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**Design and Control of
Novel Naphthalene-Containing Polymers
via Living Cationic Polymerization**

(リビングカチオン重合によるナフタレン環
含有ポリマーの設計と制御)

A Doctoral Thesis

by

Yu Shinke

Submitted to
the Graduate School of Science
Osaka University

August, 2013

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Chapter 1

GENERAL INTRODUCTION

1. Back Ground

1.1 The Science of Aromatics (Phenyl Group vs. Naphthyl Group)

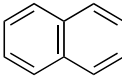
Because of the dual nature of stability and ready reactivity, aromatic compounds compose an important class of organic chemicals. A variety of aromatic structures play critical roles as key stable moieties in the fundamental skeletons of various useful biological and artificial molecules. The reactivity of aromatic compounds is attributed to their abundance of π -electrons, which makes them highly susceptible to electrophiles. Aromatic compounds are good substrates for numerous electrophilic substitution reactions, such as aromatic nitration,¹ aromatic halogenation,² aromatic sulfonation,³ and Friedel-Crafts acylation/alkylation reactions.⁴ These reactions have been widely investigated and used in the production of a variety of chemicals, such as pharmaceuticals and plastics.⁵

The reactivity of aromatic compounds, which is based on their electronic properties, is strongly dependent on the degree of conjugation or the number of conjugated rings. This dependence is clearly evident in a comparison between the simplest aromatics, benzene and naphthalene, as summarized in Table 1. Naphthalene is dozens to thousands of times more reactive than benzene in electrophilic substitution,⁶ oxidation,⁷ or Diels-Alder cycloaddition reactions.⁸ Increased conjugation in an aromatic compound leads to an enhancement of the highest occupied molecular orbital (HOMO) energy of an arene (e.g., -8.14 eV for naphthalene and -9.25 eV for benzene)⁹ and reduces its energy gap relative to the energy of the lowest unoccupied molecular orbital (LUMO) of an electrophile; hence, the HOMO of naphthalene tends to overlap the LUMO of an electrophile more easily than does that of benzene. The effects of other factors, such as the nature of substrate arenes,^{6(c),10} the substituents,¹¹ the solvents,¹² and the catalysts,¹³ have also been investigated at various reaction temperatures.¹¹ A recent development in computational chemistry has allowed reasonable explanations of experimental results on the basis of precise and quantitative calculations of the reactivity.¹⁴

In addition to their stability and reactivity, rigidity is another important feature of aromatic structures. The rigidity is a decisive factor in fixing the whole structure of a molecule by reducing its mobility. This aspect of arenes significantly contributes to improvements in the

physical properties of a polymer chain. For example, polystyrene [poly(St)], one of the most widely used general-purpose plastics, exhibits good thermal properties, with high values of T_g and T_m of 100 and 240 °C, respectively. Polymeric materials with naphthyl rings exhibit higher T_g and T_m values; for example, those of poly(2-vinylnaphthalene) are 127 and 360 °C, respectively. Therefore, these materials have been used as film-forming segments.^{15,16}

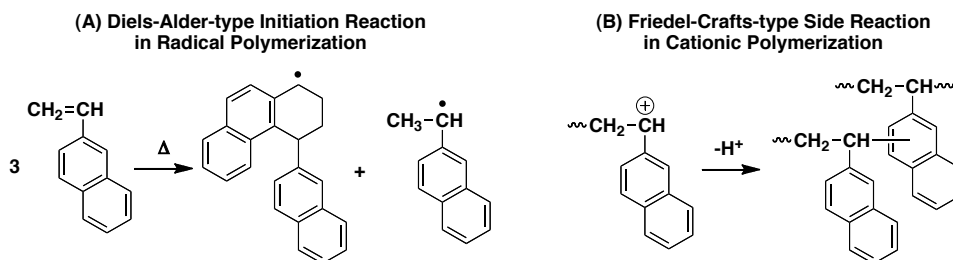
Table 1. Comparison of benzene and naphthalene in their reaction relative rates

		
Cycloaddition ⁸	1	3.2×10^4
Nitration ^{6(b)}	1	3.0×10^2
Bromination ^{6(a)}	1	1.84×10^5 (for 1-position) 1.86×10^3 (for 2-position)
Friedel-Crafts reaction ^{6(c)}	1	44 ($\alpha/\beta = 65/35$)
Dimerization by $h\nu$ ¹⁷	no dimer	

Naphthyl-containing polymers are the focus of significant attention in both the academic arena and in industrial fields because of their unique and excellent properties, which include their mechanical behavior,¹⁸ optical properties,¹⁹ and thermal properties.¹⁵ For example, poly(2-vinylnaphthalene) can be used as a probing fluorescence tag due to its excimer emission [excimer fluorescence $\lambda_{\max} = 335$ nm for poly(styrene) and 410 nm poly(2-vinylnaphthalene)].²⁰ In addition, naphthyl-carrying polymers have been used as a thermoplastic resin and as a base material for photoresists because of their better thermal resistance in comparison with those of their phenyl counterparts and their more efficient light-absorption nature.²¹

Despite these interesting features, the number of polymers with naphthalene rings has been limited because undesired reactions caused by naphthyl groups often occur during polymerization.^{22,23,24} In radical polymerization, the thermal initiation by Diels-Alder-type reactions exhibits an activation energy that is significantly lower than that of St and was found to occur concurrently in the stable free-radical polymerization of 2-vinylnaphthalene [Scheme 1(A)].²³ Consequently, two types of initiations led to uncontrolled polymerization. In cationic polymerization, the high reactivity toward Friedel-Crafts-type reactions, as previously

mentioned, disturbed the control of the reaction ($k_{\text{transfer}} / k_{\text{propagation}} = 17.7 \times 10^4$ for styrene and 100.4×10^4 for 2-vinylnaphthalene) [Scheme 1(B)].²² Although anionic polymerization is the only additional polymerization mechanism that allows living polymerization of 2-vinylnaphthalene, strict purification of the monomer was required to prevent termination by an impurity.²⁴



Scheme 1. Undesired reactions caused by naphthyl groups in (A) radical or (B) cationic polymerization of 2-vinylnaphthalene

1.2 The Use of Living Polymerization for Precise Polymer Design

Living polymerization of vinyl-type monomers is an effective way to incorporate reactive groups into a polymer chain because the stable growing ends tend to remain intact even in the presence of polar and/or reactive compounds. Since the discovery of living anionic polymerization by M. Szwarc,²⁵ the development of living polymerization techniques via several mechanisms has resulted in the preparation of various polymers with features that include precisely controlled molecular weight (MW), molecular weight distribution (MWD), polymer sequence, and/or chain-end functionality. In particular, living cationic and radical polymerizations have allowed the well-controlled polymerization of polar and/or functional monomers. A current trend in precise polymer synthesis is the incorporation of potentially reactive but not protected groups at predetermined positions for the synthesis of block or multibranched copolymers via a post-polymerization reaction.

