸ or carboxy¹⁹ groups. Subsequently, various strategies for synthesis of functionalized polymers were developed.⁵

1.1.2 Characteristics of Cationic Polymerization

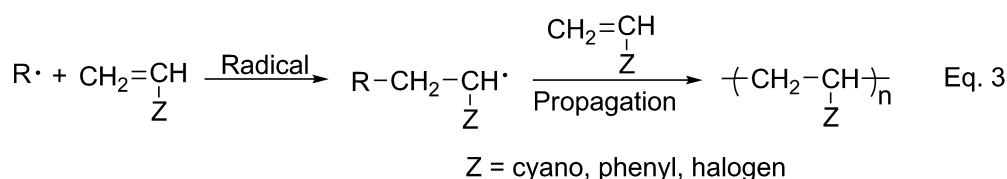
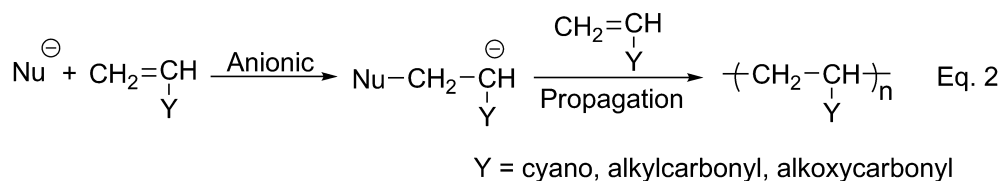
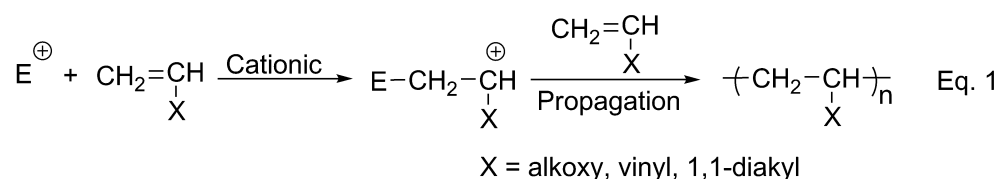
Cationic polymerization is highly selective, similar to anionic polymerization. Some monomers may not polymerize with ionic initiators. In contrary, most monomers will undergo radical polymerization. The polymerization behaviors of various monomers are shown in Table 1.1.²⁰

Table 1.1 Types of Chain Polymerization Suitable for Unsaturated Monomers²⁰

Monomer type	Type of Initiation		
	Radical	Cationic	Anionic
Ethylene	+	—	+
1-Alkyl olefins (α -olefins)	—	—	+
1,1-Dialkyl olefins	—	+	—
1,3-Dienes	+	+	+
Styrene, α -methyl styrene	+	+	+
Halogenated olefins	+	—	—
Vinyl esters ($\text{CH}_2=\text{CHOCOR}$)	+	—	—
Acrylates, methacrylates	+	—	+
Acrylonitrile, methacrylonitrile	+	—	+
Acrylamide, methacrylamide	+	—	+
Vinyl ethers	—	+	—
<i>N</i> -Vinyl carbazole	+	+	—
<i>N</i> -Vinyl pyrrolidone	+	+	—
Aldehydes, ketones	—	+	+

The cationic polymerization is conducted by addition of an electrophile to a monomer. Therefore, the propagation species becomes a carbocation, as shown in Scheme 1.3.^{21,22} In the cationic polymerization, monomer mostly has an electron donating group, such as alkoxy, vinyl, and 1,1-diakyl group. The electron donating substituent is capable of stabilizing the growing carbocation through resonance or induction, which can facilitate the cationic polymerization (Eq. 1). In the anionic polymerization, the propagating species is anion. Initiation is conducted by addition of a nucleophile to a monomer having an electron withdrawing group such as cyano, carbonyl, and

alkoxycarbonyl group (Eq. 2). The electron withdrawing substituent can stabilize the anionic intermediate to accelerate the anionic polymerization. Thus the high selectivity of ionic polymerization attributes to the stringent requirements for stabilizing the cationic and anionic propagating species. Unlike the ionic polymerization, the radical polymerization is started by radical species which is formed by addition of a radical to a monomer molecular as shown in Eq. 3. Radical intermediates are neutral and do not have strict requirements for stabilization of the propagating species.



Scheme 1.3 Ionic Polymerization and Radical Polymerization^{21,22}

Comparing cationic, anionic and radical polymerizations (Table 1.2), it is clearly shown that the polymerization conditions and behaviors are quite different.^{21,22}

Table 1.2 Comparison among Cationic Polymerization, Anionic Polymerization and Radical Polymerization^{21,22}

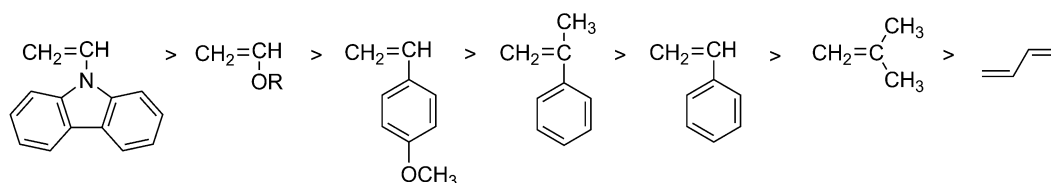
Factor	Cationic	Anionic	Radical
Propagating species	Cationic ion pair	Anionic ion pair	Radical ion pair
Impurity sensitivity	Large	Large	Small
Solvent	Prefer polar solvent	Aliphatic/aromatic hydrocarbon and ether	Nonpolar solvent
Halogenated solvent	Yes	No ^a	Yes
Living polymerization	Seldom	Most	Small

^a Facile nucleophilic substitution.

1.1.3 Monomers for Cationic Polymerization

The scope of monomer for cationic polymerization is separated into two main types,

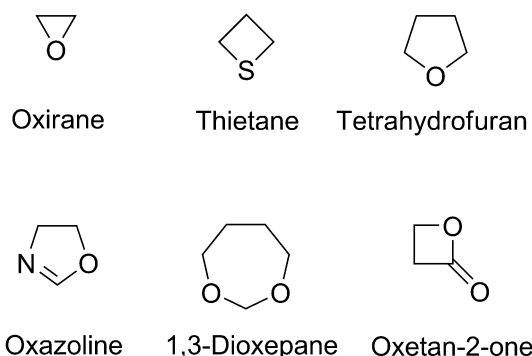
as mentioned before (Scheme 1.1): olefins and heterocyclic monomers. The cationic polymerizations of olefins proceed by nucleophilic addition of the monomer to a growing chain carbocation. The monomers for cationic polymerization contain electron-donating substituents. Because these electron-donating groups make the olefins nucleophilic enough to be conducted by electrophilic initiators and stabilize the growing chain carbocations. Some reactive vinyl monomers are listed in Scheme 1.4 in order of decreasing of reactivity, which corresponds to the electron donating ability of substituents.²³



Scheme 1.4 Reactivity Order of Olefin Monomers.²³

Olefins with heteroatoms are more reactive than that with aryl or alkyl groups because of their higher nucleophilicity which caused resonance stabilization of vinyl group. *N*-Vinyl carbazole is more reactive than vinyl ethers due to the higher nucleophilicity of nitrogen. However, contrary to the reactivity of monomers shown above, the reactivity of growing carbenium ions is opposite.

Heterocyclic monomers including lactones, lactams, and cyclic amines (Scheme 1.5) are cationically polymerized by nucleophilic attack of a cationic initiator or growing ion to a monomer. Most of cyclic monomers are only polymerized cationically. Some heterocyclic monomers (for example oxirane, oxetan-2-one) can be used both in cationic and anionic polymerization. For the homologous series of ring monomers, the general reactivity order of the ring size is $3 > 4 > 8-11 > 7 > 5 > 6$.¹⁵ The increase of propagation rate corresponds to the increase of ring strain for the homologous series of heterocycles. Six membered rings generally can not be used as monomers for cationic polymerization due to its low ring-strain.

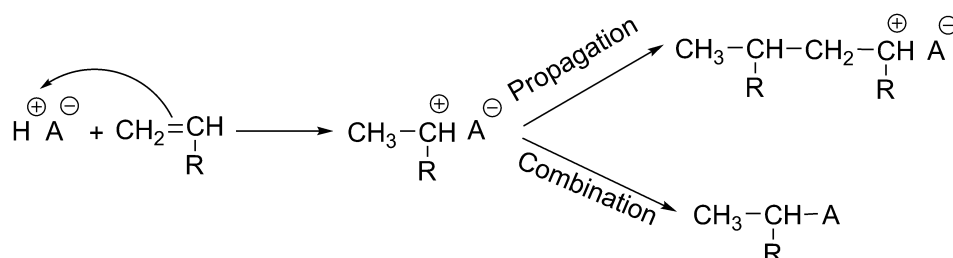


Scheme 1.5 Examples of Heterocyclic Monomers.

1.1.4 Conventional Catalysts for Cationic Polymerization

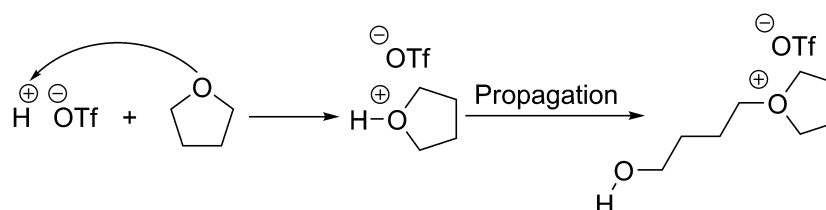
The first step in cationic polymerization is called “initiation”. The initiators induce a monomer to generate a carbenium ion. During polymerization, the counterion should be non-nucleophilic, so that the polymerization proceeds smoothly. Otherwise, the strong interaction between counterion and carbenium ion causes termination.²⁴ Kennedy firstly described the initiation step of cationic polymerization in detail.²⁵ The absolutely purified, dry isobutene (IB) failed to polymerize when dry Ziegler-Natta related catalyst, Et_2AlCl , was used. However, the polymerization ensued upon the introduction of a small amount of water or a Brønsted acid, HCl . It was postulated that the polymerization was initiated by the protons derived from water or acid. Surprisingly, when using *tert*-butyl chloride as an initiator, the polymerization also occurred. *tert*-Butyl chloride is regarded as the adduct of IB with HCl . In this case, the abstraction chloride atom from *tert*-butyl chloride by Et_2AlCl produced a stable carbocation which further conducted cationic polymerization. Hence, *tert*-butyl chloride is called a cationogen. This indicated that the proton donors and cationogenic compounds are the real initiators.

A wide variety of available initiators have been developed for cationic polymerization. Strong protonic acids (Brønsted) can form initiating species. Common mineral acids are perchloric, phosphoric, sulfuric, triflic, and trifluoroacetic acids (HClO_4 , H_3PO_4 , $\text{CF}_3\text{SO}_3\text{H}$ (HOTf) and CF_3COOH). The counterion (A^-) should be weakly nucleophilic enough to avoid termination caused by recombination with the protonated vinyl monomer (Scheme 1.6).^{26,27}



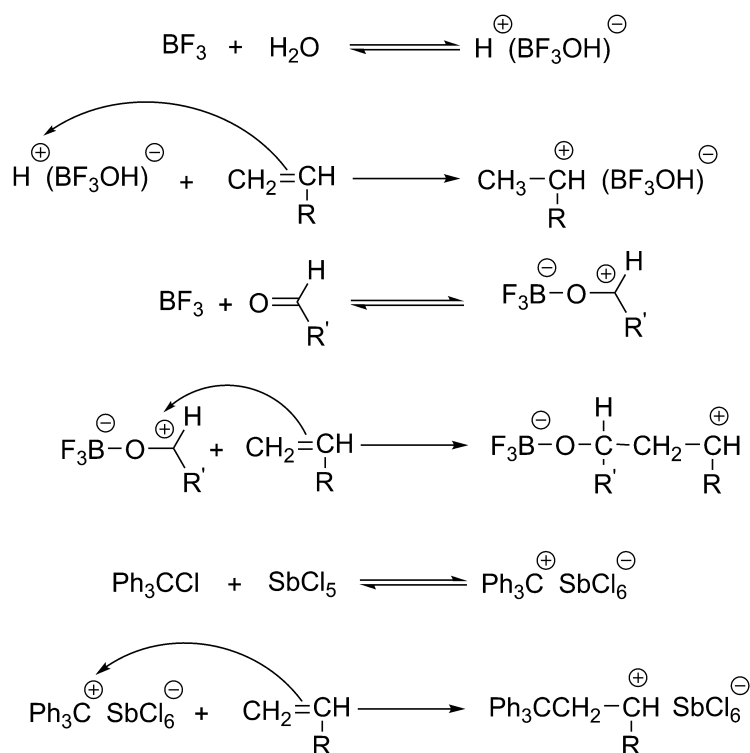
Scheme 1.6 Initiation by Brønsted Acid.^{26,27}

Cationic ring-opening polymerization follows the similar initiation mechanism as polymerization of vinyl monomers. Strong mineral acids are also common catalysts such as HOTf, HClO_4 , fuming sulfuric acid and heteropolyacids (Scheme 1.7).^{23,28}



Scheme 1.7 Cationic Ring Opening Polymerization.^{23,28}

The most common compounds used for initiation of cationic polymerization are Lewis acids (Friedel-Crafts catalysts). Most Friedel-Crafts catalysts (SnCl_4 , AlCl_3 , BF_3 , TiCl_4 , et al.) can serve as catalysts (coinitiator) for cationic polymerization.²⁹ In fact, during the initiation reaction, in the “super dry” conditions, most Lewis acids are not capable to conduct polymerization.²⁶ Various cation sources, from proton donor such as water or alcohol to a carbocation donor such as an aldehyde, an ester, an anhydride or an haloalkane, are employed as an initiator (Scheme 1.8).^{30–32} For example, the reaction of Lewis acid and aldehyde produces zwitterionic species as an active species and initiates polymerization. Trityl and trimethylsilyl cations are common carbenium ions.^{33,34} In these initiating systems, Lewis acids are also used as coinitiator to activate the cation source, then to generate cationogen. An intermediate complex formed by the reaction of the initiator with the coinitiator goes on to react with the monomer unit.



Scheme 1.8 Initiation by Lewis Acids.^{30–32}

1.1.5 Industrial Cationic Polymerization

A number of important commercial polymers are produced by cationic polymerization. The vinyl and ring-opening cationic methods enable the synthesis of polymers with novel structures that are utilized in a wide scope of commercial applications.^{20,34,35} Industrial polymers prepared by cationic ring-opening polymerization include poly(tetrahydrofuran), poly(epichlorohydrin), poly(oxymethylene), poly(ethylene imine) and others. For example, poly(tetrahydrofuran) is an important raw material to produce spandex fibers for ski boots and swimsuits. Poly(epichlorohydrin) is used in

production of hoses, air ducts and other rubber products.

Industrial polymers obtained by cationic polymerization of alkene based monomers include such as poly(vinyl ether)s and poly(*N*-vinyl carbazole). Among these polymers, poly(isobutylene) and its copolymer with isoprene (butyl rubber) are well known to be important commercial polymers in the industry. Poly(styrene)s can also be obtained by cationic polymerization, although they are usually produced radically. For example, poly(styrene)s with low molecular weight obtained by cationic polymerization are used as a raw material for disc jackets and videocassettes. In Table 1.3, some commercial products produced by cationic polymerization are listed.^{35,36}

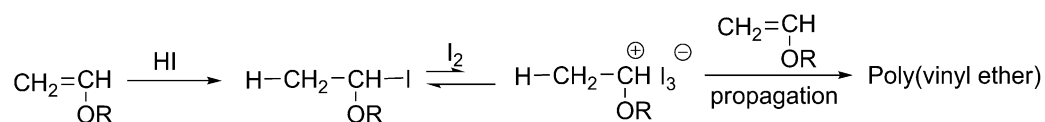
Table 1.3 Commercial Polymers via Cationic Polymerization^{35,36}

Monomer	Polymer name	Trade name
$\text{CH}_2=\underset{\text{OCH}_3}{\text{CH}}$	Polyvinyl methyl ether	Lutonal M 40
$\text{CH}_2=\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}$	Polyisobutylene	Vistanox, Oppanol
$\text{CH}_2=\underset{\text{C}_6\text{H}_5}{\text{CH}}$	Polystyrene	Styrofoam
$\text{Cl}-\text{CH}_2-\text{C}_2\text{H}_3\text{O}$	Polyepichlorohydrin	Hydrin Rubber
$\text{C}_4\text{H}_8\text{O}$	Polytetrahydrofuran	Lycra, Spandex

1.2 Living Cationic Polymerization of Vinyl Monomers

1.2.1 Background of Living Cationic Polymerization

Controlled/living polymerization is very important both in academia and industry because of its significant advantages, narrow molecular weight distribution, predetermined molar mass and controllable polymer chain ends. It is a useful method to synthesize well-defined polymers and induce functional chain end groups. In 1984, Higashimura and coworkers firstly reported living polymerization using isobutyl vinyl ether as a monomer and hydrogen iodide-iodine as an initiating system.^{11,12} This ideal living polymerization of alkyl VE was observed in hexane at -15°C (Scheme 1.9).

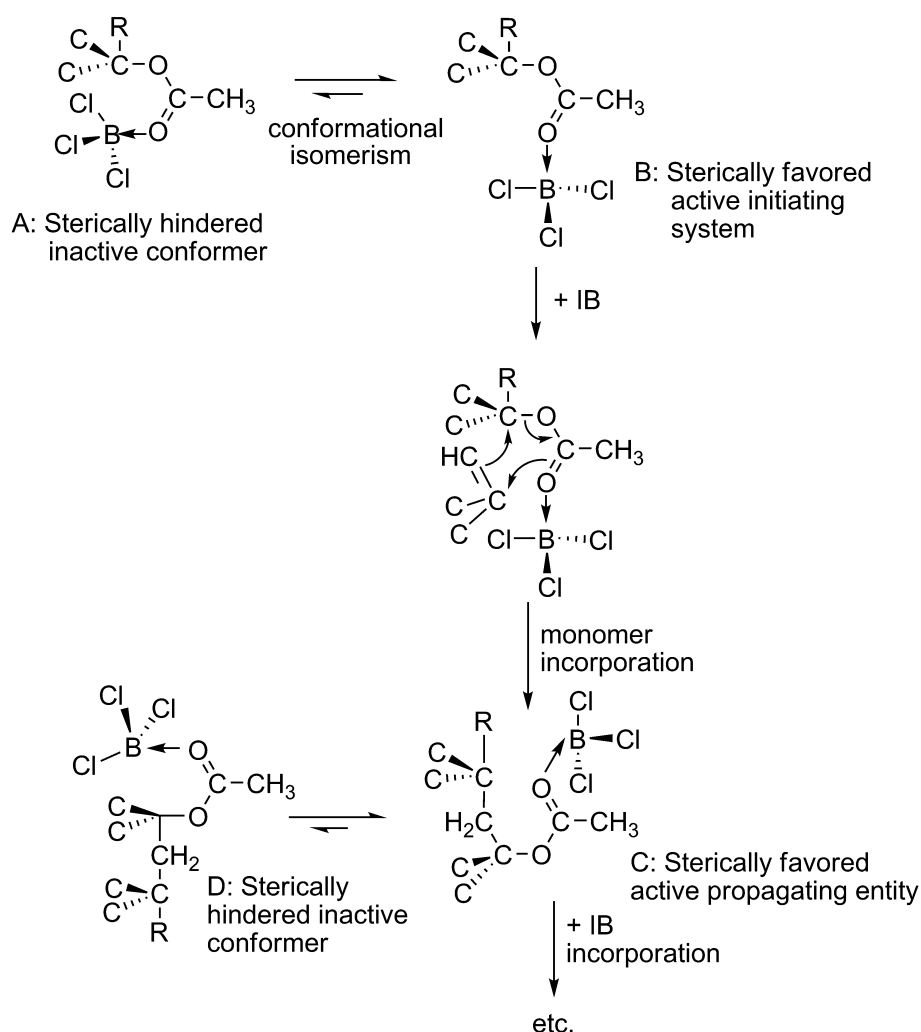


Scheme 1.9 Living Polymerization of Vinyl Ethers.^{11,12}

Subsequently, living polymerization of isobutene was observed by Kennedy and Faust.^{13,14} Living polymerization of isobutylene was achieved by the organic

acetate/ BCl_3 initiating system under conventional conditions at low reaction temperature (from -10 to -50 $^{\circ}\text{C}$). Various esters (cumyl acetate, 2,4,4-trimethylpentyl acetate, *t*-butyl acetate) were used as initiators and BCl_3 was employed as coinitiator. The ester/ BCl_3 complexes induced living polymerization in CH_2Cl_2 /hexane mixed solvent. A counteranion generated by suitable coordination of ester to BCl_3 obviously suppressed chain transfer reaction. The authors proposed the mechanism which well explained the features of living cationic polymerization of isobutylene (Scheme 1.10).¹⁴

