

氏 名	林 麗
博士の専攻分野の名称	博士（工学）
学位記号番号	博理工甲第993号
学位授与年月日	平成27年9月18日
学位授与の条件	学位規則第4条第1項該当
学位論文題目	A Benign Initiating System for Cationic Polymerization of Vinyl Ethers and Styrene Derivatives: Silver Salt/Arylmethyl 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／アリアルハロゲン化メチル／ルイス塩基)
論文審査委員	委員長 教授 廣瀬 卓司 委員 教授 三浦 勝清 委員 教授 斎藤 雅一 委員 教授 黒川 秀樹

## 論文の内容の要旨

This thesis describes the development of an eco-friendly catalyst system for living cationic polymerization. The thesis is composed of four chapters, each of them dealing with different aspects of investigation and application of cationic polymerization.

Chapter 1 is the introduction of cationic polymerization and clarifies basic researching field studied in the thesis. Firstly, it describes the historical background of cationic polymerization. The inceptive achievement of cationic polymerization was in 18th century, but it was in 1984 that the first cationic living polymerization was developed by Higashimura and Sawamoto. Then, comparing of the characteristics of cationic, anionic and radical polymerizations, their polymerization behaviors are shown to be different in reaction conditions and available monomers due to the mechanism. The scope of monomer for cationic polymerization was shown that there are two main types: electron rich olefins and heterocyclic monomers. Base on the cationic polymerization mechanism, Lewis acids (most Friedel-Crafts catalysts) and strong mineral acids are the conventional catalysts and proton donors and cationogenic compounds are used as an initiator. As a result of development of cationic polymerization, it was shown that a large number of commercial polymers have been produced in industry.

Controlled/living polymerization has attracted more attention due to significant advantages. Therefore various methods have been used for preparation of well-defined polymers. The design of living system is based on nucleophilic stabilization of inherently unstable growing terminals. 1) Generating suitable counter anion derived from activation of anion by Lewis acid and 2) forming dormant intermediate by coordination of base to growing carbocation are the two main methods. Controlled/living polymerization is an important method not only for synthesis of functional polymers but also for basic theoretical study. In the end, considering the increasing concerns about environmental problems, this study aimed to develop a benign initiating system to overcome the drawbacks of conventional catalysts; removal the metal catalyst residue is a complicated process, and strong mineral acid requires troublesome technique.

In Chapter 2, benzyl cation readily formed by the reaction of  $\text{AgClO}_4$  and  $\text{BnBr}$  was selected and studied as an initiator due to its suitable stability, and isobutyl vinyl ether (IBVE) was employed as the first monomer for cationic polymerization. Effects of Lewis base, solvent and temperature were studied. It was found that  $\text{Me}_2\text{S}$  effectively improved the polymerization at low reaction temperature. The results of relationship between conversion and time or molecular weight suggested that cationic polymerization using  $\text{AgClO}_4/\text{BnBr}/\text{Me}_2\text{S}$  was partly controlled. Furthermore, the use of more stable and bulkier arylmethyl cation,  $\text{Ph}_2\text{CH}^+$ , resulted in a controlled polymerization with suitable amount of  $\text{Me}_2\text{S}$ . The living nature of the polymerization was examined by a successful chain extension experiment. The MALDI-TOF-MS spectrum of product polymer, which revealed the main peaks separating by an interval corresponding to the monomer repeating unit, further confirmed the controlled polymerization. The molecular weights of well-defined polymers were also estimated by  $^1\text{H}$  NMR spectrum and agreed with those from GPC analysis.

In addition, it was found that the kinds of halide of initiator and anion of silver salt affected the polymerization behavior;  $\text{BnBr}$  gave higher reaction rates than  $\text{BnCl}$ . The non-coordinating anion,  $\text{TfO}^-$ , similar to  $\text{ClO}_4^-$ , caused a vigorous reaction, while strongly nucleophilic ones ( $\text{NO}_3^-$ ,  $\text{SO}_4^-$ , and  $\text{AcO}^-$ ) dramatically suppressed the polymerization. In order to elucidate the reaction mechanism, the effects of Lewis bases,  $\text{Et}_2\text{O}$  and  $\text{Me}_2\text{S}$ , arylmethyl halides ( $\text{BnBr}$ ,  $\text{Ph}_2\text{CHBr}$  and  $\text{Ph}_3\text{CCl}$ ) and the addition order were studied in detail; the electronic and steric features of initiators and Lewis bases appeared to affect the initiation and/or propagation.  $^1\text{H}$  NMR of the initiating system demonstrated the differences in the modes of coordination of benzyl cation to the added bases.