1.3 The Scope and Limitation of Living Cationic Polymerization

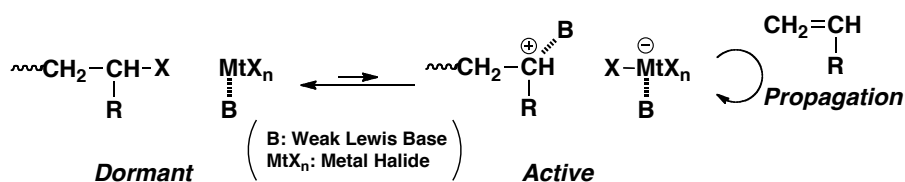
The potential reactive sites in a polymer chain are useful for the design of well-defined polymers with various sequences and/or shapes; however, the moieties can react with the growing species, thereby harming the polymerization reactions. In cationic polymerization, polar or aromatic compounds can play the role of transfer and/or terminating agents. The electron-deficient carbocation exhibits high reactivity toward nucleophilic compounds, such as

amides,²⁶ esters,²⁷ and aromatic groups.^{28,29,30} This high reactivity also facilitates end-capping reactions through the use of various functionalized nucleophiles, such as silyl enol ethers for styrene polymerizations,³¹ sodium dialkylmaronates for vinyl ether (VE) polymerizations,³² and furans,²⁸ pyrroles,²⁹ and alkoxybenzenes³⁰ for isobutylene polymerizations.

Highly efficient cationic polymerization did not become viable for monomers with polar functional groups until the advent of living cationic polymerization systems; the polar functional groups can directly cause transfer and/or termination reactions in conventional cationic polymerization. The total suppression of these side reactions was achieved through the establishment of reaction systems with an extremely small amount of cationic species, which invariably are involved in an appropriate equilibrium between dormant (covalent) and cationic species.³³ This type of equilibrium was realized through control via (1) a nucleophilic counteranion,³⁴ (2) a weak Lewis base through moderate nucleophilic interactions with a carbocation and a Lewis acid,³⁵ and (3) an ammonium salt through the common-ion effect.³⁶ Cationic processes were regarded as the most powerful methods for the synthesis of well-defined polymers with polar functional groups before controlled/living radical polymerization was discovered.³⁷

Another group of monomers with potentially reactive sites is styrene derivatives. The cationic polymerization reactions of those monomers are often disturbed by intra- or intermolecular Friedel-Crafts-type side reactions. This drawback was responsible for the later development of the nearly ideal living cationic polymerization of styrene compared to those of alkyl VEs³⁴ and isobutylene,³⁸ which were prepared using the HI/I₂ initiating system and the tertiary ester/BCl₃ system, respectively. Because of the relatively high electron density of naphthyl groups, the controlled cationic polymerization of naphthyl-containing monomers is undoubtedly difficult and has never been reported. The previously cited report showed that Friedel-Crafts-type reactions occur frequently in the cationic polymerizations of 1- and 2-vinylnaphthalenes.²²

The feasibility of the electrophilic reaction of carbocations depends on a balance between the reactivity of the carbocation from a certain monomer and the nucleophilicity or electron density of a nucleophile. For example, in the living cationic polymerization of isobutyl VE, an aromatic compound with high electron density, such as 1,3,5-trimethoxybenzene, reacts with the propagating carbocation via Friedel-Crafts-type reactions and functions as a chain transfer reagent.³⁹ In contrast, anisole, which is a less electron-dense compound, did not react with the propagating carbocations of isobutyl VE.



Scheme 2. Living cationic polymerization of vinyl monomers with an added base [Method (2)].

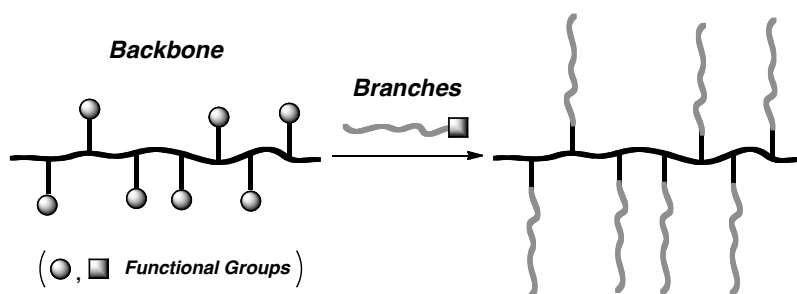
The recent second wave of the significant progress made with initiating systems, especially the base-containing versions (Scheme 2), for living cationic polymerization expanded the scope of monomers that can be polymerized in a controlled or living manner. This revolutionary change was produced as a result of the diversity of available metal halides as catalysts. Motivated by this recent progress, the author decided to examine controlled homopolymerization and copolymerizations with various cationically polymerizable monomers to synthesize functional block, random, and star-shaped polymers with specific properties based on naphthyl groups. The fluorescence property aids in the analysis of polymer morphologies. Furthermore, this research will lead to the development of controlled polymerizations of vinyl monomers with more conjugated aromatic rings, such as anthracene or pyrene rings.

1.4 Graft Copolymers

Persistent progress in living polymerization techniques has allowed for the precision syntheses of a range of well-defined graft copolymers with desirable branched positions as well as controlled MW and MWD of the backbone and branches. Since the development of living anionic polymerization,⁴⁰ this type of polymer has been synthesized via three general methodologies, including the “grafting-from,” the “grafting-through,” and the “grafting-onto” methods, because these polymers show unusual properties that are attributable to their confined and compact structures and to their chain-end effects. For example, surface property control using a graft copolymer is a useful technique for various applications, such as coatings and adhesives.⁴¹ Chujo et al.⁴² have reported that 1 wt% of a poly[methyl methacrylate (MMA)-*graft*- 2-dimethylaminoethyl methacrylate] was sufficient to make a surface hydrophilic when mixed with a poly(MMA).

Among the three approaches, the “grafting-onto” method is better suited for the precise control and characterization of the structures of the backbone and branches because living

polymerizations are independently conducted for linear polymers. However, conventional graft copolymer synthesis often requires the use of protecting and deprotecting functional groups for side-chain polymerization or coupling reactions when linear polymers are to be used as side chains. One common way to avoid such transformations is the use of two polymerization reactions that proceed via different mechanisms. For example, the chloromethylation of polystyrene is required for subsequent reaction with living anionic polymer chains.⁴³ In this procedure, the modification and purification of the backbone are cumbersome tasks. Deffieux's work is a good example of synthesis based on a coupling reaction without modification; the synthesis consists of two types of polymerization reactions: the living anionic polymerization and living cationic polymerization of poly(2-chloroethyl vinyl ether; CEVE) for the side and main chains, respectively.⁴⁴



Scheme 3. Synthesis of graft copolymers by “grafting-onto” method

The recent development of combinations of “click”-type polymer chemistry reactions has enabled the efficient synthesis of graft copolymers by the grafting-onto method, thereby leading to an increasing number of studies that involve this method.⁴⁵ In addition to the grafting efficiency, the fewer steps required for the functional group transformation of a branching reaction is another merit of processes that involve “click” reactions.