After the above two main breakthroughs, numerous studies for living polymerization were performed and various initiating systems were extensively developed for well-defined polymer.^{5,36,37}



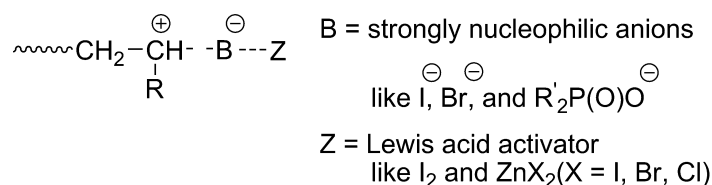
Scheme 1.10 Living Polymerization of Isobutylene.¹⁴

1.2.2 Design of Living Cationic Polymerization

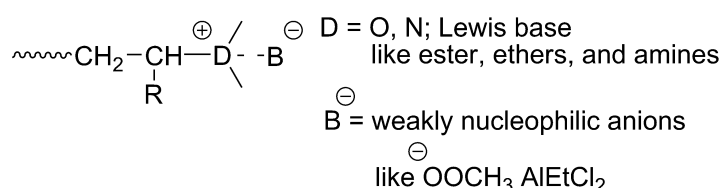
The synthesis of controlled polymer architectures can fulfill the requirements in polymer science and technology. Various initiating systems from Friedel-Crafts catalysts to Lewis acid-free catalysts were extensively developed for different

controlled polymerizations.³⁷⁻⁴⁰ The design of living initiating systems is based on nucleophilic stabilization of the inherently unstable growing carbocations. There are two main stabilization methods: by suitable counteranion or by added Lewis base (Scheme 1.11).⁴¹

Method I: Carboction stabilization by counteranions



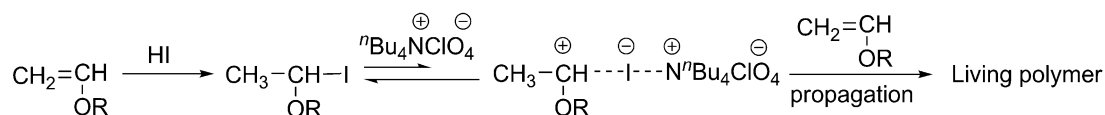
Method II: Carbocation stabilization with added Lewis base



Scheme 1.11 Design of Initiating Systems.⁴¹

In Method I, Lewis acids coordinate the anions to generate the transition species, which conduct living propagation (Scheme 1.11).⁴¹ As shown in Scheme 1.9, the first cationic living polymerization reported by Higashimura and coworkers was initiated by HI/I_2 .^{11,12} The initiator HI firstly adds to the vinyl group of monomer to produce an adduct. The vinyl ether-hydrogen halide adduct is subsequently activated by Lewis acid, I_2 , making I_3^- to induce the living propagation.

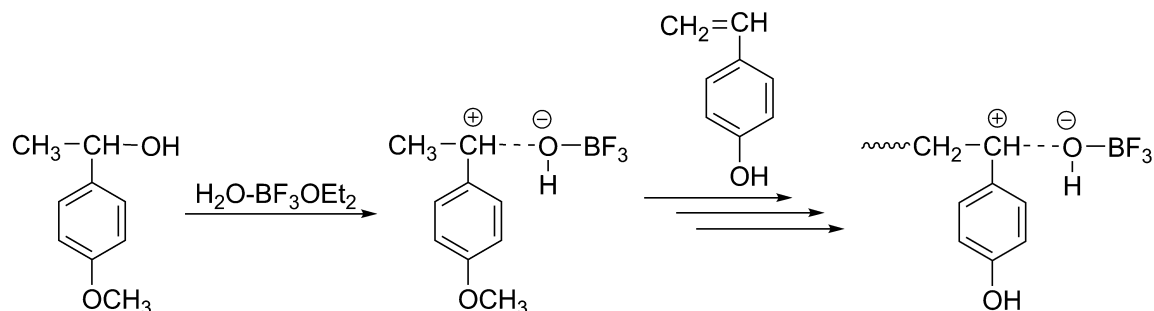
Ammonium salt with a noncoordinating anion can also replace I_2 to interact the iodide anion of the vinyl ether-hydrogen iodide adduct, then, to generate the active intermediates, which lead to the living cationic polymerization (Scheme 1.12).⁴² The mechanism is similar to those for the systems using HI/I_2 . Importantly, these results indicate that the ammonium salt is effective as I_2 in the nucleophilic stabilization of the growing carbocations.



Scheme 1.12 Living Polymerization of Vinyl Ether by HI /Ammonium Salt Initiating System.⁴²

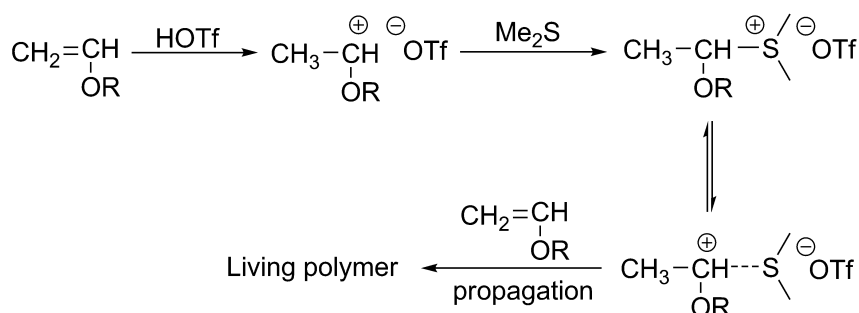
The living polymerization of styrene was achieved by an initiating system based on alcohol and BF_3OEt_2 in the presence of water.^{43,44} For example, the controlled cationic polymerization of *p*-hydroxystyrene was obtained with an alcohol as an initiator that was produced by addition of water and BF_3OEt_2 to *p*-methoxystyrene in the mixed solvent of CH_3CN and CH_2Cl_2 (Scheme 1.13).⁴⁴ It is surprising that the ionic

polymerization proceeded even in the presence of water to afford polymers with narrow MWDs and the M_n increased in proportion of monomer conversion.



Scheme 1.13 Living Polymerization of Styrene by R-OH/H₂O-BF₃OEt₂ Initiating System.⁴⁴

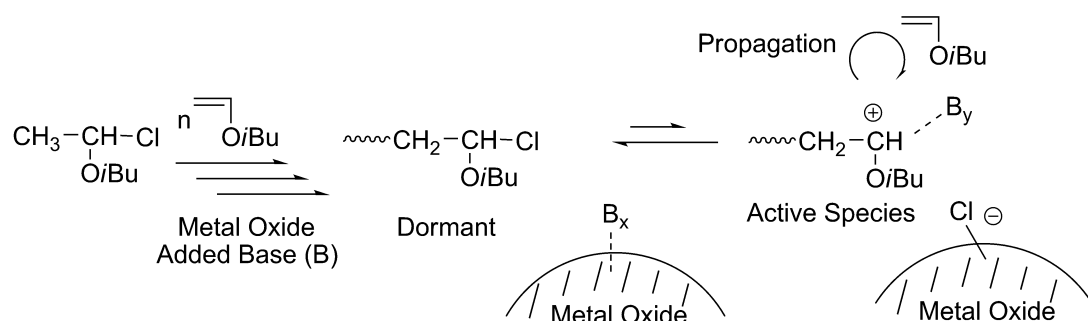
In Method II (Scheme 1.11), Lewis bases are employed to stabilize the growing carbocations by coordination.⁴¹ A wide variety of added bases, such as ether, bulky amine and sulfide, are well developed in cationic polymerization.^{32,34,41,45} For example, the cationic polymerization of vinyl ether initiated by triflic acid (HOTf) was vigorous and uncontrolled, but, when dialkyl sulfides were employed as added base, the polymerization proceeds in a living manner.⁴⁵ As shown in Scheme 1.14, in the presence of Me₂S, the formation of sulfonium ions suppressed side reactions to afford living polymers.



Scheme 1.14 Living Polymerization of Vinyl Ether by HOTf/Dialkyl Sulfide Initiating System.⁴⁵

It is well-known that most Friedel–Crafts catalysts can be used for cationic polymerization.⁵ The addition of appropriate added base to the reaction mixture initiated by Friedel–Crafts catalysts tends to lead into a living polymerization, yielding polymers with well-defined structures. Lewis acids with strong acidity induce rapid and uncontrolled polymerization. The coordination of added base to growing carbocations causes an equilibrium between dormant and active species, which can suppress the side reactions and lead to controlled polymerization. For example, although metal oxide polymerized IBVE uncontrolled, the addition of weak Lewis bases resulted in an increase of livingness. The propagating carbocation is

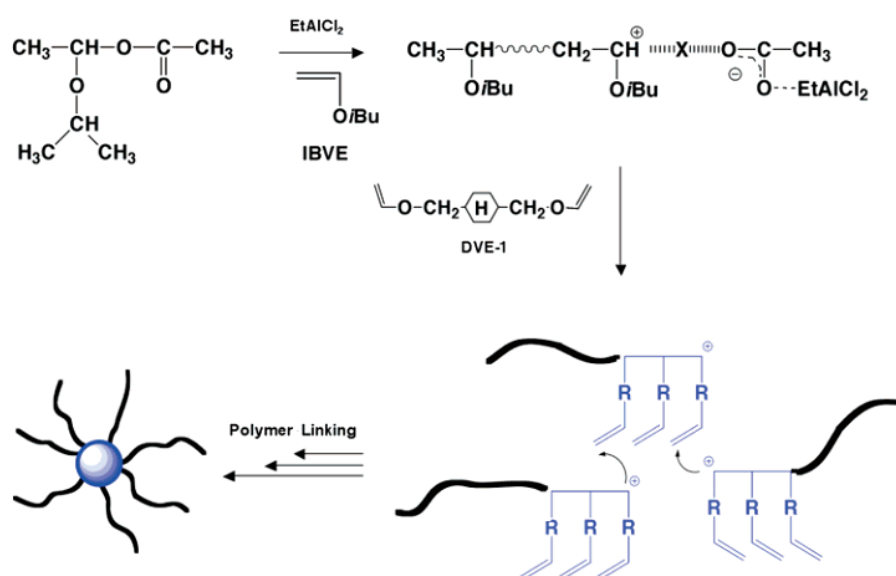
produced by the abstraction of chloride anion by metal oxide. A weak Lewis base is responsible for the production of the long-lived species by stabilizing the carbocation (Scheme 1.15).⁴⁶



Scheme 1.15 Living Polymerization of IBVE by Metal Oxide/Weak Lewis Base Initiating System.⁴⁶

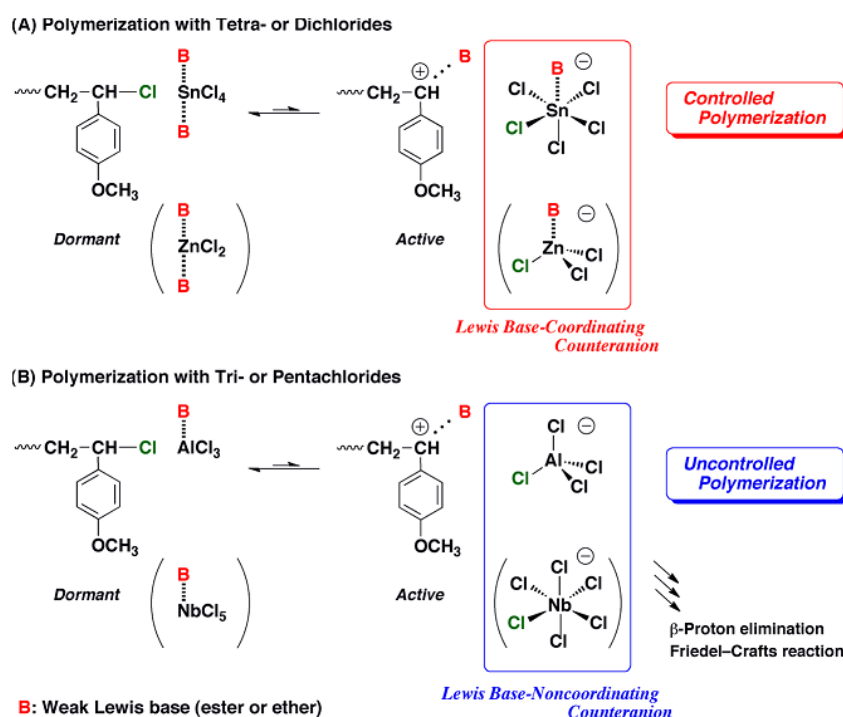
1.2.3 Application of Living Cationic Polymerization

Living cationic polymerization is useful to synthesize a wide variety of homo-, block-, graft-, star- shaped and functional polymers. The first preparation of block copolymer with a narrow MWD was reported in 1984.¹⁶ For example, CVE (cetyl vinyl ether) - MVE (methyl vinyl ether) blocks were first synthesized by blocking from living poly(CVE) with HI/I_2 initiating system. The resulting polymers had narrow MWDs and shifted toward higher M_n s. Since this successful synthesis of diblock copolymer, various functional polymers were obtained.^{5,17,37} Recently, Aoshima's group reported that the star-shaped poly(VE)s with narrow MWDs were quantitatively synthesized by living cationic polymerization with EtAlCl_2 in the presence of added base (Scheme 1.16).²



Scheme 1.16 Synthesis of Star-shaped Polymers by Living Cationic Polymerization.²

Living cationic polymerization systems can be used to reveal the catalytic activities of metal halides.^{47,48} Because the polymerization rates and side reactions, which can be determined in a straightforward fashion, are mostly due to the nature of the central metal ion. For example, a variety of metal halides were employed as catalysts for the cationic polymerization of *p*-methoxystyrene and the results indicated the structural effects of the metal halides on the cationic polymerization behaviors. In the presence of a weak added base, metal tetrachlorides and dichloride like SnCl₄, TiCl₄, ZrCl₄, HfCl₄, and ZnCl₂ induced the living polymerization, resulting in polymer with narrow MWDs and predetermined *M_n*s. In contrast, metal trichlorides and pentachlorides like AlCl₃, FeCl₃, GaCl₃, NbCl₅, and TaCl₅ conducted polymerization in an uncontrolled manner, and frequent side reactions such as β-proton elimination or Friedel-Crafts reactions occurred, yielding polymers with broad MWDs. The results suggest that the differences of polymerization behaviors stem from the structures of the counteranions based on the nature of the metal halides (Scheme 1.17).⁴⁸



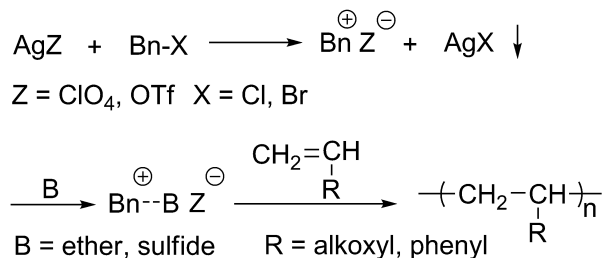
Scheme 1.17 Plausible Mechanisms for Cationic Polymerization of *p*MOS with Various Metal Chlorides.⁴⁸

1.3 Aim of This Work

Since the discovery of living cationic polymerization, a wide variety of Brønsted acids and Lewis acids have been used as catalysts in controlled/living cationic polymerization processes. As metal catalysts, various metal halides and metal oxides have been used as Lewis acid catalysts for many functional VEs and styrene derivatives. However, removal of the metal catalyst residue is generally a complicated process, which is a major limitation to their use. Therefore, a variety of metal-free

initiating systems have also been developed for living polymerization of active vinyl monomers, such as HI-I₂,¹¹ HI,⁴⁹ HI-tetraalkylammonium salt,⁴² CF₃SO₃H-sulfide,⁴⁵ HCl-aliphatic ether,⁵⁰ BF₃OEt₂-alcohol,²⁹ and CF₃SO₃H-tetrabutylammonium salt systems.⁴⁰ However, these strong Brønsted acids may cause equipment corrosion and require the use of complicated procedures because of their toxicity and/or instability. Increasing concern about environmental problems in recent years has fueled the drive toward the development of new, more environmentally friendly catalysts for the cationic polymerization.

In this regard, this study aims to develop a new, facile and eco-friendly initiation system for cationic polymerization. The benzyl cation is selected as an initiator because of its stability and eco-friendliness. The benzyl cation is readily formed by the reaction between an aryl methyl halide and a silver salt, and the reaction product, AgX, readily precipitates and is easily removed by filtration (Scheme 1.1). Among various cationically polymerizable compounds, vinyl ethers and styrene derivatives are employed as monomers. In order to establish the optimum conditions for use, IBVE is selected as the first monomer, and we evaluate the effects of the type of added base, order of addition of the reagents, and types of silver salts on the polymerization reaction. Based on the results, other vinyl ethers (ethyl vinyl ether and isopropyl vinyl ether) and styrene derivatives (such as styrene, methoxystyrene and alkoxyethyl styrene) are investigated for cationic polymerization. The copolymerization of vinyl ethers is also studied.



Scheme 1.1 Strategy of a Benign Metal-Free Cationic Polymerization System.

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Chapter 2 Synthesis of Living Poly(vinyl ether)s and Block Copolymers by the Silver Salt / Aryl Methyl Halide /Lewis Base Initiating System

2.1 Introduction

Cationic polymerizations are not only commercially important processes for producing numerous types of materials but are also academically interesting methods for preparing polymers and copolymers using certain monomers such as vinyl ethers (VEs).¹⁻⁶ Since the inception of living cationic polymerization of vinyl ethers in the 1980s,⁷ a wide variety of Brønsted acids and Lewis acids have been used as catalysts in various controlled/living cationic polymerization processes. Various metal catalysts including metal halides (SnCl_4 , ZnI_2 , EtAlCl_2 , etc.) and metal oxides (Fe_2O_3 , ZnO , Ga_2O_3 , etc.) have been used as Lewis acid catalysts for cationic polymerization of a variety of VEs.⁸⁻¹² However, removal of the metal catalyst residue is generally a complicated process, which is a major limitation to their use. Therefore, various metal-free initiating systems have been developed for living polymerization of vinyl ethers and active vinyl monomers, such as HI-I_2 ,⁷ HI ,¹³ $\text{HI-tetraalkylammonium salt}$,¹⁴ $\text{CF}_3\text{SO}_3\text{H-sulfide}$,¹⁵ $\text{HCl-aliphatic ether}$,¹⁶ $\text{BF}_3\cdot\text{OEt}_2\text{-alcohol}$,¹⁷ and $\text{CF}_3\text{SO}_3\text{H-tetrabutylammonium salt}$ ¹⁸ systems. However, these strong Brønsted acids may cause equipment corrosion and require the use of complicated procedures because of their toxicity and/or instability.

Increasing concern about environmental problems in recent years has fueled the drive toward the development of new, more environmentally friendly catalysts for the cationic polymerization of VEs. With the objective to develop a cationic polymerization system that is simple as well as ecofriendly for this purpose, we selected the benzyl cation as an initiator. The benzyl cation is readily formed by the reaction between an aryl methyl halide (Ph(R)CHX ; $\text{R} = \text{H}$ or Ph) and a silver salt, and AgX readily precipitates and is easily removed by filtration.

Previous studies using benzyl cations as initiators conducted by Praill¹⁹ and Matyjaszewski and Sigwalt²⁰ suggested that it is necessary to control the reactivity of the benzyl cation. In order to establish the best system for use, we evaluate herein the effects of the types of added bases, addition order of the reagents, and types of silver salts on the polymerization reaction. Vinyl ethers (IBVE, EVE, IPVE) are selected as the monomers, and are known to be active monomers for cationic polymerization.²¹⁻²³

The versatile polymers, poly(VE)s, may be used in various applications by exploiting their high polarizability and the flexibility of their side chains.^{1,24-27} The copolymerization of VEs is also studied.