Furthermore, polymerization of other vinyl ethers, ethyl vinyl ether (EVE), isopropyl vinyl ether (IPVE), were also shown to proceed in a controlled manner using  $\text{AgClO}_4/\text{BnBr}/\text{Me}_2\text{S}$  system under a suitable temperature condition depending on monomer reactivity. The spectral features of  $^1\text{H}$  NMR were assigned to well-defined structures of polymer chains and the MALDI-TOF-MS spectroscopy further demonstrated highly controlled polymerization due to clearly resolved peaks corresponding to monomer unit. Some other sulfides,  $\text{Et}_2\text{S}$  and tetrahydrothiophene (THT), were also investigated. The results indicate that choosing a sulfide with suitable nucleophilicity and reaction temperature was essential to control polymerization. The living initiating system,  $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{Me}_2\text{S}$ , was also used for copolymerization of IBVE and EVE.

Chapter 3 extends the application of arylmethyl halide/silver salt/Lewis base initiating systems for cationic polymerization of styrene derivatives. Less reactive monomers (styrene, *p*-methoxymethylstyrene and *p*-butoxymethylstyrene) proceeded in an uncontrolled fashion, yielding polymer with low conversion and broad MWD at  $25^\circ\text{C}$  in a long reaction time (at least 18 h), even employing bulky Lewis base and ammonium salt as an additive. For the highly reactive monomer, *p*-methoxystyrene, the use of sulfides ( $\text{Me}_2\text{S}$ , THT and  $\text{Et}_2\text{S}$ ) effectively controlled polymerization at suitable temperature. However, the polymerization with some other sulfur containing reagents (thiophene, DMSO,  $\text{PhSMe}$ , and  $\text{PhSPh}$ ), which could not generate effective dormant form with growing carbocation, proceeded in a less controlled manner. In addition, differences in modes of coordination of benzyl cation to the added bases were demonstrated by  $^1\text{H}$  NMR. Benzyl sulfonium generated by strong coordination of  $\text{Me}_2\text{S}$  to  $\text{Bn}^+$  dramatically suppressed initiation. The more stable and bulkier initiators,  $\text{Ph}_2\text{CHBr}$  and  $\text{Ph}_3\text{CCl}$ , appeared to be relatively unaffected by added base for polymerization.

Conclusions are drawn in Chapter 4. The cationic polymerization results of vinyl ethers and styrene derivatives were summarized. The presented eco-friendly initiating system using neutral initiators, arylmethyl halide and silver salt, was emphasized to surpass the limitations of conventional catalyst systems due to their instability and/or troublesome purification. The effect of Lewis base ( $\text{Me}_2\text{S}$ ,  $\text{Et}_2\text{S}$  and THF) on controlled polymerization was also recognized.

The investigation of the modes of interaction between arylmethyl cations and Lewis bases contributed to realize the polymerization mechanism well. Extension of the scope of available silver salts and arylmethyl halides is expected to be useful for the development of new initiating systems for cationic living polymerization and copolymerization.

## 論文の審査結果の要旨

This thesis describes the development of an eco-friendly catalyst system for living cationic polymerization. The thesis is composed of four chapters, each of them dealing with different aspects of investigation and application of cationic polymerization.

Chapter 1 is the introduction of cationic polymerization and clarifies basic researching field studied in the thesis. Firstly, it describes the historical background of cationic polymerization. The inceptive achievement of cationic polymerization was in 18 th century, but it was in 1984 that the first cationic living polymerization was developed by Higashimura and Sawamoto. Then, comparing of the characteristics of cationic, anionic and radical polymerizations, their polymerization behaviors are shown to be different in reaction conditions and available monomers due to the mechanism. The scope of monomer for cationic polymerization was shown that there are two main types: electron rich olefins and heterocyclic monomers. Base on the cationic polymerization mechanism, Lewis acids (most Friedel-Crafts catalysts) and strong mineral acids are the conventional catalysts and proton donors and cationogenic compounds are used as an initiator. As a result of development of cationic polymerization, it was shown that a large number of commercial polymers have been produced in industry.

Controlled/living polymerization has attracted more attention due to significant advantages. Therefore various methods have been used for preparation of well-defined polymers. The design of living system is based on nucleophilic stabilization of inherently unstable growing terminals. 1) Generating suitable counter anion derived from activation of anion by Lewis acid and 2) forming dormant intermediate by coordination of base to growing carbocation are the two main methods. Controlled/living polymerization is an important method not only for synthesis of functional polymers but also for basic theoretical study. In the end, considering the increasing concerns about environmental problems, this study aimed to develop a benign initiating system to overcome the drawbacks of conventional catalysts; removal the metal catalyst residue is a complicated process, and strong mineral acid requires troublesome technique.