Given the previously discussed background information, the direct synthesis of well-defined polymers with latent pendants would lead to the facile synthesis of graft copolymers via a single polymerization mechanism. The potential reactive groups, if they survive the polymerization reactions, can be used without further transformation for termination with living polymer chains to yield graft copolymers. Such simple “grafting-onto” methods usually require two different polymerization mechanisms because a functional group, which reacts easily in the branching step, is unable to survive the first polymerization if both steps are conducted through the same mechanism.

On the basis of their possible high reactivity toward cationic species, naphthyl groups may be used as capping sites for a “grafting-onto” method in cationic polymerizations. However, the literature contains no examples of Friedel-Crafts-type capping reactions of cationically prepared living polymers, even with a low-molecular-weight naphthalene-containing compound. Because Friedel-Crafts alkylation and cationic polymerization proceed under very similar conditions, a judicious choice of the initiating systems and other reaction conditions is required. The results of termination mechanisms based on the highly nucleophilic naphthyl group would lead to the synthesis of various well-defined branched polymers, i.e., not only graft copolymers but also star-shaped polymers.

1.5 pH-Responsive Polymers

From the perspective of physical properties, naphthyl groups are expected to interact strongly with each other in aqueous solution due to the hydrophobic interaction that can be achieved with the assistance of π - π stacking interaction. The strong hydrophobicity of naphthyl groups is exemplified by the fact that the free energy value for the stacking of naphthyl groups is twice as large as that of phenyl groups (free energy of stacking $\Delta\Delta G^\circ = 1.4 \pm 0.2$ for benzene and 2.9 ± 0.2 for naphthalene).⁴⁶ In addition, the stacking ability of naphthyl groups was assessed on the basis of the calculated values for the hydrophobicity, the dipole moment, the polarizability, and the surface areas of various aromatic analogues in a self-complementary DNA duplex.⁴⁶ Such strong hydrophobic interactions based on naphthyl groups are expected to function as a driving force toward the unique self-assembly of polymer segments.

The precise control of the self-assembling behavior of a stimuli-responsive polymer cannot be realized without well-defined polymeric structures with functional groups. The recent development of the living cationic polymerization technique has permitted a high degree of control of primary structures and the tolerance of a wide range of polar groups, such as ether,⁴⁷ carboxyester,⁴⁸ phthalimide,⁴⁹ silyloxy,⁵⁰ and azobenzene⁵¹ groups. This accomplishment is expected to lead to the development of more sophisticated self-assembly systems that respond to various external stimuli, such as temperature,^{47,50} pH,^{48,49} and light.⁵¹

Carboxy-containing polymers contain ionizable functional groups capable of donating or accepting protons upon changes in the pH of their environment; hence, the hydrophobicity of the functional groups changes depending on the pH when the polymer is in water. This specific behavior is expected to be useful in many applications, particularly in biomedical systems.⁵² However, poly(acrylic acid),⁵³ poly(methacrylic acid),⁵⁴ and poly(vinyl benzoate),⁵⁵ which are

the most extensively studied pH-responsive polymers, respond in the acidic region, i.e., in the approximate pH range of 4–5. In contrast, property changes that occur at intermediate or higher pH values are usually required in biomedical fields.⁵⁶ For example, phosphate- and tris-buffered salines, which are commonly used buffer solutions in biological investigations, maintain the pH of the solution at 7–8.

Hydrophobicity in a pH-responsive polymer chain would increase the critical pH value at which phase separation occurs. Recently, Aoshima et al.^{49(c)} demonstrated that novel pH-responsive poly(VE)s with carboxyphenyl groups undergo pH-responsive phase separation in water at approximately pH 6, which is higher than the phase-separating pH of a poly(VE) with short alkyl chains that are less hydrophobic. Thus, a key for controlling the response pH is the introduction of hydrophobic groups with different hydrophobicities in the side group at the position adjacent to a carboxylic group. The introduction of naphthalene rings, which are highly hydrophobic groups with π - π stacking ability, is expected to further increase the phase-separating pH and thereby lead to the practical use of such polymers in the biomedical field.

2. Objectives and Outline of This Thesis

As a result of the dearth of studies on the synthesis of various well-defined naphthalene-containing polymers, the author grew interested in the precise synthesis of novel polymeric materials using naphthalene as a key compound via base-assisting living cationic polymerization. The increased reactivity of a naphthyl group is likely to cause frequent Friedel-Crafts-type side reactions in the cationic polymerization of naphthalene-containing monomers, unlike the case with phenyl-counterparts undergoing living polymerization. Thus, the author first examined the cationic polymerizations of VE monomers with naphthyl groups. Furthermore, because the carbocations generated from vinylnaphthalene derivatives usually exhibit reactivities that vary from those exhibited by naphthyl-containing VEs or styrene derivatives. Thus, the appropriate conditions for the living cationic polymerization of vinylnaphthalene monomers were also investigated with particular focus on the initiating systems.

A novel synthetic methodology for well-defined graft copolymers was then designed around the high reactivity of a naphthyl ring. In addition, the precise synthesis of pH-responsive polymers that contain naphthyl rings and their stimuli-sensitive behavior based on the high hydrophobicity of the naphthyl ring was demonstrated.

This thesis consists of two parts: Part I describes the precision synthesis of naphthalene-containing polymers via base-assisting living cationic polymerization (Chapters 2 and 3). In Part II, the novel design of functional materials through the specific reactivity and properties of the identified naphthyl ring is described (Chapters 4 and 5).

Chapter 2 presents the living cationic polymerization of a naphthalene-containing VE. The naphthyl ring is potentially attacked by an electrophile at two positions: the 1 (α)- and 2 (β)-positions. The cationic polymerization of a β -substituted naphthalene-containing VE was controlled under conditions similar to those used for the living cationic polymerization of its phenyl-containing counterpart. In contrast, the polymerization of an α -substituted monomer was accompanied by side reactions. The cause of the side reactions was investigated through an analysis of the obtained polymers and through theoretical calculations.

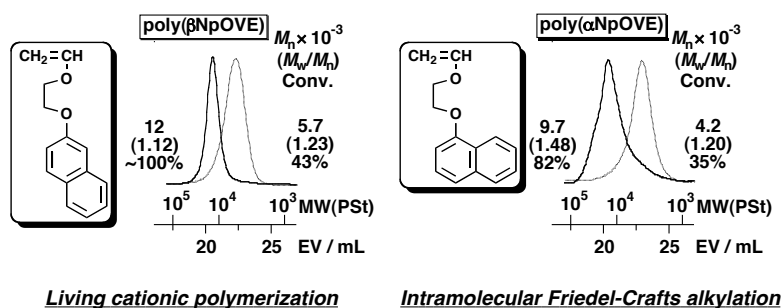


Figure 1. Cationic polymerizations of naphthalene-containing VEs.