2.2 Experimental

2.2.1 Materials

All commercially available chemicals were used as received unless otherwise specified. Isobutyl vinyl ether (IBVE, Aldrich), ethyl vinyl ether (EVE) and

isopropyl vinyl ether (IPVE) were distilled over sodium before use. All ethers (diethyl ether (Et_2O , Wako), diisopropyl ether ($i\text{Pr}_2\text{O}$, Kanto), cyclopentyl methyl ether (CPME, kindly supplied from Zeon), tetrahydrofuran (THF, Kanto) and dioxane (DO, Wako)), dimethyl sulfide (Me_2S , TCI), diethyl sulfide (Et_2S , TCI) and toluene (Kanto) were distilled over sodium. *N,N*-Diisopropylethylamine ($i\text{Pr}_2\text{NEt}$, Wako) was distilled from sodium hydroxide. Ethyl acetate (AcOEt , Wako) and dichloromethane (CH_2Cl_2 , Wako) were distilled from calcium hydride. Benzyl bromide (BnBr, Wako) and benzyl chloride (BnCl, Kanto) were purified by distillation under reduced pressure. Silver perchlorate (AgClO_4 , Wako), silver triflate (AgOTf , Wako), silver nitrate (AgNO_3 , Kanto), silver sulfate (Ag_2SO_4 , Wako), and silver acetate (AgOAc , Wako) were vacuum dried before use.

2.2.2 Polymerization

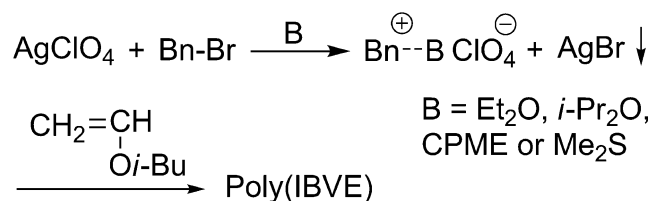
The following is a typical polymerization procedure. A solution of BnBr (0.025 mmol) in Et_2O was added to a solution of AgClO_4 (0.028 mmol) in Et_2O (0.5 mL) in a round-bottomed flask at 0 °C under nitrogen. After stirring for 10 min at this temperature, the mixture was cooled to the given reaction temperature. The polymerization was initiated by the addition of a prechilled mixture of IBVE (5.0 mmol) and Me_2S (0.75 mmol) in CH_2Cl_2 (4.0 mL). The reaction was quenched by adding methanol (5.0 mL) containing a small amount of aqueous ammonia (0.1 vol%). After adding CH_2Cl_2 (20 mL) to the quenched mixture, the solution was filtered to remove AgBr and washed with water, the organic phase was then separated and concentrated to obtain poly(IBVE). The monomer conversion was determined by gravimetry.

2.2.3 Characterization

^1H NMR spectra were recorded in CDCl_3 at 25 °C on a Bruker Avance-300 or Bruker Avance-500 spectrometer. The number-average molecular weight (M_n) and molecular weight distribution (MWD, M_w/M_n) of the polymers were measured by gel permeation chromatography (GPC) in THF at 40 °C with a Shodex GPC KF-806 L column (flow rate: 1.0 mL/min). The M_n was calibrated with polystyrene standards (TSK: $945\text{--}7.1 \times 10^5$, $M_w/M_n \leq 1.1$). MALDI-TOF-MS data were recorded on a Bruker Autoflex III Smartbeam MALDI-TOF mass spectrometer (linear/positive mode; voltage: 19 kV) using dithranol as a matrix and sodium trifluoroacetate as an ion source (polymer/matrix/ion source = 1 mg/8 mg/1 mg in 1 mL of THF).

2.3 Results and Discussion

2.3.1 Cationic Polymerization Initiated by AgClO₄/BnBr System



Scheme 2.1 Cationic Polymerization of IBVE.

Table 2.1 Screening of Added Base and Solvent Systems for Cationic Polymerization of IBVE Using the AgClO₄/BnBr Initiating System at 0 °C^a

Entry	Added base	Solvent	Time (min)	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	–	CH ₂ Cl ₂	5	2.7	5.63
2	Et ₂ O	CH ₂ Cl ₂	5	4.1	4.09
3	CPME	CH ₂ Cl ₂	5	3.7	4.40
4	<i>i</i> -Pr ₂ O	CH ₂ Cl ₂	5	3.7	4.83
5	Et ₂ O	Et ₂ O	5	4.0	3.02
6	Et ₂ O/Me ₂ S	CH ₂ Cl ₂	30	7.7	2.43

^a BnBr: 0.025 mmol, molar ratio: AgClO₄/BnBr/IBVE = 1.1/1.0/200, solvent: 4.0 mL, temp: 0 °C, addition order: AgClO₄, ether (0.5 mL), BnBr + ether (0.5 mL), IBVE + solvent (+ Me₂S 0.75 mmol), conversion = 100%.

^b By GPC (polystyrene calibration).

The synthesis of poly(IBVE) was initially performed in CH₂Cl₂ at 0 °C, initiated by the benzyl cation that is readily formed by the reaction of AgClO₄ and BnBr (Table 2.1, entry 1). The polymerization proceeded in an uncontrolled manner but reached quantitative conversion in 5 min. Benzyl perchlorate is expected to be highly reactive, possibly resulting in the alkylation of the aromatic rings, which is similar to the mechanism proposed by Matyjaszewski and Sigwalt for the self-alkylation reaction between 1-phenylethyl bromide and silver triflate.²⁰ In fact, when the initiation reaction (i.e., the mixture of AgClO₄ and BnBr in CH₂Cl₂) was quenched with prechilled water at 0 °C after 10 min, the resulting solution contained intractable products along with unreacted BnBr. The ¹H NMR profile shows peaks of complex aromatic (~ 7.5–7.0 ppm) and benzylic (~ 4.5 ppm and ~ 4.0–3.8 ppm) peaks (Figure 2.1), suggesting self-coupling as side reactions.

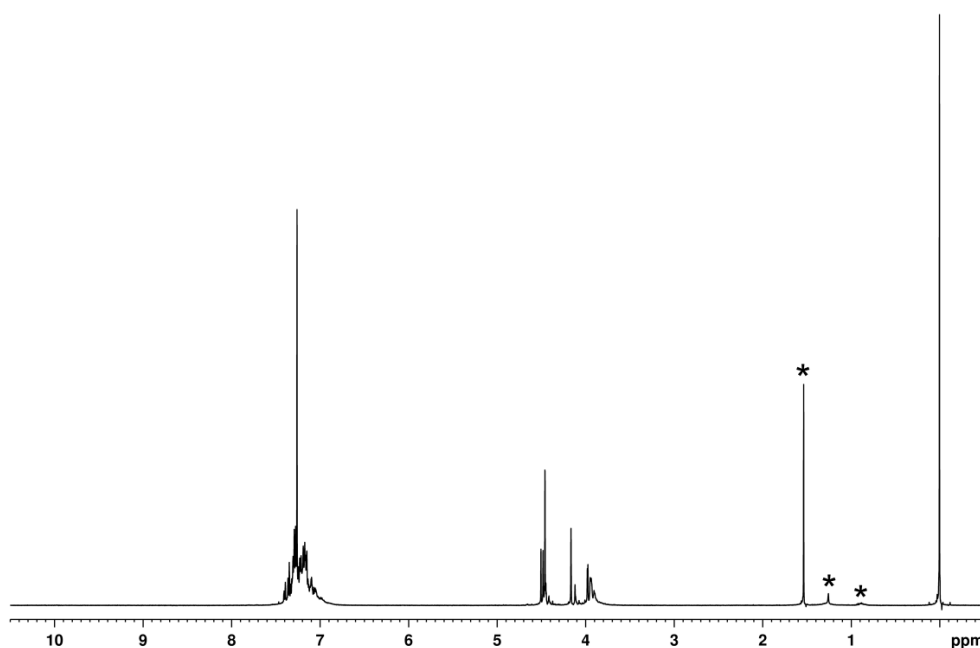


Figure 2.1 ^1H NMR spectrum of the product mixture obtained by the reaction of AgClO_4 and BnBr in CH_2Cl_2 in 10 min at $0\text{ }^\circ\text{C}$. BnBr : 0.25 mmol, molar ratio: $\text{AgClO}_4/\text{BnBr} = 1.1/1.0$, CH_2Cl_2 : 10 mL, quencher: prechilled water, purification: PTLC ($\text{EA/Hexane} = 1/10$), product mixture: 13.4 mg (slight yellow oil), *: water and Vaseline, recorded at $25\text{ }^\circ\text{C}$.

Thus, respective ethers were added that function as a Lewis base to stabilize the benzyl cation as well as the propagating carbocation of IBVE (Scheme 2.1, entries 2–4).^{28,29} These cationic polymerizations were also completed in 5 min and were uncontrolled, which resulted in products with low M_n values ($M_n \sim 4.0 \times 10^3$) and broad MWDs ($M_w/M_n \sim 4.1\text{--}4.8$). The ^1H NMR spectrum of the product revealed the presence of an internal $\text{C}=\text{C}$ bond and two kinds of chain-end structures, acetal and aldehyde, suggesting that side reactions occurred, such as side-chain abstraction (Figure 2.2).^{18,26,30} The MWD values of the polymers tended to decrease with an increase in the basicity of the ethers (Et_2O ($\text{p}K_a = -3.59$) > $i\text{Pr}_2\text{O}$ ($\text{p}K_a = -4.30$)). The result is consistent with previous observations that the propagating carbocation was strongly stabilized in the presence of more basic ethers.^{28,29} Another possible factor influencing the control of the propagation is the steric hindrance of the added bases (Et_2O , $i\text{Pr}_2\text{O}$, and CPME); $i\text{Pr}_2\text{O}$ and CPME respectively have bulky isopropyl and cyclopentyl groups that lead to weak interaction with the growing terminal cation, resulting in polymers with broad MWDs (Table 2.1, entries 3 and 4). Consequently, Et_2O was used in the ensuing evaluation.

Because Et_2O functions as a Lewis base, it was used as a reaction solvent at $0\text{ }^\circ\text{C}$, giving rise to a polymer with a low M_n and narrow MWD (Table 2.1, entry 5). Webster et al. used alkyl sulfides as added bases to control cation polymerization and enhance the ‘livingness’ of the polymerization.^{15,31} Herein, Me_2S was examined as a co-added base for the reaction system because it is less sterically hindered than Et_2O .

and the sulfur atom has higher nucleophilicity than oxygen. With a molar ratio of Me₂S:BnBr of 30:1, the reaction at 0 °C yielded polymers with higher *M_n* values and narrower MWDs than those obtained in the absence of Me₂S (Table 2.1, entry 6 vs. entry 2).

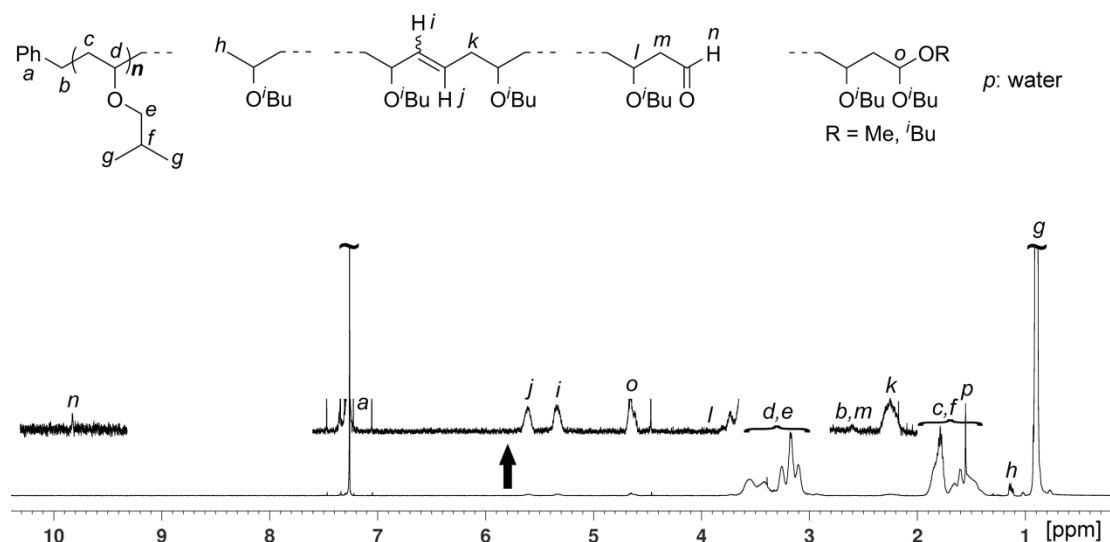
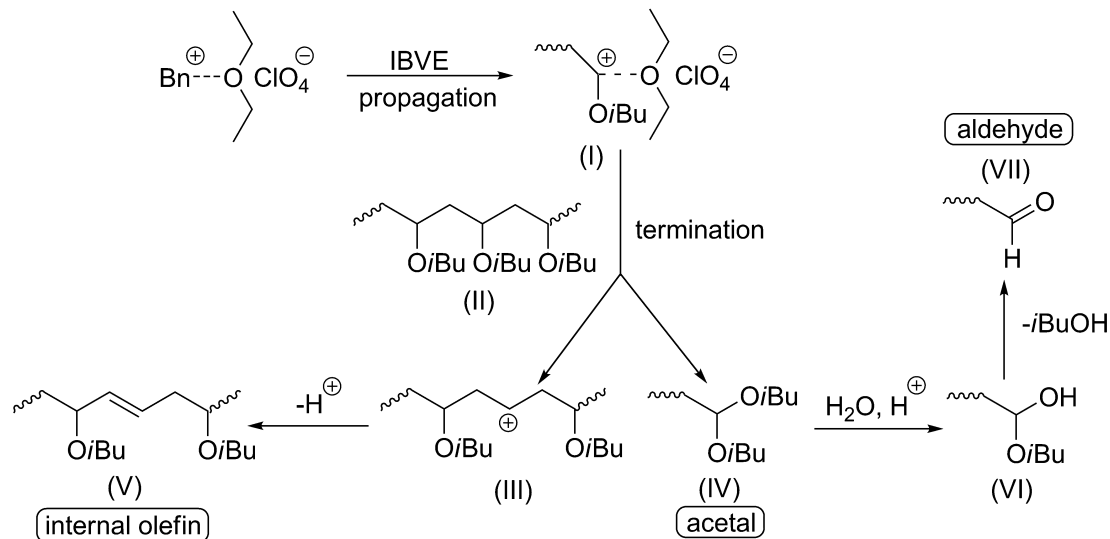


Figure 2.2 ¹H NMR spectrum of poly(IBVE) obtained using AgClO₄/BnBr initiating system in CH₂Cl₂ at 0 °C (Table 2.1, entry 2).



Scheme 2.2 Proposed Mechanism for the Cationic Polymerization of IBVE (Table 2.1, entry 2).

According to ¹H NMR, the possible detailed mechanism for side reaction during the cationic polymerization of IBVE at 0 °C is shown in Scheme 2.2. The polymerization is initiated by benzyl cationic, Bn⁺, generated by the reaction of AgClO₄ and BnBr. The growing carbocation (I) leads to the occurrence of abstraction of the isobutoxy group from the polymer chain (II) due to the weak coordination to added base, thus

generating an acetal end group (IV) and a mid-chain (internal) olefin group (V). A small amount of unstable acetal group further transforms into an aldehyde group by adventitious water from common quenching solvent (MeOH) (VII).

2.3.2 Effects of Solvent, Added Base, and Temperature on AgClO₄/BnX Initiating System

Table 2.2 Effects of Reaction Solvent, Added Base, and Temperature on the Cationic Polymerization Behavior of IBVE Using Various Benzyl Halide Initiators^a

Entry	Initiator	Solvent	Added base	Temp (°C)	Time (min)	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	BnBr	CH ₂ Cl ₂	Et ₂ O	−23	5	100	11.0	2.93
2	BnBr	CH ₂ Cl ₂	Et ₂ O	−41	30	—	—	—
3	BnBr	Et ₂ O	Et ₂ O	−23	5	—	—	—
4	BnBr	Et ₂ O	Et ₂ O	−23	30	100	13.5	2.46
5	BnBr	CH ₂ Cl ₂	Et ₂ O/Me ₂ S	−23	30	21	2.8	2.17
6	BnCl	CH ₂ Cl ₂	Et ₂ O/Me ₂ S	−23	60	5.4	—	—
7	BnCl ^c	CH ₂ Cl ₂	Et ₂ O/Me ₂ S	−23	60	100	7.6	2.29
8	Ph ₂ CHBr	Et ₂ O	Et ₂ O	−23	5	100	3.3	2.27
9	Ph ₂ CHBr	CH ₂ Cl ₂	Et ₂ O	−41	5	100	5.6	2.14
10	Ph ₂ CHBr	Et ₂ O	Et ₂ O	−41	5	100	13.1	1.34
11	Ph ₂ CHBr	CH ₂ Cl ₂	Et ₂ O/Me ₂ S	0	30	100	4.1	2.05
12	Ph ₂ CHBr	CH ₂ Cl ₂	Et ₂ O/Me ₂ S	−23	30	100	15.6	1.37
13	Ph ₂ CHBr	CH ₂ Cl ₂	Et ₂ O/Me ₂ S	−41	30	—	—	—
14	Ph ₂ CHBr	toluene	Et ₂ O/Me ₂ S	−23	30	70	10.3	1.36

^a Initiator: 0.025 mmol, molar ratio: AgClO₄/initiator/IBVE = 1.1/1.0/200, solvent: 4.0 mL, addition order: AgClO₄, Et₂O (0.5mL), initiator + Et₂O (0.5 mL), 10 min at 0 °C, IBVE + solvent (+ Me₂S 0.75mmol).

^b By GPC (polystyrene calibration).

^c Addition order: AgClO₄, Et₂O (0.5 mL), initiator + Et₂O (0.5 mL), 2 h at 25 °C, IBVE + solvent + Me₂S (0.75 mmol).

In order to further control the reaction, the effects of the reaction solvent, added base, and temperature were investigated and are summarized in Table 2.2. Lowering the temperature from 0 °C to −23 °C induced a noticeable increase in M_n (from 4.1 to 11.0×10^3) and a narrower MWD (from 4.09 to 2.93) (Table 2.2, entry 1) was obtained (cf. Table 2.1, entry 2). At −41°C, however, no polymerization occurred within 30 min (entry 2).

When Et₂O was used as a solvent, no polymerization was observed within the first 5 min at −23 °C but the reaction reached completion in 30 min (entries 3 and 4), which suggested that an induction period was necessary at −23 °C. The obtained polymers (entry 4) had higher M_n values and narrower MWDs than achieved with the use of CH₂Cl₂ (entry 1). These results indicate that the interaction between Et₂O and the benzyl cation became influential, which may account for the required induction time.

On the other hand, when Me₂S was used as an added base at –23 °C, the extent of polymerization decreased greatly, and only 21% conversion was achieved in 30 min (entry 5). More effective or stronger coordination between the carbocation and Me₂S is obvious.

The replacement of BnBr (entry 5) with BnCl (entry 6) decreased the conversion significantly to 5% under similar conditions. The lower reactivity may be due to the lower leaving ability of Cl[–] than Br[–]. In order to increase the concentration of the benzyl cation and its reactivity, the initiation reaction temperature was raised to 25 °C and the reaction time was extended to 2 h for BnCl (entry 7), resulting in effective polymerization, $M_n = 7.6 \times 10^3$ and MWD = 2.29.

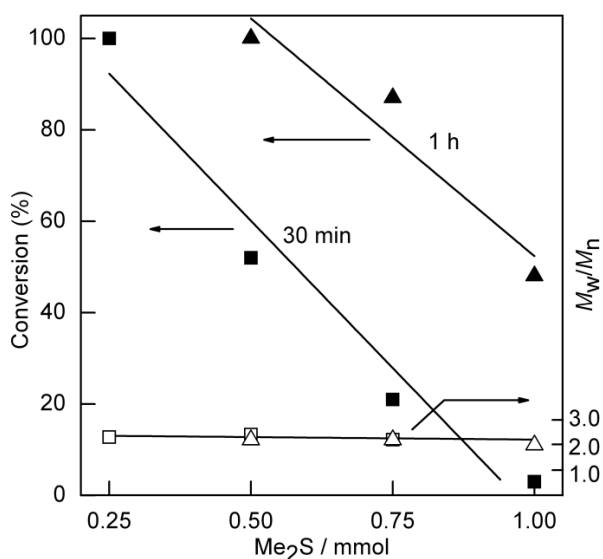


Figure 2.3 The amount of Me₂S-conversion plots for polymerization of IBVE using AgClO₄/BnBr in mixed solvent of CH₂Cl₂ (4.0 mL) and Et₂O (1.0 mL) at –23 °C. BnBr: 0.025 mmol, AgClO₄/BnBr/IBVE = 1.1/1.0/200 (Table 2.3).