In Chapter 2, benzyl cation readily formed by the reaction of  $\text{AgClO}_4$  and  $\text{BnBr}$  was selected and studied as an initiator due to its suitable stability, and isobutyl vinyl ether (IBVE) was employed as the first monomer for cationic polymerization. Effects of Lewis base, solvent and temperature were studied. It was found that  $\text{Me}_2\text{S}$  effectively improved the polymerization at low reaction temperature. The results of relationship between conversion and time or molecular weight suggested that cationic polymerization using  $\text{AgClO}_4/\text{BnBr}/\text{Me}_2\text{S}$  was partly controlled. Furthermore, the use of more stable and bulkier arylmethyl cation,  $\text{Ph}_2\text{CH}^+$ , resulted in a controlled polymerization with suitable amount of  $\text{Me}_2\text{S}$ . The living nature of the polymerization was examined by a successful chain extension experiment. The MALDI-TOF-MS spectrum of product polymer, which revealed the main peaks separating by an interval corresponding to the monomer repeating unit, further confirmed the controlled polymerization. The molecular weights of well-defined polymers were also estimated by  $^1\text{H}$  NMR spectrum and agreed with those from GPC analysis.

In addition, it was found that the kinds of halide of initiator and anion of silver salt affected the polymerization behavior;  $\text{BnBr}$  gave higher reaction rates than  $\text{BnCl}$ , The non-coordinating anion,  $\text{TfO}^-$ , similar to  $\text{ClO}_4^-$ , caused a vigorous reaction, while strongly nucleophilic ones ( $\text{NO}_3^-$ ,  $\text{SO}_4^-$ , and  $\text{AcO}^-$ ) dramatically suppressed the polymerization. In order to elucidate the reaction mechanism, the effects of Lewis bases,  $\text{Et}_2\text{O}$  and  $\text{Me}_2\text{S}$ , arylmethyl halides ( $\text{BnBr}$ ,  $\text{Ph}_2\text{CHBr}$  and  $\text{Ph}_3\text{CCl}$ ) and the addition order were studied in detail; the electronic and steric features of initiators and Lewis bases appeared to affect the initiation and/or propagation.  $^1\text{H}$  NMR of the initiating system demonstrated the

differences in the modes of coordination of benzyl cation to the added bases.

Furthermore, polymerization of other vinyl ethers, ethyl vinyl ether (EVE), isopropyl vinyl ether (IPVE), were also shown to proceed in a controlled manner using  $\text{AgClO}_4/\text{BnBr}/\text{Me}_2\text{S}$  system under a suitable temperature condition depending on monomer reactivity. The spectral features of  $^1\text{H}$  NMR were assigned to well-defined structures of polymer chains and the MALDI-TOF-MS spectroscopy further demonstrated highly controlled polymerization due to clearly resolved peaks corresponding to monomer unit. Some other sulfides,  $\text{Et}_2\text{S}$  and tetrahydrothiophene (THT), were also investigated. The results indicate that choosing a sulfide with suitable nucleophilicity and reaction temperature was essential to control polymerization. The living initiating system,  $\text{AgClO}_4/\text{Ph}_2\text{CHBr}/\text{Me}_2\text{S}$ , was also used for copolymerization of IBVE and EVE.

Chapter 3 extends the application of arylmethyl halide/silver salt/Lewis base initiating systems for cationic polymerization of styrene derivatives. Less reactive monomers (styrene, *p*-methoxymethylstyrene and *p*-butoxymethylstyrene) proceeded in an uncontrolled fashion, yielding polymer with low conversion and broad MWD at 25 °C in a long reaction time (at least 18 h), even employing bulky Lewis base and ammonium salt as an additive. For the highly reactive monomer, *p*-methoxystyrene, the use of sulfides ( $\text{Me}_2\text{S}$ , THT and  $\text{Et}_2\text{S}$ ) effectively controlled polymerization at suitable temperature. However, the polymerization with some other sulfur containing reagents (thiophene, DMSO, PhSMe, and PhSPh), which could not generate effective dormant form with growing carbocation, proceeded in a less controlled manner. In addition, differences in modes of coordination of benzyl cation to the added bases were demonstrated by  $^1\text{H}$  NMR. Benzyl sulfonium generated by strong coordination of  $\text{Me}_2\text{S}$  to  $\text{Bn}^+$  dramatically suppressed initiation. The more stable and bulkier initiators,  $\text{Ph}_2\text{CHBr}$  and  $\text{Ph}_3\text{CCl}$ , appeared to be relatively unaffected by added base for polymerization.

Conclusions are drawn in Chapter 4. The cationic polymerization results of vinyl ethers and styrene derivatives were summarized. The presented eco-friendly initiating system using neutral initiators, arylmethyl halide and silver salt, was emphasized to surpass the limitations of conventional catalyst systems due to their instability and/or troublesome purification. The effect of Lewis base ( $\text{Me}_2\text{S}$ ,  $\text{Et}_2\text{S}$  and THF) on controlled polymerization was also recognized. The investigation of the modes of interaction between arylmethyl cations and Lewis bases contributed to realize the polymerization mechanism well. Extension of the scope of available silver salts and arylmethyl halides is expected to be useful for the development of new initiating systems for cationic living polymerization and copolymerization.