In Chapter 3, the cationic polymerizations of various vinylnaphthalene derivatives are examined. The frequent chain transfer reactions that occur under the conditions suited for the corresponding styrene derivative were completely suppressed with the use of appropriate initiating systems at a low temperature, which led to the first living cationic polymerization of vinylnaphthalene derivatives.

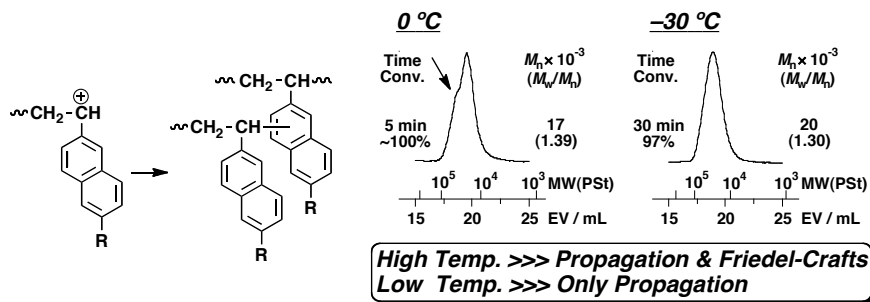
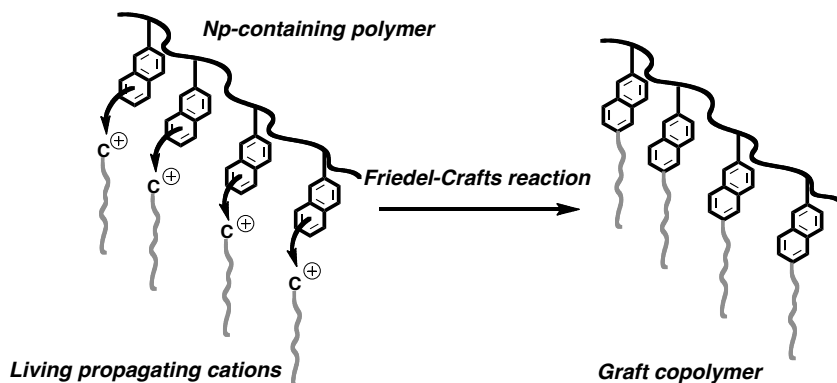


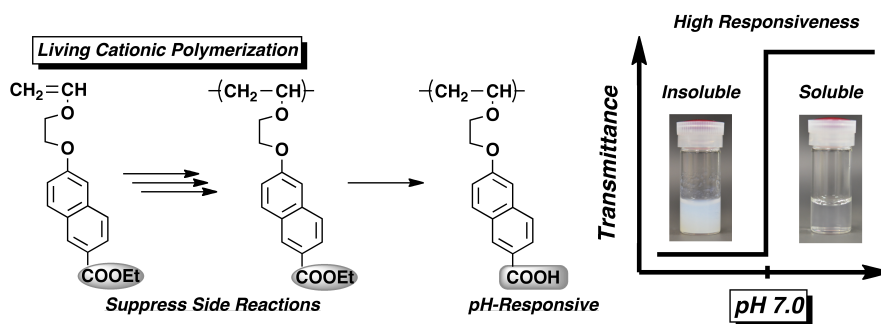
Figure 2. Cationic polymerizations of 6-*tert*-butoxy-2-vinylnaphthalene at various temperatures.

Chapter 4 focuses on the high reactivity of naphthalene for electrophilic substitution reactions. A facile synthesis of graft copolymers was achieved through the use of the naphthalene-containing homopolymer as a quencher for the living cationic polymerization of various styrene derivatives. Living polymers of styrene derivatives that produce less-stable carbocations, such as the *p*-chlorostyrene or *p*-acetoxystyrene polymers, were suited for the highly efficient reactions with naphthyl groups and yielded well-defined graft copolymers.



Scheme 4. Conceptual illustration for synthesis of graft copolymer by living cationic polymerization and subsequent Friedel-Crafts reaction.

Chapter 5 describes the synthesis of a pH-responsive polymer with naphthyl groups. pH-responsive carboxy groups were introduced through deprotection of the carboxy ester groups of a naphthalene-containing VE polymer that was prepared by a living cationic polymerization. The pH-responsive behavior of the obtained homopolymer and copolymer with other functional segments in water was investigated.



Scheme 5. Synthesis of pH-responsive polymer with naphthyl rings and its pH-driven phase separation in water.

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Part I

Living Cationic Polymerization of Naphthalene-Containing Monomers

Chapter 2

Living Cationic Polymerization of Vinyl Ethers with a Naphthyl Group: Decisive Effect of the Substituted Position on Naphthalene Ring

INTRODUCTION

Although the living polymerization of monomers with polar functional groups is a challenge in cationic polymerization, the development of various initiating systems over the past few decades has overcome these problems to a large degree.¹ This progress has led to the precise synthesis of various polyVEs containing functional groups such as oxyethylene,^{2,3} hydroxy,⁴⁻⁶ carboxy,⁷⁻¹⁰ and amine groups.¹¹⁻¹³ Recent developments in initiating systems consisting of various Lewis acids with added bases exhibit high durability toward highly Lewis basic groups, such as azobenzene,¹⁴ urethane¹⁵ and amide¹⁶ groups, and well-controlled synthesis from such monomers has become possible. This extension of the scope of polymerizable monomers has contributed to the synthesis of stimuli-responsive polymers with high sensitivity to temperature, light, and pH in solution^{1,17} or on bulk surfaces.¹⁸⁻²⁰

As described in General Introduction, cationic polymerization of a monomer with an aromatic functional group is often difficult because the aromatic ring can react readily with a carbocation by Friedel-Crafts-type mechanisms under certain reaction conditions. For example, chain transfer reactions with intramolecular alkylation forming an indanyl-ring at the propagating chain end frequently occur in cationic polymerizations of styrene derivatives.^{21,22} Furthermore, naphthalene and its derivatives have high reactivities toward cationic species and electrophilic reagents due to the rich π -electrons in their rings. In fact, the higher reactivity of naphthalene derivatives in electrophilic substitution reactions compared with the corresponding benzenes has been clearly demonstrated.²³⁻²⁵ The rates of nitration of the 1- and 2-positions of naphthalene were estimated to be 470- and 50-fold greater than the corresponding rates for benzene, respectively.²⁴ Furthermore, the rate of chlorination at the 1-position of naphthalene is 6.6×10^4 -fold greater than that of benzene.²⁵ Because of this high reactivity toward electrophilic species, it is often difficult to control the cationic polymerization of vinyl monomers containing a naphthalene ring, such as 2-vinylnaphthalene,²⁶ although various studies achieved controlled cationic polymerization of styrene derivatives and phenyl

group-containing VEs by suppressing Friedel-Crafts-type side reactions under appropriate reaction conditions.