The influence of the amount of Me₂S on the extent of polymerization was also investigated at –23 °C over respective periods of 30 and 60 min (Figure 2.3, Table 2.3). Increasing the amount of Me₂S (from 0.25 to 1.0 mmol) noticeably lowered the reaction rate (from 100% to 3% conversion in 30 min) and led to a decrease of M_n in direct proportion to the monomer conversion, while the MWD values were not significantly affected and remained in the range of 2.0–2.4.

Table 2.3 Effects of the Amount of Me₂S on Conversion and Molecular Weight in 30 min and 60 min^a

Entry	Initiator	Time	Me ₂ S (mmol)	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	BnBr	30 min	0.25	100	4.4	2.28
2			0.50	52	4.7	2.40
3			0.75	21	2.8	2.17
4			1.0	3	—	—
5	BnBr	1 h	0.50	100	8.6	2.17
6			0.75	87	7.4	2.23
7			1.0	48	4.8	1.96

^aBnBr: 0.025 mmol, molar ratio: AgClO₄/BnBr/IBVE = 1.1/1.0/200, CH₂Cl₂: 4.0 mL, temp: -23 °C, addition order: AgClO₄, Et₂O (0.5 mL), BnBr + Et₂O (0.5 mL), IBVE + CH₂Cl₂ + Me₂S. ^bBy GPC (polystyrene calibration).

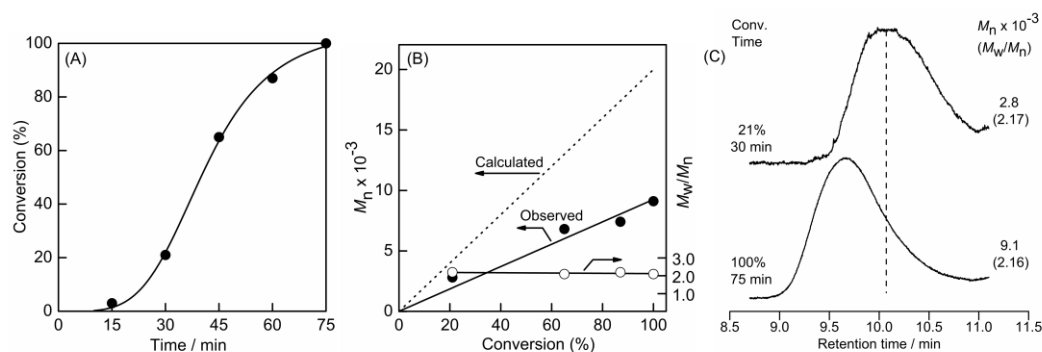


Figure 2.4 (A) Time-conversion curves, (B) relationship between conversion of IBVE and M_n or M_w/M_n of poly(IBVE) and (C) GPC curves for poly(IBVE) obtained using AgClO₄/BnBr initiating system in the presence of Me₂S (0.75 mmol) in mixed solvent of CH₂Cl₂ (4.0 mL) and Et₂O (1.0 mL) at -23 °C. BnBr: 0.025 mmol, molar ratio: AgClO₄/BnBr/IBVE = 1.1/1.0/200.

The time course of the cationic polymerization of IBVE by the AgClO₄/BnBr initiating system was investigated in the presence of Me₂S (Figure 2.4, Table 2.4). Figure 2.4(A) shows the time-conversion curves obtained with the use of a Me₂S:BnBr molar ratio of 30:1 at -23 °C. An induction period (about 10 min) was required and the polymerization was slowed down to reach quantitative conversion in 75 min. The observed induction period is considered to be related to the strong interaction between the benzyl cation and the added base, which is similar to the case of cationic IBVE polymerization using metal oxides in the presence of ethyl acetate or 1,4-dioxane.¹² Figure 2.4(B) shows the increase of M_n and M_w/M_n of poly(IBVE) as a function of monomer conversion. In the presence of Me₂S, M_n increased in direct proportion to the monomer conversion, but the M_n values were lower than the theoretical values and the MWDs were still broad ($M_w/M_n \sim 2.2$), indicating that the cationic polymerization was partially controlled. As shown in Figure 2.4(C), The GPC

curves of products clearly showed a shift to higher M_n .

Table 2.4 Effects of Reaction Time in the Cationic Polymerization of IBVE in the Presence of Me_2S ^a

Entry	Time (min)	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	15	3	–	–
2	30	21	2.8	2.17
3	45	65	6.8	2.14
4	60	87	7.4	2.23
5	75	100	9.1	2.16

^aBnBr: 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{BnBr}/\text{IBVE} = 1.1/1.0/200$, CH_2Cl_2 : 4.0 mL, temp: $-23\text{ }^\circ\text{C}$, addition order: AgClO_4 , Et_2O (0.5 mL), BnBr + Et_2O (0.5 mL), IBVE + Me_2S (0.75 mmol) + CH_2Cl_2 . ^bBy GPC (polystyrene calibration).

2.3.3 Cationic Polymerization by $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ Initiating System

In order to control the polymerization, the more stable benzyl cation, Ph_2CH^+ , was evaluated and the results are summarized in Table 2.2. Because of the electronic effect of an additional Ph group, Ph_2CHBr and Ag salt are expected to easily generate the Ph_2CH^+ cation, and this system resulted in a polymer with a low M_n and quantitative conversion within 5 min at $-23\text{ }^\circ\text{C}$ (entry 8 vs. entry 3). As shown in Table 2.2, the reaction employing the $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system at a lower temperature ($-41\text{ }^\circ\text{C}$) and the reaction using Et_2O as a solvent yielded polymers with higher M_n s, (up to 13.1×10^3) and narrower MWDs (2.14 and 1.34 for entries 9 and 10, respectively).

The effect of Me_2S was also studied using the Ph_2CH^+ initiating system; however, the reaction at $0\text{ }^\circ\text{C}$ proceeded in an uncontrolled manner (entry 11). Coordination between the carbocation and Me_2S became stronger and more effective at $-23\text{ }^\circ\text{C}$, resulting in a polymer with a high M_n of 15.6×10^3 and a narrow MWD of 1.37 (entry 12). The controlled reaction was confirmed by ^1H NMR analysis of the polymer (Figure 2.5), which showed no olefin peaks from β -proton elimination or side-chain abstraction, as suggested in Figure 2.2. Under similar conditions, however, no polymerization was achieved when the reaction temperature was further lowered to $-41\text{ }^\circ\text{C}$ (entry 13). Using toluene as the solvent, good conversion (70%) was achieved to yield a polymer with a narrow MWD in 30 min in the presence of Me_2S at $-23\text{ }^\circ\text{C}$ (entry 14).

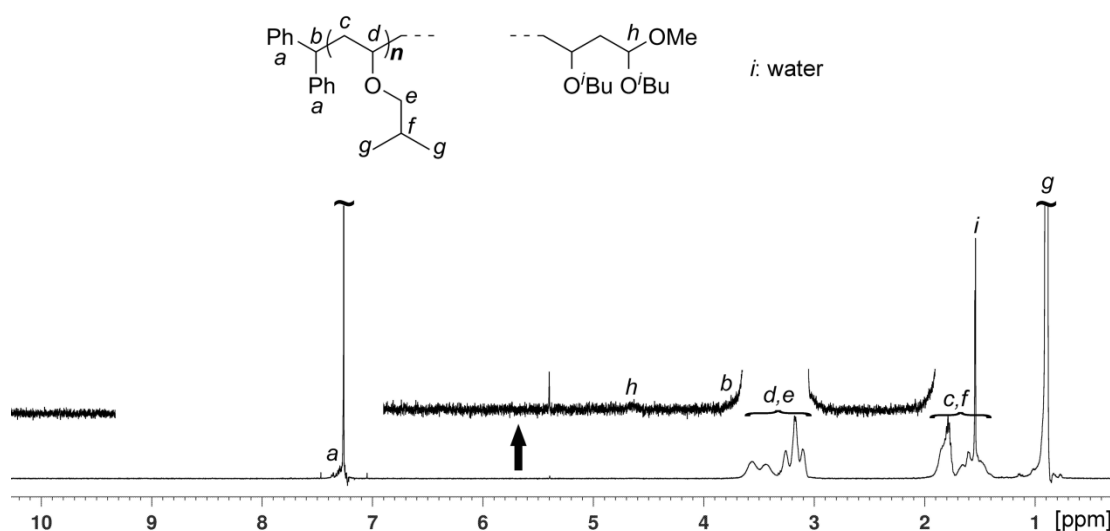


Figure 2.5 ^1H NMR spectrum of poly(IBVE) obtained using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in CH_2Cl_2 at $-23\text{ }^\circ\text{C}$ (Table 2.2, entry 12).

Table 2.5 Effects of Additive in the Cationic Polymerization of IBVE Using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ Initiating System^a

Entry	Additive	Temp ($^\circ\text{C}$)	Time (min)	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	None	-23	5	100	3.8	3.56
2	EA (20 vol%)	-23	5	100	6.6	3.22
3		-41	5	100	7.1	2.68
4	THF (20 vol%)	-23	5	100	6.0	2.99
5		-41	5	100	9.7	2.81
6	DO (20 vol%)	-23	5	100	5.1	2.89
7		-41	5	100	6.4	2.54
8	<i>i</i> -Pr ₂ NEt (0.75 mmol)	-23	30	—	—	—
9	<i>n</i> -Bu ₄ NBr (0.25 mmol)	-23	30	14	2.3	1.90

^aUnless otherwise noted, solvent: CH_2Cl_2 , Ph_2CHBr : 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{IBVE} = 1.1/1.0/200$, addition order: AgClO_4 , Et_2O (0.5 mL), $\text{Ph}_2\text{CHBr} + \text{Et}_2\text{O}$ (0.5 mL), IBVE + solvent (4.0 mL) + additive. ^bBy GPC(polystyrene calibration). EA = ethyl acetate, DO = dioxane.

Some oxygen containing solvents, which are also known to act as weak Lewis bases to control the cationic polymerization,^{12,32} were studied. However, the molecular weights and MWDs of the obtained poly(IBVE)s were uncontrolled ($M_w/M_n > 2.5$, Table 2.5, entries 2–7). Other additives (bulky Hünig's base and ammonium salt) were also examined,^{14,18,33} but no notable effect was observed (entries 8 and 9).

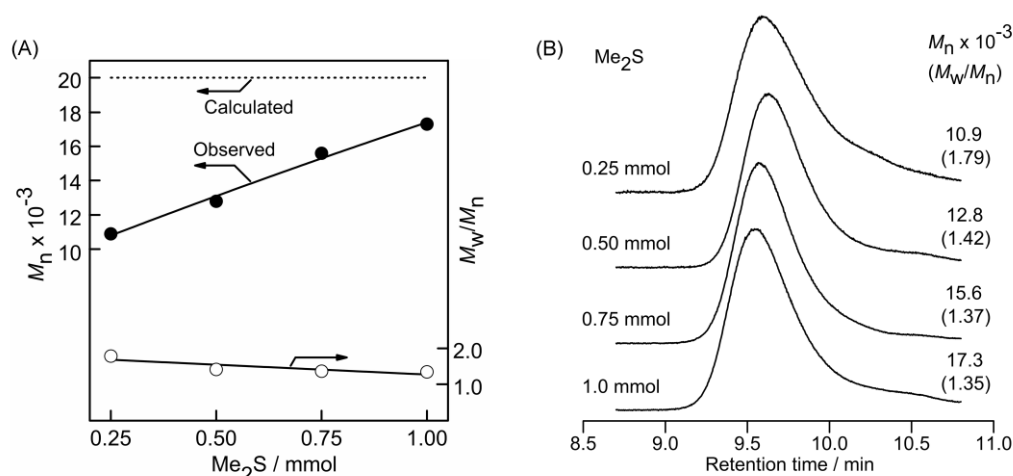


Figure 2.6 (A) Relationship between the amount of Me_2S and M_n or M_w/M_n and (B) GPC curves for poly(IBVE) obtained using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in mixed solvent of CH_2Cl_2 (4.0 mL) and Et_2O (1.0 mL) at -23°C . Ph_2CHBr : 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{IBVE} = 1.1/1.0/200$.

The above results indicate that changes in the reaction temperature, Lewis bases, and/or initiators strongly influence control of the polymerization reaction. The influence of the amount of Me_2S on the polymerization initiated by Ph_2CH^+ was also investigated at -23°C , as shown in Figure 2.6(A). As expected from Table 2.2, all reactions were completed in 30 min and, in contrast to PhCH_2^+ , increasing the amount of Me_2S favorably resulted in a significant increase of the M_n (from 11.0 to 17.0 $\times 10^3$) and a decrease of the MWD (from 1.79 to 1.35) (Table 2.6). The GPC curves of the products clearly showed a shift to higher M_n (Figure 2.6(B)).

Table 2.6 Effects of the Amount of Me_2S in the Cationic Polymerization of IBVE at -23°C in 30 min^a

Entry	Initiator	Added base	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	Ph_2CHBr	Et_2O , Me_2S 0.25 mmol	10.9	1.79
2		Et_2O , Me_2S 0.50 mmol	12.8	1.42
3		Et_2O , Me_2S 0.75 mmol	15.6	1.37
4		Et_2O , Me_2S 1.0 mmol	17.3	1.35

^a Ph_2CHBr : 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{IBVE} = 1.1/1.0/200$, CH_2Cl_2 : 4.0 mL, temp: -23°C , conversion: 100%, addition order: AgClO_4 , Et_2O (0.5 mL), Ph_2CHBr + Et_2O (0.5 mL), IBVE + CH_2Cl_2 + Me_2S . ^bBy GPC (polystyrene calibration).

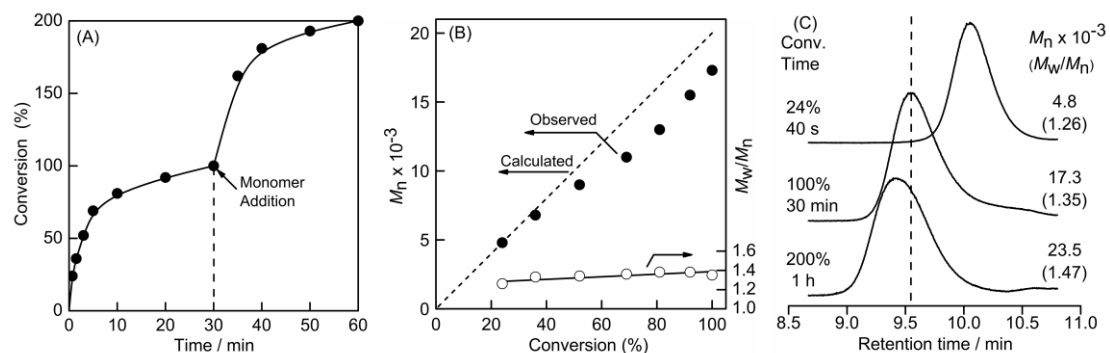


Figure 2.7 (A) Time-conversion curves, (B) relationship between conversion of IBVE and M_n or M_w/M_n , and (C) GPC curves for poly(IBVE) obtained using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in the presence of Me_2S (1.0 mmol) in mixed solvent of CH_2Cl_2 (4.0 mL) and Et_2O (1.0 mL) at -23°C . Ph_2CHBr : 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{IBVE} = 1.1/1.0/200$.

Considering the reduced MWD, the chain extension experiment was conducted to examine the living nature of the polymerization under the given conditions, and the results are shown in Figure 2.7 (Table 2.7). The first polymerization by $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ involved no induction period and was completed in 30 min (Figure 2.7(A)). The M_n values increased in proportion to the monomer conversion and were in good agreement with the theoretical values calculated from the molar ratio of IBVE to Ph_2CHBr (Figure 2.7(B)). In addition, a fresh feed of monomer was added to the reaction mixture when the initial charge of monomer was almost consumed. The second-stage of polymerization was rapidly initiated with no induction time and high conversion was also achieved within 30 min (Figure 2.7(A)). The GPC curves of the products clearly showed a shift to higher M_n (Figure 2.7(C)).

Table 2.7 Effects of Reaction Time in the Living Cationic Polymerization of IBVE Using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ Initiating System in the Presence of $\text{Me}_2\text{S}^{\text{a}}$

Entry	Time (min)	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	40s	24	4.8	1.26
2	1.5	36	6.8	1.33
3	3	52	9.0	1.34
4	5	69	11.0	1.36
5	10	81	13.0	1.38
6	20	92	15.5	1.38
7	30	100 (99.7)	17.3	1.35
8	30 + 5	162	18.4	1.52
9	30 + 10	181	20.1	1.47
10	30 + 20	193	21.3	1.44
11	30 + 30	200	23.5	1.47

^a Ph_2CHBr : 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{IBVE} = 1.1/1.0/200$, CH_2Cl_2 : 4.0 mL, temp: $-23\text{ }^\circ\text{C}$, addition order: AgClO_4 , Et_2O (0.5 mL), $\text{Ph}_2\text{CHBr} + \text{Et}_2\text{O}$ (0.5 mL), $\text{IBVE} + \text{Me}_2\text{S}$ (1.0 mmol) + CH_2Cl_2 . ^bBy GPC (polystyrene calibration).

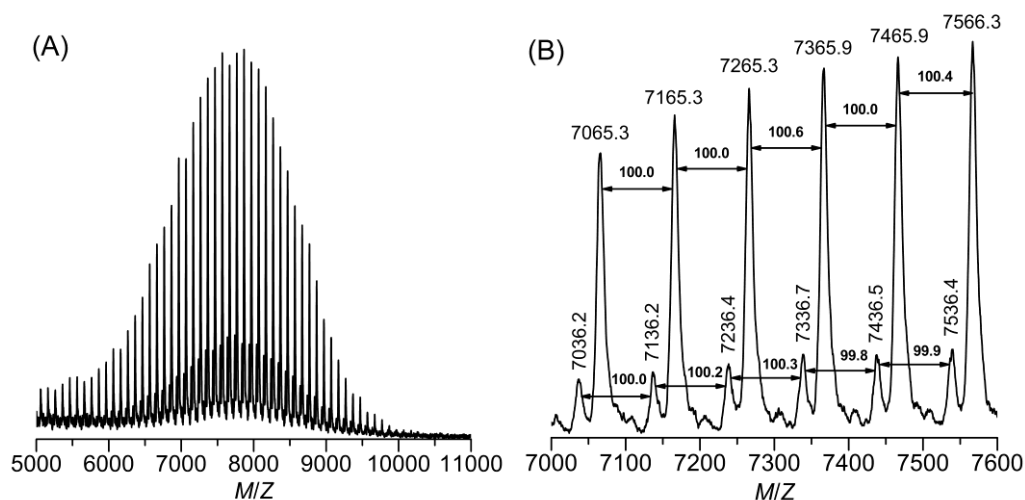


Figure 2.8 MALDI-TOF-MS spectra of poly(IBVE) obtained using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in the presence of Me_2S (1.0 mmol) in mixed solvent of CH_2Cl_2 (4.0 mL) and Et_2O (1.0 mL) at $-23\text{ }^\circ\text{C}$. Ph_2CHBr : 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{IBVE} = 1.1/1.0/200$ (Table 2.7, entry 2).

Controlled polymerization was further confirmed by MALDI-TOF-MS and ^1H NMR measurements. The spectrum of poly(IBVE) obtained using the $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in the presence of Me_2S (Table 2.7, entry 2) had clearly resolved peaks (Figure 2.8(A)). Importantly, two series of main peaks were separated by an interval corresponding to an IBVE repeating unit (100.2 mass unit, Figure 2.8(B)). The smaller peaks were attributed to individual polymer chains in the ionized adduct

forms with single alkali metals $[\text{Ph}_2\text{CH}-(\text{IBVE})_n-\text{OMe} + \text{Na}^+]$ (for example $7235.2 = 167.2 + 100.2 \times 70 + 31.0 + 23.0$, where 167.2, 100.2, 31.0, and 23.0 are the molar mass of Ph_2CH , IBVE, OMe, and Na^+ , respectively; obsd: 7236.4). On the other hand, the higher main series corresponded to $[\text{H}-(\text{IBVE})_n-\text{OMe} + \text{Na}^+]$ because of the loss of the Ph_2CH residue (for example $7069.0 = 1.0 + 100.2 \times 70 + 31.0 + 23.0$, obsd: 7065.3). The presence of these peaks plausibly indicates fragmentation during ionization in the MALDI-TOF-MS analysis, as reported by other authors.^{34–36}

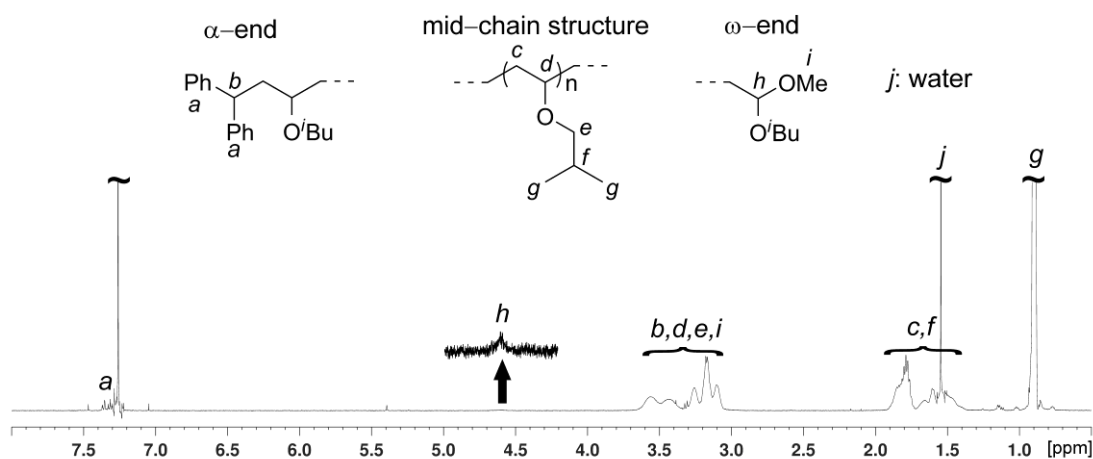


Figure 2.9 ^1H NMR spectrum of poly(IBVE) obtained using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in CH_2Cl_2 at $-23\text{ }^\circ\text{C}$ (Table 2.7, entry 2, $M_n(\text{GPC}) = 6800$, $M_n(\text{NMR},\alpha) = 7400$, $M_n(\text{NMR},\omega) = 8000$).

The ^1H NMR spectrum (Figure 2.9) confirmed the presence of an α -end ($\text{H}(a)$) derived from the initiator and an ω -end ($\text{H}(h)$) derived from the methanol quencher. No peaks from terminal olefins, generated via β -proton elimination, were observed. The molecular weights were estimated from the ratios of the methylene and methine protons ($\text{H}(c) + \text{H}(f)$) of the monomer and the M_n values ($M_n(\text{NMR},\alpha) = \sim 7400$ and $M_n(\text{NMR},\omega) = \sim 8000$) agreed with those from GPC analysis ($M_n(\text{GPC}) = 6800$).

2.3.4 Cationic Polymerization by Various Silver Salt/Aryl Methyl Halide Initiating Systems

Table 2.8 Effects of Several Types of Silver Salts on the Cationic Polymerization Behavior of IBVE^a

Entry	Initiator	Added base	Silver Salt	Temp (°C)	Time (min)	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^c	M_w/M_n
1	BnBr	–	AgOTf	–23	5	100	4.6	2.71
2	BnBr	Me ₂ S	AgOTf	–23	60	100	8.2	1.91
3	BnBr	–	AgOTf	–41	30	100	11.5	2.14
4	BnBr	–	AgClO ₄	–23	5	100	11.0	2.93
5	BnBr	Me ₂ S	AgClO ₄	–23	60	87	7.4	2.23
6 ^b	BnBr	–	Ag ₂ SO ₄	0	30	1.4	–	–
7	BnBr	–	AgNO ₃	0	30	–	–	–
8	BnBr	–	AgOAc	0	30	–	–	–
9	Ph ₂ CHBr	–	AgClO ₄	–23	5	100	3.8	3.56
10	Ph ₂ CHBr	Me ₂ S	AgClO ₄	–23	30	100	15.6	1.37
11	Ph ₂ CHBr	Me ₂ S	AgOTf	–23	30	100	15.4	1.38

^a Initiator: 0.025 mmol, molar ratio: silver salt/initiator/IBVE = 1.1/1.0/200, CH₂Cl₂: 4.0 mL, addition order: silver salt, Et₂O (0.5 mL), initiator + Et₂O (0.5 mL), IBVE + CH₂Cl₂ (+ Me₂S 0.75 mmol).

^b Ag₂SO₄/BnBr = 0.55/1.0.

^c By GPC (polystyrene calibration).

The data in Table 2.8 show the influence of the counter anion of the silver salts on the conversion, M_n , and MWD. Polymerization using AgOTf and BnBr was completed in 5 min but was uncontrolled, resulting in a lower M_n than achieved with the use of AgClO₄ (entry 1 vs. entry 4). When Me₂S was employed as an added base (entry 2) or when the temperature was lowered to –41 °C (entry 3), the M_n values increased and the MWD values decreased. Comparison with the results obtained with AgClO₄ (entry 2 vs. entry 5; entry 3 vs. entry 2 (Table 2.2)) suggested that the AgOTf/BnBr initiating system was more active. In contrast, the use of other silver salts lead to dramatic suppression (entry 6) or no polymerization obtained with AgNO₃ or AgOAc in 30 min at 0 °C (entry 7 and entry 8). Anions with higher nucleophilicity (SO₄^{2–}, NO₃[–], and AcO[–]) may undergo stronger interactions with the benzyl cation and/or the propagating terminal.

The effect of the silver salt was also studied using Ph₂CHBr with AgClO₄ and AgOTf, where the more stable and bulkier benzyl cation, Ph₂CH⁺, induced cationic polymerization in a less controlled manner (entry 4 vs. entry 9). As expected, in the presence of Me₂S, the reaction using the AgOTf/Ph₂CHBr initiating system at –23 °C proceeded smoothly, reaching quantitative conversion in 30 min, and producing a polymer with a narrow MWD, similar to the results achieved with AgClO₄/Ph₂CHBr (entry 11 vs. entry 10) given that CF₃SO₃[–] is a noncoordinating anion, similar to ClO₄[–].¹⁸

2.3.5 Polymerization Mechanism with AgClO₄/Aryl Methyl Halide Initiating System

Table 2.9 Effects of Dimethyl Sulfide Addition Order on the Cationic Polymerization Behavior of IBVE^a

Entry	Addition order	Initiator	Temp (°C)	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	I	BnBr	0	100	7.7	2.43
2	II	BnBr	0	—	—	—
3	I	Ph ₂ CHBr	0	100	4.1	2.05
4	II	Ph ₂ CHBr	0	100	6.3	3.15
5	I	Ph ₂ CHBr	−23	100	15.6	1.37
6	II	Ph ₂ CHBr	−23	9.3	—	—
7	I	Ph ₃ CCl	−23	100	14.1	1.35
8	II	Ph ₃ CCl	−23	100	14.6	1.40

^a Initiator: 0.025 mmol, molar ratio: AgClO₄/initiator/IBVE = 1.1/1.0/200, CH₂Cl₂: 4.0 mL, reaction time: 30 min, addition order I: AgClO₄, Et₂O (0.5 mL), initiator + Et₂O (0.5 mL), IBVE + CH₂Cl₂ + Me₂S (0.75 mmol), addition order II: AgClO₄, Et₂O (0.5 mL), initiator + Et₂O (0.5 mL) + Me₂S (0.75 mmol), IBVE + CH₂Cl₂.

^b By GPC (polystyrene calibration).

To investigate the reaction mechanism, the effect of Me₂S was further studied by switching the order of addition of the reagents, and the results are presented in Table 2.9. When Me₂S and BnBr were simultaneously added to a solution of AgClO₄ in Et₂O (addition order II), no polymerization occurred at 0 °C (entry 2 vs. entry 1 [addition order I]). This drastic change, therefore, is attributed to the strong interaction between the benzyl cation and Me₂S.

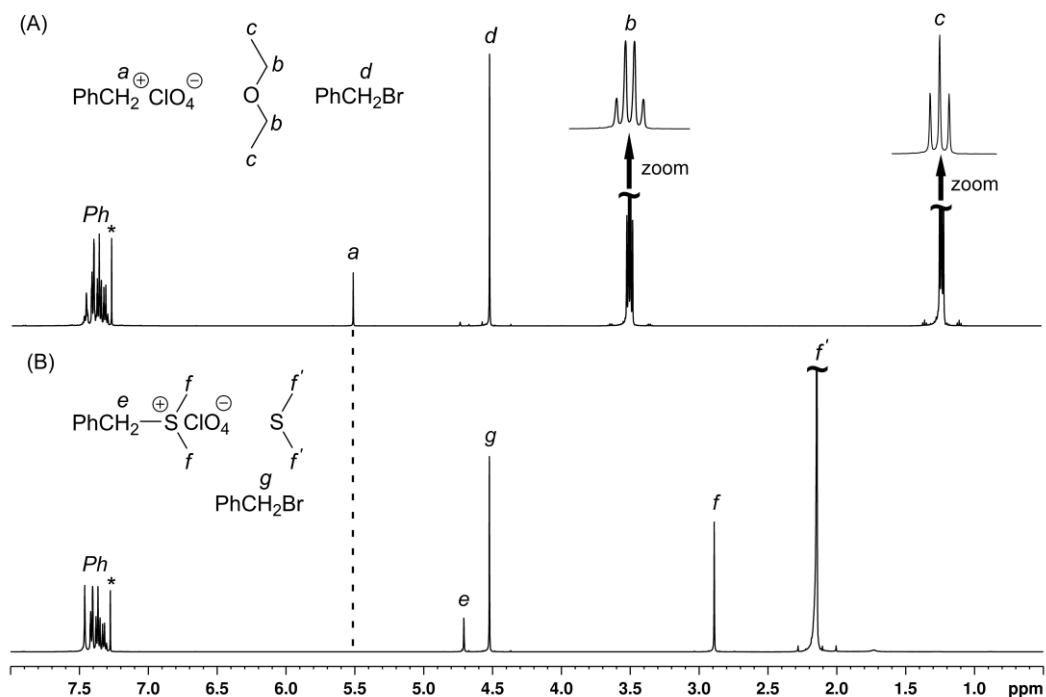
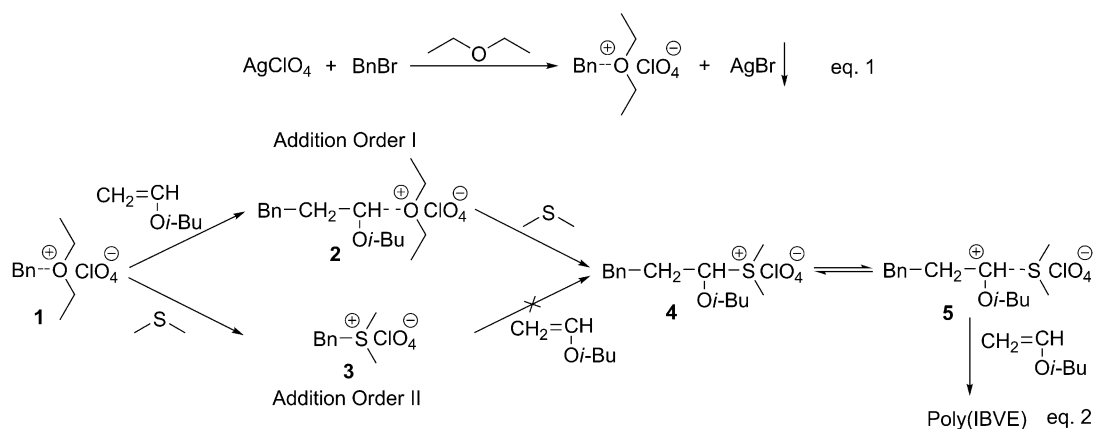


Figure 2.9 ^1H NMR spectra of reaction mixture of AgClO_4 , BnBr , and added base in CDCl_3 at 0°C , (A) Et_2O , (B) Me_2S . $\text{BnBr} = 0.025$ mmol, molar ratio: $\text{BnBr}/\text{AgClO}_4/\text{added base} = 1.0/1.1/2.0$, $\text{CDCl}_3 = 0.6$ mL, the reaction mixture was shaken for 5 s and kept for 30 min at 0°C before the measurement, *: CDCl_3 .

The interaction was studied by ^1H NMR analysis of the mixture of AgClO_4 , BnBr , and added base in a 1.1:1.0:2.0 molar ratio at 0°C . As seen in Figure 2.9, only single ethyl proton signals (peaks *b* and *c*) were detected for the $\text{AgClO}_4/\text{BnBr}/\text{Et}_2\text{O}$ system (Figure 2.9(A)), while two kinds of methyl proton peaks (peaks *f* and *f'*) were observed for the $\text{AgClO}_4/\text{BnBr}/\text{Me}_2\text{S}$ system (Figure 2.9(B)). This chemical shift of peak *f* ($\delta = 2.89$ ppm) relative to peak *f'* ($\delta = 2.15$ ppm) agrees with the result reported by Webster et al.¹⁵ On the other hand, both figures show an additional benzylic proton signal (peak *a* in Figure 2.9(A) and peak *e* in Figure 2.9(B)) with peaks *d* and *g* of BnBr . Because peak *a* appears more downfield ($\delta = 5.51$ ppm) than peak *e* ($\delta = 4.71$ ppm), the former can be assigned to the benzylic proton of PhCH_2^+ and the latter to that of benzyl sulfonium perchlorate. These results clearly indicate that there is little interaction between PhCH_2^+ and Et_2O at this molar ratio, while PhCH_2^+ interacts well with Me_2S and the sulfonium ion suppresses and controls the propagation.

In the case of Ph_2CHBr , on the other hand, polymerization occurred at 0°C using both addition orders (Table 2.9, entries 3 and 4), plausibly because the interaction with Me_2S was weakened owing to the electronically more stable cation, Ph_2CH^+ , that is also bulkier than PhCH_2^+ . However, the reaction was less controlled for entry 4 (order II), leading to a polymer with a higher M_n and a broader MWD than that of entry 3. At -23°C , polymerization via addition order I produced the best result (entry 5), in contrast with the very low conversion obtained using addition order II (entry 6). On the other hand, the more stable and bulky triphenylmethyl cation appears to be

relatively unaffected by the addition order (entries 7 and 8), i.e., by Me_2S , at $-23\text{ }^\circ\text{C}$.^{21,37,38}



Scheme 2.3 Possible Mechanism of IBVE Polymerization Using $\text{AgClO}_4/\text{BnBr}$ Catalyst System.

Based on the results, the proposed mechanism for cationic polymerization of IBVE is shown in Scheme 2.3. In the initiation step, the active benzyl cation prepared from $\text{AgClO}_4/\text{BnBr}$ is stabilized by the nucleophilic interaction of Et_2O , which acts as a solvent (eq. 1). When the monomer and Me_2S mixture is added to the initiating system (addition order I), the benzyl cation reacts smoothly with the monomer to form oxonium perchlorate, **2**, which is weakly coordinated by Et_2O . Substitution of Et_2O by Me_2S then converts **2** to sulfonium perchlorate, **4** (the dormant form), but continues to polymerize via **5** (the active form). On the other hand, when BnBr and Me_2S are simultaneously added (addition order II), Me_2S easily replaces Et_2O to form benzyl sulfonium ion **3**, and almost suppresses the propagation. At higher temperatures or with more stable cations, polymerization occurs in accordance with the conditions.

This mechanism assumes that there is a difference between the coordination of Me_2S to the cations, benzyl cation, and propagating polymer cation owing to electronic and steric factors. Given that the influence of Me_2S on Ph_2CH^+ is less pronounced than the influence on PhCH_2^+ (Table 2.9, entry 2 vs. entry 4), coordination to the propagating terminal $\text{R}(\text{BuO})\text{CH}^+$, which is a secondary carbocation with an alkoxy group, is weaker than coordination to PhCH_2^+ , which is a less stable primary carbocation (**3** vs. **4** in Scheme 2.3). Furthermore, the second phenyl group of Ph_2CH^+ , two additional phenyl groups of Ph_3C^+ (Table 2.9, entries 7 and 8), and the $i\text{Bu}$ group of IBVE should cause greater steric hindrance to the propagating carbocation than PhCH_2^+ .

2.3.6 Effects of Alkyl Sulfide on the Cationic Polymerization Behavior of VEs

In order to investigate the applicability of the present system, cationic polymerization of alkyl vinyl ethers with different reactivities were studied using some alkyl sulfides. The results are summarized in Table 2.10.

Table 2.10 Cationic Polymerization of VEs Using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ Initiating System in the Presence of Alky Sulfide^a

Entry	Monomer	Added base	Temp (°C)	Time (min)	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^b	$M_n \times 10^{-3}$ (calcd)	M_w/M_n
1	IBVE	Me_2S	−23	30	100	17.3	20.0	1.35
2		Me_2S	−41	30	—	—	—	—
3		Et_2S	−23	30	100	8.1	20.0	1.56
4		Et_2S	−41	30	63	7.6	12.6	1.53
5		THT	−23	30	100	15.0	20.0	1.34
6		THT	−41	30	13	2.6	2.6	1.24
7	EVE	Me_2S	−23	30	100	12.5	14.4	1.42
8		Me_2S	−41	30	5	—	—	—
9		Et_2S	−23	30	100	5.0	14.4	1.75
10		Et_2S	−41	30	73	8.4	10.5	1.40
11		THT	−23	30	100	10.6	14.4	1.44
12		THT	−41	30	16	2.3	2.3	1.23
13	IPVE	Me_2S	−23	20	100	5.1	17.2	1.68
14		Me_2S	−41	20	78	10.8	13.4	1.32
15		Et_2S	−41	20	93	13.1	16.0	1.29
16		THT	−41	20	100	14.2	17.2	1.35
17	EVE	Me_2S	−23	2	28	4.1	4.0	1.25
18	IPVE	Me_2S	−41	5	24	4.2	4.1	1.24

^a Ph_2CHBr : 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{monomer} = 1.1/1.0/200$, solvent: 4.0 mL, addition order: AgClO_4 , Et_2O (0.5mL), $\text{Ph}_2\text{CHBr} + \text{Et}_2\text{O}$ (0.5 mL), monomer + solvent + added base (1.0 mmol).

^b By GPC (polystyrene calibration).

As shown in Table 2.10, the cationic polymerization of IBVE in the presence of different alkyl sulfides proceeded at low reaction temperature. When Me_2S was used as an added base, the polymerization proceeded in a highly controlled manner, yielding polymer with high M_n and narrow MWD at −23 °C (entry 1), but no polymer was obtained at −41 °C (entry 2). In contrast, polymers with low M_n and broader MWD were prepared in the presence of Et_2S at −23 °C (entry 3). These results indicate that the bulkier Et_2S led to weak interaction with the growing carbocation, resulting in less controlled polymerization than that using Me_2S with less steric hindrance. The ^1H NMR analysis of product polymers revealed the undesired structures derived from chain transfers occurred by uncontrolled polymerization (Figure 2.10). When lowering temperature to −41 °C, the polymerization still proceeded smoothly, giving polymers with moderate conversion in a little controlled manner (entry 4). The polymerization using tetrahydrothiophene (THT) at −23 °C was well controlled, which resulted in polymers with narrow MWDs but a little lower M_n s than that using Me_2S (entry 5 vs. entry 1). In addition, the polymerization at −41 °C was very slow and highly controlled, yielding polymers with low conversion and

narrow MWD (entry 6). The above results indicate that as the bulkiness of sulfide increased, the coordination between the added base and a growing carbocation become weak, which was responsible for the occurrence of side reactions.