Despite their potential problems, naphthalene rings are of great interest as main-chain or side-chain groups in polymer chains because these groups have attractive physical properties, such as higher thermal stability and desirable optical properties compared to benzene rings. In addition, the bulkiness of naphthalene rings restricts the mobility of the polymer chain, and therefore, the glass transition temperatures (T_g) of polymers containing naphthalene rings are generally higher than those of polymers containing phenyl rings. For example, the T_g of poly(ethylene terephthalate) and poly(ethylene naphthalene-2,6-dicarboxylate) are 84 °C and 134 °C, respectively.²⁷ In addition, vinyl monomers with a naphthyl group in their side-chains are copolymerizable with other vinyl monomers, giving various properties described above to copolymers. In fact, a poly(2-vinylnaphthalene) segment was introduced as a film-forming segment into block copolymers with ionic segments^{28,29}

In this chapter, the author investigates the cationic polymerization of VEs with alkoxy-substituted naphthalene rings in the side chain, as illustrated in Chart 1. Polymerization is conducted using a base-assisted initiating system consisting of a metal halide with a Lewis base, such as an ether or an ester, because this system produces stable and robust cationic growing species. The polymerization properties of monomers with α - or β -substituted naphthalene rings are compared in terms of the reaction rate and the livingness of the reactions. The difference between the two monomers is discussed based on theoretical calculations using methoxynaphthalenes as model compounds.

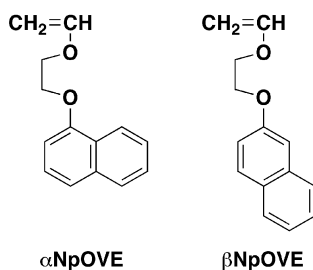


Chart 1. Monomer structures examined in this Chapter

EXPERIMENTAL

Materials

1-Naphthoxyethyl VE [α NpOVE (> 99.5%)] and 2-naphthoxyethyl VE [β NpOVE (> 99.5%)], both of which were supplied by Canon Inc., were recrystallized from methanol and then from dry hexane and vacuum-dried for over 3 h prior to use. 2-Phenoxyethyl VE (PhOVE) was prepared by the reaction of 2-chloroethyl VE (TCI; 97.0%) with phenol and purified by double distillation over calcium hydride under reduced pressure before use.³⁰ Ethyl acetate (Wako; > 99.5%) was dried overnight over molecular sieves 3A and 4A and distilled twice over calcium hydride before use. 1,4-Dioxane (Wako; > 95%) was dried overnight over molecular sieves 3A and 4A and distilled over calcium hydride and then lithium aluminum hydride. Toluene (Wako; 99.5%) was dried by passage through solvent purification columns (Glass Contour). 1-(Isobutoxy)ethyl acetate [IBEA; $\text{CH}_3\text{CH}(\text{O}i\text{Bu})\text{OCOCH}_3$]³¹ and 1-(isobutoxy)ethyl chloride [IBVE-HCl; $\text{CH}_3\text{CH}(\text{O}i\text{Bu})\text{Cl}$],³² used as cationogens, were prepared by addition reactions of IBVE with acetic acid and dry HCl, respectively, according to literature methods. 1-Methoxynaphthalene (α MeONp) was distilled over calcium hydride under reduced pressure, and 2-methoxynaphthalene (β MeONp) was recrystallized from methanol and then dry hexane and vacuum-dried for over 1 h prior to use. Commercial $\text{Et}_{1.5}\text{AlCl}_{1.5}$ (Nippon Aluminum Alkyls; 1.0 M solution in toluene), SnCl_4 (Aldrich; 1.0 M solution in heptane), and ZnCl_2 (Aldrich; 1.0 M solution in ethyl acetate) were used without further purification. A stock solution of FeCl_3 in diethyl ether was prepared from anhydrous FeCl_3 (Aldrich; 99.99%). All materials except for toluene were stored in brown ampoules under dry nitrogen.

Procedures

Polymerization was carried out in a dry nitrogen atmosphere in a glass tube equipped with a three-way stopcock that was baked at over 300 °C under dry nitrogen for 10 min before use. A typical example of the polymerization of β NpOVE in toluene at 0 °C is as follows: β NpOVE monomer was dried for over 3 h in a baked glass tube under vacuum and dissolved in toluene. The reaction was initiated by the addition of a prechilled $\text{Et}_{1.5}\text{AlCl}_{1.5}$ solution in toluene to a mixture of the β NpOVE solution, 1,4-dioxane, and the cationogen (IBEA) at 0 °C with a dry syringe. The polymerization was terminated with prechilled methanol containing a small amount of aqueous ammonia (0.1 wt%). The quenched reaction mixture was diluted with dichloromethane and washed successively with dilute hydrochloric acid, aqueous sodium

hydroxide solution, and water to remove the initiator residues. The volatiles were then removed under reduced pressure at 50 °C, and the residue was purified by reprecipitation in methanol to remove residual monomers. The product polymer was vacuum-dried overnight at room temperature to yield a white rigid polymer. The extent of the monomer conversion was determined by gravimetry.

Characterization

The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with three polystyrene gel columns [Tosoh; TSKgel G-4000H_{XL}, G-3000H_{XL}, and G-2000H_{XL}; exclusion limit molecular weights = 4×10^5 , 6×10^4 , and 1×10^4 , respectively, or TSKgel MultiporeH_{XL}-M $\times 3$; exclusion limit molecular weight = 2×10^6 ; column size = 7.8 mm (internal diameter) $\times$ 300 mm; flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and the polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh; $M_n = 291\text{--}1.09 \times 10^6$, $M_w/M_n < 1.1$). ¹H NMR spectra of the obtained polymers were recorded at 30 °C in CDCl₃ using a JEOL ECA-500 spectrometer at 500 MHz. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were recorded using a Shimadzu/Kratos AXIMA-CFR spectrometer (linear mode) with dithranol (1,8,9-anthracenetriol) as the matrix and sodium trifluoroacetate as the ionizing agent. Differential scanning calorimetry (DSC) was performed with a Seiko Instruments EXSTAR6000 DSC6220 in the range from –20 to 120 °C. The DSC measurements were conducted under a nitrogen purge (50 mL/min.), and the heating and cooling rates were 10 °C/min. The glass transition temperature (T_g) of the polymers was defined as the temperature corresponding to the midpoint of the heat capacity change in the second heating scan.