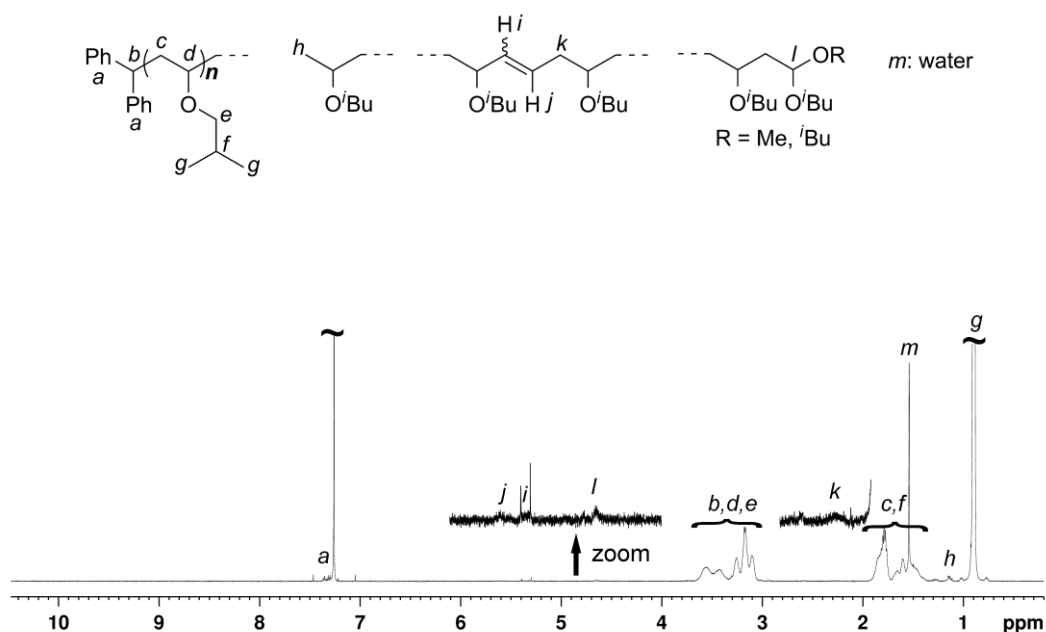


Figure 2.10 ^1H NMR spectrum of poly(IBVE) obtained using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in CH_2Cl_2 at $-23\text{ }^\circ\text{C}$ (Table 2.10, entry 3).

The cationic polymerization of EVE at $-23\text{ }^\circ\text{C}$ reached quantitative conversion in 30 min and produced polymers with a little broader MWD than poly(IBVE) (entry 1 vs. entry 7, entry 3 vs. entry 9, entry 5 vs. entry 11). In the presence of Et_2S , the difference of M_n between GPC result and the theoretical value was also very large, similar to that for poly(IBVE) (entry 9). Because coordination between growing chain terminal and bulky sulfide, Et_2S , was weak. The uncontrolled polymerization was confirmed by the ^1H NMR analysis of product polymers (Figure 2.11(A)). The spectrum revealed the occurrence of chain transfer due to the presence of olefin peaks.

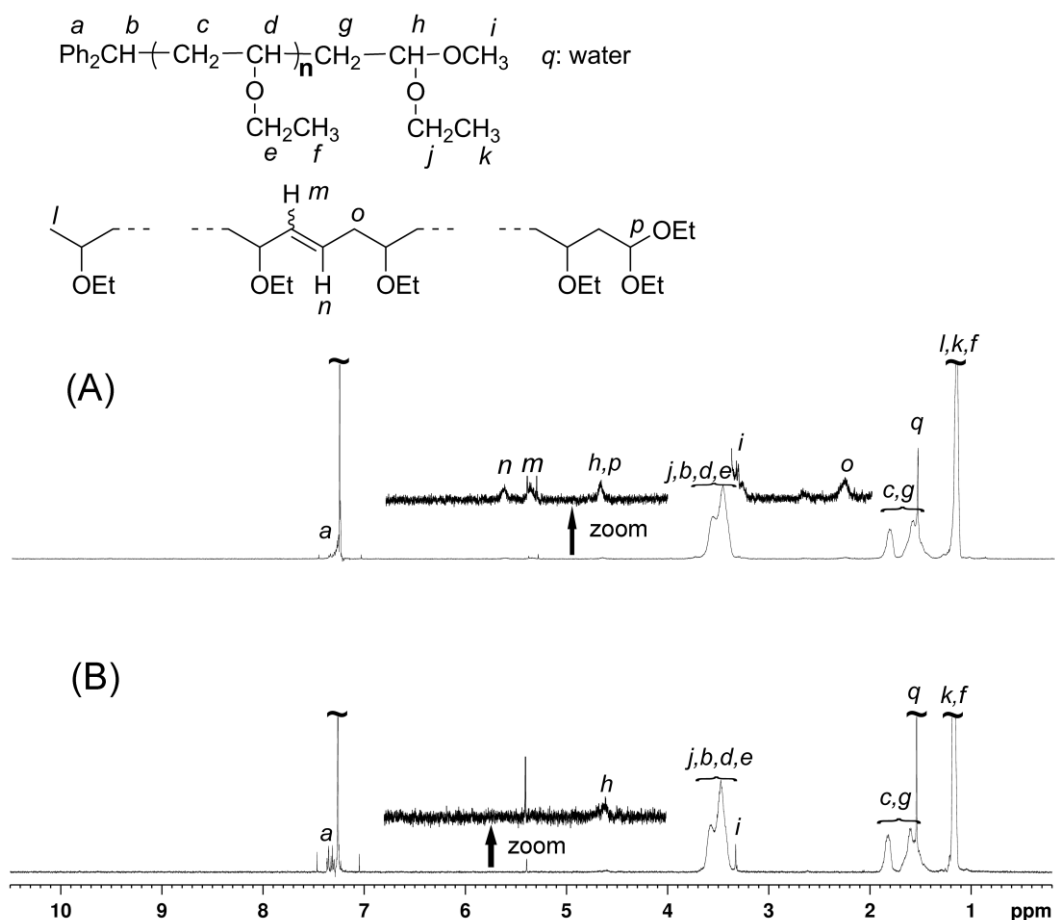


Figure 2.11 ¹H NMR spectrum of poly(EVE) obtained using AgClO₄/Ph₂CHBr initiating system in CH₂Cl₂ at -23 °C, (A) entry 9, (B) entry 17 (Table 2.10).

In comparison to the results of polymerization of IBVE at -41 °C, the polymerization of EVE proceeded smoothly, giving polymers in higher conversion with Et₂S and THF (entries 10 and 12). When using Me₂S, a small amount of polymer was obtained (entry 8). These results suggested that the monomer EVE was a little more active than IBVE. Interaction between the growing chain carbocation and Me₂S was stronger and more effective than Et₂S and THT. Thus, the controlled polymerization under the typical conditions was quenched after 2 min (entry 17) and the well-defined polymers was confirmed by ¹H NMR and MALD-TOF-MS. As shown in (Figure 2.11(B)), it shows no olefin peaks from chain abstraction, as suggested in Figure 2.11(A).

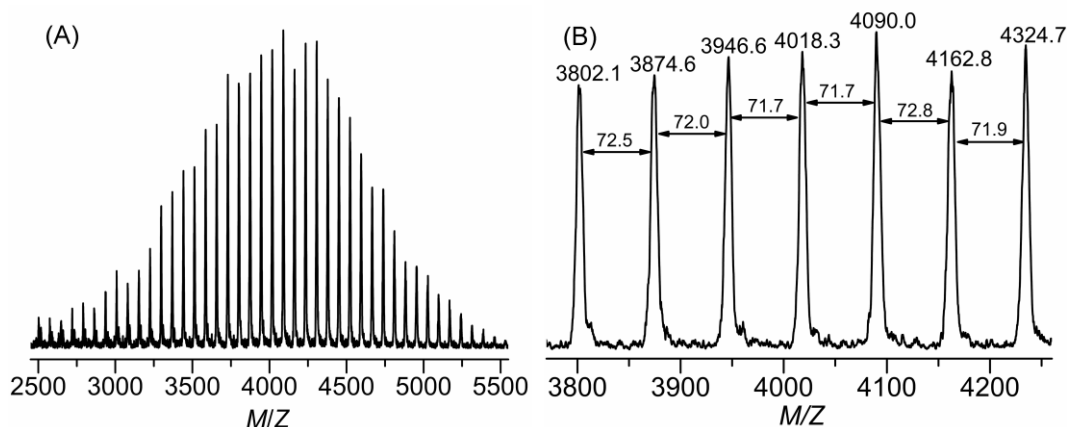


Figure 2.12 MALDI-TOF-MS spectra of poly(EVE) obtained using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in the presence of Me_2S (1.0 mmol) in mixed solvent of CH_2Cl_2 (4.0 mL) and Et_2O (1.0 mL) at -23°C . Ph_2CHBr : 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{EVE} = 1.1/1.0/200$ (Table 2.10, entry 17).

The MS spectra of the polymers appear clearly resolved peaks (Figure 2.12(A)). Importantly, the main peaks were separated by an interval corresponding to an EVE repeating unit (72.1 mass unit, Figure 2.12(B)). The main series corresponded to $[\text{H}-(\text{EVE})_n-\text{OMe} + \text{Na}^+]$ because of the loss of the Ph_2CH residue (for example $4092.6 = 1.0 + 72.1 \times 56 + 31.0 + 23.0$, where 1.0, 72.1, 31.0, and 23.0 are the molar mass of H, EVE, OMe, and Na^+ , respectively; obsd: 4090.0). The presence of these peaks plausibly indicates fragmentation during ionization in the MALDI-TOF-MS analysis, as reported by other authors.^{34–36}

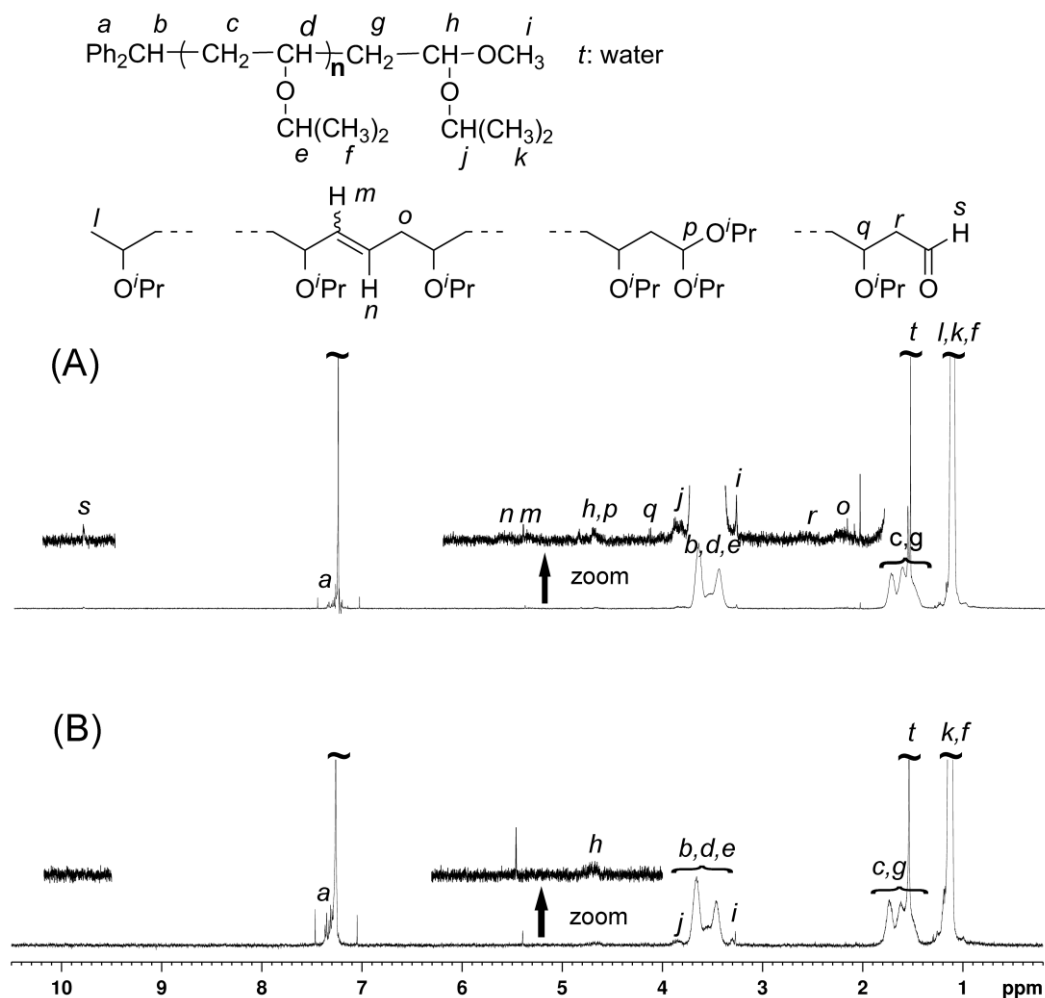


Figure 2.13 ^1H NMR spectrum of poly(IPVE) obtained using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in CH_2Cl_2 at $-23\text{ }^\circ\text{C}$, (A) entry 13, (B) entry 18 (Table 2.10).

Isopropyl vinyl ether (IPVE), a more reactive VE than IBVE and EVE, was also employed for polymerization under the typical conditions. Polymerization using Me_2S at $-23\text{ }^\circ\text{C}$ proceeded faster and completed in 20 min, which resulted in polymers with broad MWD and low M_n (entry 13). The occurrence of uncontrolled polymerization was further confirmed by ^1H NMR (Figure 2.13(A)). The spectrum revealed internal olefin, acetal and aldehyde structures derived from side reactions including elimination and chain abstraction. In order to control the reaction, lowering the temperature to $-41\text{ }^\circ\text{C}$ induced controlled polymerization. To confirm the highly controlled polymerization, the polymerization under the similar conditions was quenched after 5 min (entry 18) and the product polymer was analyzed by ^1H NMR and MALD-TOF-MS. The ^1H NMR (Figure 2.13(B)) showed no undesired peaks from side chain transfer, as suggested in Figure 2.13(A).

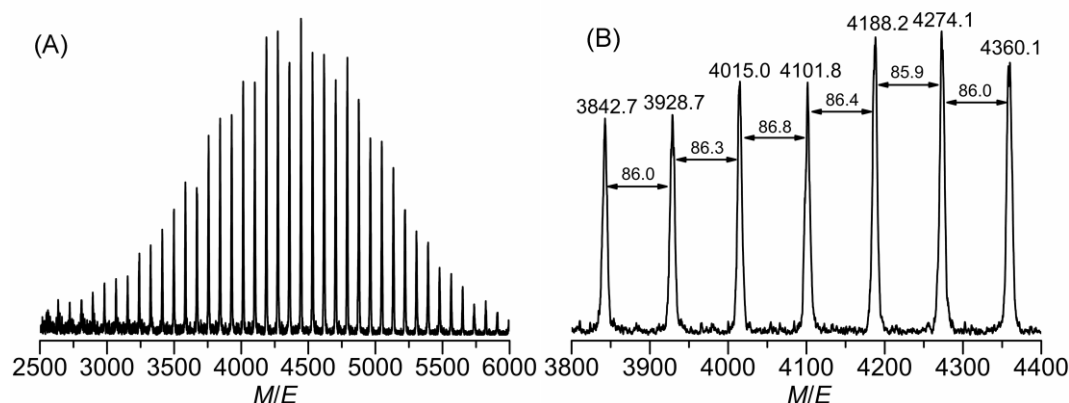


Figure 2.14 MALDI-TOF-MS spectra of poly(IPVE) obtained using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in the presence of Me_2S (1.0 mmol) in mixed solvent of CH_2Cl_2 (4.0 mL) and Et_2O (1.0 mL) at -41°C . Ph_2CHBr : 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{IPVE} = 1.1/1.0/200$ (Table 2.10, entry 18).

As shown in Figure 2.14, the main peaks were separated by an interval corresponding to an IPVE repeating unit (86.1 mass unit, Figure 2.14(B)). The main series corresponded to $[\text{H}-(\text{IPVE})_n-\text{OMe} + \text{Na}^+]$ due to the loss of the Ph_2CH residue (for example $4187.8 = 1.0 + 86.1 \times 48 + 31.0 + 23.0$, where 1.0, 86.1, 31.0, and 23.0 are the molar mass of H, IPVE, OMe, and Na^+ , respectively; obsd: 4188.2).

2.3.7 Copolymerization of VEs by $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ Initiating System

Living cationic block copolymerization is another simple and convenient method for the synthesis of well-defined copolymers. Thus, the synthesis of copolymers of VEs via sequential monomer addition was also investigated by the $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in the presence of alkyl sulfide.

Table 2.11 Copolymerization of VEs Using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ Initiating System in the Presence of Alky Sulfide^a

Entry	Monomer	Time (min)	Conv (%) ^c IBVE/EVE	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	IBVE	15	94/0	4.8	1.32
2	IBVE + EVE	15+15	100/61	6.2	1.62
3	EVE + IBVE	15+15	100/66 ^d	3.9	1.74

^a Ph_2CHBr : 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{IBVE}/\text{EVE} = 1.1/1.0/100/100$, CH_2Cl_2 : 4.0 mL, temp: -23°C , addition order: AgClO_4 , Et_2O (0.5 mL), Ph_2CHBr + Et_2O (0.5 mL), monomer + CH_2Cl_2 + Me_2S (1.0 mmol), (after first stage polymerization + another monomer).

^b By GPC (polystyrene calibration).

^c Determined by ^1H NMR.

^d Conversion (%): EVE/IBVE.

As shown in Table 2.11, the polymerization of IBVE in the presence of Me₂S reached high conversion (up to 94%) in 15 min at -23 °C (entry 1). To confirm the occurrence of highly controlled polymerization, the ¹H NMR was measured for the product polymer. As shown in Figure 2.15, no structures derived from side reactions were detected.

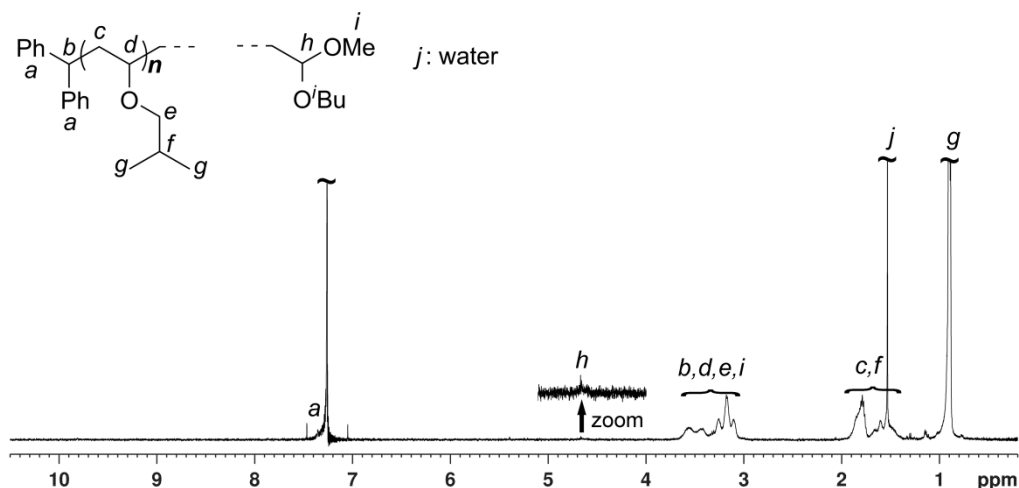


Figure 2.15 ¹H NMR spectrum of poly(IBVE) obtained using AgClO₄/Ph₂CHBr initiating system in CH₂Cl₂ at -23 °C (Table 2.11, entry 1).

A fresh feed of monomer, EVE, was charged to the reaction mixture when the initial monomer, IBVE, was almost consumed. The second stage polymerization proceeded smoothly to yield the copolymers with higher molecular weight and increased conversion (entry 2 vs. entry 1). The product copolymer was studied by ¹H NMR to confirm the structures. As shown in Figure 2.16, the ¹H NMR spectrum revealed the presence of side chain end structures: one methyl group derived from IBVE and another methyl group stem from EVE.

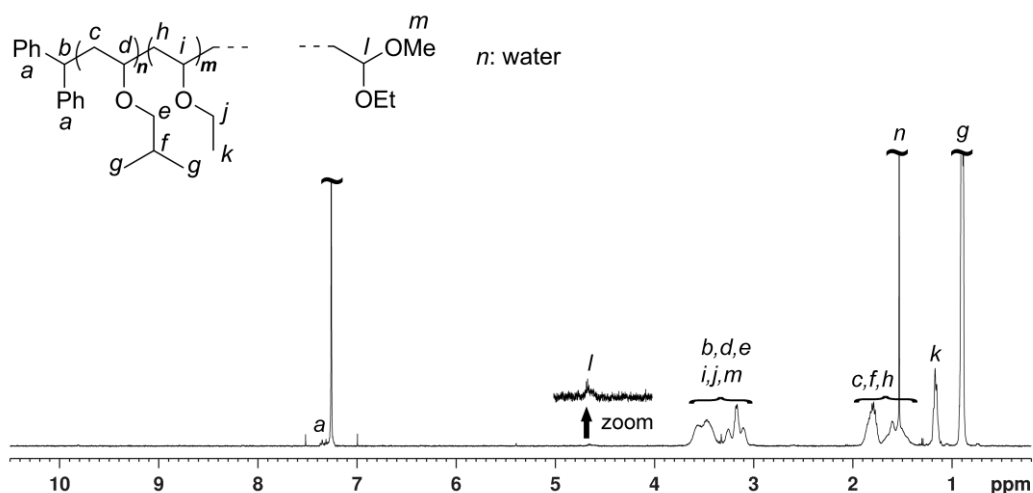


Figure 2.16 ¹H NMR spectrum of poly(IBVE)-*b*-poly(EVE) obtained using AgClO₄/Ph₂CHBr/Me₂S initiating system in CH₂Cl₂ at -23 °C (Table 2.11, entry 2).