Computational Methods

All calculations were performed with Gaussian 03 at the density functional calculation (DFT)/B3LYP level of theory with the 6-31G** basis set.³³

RESULTS AND DISCUSSION

Cationic Polymerizations of NpOVEs: Effect of Lewis Acids

Table 1. Cationic Polymerizations of VEs ^a

entry	monomer	activator	added base	time	conv. (%)	$M_n \times 10^{-4}$ ^b	M_w/M_n ^b
1	α NpOVE	$\text{Et}_{1.5}\text{AlCl}_{1.5}$	–	2 sec	94	1.9	3.68
2		$\text{Et}_{1.5}\text{AlCl}_{1.5}$	EtOAc	31 h	89	1.1	1.30
3		$\text{Et}_{1.5}\text{AlCl}_{1.5}$	DO	3 h	66	0.76	1.29
4		SnCl_4	DO	1 min	90	0.44	1.53
5		FeCl_3	DO	7 sec	35	0.27	1.26
6		ZnCl_2	DO	1.5 h	75	0.48	1.41
7	β NpOVE	$\text{Et}_{1.5}\text{AlCl}_{1.5}$	–	1 sec	92	2.0	1.85
8		$\text{Et}_{1.5}\text{AlCl}_{1.5}$	EtOAc	20 h	93	1.3	1.10
9		$\text{Et}_{1.5}\text{AlCl}_{1.5}$	DO	3 h	80	1.0	1.12
10		SnCl_4	DO	1 min	97	0.69	1.33
11		FeCl_3	DO	7 sec	57	0.52	1.28
12		ZnCl_2	DO	1 h	72	0.69	1.29
13	PhOVE	$\text{Et}_{1.5}\text{AlCl}_{1.5}$	DO	4 h	92	1.2	1.05

^a [monomer]₀ = 0.40 M, [IBEA (for $\text{Et}_{1.5}\text{AlCl}_{1.5}$) or IBVE–HCl]₀ = 4.0 mM, [Lewis acids]₀ = 20 mM. [added base] = 1.0 M (for EtOAc) or 1.2 M (for 1,4-dioxane; DO), in toluene at 0 °C.

^b Determined by GPC, polystyrene calibration.

The cationic polymerizations of α NpOVE and β NpOVE were performed using $\text{Et}_{1.5}\text{AlCl}_{1.5}$ as a Lewis acid in conjunction with IBEA as a cationogen in toluene at 0 °C without any additives. The polymerizations of both monomers were complete in a few seconds but were not controlled, producing polymers with broad MWDs (entries 1 and 7 in Table 1). To control the reactions, the polymerizations were conducted in the presence of ethyl acetate, a weak Lewis base capable of inducing the living cationic polymerization of various alkyl VEs.^{1,3,6,9,10,13–20} The reactions of NpOVEs proceeded without induction periods at similar rates to reach almost quantitative conversions (Figure 1A; entries 2 and 8 in Table 1). The rates were comparable to that of the living polymerization of PhOVE, a phenyl-substituted counterpart, under similar conditions (entry 13). The polymerization rates of VEs are often affected by the

nature of their functional substituents.^{2,34} The polymerizations of NpOVEs proceeded much more slower compared to the case of alkyl VEs such as isobutyl, tetradecyl, or dodecyl VE.³⁵ The smaller reactivity may be due to an intramolecular interaction between a growing carbocation and the naphthyl groups in the side chain. The shift of the MWD curves with the consumption of the monomers confirmed the generation of long-lived species (Figure 1D). Furthermore, the M_n values of the α NpOVE and β NpOVE polymers increased in direct proportion to the monomer conversions (Figure 1B). However, an obvious difference in controllability was observed between the polymerizations. The MWDs of poly(β NpOVE) became narrower as the reaction proceeded, but those of poly(α NpOVE) broadened with increasing monomer conversion (Figure 1C). A shoulder peak in a higher MW region and tailing also appeared at the latter stage of the polymerization, as shown in Figure 1D. These facts suggested that undesired reactions involving coupling and chain transfer reactions occurred during the polymerization of α NpOVE.

Cationic polymerizations of NpOVEs using various Lewis acids (SnCl_4 , FeCl_3 , and ZnCl_2) as catalysts were also examined in the presence of an added base. The polymerizations proceeded with all catalysts, but the product polymers had lower MWs and broader MWDs compared with those obtained using the Al catalyst. In addition, the MWDs of the resultant poly(α NpOVE)s were broader than those of their poly(β NpOVE)s counterparts, irrespective of the catalyst used. Based on these results, the author investigated the cationic polymerization of these two monomers in detail using $\text{Et}_{1.5}\text{AlCl}_{1.5}$ as a catalyst.

Living Cationic Polymerization of β NpOVE with $\text{Et}_{1.5}\text{AlCl}_{1.5}$

The linear increase in the M_n values and the narrow MWDs should be evidence that the polymerization of β NpOVE using IBEA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ proceeded in a living fashion (Figure 1B). However, the M_n values determined by GPC were smaller than the theoretical values. This difference is most likely the result of the M_n values being determined relative to polystyrene standards. In fact, the degree of polymerization calculated from the integral ratio of the peaks assigned to the α -end and the main chain in the ^1H NMR spectrum (see Figure 4) agreed well with the calculated value [conv. = 50%, $M_n(\text{GPC}) = 0.68 \times 10^4$, $M_n(\text{NMR}) = 1.1 \times 10^4$, and $M_n(\text{calcd.}) = 1.1 \times 10^4$]. The living nature of the polymerization using the IBEA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ initiating system was further evaluated by a monomer addition experiment in which a fresh feed of β NpOVE solution was added to the reaction mixture when the monomer conversion reached 93% during the first stage of the polymerization. The added monomer was smoothly

consumed to reach almost quantitative conversion (Figure 2A). The molecular weights increased in direct proportion to monomer conversion (Figure 2B), and the GPC peaks shifted to the higher molecular weight region, maintaining a unimodal shape and a narrow MWD (Figure 2C).

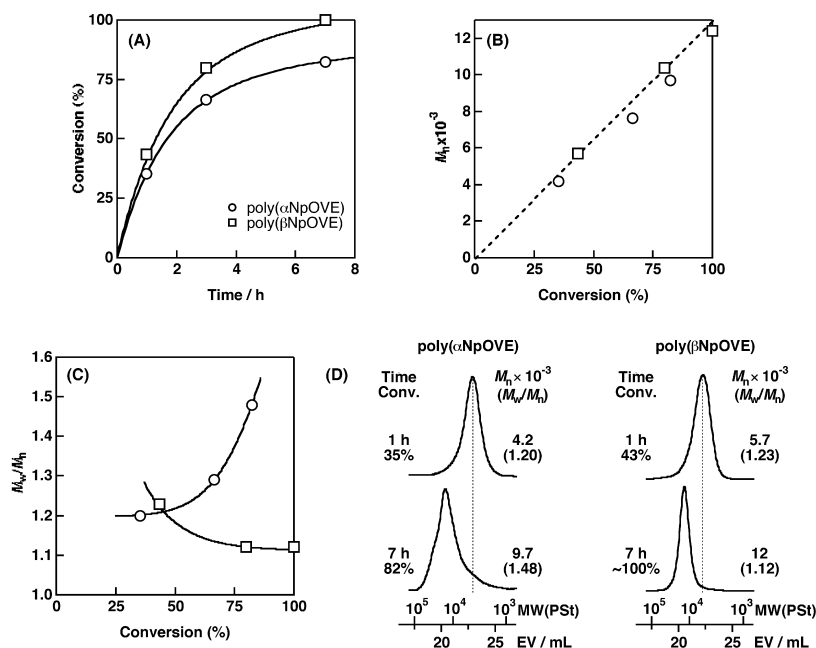


Figure 1. (A) Time-conversion curves, (B) M_n - and (C) M_w/M_n -conversion plots for the polymerization of α NpOVE (circle) and β NpOVE (square), and (D) MWD curves of the obtained polymers using IBEA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ initiating system in toluene in the presence of 1,4-dioxane at 0 °C: $[\text{monomer}]_0 = 0.40$ M, $[\text{IBEA}]_0 = 4.0$ mM, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 20$ mM, $[\text{1,4-dioxane}] = 1.2$ M.

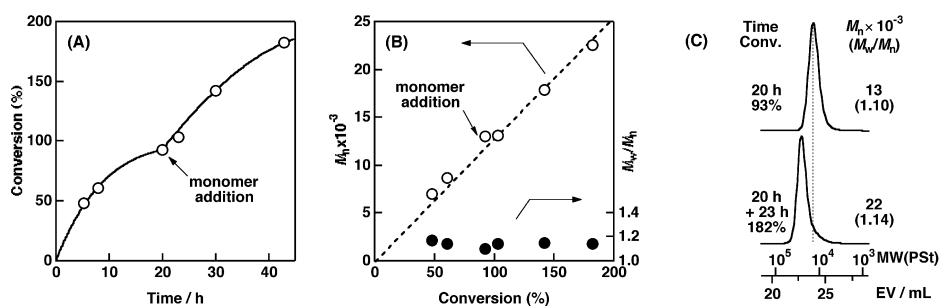


Figure 2. (A) Time-conversion curve, (B) M_n - and M_w/M_n -conversion plots for the polymerization of β NpOVE, and (C) MWD curves of the obtained polymers in the monomer addition experiment using IBEA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ initiating system in toluene in the presence of ethyl acetate at 0 °C: $[\beta\text{NpOVE}]_0 = [\beta\text{NpOVE}]_{\text{add}} = 0.40$ M, $[\text{IBEA}]_0 = 4.0$ mM, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 20$ mM, $[\text{ethyl acetate}] = 1.0$ M.

The absence of side reactions was confirmed by MALDI-TOF-MS and ^1H NMR analyses. In the MS spectrum of the product polymer with $M_n(\text{GPC}) = 0.57 \times 10^4$, only a single series of peaks was observed at constant intervals close to the βNpOVE monomer mass of 214.3 (Figure 3). Furthermore, the m/z of 5943.6 is very close to 5940.2, the calculated mass of the structure with an α -end derived from the cationogen and an ω -end from the quenching agent $[\text{CH}_3\text{CH}(\text{OiBu})-(\beta\text{NpOVE})_{27}-\text{OCH}_3/\text{Na}^+]$. The ^1H NMR spectrum also showed no undesirable structures.

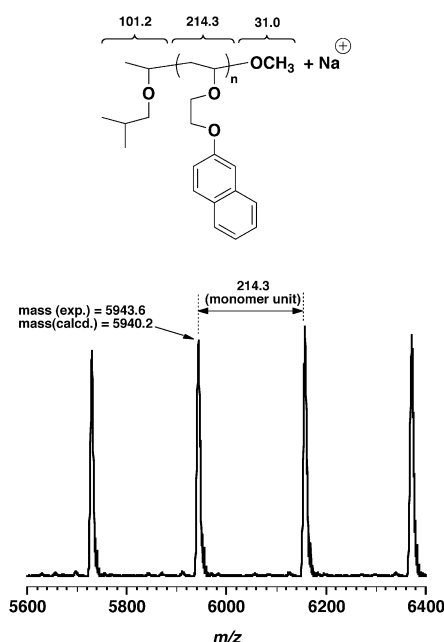


Figure 3. MALDI-TOF-MS spectrum of poly(βNpOVE) (polymerization conditions: $[\beta\text{NpOVE}]_0 = 0.40$ M, $[\text{IBEA}]_0 = 4.0$ mM, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 20$ mM, $[1,4\text{-dioxane}] = 1.2$ M, in toluene at 0°C).

Side Reactions in the Polymerization of αNpOVE

In contrast to the living polymerization of βNpOVE , the polymerization of αNpOVE involved appreciable side reactions, as indicated by the broad MWD curves with two shoulders for the products (Figure 1D). A ^1H NMR analysis of the product polymers revealed the types of side reactions. Figure 4 shows the ^1H NMR spectra of poly(αNpOVE) and poly(βNpOVE) obtained with the $\text{IBEA}/\text{Et}_{1.5}\text{AlCl}_{1.5}$ initiating system in the presence of 1,4-dioxane in toluene at 0°C . The ^1H NMR spectrum of poly(αNpOVE) contained some small peaks in the range of 5–6 ppm, whereas no peaks appeared in this region for poly(βNpOVE). The peaks were

assigned to the methine protons (*p*: see Scheme 1) of the structures resulting from Friedel-Crafts reactions³⁶ and to the olefin protons (*q* and *r*: see Scheme 1) due to side-chain alcohol abstraction.^{38,39} The comparison of the integral ratios of peak *r* and the other peaks (*p* and *q*) suggested that Friedel-Crafts reactions were the primary side reactions.

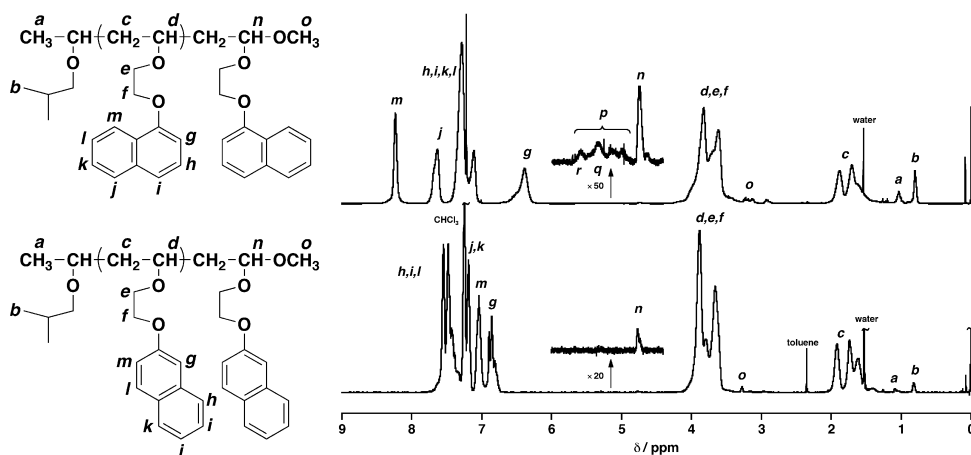
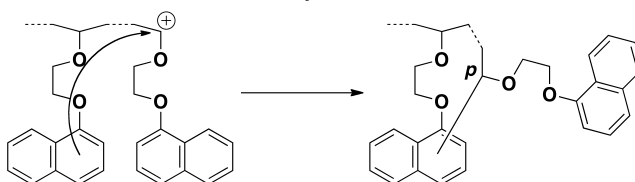
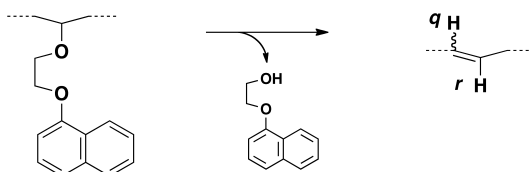