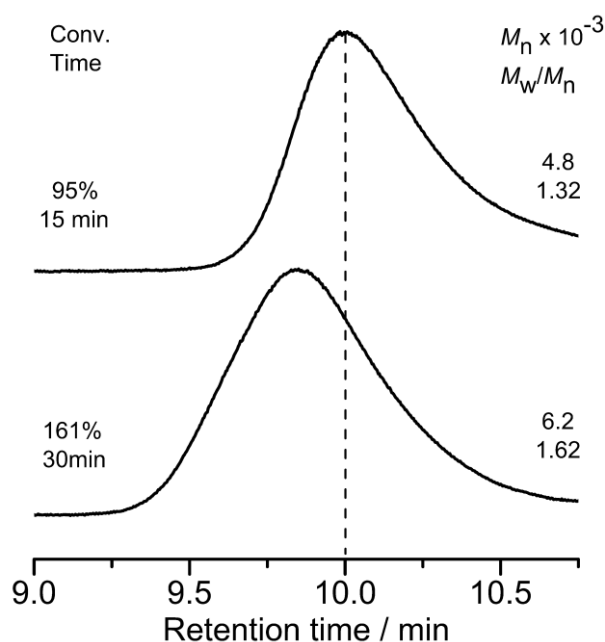


Figure 2.17 GPC curves for poly(IBVE) obtained using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system in mixed solvent of CH_2Cl_2 (4.0 mL) and Et_2O (1.0 mL) at -23°C . Ph_2CHBr : 0.025 mmol, molar ratio: $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{Me}_2\text{S}/\text{IBVE}/\text{EVE} = 1.1/1.0/40/100/100$ (Table 2.11, entry 1 and entry 2).

The GPC curve of the product clearly showed a shift to higher M_n in comparison to the result of poly(IBVE) (Figure 2.17). These results indicated that the copolymerization of VEs was successfully obtained by sequential monomer addition method. In entry 3 (Table 2.11), the order of monomers was switched, resulting polymers with lower M_n and broader MWD, although the conversion became higher (entry 3 vs. entry 1). The results might be due to the higher reactivity of monomer, EVE, which induced the first stage polymerization in a little less controlled manner.

2.4 Conclusions

Cationic polymerization of IBVE was successfully achieved using the $\text{AgClO}_4/\text{aryl methyl halide}$ initiating system in a mixed solvent of CH_2Cl_2 and Et_2O , with Me_2S as an added base. This new method is facile, mild, and free from complex catalysts, and only requires simple experimental techniques with ordinary apparatus. It was found that Me_2S exerts a strong effect on the rate of polymerization, resulting in a narrower MWD range than the system without it. The living nature of poly(IBVE) synthesized using the $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{Me}_2\text{S}$ system was examined by a successful chain extension experiment. In order to elucidate the reaction mechanism, the effects of added bases, such as Et_2O and Me_2S , initiators, such as BnBr , Ph_2CHBr and Ph_3CCl , and the addition order were studied in detail; the electronic and steric features of added bases and aryl methyl halides appeared to affect the initiation and/or

propagation. Differences in the modes of coordination of benzyl cation to the added bases were demonstrated by ^1H NMR. In addition, it was found that IBVE polymerization was affected by the kinds of halides used in the initiators; BnBr gave high reaction rates, while BnCl resulted in poor results. In the initiation step, the side reaction, alkylation of aromatic ring, occurred during the generation of benzyl cation from the silver salt with noncoordinating anion, AgClO_4 , and BnBr in CH_2Cl_2 . Because the benzyl perchlorate is highly reactive. Thus, Et_2O was employed to stabilize the initiator cation effectively and also as solvent to dissolve silver salt. The anion of the silver salt also changed the reaction rates; noncoordinating anion, TfO^- , similar to ClO_4^- , caused a vigorous reaction, while strongly nucleophilic anions (NO_3^- , SO_4^{2-} , and CH_3CO_2^-) significantly retarded the polymerization.

Furthermore, polymerizations of other vinyl monomers, such as EVE, IPVE, also proceeded in a controlled fashion using $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{Me}_2\text{S}$ system under different temperature according to monomer reactivity. The types of sulfide also affected polymerization behaviors. The controllability of polymerization becomes weaker as the bulkiness of the sulfide increases, which is due to the weak coordination between the growing carbocation and sulfide. Choosing a sulfide with suitable nucleophilicity was important for achievement of controlled polymerization. In addition, selecting the reaction temperature according to monomer reactivity was also essential for suppressing side reactions. The copolymerization of IBVE and EVE was successfully achieved by $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ system with Me_2S in CH_2Cl_2 at -23°C . The addition order of monomer dramatically influenced the polymerization behavior.

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Chapter 3 Cationic Polymerization of Styrene Derivatives by the Silver Salt/Aryl Methyl Halide/Lewis Base Initiating System

3.1 Introduction

Quite recently, we have achieved the controlled/living cationic polymerization of IBVE initiated by $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ system in CH_2Cl_2 in the presence of Me_2S at $-23\text{ }^\circ\text{C}$.¹ However, without Me_2S , the $\text{AgClO}_4/\text{Ph}_2\text{CHBr}$ initiating system leads to uncontrolled polymerization. In addition, it was found that the kinds of aryl methyl halides also influenced the polymerization behavior and the $\text{AgClO}_4/\text{BnBr}/\text{Me}_2\text{S}$ system induced polymerization in a partly controlled fashion.

Based on these results, other VEs were also investigated in the combination with some sulfides. We have noticed that choosing a sulfide with suitable nucleophilicity was important for achievement of controlled polymerization. In addition, according to the monomer reactivity selecting the reaction temperature was also essential for suppressing side reactions.

In order to extend the application of aryl methyl halide/silver salt /Lewis Base initiating system, styrene derivatives (St)s were employed and studied. Since the first discovery of living cationic polymerization in 1980s,² a wide variety of initiating systems have been developed for various styrene monomers, such as HI/ZnI_2 ,³ HI/I_2 ,⁴ $\text{IBVE-HCl}/\text{ZnX}$,⁵ alcohol/ BF_3OEt_2 ,⁶ 1-(4-methoxyphenyl)-ethanol/ $\text{B}(\text{C}_6\text{F}_5)_3$ ⁷ and $\text{St-HCl}/\text{FeCl}_3$.⁸ However, most of the initiating systems contain strong Lewis acids or mineral acids. These strong Brønsted acids may cause equipment corrosion and require the use of complicated procedures because of their toxicity and/or instability. Removal of the metal catalyst residue is generally a complicated process, which is a major limitation to their use.

Consequently, we became interested in applying our new initiating system for the polymerization of styrene derivatives.

3.2 Experimental

3.2.1 Materials

p-Methoxystyrene (pMOS, Wako), styrene (St, Wako) and *p*-alkoxymethyl styrene prepared as described elsewhere⁹ were distilled under vacuum before use.

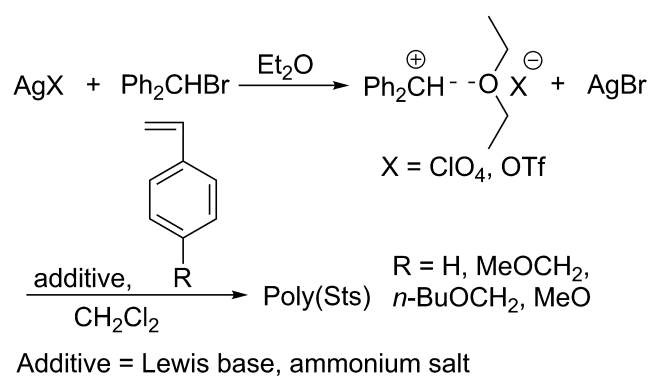
3.2.2 Polymerization

The following is a typical polymerization procedure. A solution of Ph_2CHBr (0.025 mmol) in Et_2O was added to a solution of AgClO_4 (0.028 mmol) in Et_2O (0.5 mL) in a round-bottomed flask at $0\text{ }^\circ\text{C}$ under nitrogen. After stirring for 10 min at this temperature, the mixture was cooled to the given reaction temperature. The polymerization was initiated by the addition of a prechilled mixture of pMOS (5.0 mmol) and Me_2S (1.0 mmol) in CH_2Cl_2 (4.0 mL). The reaction was quenched by

adding methanol (5.0 mL) containing a small amount of aqueous ammonia (0.1 vol%). After adding CH₂Cl₂ (20 mL) to the quenched mixture, the solution was filtered to remove AgBr and washed with water, the organic phase was then separated and concentrated to remove volatiles. The polymer was recovered by precipitation in methanol and dried under vacuum.

3.3 Results and Discussion

3.3.1 Cationic polymerization of Poly(St)s Initiated by AgClO₄ (AgOTf) /Ph₂CHBr



Scheme 3.1 Cationic Polymerization of Styrene Derivatives.

Table 3.1 Screening of Styrene Monomers and Additives for Cationic Polymerization Using AgClO₄ (or AgOTf)/Ph₂CHBr at 25 °C^a

Entry	Monomer	Additives	Time (h)	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	Styrene	Me ₂ S (0.25 mmol)	22	Not polymerized		
2		PhSMe (0.25 mmol)	18	6 ^c	—	—
3		PhSMe (0.125 mmol)	18	9	6.7	2.13 ^f
4		None	18	18	9.5	1.78 ^f
5	<i>p</i> -Methoxymethylstyrene	PhSMe (0.25 mmol)	18	20 ^c	—	—
6		None	18	45 ^c	—	—
7 ^d		None	18	15 ^c	—	—
8		<i>n</i> -Bu ₄ NClO ₄ (0.028 mmol)	18	57 ^c	—	—
9		<i>n</i> -Bu ₄ NClO ₄ (0.075 mmol)	18	66 ^c	—	—
10	<i>p</i> - <i>n</i> -Butoxymethylstyrene	None	18	30	2.5	1.38
11		None	24	32	2.4	1.37
12 ^e		None	18	65	2.2	1.84
13	<i>p</i> -Methoxystyrene	Me ₂ S (0.25 mmol)	12	93	10.2	1.58

^a Unless otherwise noted, Ph₂CHBr: 0.025 mmol, CH₂Cl₂: 4.0 mL, temp: 25 °C, molar ratio: AgClO₄/Ph₂CHBr/monomer = 1.1/1.0/200, addition order: AgClO₄, Et₂O (0.5mL), Ph₂CHBr + Et₂O (0.5 mL), monomer + CH₂Cl₂ (+ additive).

^b By GPC (polystyrene calibration).

^c Determined by ¹H NMR.

^d Using AgOTf

^e Without solvent (Et₂O + CH₂Cl₂).

^f For high molecular weight polymer.

We first carried out cationic polymerizations of various styrene derivatives with AgClO₄(AgOTf)/Ph₂CHBr initiating system using Lewis base or ammonium salt as an additive in CH₂Cl₂ at 25 °C (Scheme 3.1). The results are summarized in Table 3.1. Polymerization of styrene in the presence of Me₂S at 25 °C (entry 1) gave no polymer due to the strong coordination of sulfide to the initiator cation. Because Me₂S has high nucleophilicity and less steric hindrance, PhSMe was employed to decrease the coordination of sulfide, but there was no obvious improvement for the monomer conversion, even though, half amount of PhSMe (entry 2 and entry 3). Without added base, the polymerization of styrene was still slow, reaching 18% conversion in 18 h. The cationic polymerization of *p*-methoxymethylstyrene proceeded faster than that of

styrene (entry 5 vs. entry 2), probably because an electron-donating group (methoxymethyl group) at the para position of aromatic ring increases the reactivity. The reaction in the presence of *n*-Bu₄NClO₄ resulted in higher conversion than that without additive (entry 8 vs. entry 6). This result suggests a fast exchange between the growing carbocations and the excess noncoordinating anions, perchlorate anions derived from ammonium salt, which increased the acidity of the carbocations. The effect of ammonium salt is similar to the case of cationic polymerization of vinyl ethers using hydrogen iodide/ammonium salts initiating system.¹⁰ The increase of amount of *n*Bu₄NClO₄ further increased the conversion (entry 9).

The use of AgOTf did not improve the polymerization (entry 7). In addition, all poly(*p*-methoxymethylstyrene) can dissolve in methanol slowly due to the low molecular weight. To confirm the polymer chain length generated during the polymerization, methanol-precipitation method was also applied to separate part of polymers in a certain time. The separated polymer was analyzed by ¹H NMR (Figure 3.1) and GPC (Figure 3.1 and Table 3.2). The ¹H NMR spectrum revealed the peaks from the monomer. The polymer with low *M_n* values ($\sim 2.0 \times 10^3$) is likely responsible for solubility in methanol.

Table 3.2 Effects of Additive in the Cationic Polymerization of *p*-Methoxymethylstyrene Using AgClO₄/Ph₂CHBr Initiating System^a

Entry	Additives	Conv (%)	<i>M_n</i> × 10 ⁻³ (GPC) ^b	<i>M_w</i> / <i>M_n</i>
1	PhSMe (0.25 mmol)	13	1.5	1.43
2	None	24	1.7	1.75
3	<i>n</i> -Bu ₄ NClO ₄ (0.028 mmol)	31	2.2	1.52
4	<i>n</i> -Bu ₄ NClO ₄ (0.075 mmol)	35	1.9	1.58

^a Unless otherwise noted, Ph₂CHBr: 0.025 mmol, CH₂Cl₂: 4.0 mL, temp: 25 °C, time: 18h, molar ratio: AgClO₄/Ph₂CHBr/*p*-methoxymethylstyrene = 1.1/1.0/200, addition order: AgClO₄, Et₂O (0.5mL), Ph₂CHBr + Et₂O (0.5 mL), monomer + CH₂Cl₂ (+ additive).

^b By GPC (polystyrene calibration). Precipitation: added 40 mL MeOH to the product, and the mixture was shaken for 5 s and kept for 2 h at room temperature, polymer was then separated.

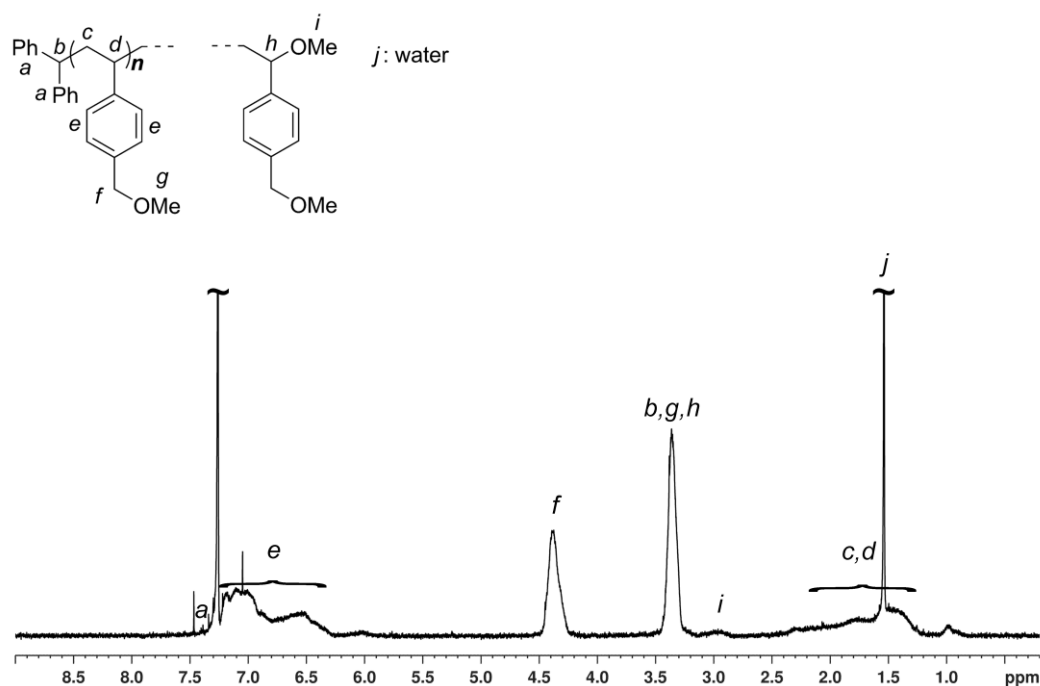


Figure 3.1 ¹H NMR spectrum of poly(*p*-methoxymethylstyrene) obtained using AgClO₄/Ph₂CHBr initiating system in CH₂Cl₂ at 25 °C (Table 3.2, entry 1).

The monomer with a longer substituent, *p*-*n*-butoxymethylstyrene, was also polymerized with the AgClO₄/Ph₂CHBr initiating system. The resulting polymer were obtained by methanol precipitation. The polymerization was slow, reaching 30 % in 18 h (entry 10, Table 3.1), but it was difficult to increase the conversion by extension of time (entry 11). Without solvent, the polymerization proceeded in an uncontrolled fashion, yielding polymer with low M_n and broad MWD (entry 12).

Among various styrene derivatives, pMOS has much higher reactivity due to the large electron-donating ability of methoxy group at the para position. As shown in Table 3.1, the polymerization of pMOS proceeded in high conversion (up to 93%) in the presence of Me₂S (entry 13). Considering the above results, we systematically investigated the cationic polymerization of pMOS.

3.3.2 Added Base Influence on Cationic polymerization Behavior of Poly(pMOS)

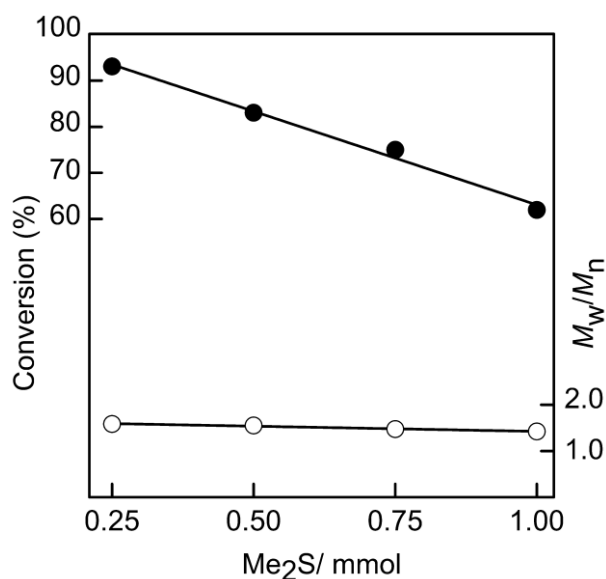


Figure 3.2 Relationship between the amount of Me₂S and conversion or M_w/M_n of poly(pMOS) obtained using AgClO₄/Ph₂CHBr initiating system in mixed solvent of CH₂Cl₂ (4.0 mL) and Et₂O (1.0 mL) at 25 °C. Ph₂CHBr: 0.025 mmol, molar ratio: AgClO₄/Ph₂CHBr/pMOS = 1.1/1.0/200 (Table 3.3).

Table 3.3 Effects of the Amount of Me₂S in the Cationic Polymerization of pMOS at 25 °C in 12h^a

Entry	Added base	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^b	$M_n \times 10^{-3}$ (calcd)	M_w/M_n
1	Me ₂ S (0.25 mmol)	93	10.2	24.9	1.58
2	Me ₂ S (0.50 mmol)	83	9.4	22.2	1.55
3	Me ₂ S (0.75 mmol)	75	9.6	20.1	1.47
4	Me ₂ S (1.0 mmol)	62	8.2	16.6	1.42

^a Ph₂CHBr: 0.025 mmol, CH₂Cl₂: 4.0 mL, temp: 25 °C, time: 12 h, molar ratio: AgClO₄/Ph₂CHBr/pMOS = 1.1/1.0/200, addition order: AgClO₄, Et₂O (0.5mL), Ph₂CHBr + Et₂O (0.5 mL), pMOS + CH₂Cl₂ + Me₂S.

^b By GPC (polystyrene calibration).

The influence of the amount of Me₂S on the polymerization behavior was investigated at 25 °C. As shown in Figure 3.2, increase of the amount of Me₂S dramatically decreased the monomer conversion. These results indicate that more effective and stronger interaction between the carbocation and Me₂S was obtained as the increase of the added base concentration. However, the differences between M_n values from GPC measurements and theoretical M_n values calculated from the ratio of initiator and

reacted monomers remained large (Table 3.3), which suggests that the increase of the amount of added base did not effectively suppress the occurrence of side reactions (β -proton elimination and the Friedel-Crafts reaction) during the polymerization.^{11,12}

Table 3.4 Effects of Reaction Temperature on the Cationic Polymerization Behavior in the presence of Me₂S (or Et₂S)^a

Entry	Added base	Temp (°C)	Conv (%)	$M_n \times 10^{-3}$ (GPC)	M_w/M_n
1	Me ₂ S (0.25 mmol)	0	19	3.6	1.29
2		5	35	4.6	1.35
3		10	62	7.9	1.44
4 ^c		25	93	10.2	1.58
5	Me ₂ S (0.125 mmol)	0	30	6.0	1.34
6	Me ₂ S (0.5 mmol)	10	31	4.7	1.36
7	Et ₂ S (0.25 mmol)	0	47	10.4	1.39
8		5	85	10.9	1.44
9		10	95	11.5	1.51
10 ^d		25	98	8.6	1.55
11	Et ₂ S (0.5 mmol)	10	84	10.7	1.47

^a Ph₂CHBr: 0.025 mmol, CH₂Cl₂: 4.0 mL, reaction time: 18 h, molar ratio: AgClO₄/Ph₂CHBr/pMOS = 1.1/1.0/200, addition order: AgClO₄, Et₂O (0.5mL), Ph₂CHBr + Et₂O (0.5 mL), pMOS + CH₂Cl₂ + added base.

^b By GPC (polystyrene calibration).

^c Reaction time: 12 h.

^d Reaction time: 8 h.

The influence of reaction temperature was investigated in the presence of alkyl sulfide (Me₂S or Et₂S). The experimental results (Table 3.4) indicate that pMOS conversion was obviously accelerated by increasing the reaction temperature. In the presence of Me₂S, the yield of poly(pMOS) increased from 19% to 62% with increasing temperature from 0 to 10 °C (from entry 1 to entry 3). The M_n values increased from 3600 to 7900 g/mol but MWDs became broader from 1.29 to 1.44. The polymerization at 25 °C proceeded smoothly to achieve high monomer conversion in 12 h (entry 4). The small amount of Me₂S resulted in polymer with higher conversion and broader MWD (entry 5 vs. entry 1). Conversely, increasing the amount of Me₂S dramatically decreased polymerization rate and slightly narrowed MWD (entry 6 vs. entry 3).

When using a bulkier sulfide, Et₂S, as an added base, the tendency of polymer

conversion and MWD was similar to that with Me₂S. Although the values of yield and MWD were higher than using Me₂S at the corresponding temperature, the M_n s were not affected much and remained about 11000 g/mol (from entries 7 to 9). The polymerization at 25 °C proceeded fast to achieve high monomer conversion in 8 h (entry 10). The increase of the amount of Et₂S did not effectively influence polymerization (entry 11 vs. entry 9). These results indicate that the weak coordination of bulky Et₂S to carbocation makes polymerization fast but its control becomes more difficult. The proposition that the bulkiness of added base decreases the interaction with carbocation is similar to the previous reports.^{13,14}

Table 3.5 Effects of Added Base on the Cationic Polymerization^a

Entry	Added base	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	Me ₂ S (0.25 mmol)	19	3.6	1.29
2	Et ₂ S (0.25 mmol)	47	10.4	1.39
3	PhSMe (1.0 mmol)	93	21.8	1.53
4	PhSPh (1.0 mmol)	100	18.1	3.02
5	Thiophene (1.0 mmol)	100	22.4	2.72
6	DMSO (1.0 mmol)	2	—	—

^a Ph₂CHBr: 0.025 mmol, added base: 1.0 mmol, CH₂Cl₂: 4.0 mL, temp: 0 °C, time: 18 h, molar ratio: AgClO₄/Ph₂CHBr/pMOS = 1.1/1.0/200, addition order: AgClO₄, Et₂O (0.5mL), Ph₂CHBr + Et₂O (0.5 mL), pMOS + CH₂Cl₂ + added base.

^b By GPC (polystyrene calibration).

A series of sulfur containing reagents were employed as added bases for cationic polymerization at 0 °C. As shown in Table 3.5, compared with alkyl sulfides, Me₂S and Et₂S, PhSMe has greater steric hindrance due to the phenyl group and less nucleophilicity caused by the resonance effect of aromatic ring. The reaction using PhSMe proceeded smoothly to reach high monomer conversion (entry 3). When using PhSPh with more steric hindrance and weaker basicity, polymerization was uncontrolled and resulted in product with broad MWD (entry 4). Other sulfur containing compounds, thiophene, DMSO, were also studied. The aromaticity of thiophene caused weak interaction with growing carbocation, yielding ill-defined polymers (entry 5). Under similar conditions, DMSO significantly suppressed polymerization probably due to strong coordination of (entry 6).

3.3.3 Initiator Influence on Cationic polymerization Behavior of Poly(pMOS)

Table 3.6 Effects of Coordination of Added Base to Initiator on Cationic Polymerization Behavior^a

Entry	Initiator	Added base	Conv (%)	$M_n \times 10^{-3}$ (GPC) ^b	M_w/M_n
1	BnBr	Me ₂ S	Trace	–	–
2	Ph ₂ CHBr	Me ₂ S	19	3.6	1.29
3	BnBr	PhSMe	97	31.4	2.15
4	Ph ₂ CHBr	PhSMe	98	26.8	1.72
5	Ph ₃ CCl	Me ₂ S	19	3.2	1.26
6	Ph ₂ CHBr	THT	22	4.0	1.29
7	Ph ₃ CCl	THT	21	3.3	1.30
8	Ph ₂ CHBr	Et ₂ S	47	10.4	1.39
9	Ph ₃ CCl	Et ₂ S	55	8.1	1.47

^a Initiator: 0.025 mmol, added base: 0.25 mmol, CH₂Cl₂: 4.0 mL, temp: 0 °C, time: 18 h, molar ratio: AgClO₄/initiator/pMOS = 1.1/1.0/200, addition order: AgClO₄, Et₂O (0.5mL), Ph₂CHBr + Et₂O (0.5 mL), pMOS + CH₂Cl₂ + added base.

^b By GPC (polystyrene calibration).

In order to investigate the effect of initiator, simple benzyl halide, BnBr was employed to conduct the cationic polymerizations in the presence of different added bases, and the results are presented in Table 3.6 The cationic polymerization initiated by AgClO₄/BnBr was remarkably suppressed in the presence of Me₂S, but the reaction proceeded fast when using PhSMe (entry 1 vs. entry 3). This drastic change is attributed to the strong interaction between benzyl cation and Me₂S. In the case of Ph₂CHBr, on the other hand, polymerization occurred in a highly controlled manner, resulting in polymer with narrow MWD (entry 2), probably because the interaction with Me₂S was weakened owing to the electronically more stable and bulkier cation, Ph₂CH⁺. As expected, the use of a bulky and low nucleophilic sulfide, PhSMe, led to less controlled polymerization, yielding product polymer with high conversion and broad MWD due to weak coordination to Ph₂CH⁺ (entry 4). In addition, a more stable and bulky triphenylmethyl cation conducted polymerization similar to Ph₂CHBr in the presence of various added base (entry 5 to entry 9).

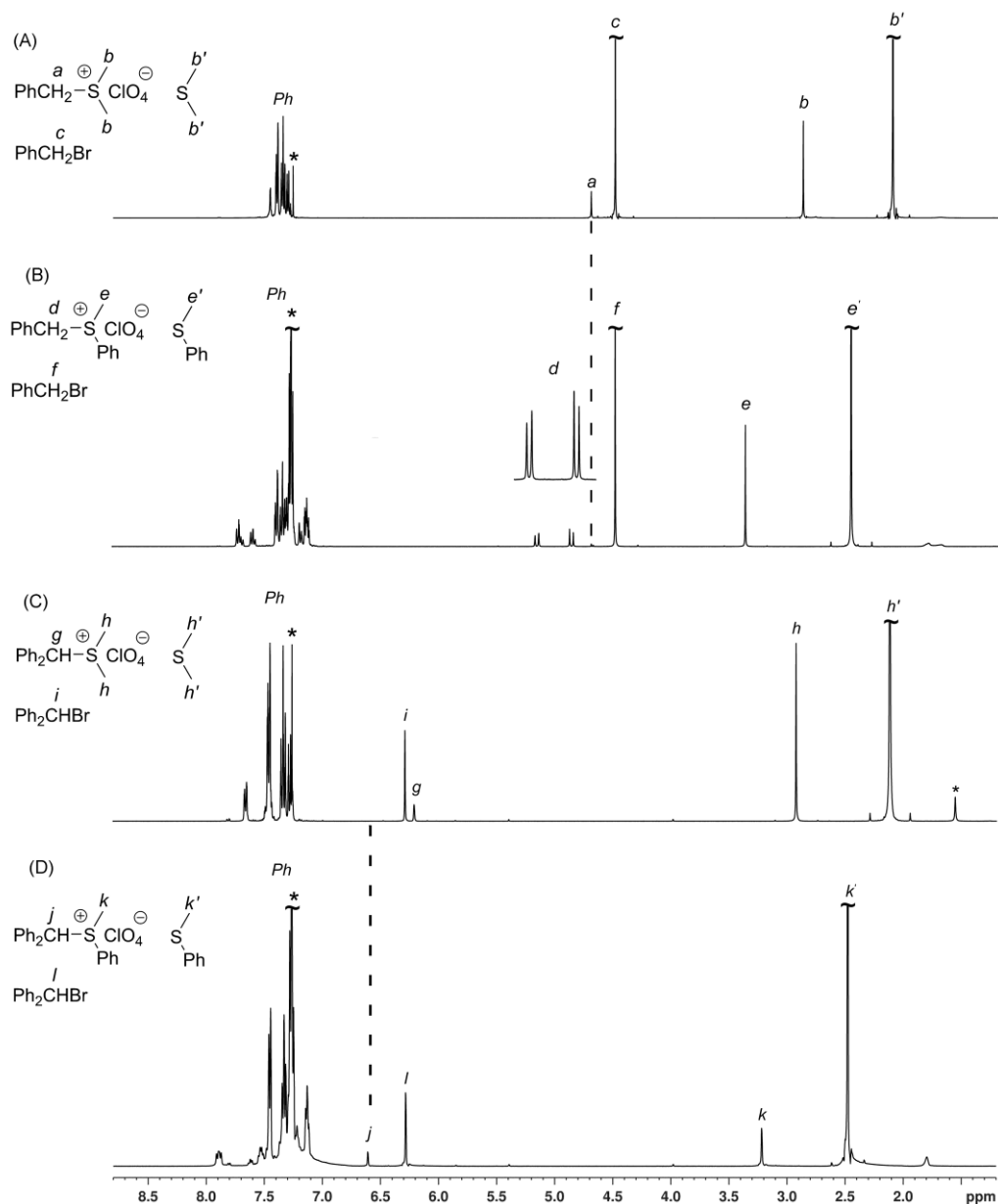


Figure 3.3 ^1H NMR spectra of reaction mixture of AgClO_4 , aryl methyl halide, and added base in CDCl_3 , recorded at 25°C , (A) BnBr , Me_2S , (B) BnBr , PhSMe , (C) Ph_2CHBr , Me_2S , (D) Ph_2CHBr , PhSMe . Aryl methyl halide = 0.025 mmol, molar ratio: aryl methyl halide/ AgClO_4 /added base = 1.0/1.1/2.0, CDCl_3 = 0.6 mL, the reaction mixture was shaken for 5 s and kept for 30 min at 0°C before the measurement, *: CDCl_3 and water.

To further study the interaction between the initiator cation and added base, it was examined by ^1H NMR analysis of the mixture of AgClO_4 , initiator, and added base in a 1.1:1.0:2.0 molar ratio at 0°C . As seen in Figure 3.3, two kinds of methyl protons of sulfides (peak b and peak b' , peak e and peak e' , peak h and peak h' , peak k and peak k') were observed for the system of AgClO_4 , aryl methyl bromide, and sulfide. These results clearly indicate initiator cations (Bn^+ or Ph_2CH^+) interact well with Me_2S or

PhSMe to generate sulfonium ions.

In Figure 3.3(A), in the presence of Me₂S, single peak (peak *a*) is assigned to the protons of benzyl group. However, the protons (peak *d*) of benzyl group are not equivalent due to different chemical environment in the presence of PhSMe, each proton is split into a doublet by adjacent proton. (Figure 3.3(B)).

Comparing to PhSMe, the interaction between Bn⁺ and Me₂S is stronger due to the stronger nucleophilicity and less steric hindrance of Me₂S than PhSMe. This stronger coordination was confirmed by ¹H NMR, peak *a* (δ = 4.71 ppm) appears more upfield than peak *d* (δ ~ 4.85–5.18 ppm) (Figure 3.3(A) vs. Figure 3.3(B)). The results indicate the coordination of Me₂S decreases the density of positive charge on methylene group of benzyl sulfonium ion a little more obviously than that with PhSMe. The stronger interaction between Bn⁺ and Me₂S dramatically suppresses the propagation (Table 3.6, entry 1 vs. entry 3).

As expected, to Ph₂CH⁺, coordination of Me₂S was also stronger than PhSMe, which led to that peak *g* (δ = 6.21 ppm) appears more upfield than peak *j* (δ = 6.61 ppm) (Figure 3.3(C) vs. Figure 3.3(D)).

As shown in Figure 3.3(A) and Figure 3.3(C), peak *g* (δ = 6.21 ppm) derived from diphenyl sulfonium perchlorate appears more downfield than peak *a* (δ = 4.71 ppm) from benzyl sulfonium perchlorate due to the resonance effects of the second phenyl group from Ph₂CH⁺.

3.4 Conclusions

Cationic polymerization of styrene derivatives was achieved using the AgClO₄/aryl methyl halide/Lewis base initiating system in a mixed solvent of CH₂Cl₂ and Et₂O. This new method is facile, mild, and free from complex catalysts, and uses simple experimental techniques with ordinary apparatus. It was found that the polymerizations of low reactive monomers (styrene, *p*-methoxymethylstyrene and *p*-butoxymethylstyrene) proceeded in an uncontrolled fashion without added base. Ammonium salt with noncoordinating anion (*n*-Bu₄ClO₄) significantly accelerated the polymerization, while added base suppressed the propagation. When using a higher active monomer, pMOS, polymerization using Me₂S at 25 °C reached high conversion and yielded polymer with high *M_n* and narrow MWD.

The effects of temperature and added base on the polymerization of pMOS were investigated. At high temperature (up to 25 °C), the polymerization rate was increased but product polymer was ill-defined. The sulfide with bulky group (Et₂S) coordinated weakly to carbocation, resulting polymerization in a less controlled fashion than using Me₂S (or THT). Some other sulfur containing reagents, such as thiophene, DMSO, PhSMe, and PhSPh, were also studied. Unfortunately, they could not generate effective dormant form with carbocation. In the initiation step, aryl methyl cation with appreciated nucleophilicity was essential for the propagation. Differences in the modes of coordination between benzyl cation and the added bases were demonstrated by ¹H NMR. Benzyl sulfonium ion formed by the reaction of Bn⁺ and Me₂S significantly suppressed polymerization. On the other hand, the more stable and bulky

initiators, Ph_2CHBr and Ph_3CCl , appear to be relatively unaffected by added base for initiation of monomer.

3.5 References

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Chapter 4 Conclusion and Outlook

A benign initiating system for cationic polymerization of VEs and Sts was developed using silver salt, aryl methyl halide and Lewis base. The benzyl cation is readily formed by the reaction between silver salt and aryl methyl halide, and silver halide readily precipitates and is easily removed by filtration. We first carried out cationic polymerization of IBVE. Me₂S was shown to be an effective Lewis base (LB) for controlling the reaction. Detailed study of various benzyl cations and the addition order of reagent addition showed that the reaction was controlled by the steric and electronic features of the benzyl halides, LBs, and IBVE. A plausible reaction mechanism was proposed. As shown in Figure 4.1, this mechanism assumes that there is a difference between the coordination of Me₂S to the benzyl cation, and propagating polymer cation owing to electronic and steric factors.

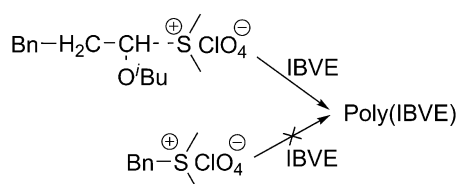


Figure 4.1 Coordination of Me₂S to benzyl cation, and propagating polymer cation.

Based on the above results, other VEs (EVE and IPVE) and sulfides (Et₂S and THF) were studied for cationic polymerization. Monomer reactivity and Lewis base basicity affected polymerization behavior (Chart 4.1). Choosing a sulfide with suitable nucleophilicity was important for achievement of controlled polymerization. In addition, depending on monomer reactivity, selecting the reaction temperature was also essential for suppressing side reactions. Furthermore, block copolymers of VEs were successfully synthesized by sequential addition method.

Chart 4.1 Cationic Polymerization Behaviors Initiated by AgClO₄/Ph₂CHBr/Lewis base^a

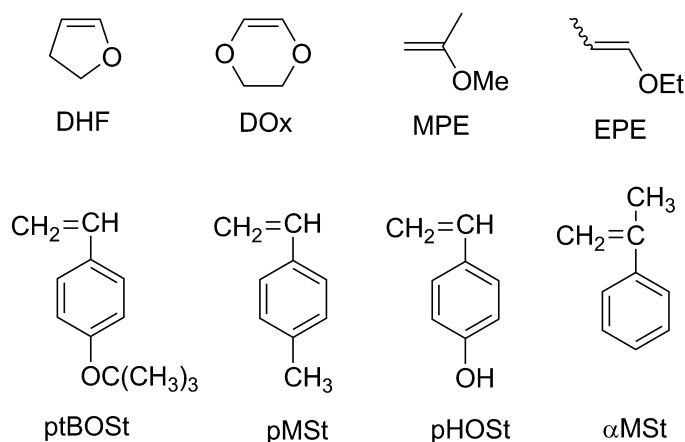
		Monomer reactivity		
Nucleophilicity ↑		IPVE	EVE	IBVE
		-23/-41 °C	-23/-41 °C	-23/-41 °C
	Me ₂ S	●/○	○/×	○/×
	THF	-/○	●/○	●/○
	Et ₂ S	-/○	●/●	●/●

^a ○: controlled, ●: partly controlled, ●: uncontrolled, ×: not polymerized or low conversion.

Styrene derivatives were also studied as monomers for the present new initiating system. Less reactive monomers (styrene, *p*-methoxymethylstyrene and *p*-butoxymethylstyrene) proceeded in an uncontrolled fashion, even employing bulky Lewis base and ammonium salt as an additive. The polymerization of highly reactive

p-methoxystyrene (pMOS) was effectively controlled by using sulfides. In addition, the interaction between aryl methyl halide and added base obviously influenced the polymerization. Detailed comparison of various modes of coordination of benzyl cation to the added bases by ^1H NMR indicated effects of electronic and steric factors of initiator and sulfide on their interaction. These results contribute to both developing benign initiating systems for cationic polymerization and establishing guidance for the effect of interaction between aryl methyl halide and sulfide on the initiation step.

This work described in this thesis contributes to the continuing trend of developing eco-friendly catalyst system for living cationic polymerization. The use of neutral initiators, silver salts and aryl methyl halides, helps to overcome the limitations of the traditional initiating systems derived from their instability and/or troublesome purification. Various Lewis bases (Me_2S , Et_2S , THT) effectively improve the polymerization. Considering the controlled/living polymerization of vinyl ethers, other active enol ethers-type monomers (Scheme 4.1), such as dihydrofuran (DHF), 1,4-dioxane (DOx), ethyl 1-propenyl ether (EPE) and methyl 2-propenyl ether (MPE), should be employed as monomers. Furthermore, based on the detailed study of polymerization of pMOS, other styrene monomers (Scheme 4.1), such as *p*-methyl styrene (pMSt), *p*-hydroxyl styrene (pHOSt), α -methyl styrene (α MSt) and *p*-tertbutoxy styrene (ptBOSSt), would be developed for controlled/living cationic polymerization by choosing suitable added bases, like EtSMe, $^i\text{PrSMe}$. Reaction temperature and solvent are also essential factors.



Scheme 4.1 Enol Ethers and Styrene Monomers.

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