Figure 4. ^1H NMR spectra (500 MHz, CDCl_3 , 30 $^\circ\text{C}$) of poly(αNpOVE) (upper) and poly(βNpOVE) (lower) obtained using IBEA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ in the presence of 1,4-dioxane at 0 $^\circ\text{C}$ (see Scheme 1 for the assignments of peaks *p*, *q*, and *r*; polymerization conditions: $[\alpha\text{NpOVE}]_0 = 0.10$ M or $[\beta\text{NpOVE}]_0 = 0.40$ M, $[\text{IBEA}]_0 = 4.0$ mM, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 20$ mM, $[1,4\text{-dioxane}] = 1.2$ M.)

(A) intramolecular Friedel-Crafts alkylation



(B) mid-chain alcohol abstraction



Scheme 1. Postulated mechanisms of side reactions in cationic polymerization of αNpOVE .

The MALDI-TOF-MS spectra also demonstrated the occurrence of side reactions in the polymerization of α NpOVE. Three series of peaks were detected, as shown in Figure 5, and each series had an interval of 214.3, corresponding to the mass of the α NpOVE monomer. The values of one series agreed with the masses of poly(α NpOVE) chains with an initiator fragment [$\text{CH}_3\text{CH}(\text{O}i\text{Bu})-$] at the α -end and a methoxy terminal [$-\text{OCH}_3$] at the ω -end derived from a methanol quencher. This structure is expected to result from propagation without side reactions. Another series with m/z values of -32 relative to the former series corresponded to two types of structures that were also suggested by the ^1H NMR analysis, i.e., chains derived from intramolecular Friedel-Crafts alkylation or intramolecular side-chain alcohol abstraction. The almost exclusive occurrence of intramolecular Friedel-Crafts reactions (rather than intermolecular reactions) was also suggested because αMeONp induced no side reactions in the living cationic polymerization of PhOVE using the $\text{IBEA}/\text{Et}_{1.5}\text{AlCl}_{1.5}$ initiating system.⁴⁰ The series with low intensity matched the masses of the structures containing internal olefins due to intermolecular or Lewis acid-mediated alcohol abstraction and an ω -end methoxy group.

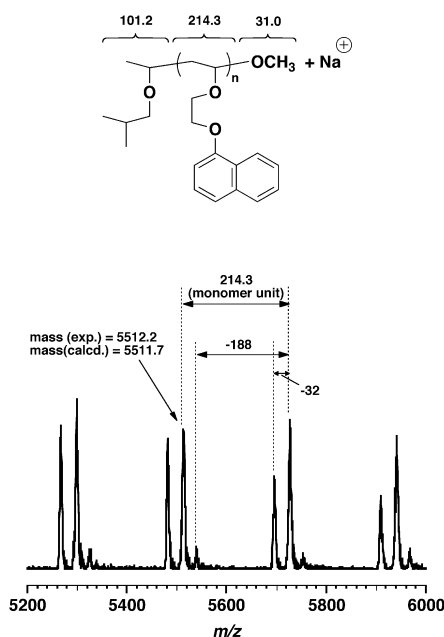


Figure 5. MALDI-TOF-MS spectrum of poly(α NpOVE) ($[\alpha\text{NpOVE}]_0 = 0.10$ M, $[\text{IBEA}]_0 = 4.0$ mM, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 20$ mM, $[1,4\text{-dioxane}] = 1.2$ M, in toluene at 0°C .)

The greater vulnerability of α NpOVE to Friedel-Crafts-type side reactions was well supported by following theoretical calculations. Using density functional theory (DFT) calculations, the highest occupied molecular orbital (HOMO) energies of 1- and 2-methoxynaphthalenes (α MeONp and β MeONp), model compounds of NpOVE monomers, were estimated to be -0.21005 a.u. (-131.84 kcal/mol) and -0.21130 a.u. (-132.59 kcal/mol), respectively. These results indicate that α MeONp is more reactive with electrophilic reagents,^{41,42} such as a growing carbocation, during cationic polymerization. In addition, the probabilities of the highest HOMO electron densities were obtained for the 4-position for α MeONp and for the 1-position for β MeONp, as shown in Figure 6, indicating that the carbons at these positions are most likely to be attacked electrophilically. The lower steric hindrance around the 4-position of α -alkoxy naphthalene relative to the 1-position of β -alkoxy naphthalene may also be responsible for the greater tendency toward electrophilic substitution reactions.

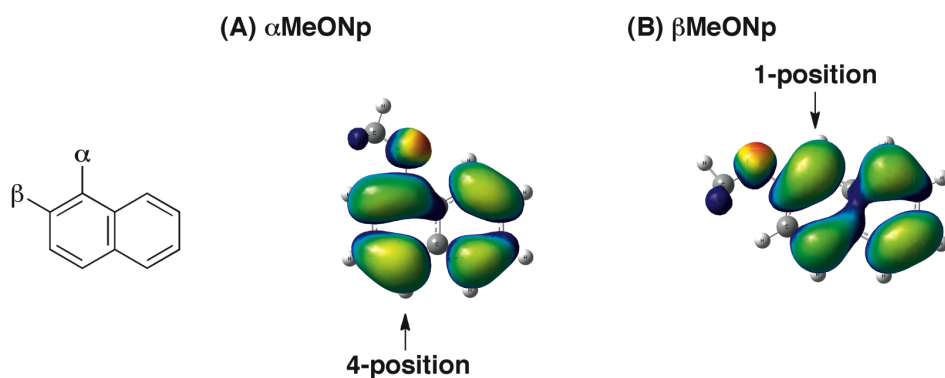


Figure 6. Geometry of (A) α MeONp and (B) β MeONp, optimized by the B3LYP/6-31G** method.

An effective method to suppress Friedel-Crafts reactions in cationic polymerization is to perform reactions at low temperatures. Thus, the cationic polymerization of α NpOVE was examined with the IBEA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ initiating system at -30 °C. However, side reactions were shown to occur by ^1H NMR and MALDI-TOF-MS analyses of the product polymers, although the peaks assigned to the uncontrolled structures were smaller in both analyses than the peaks for the polymers obtained at 0 °C. Polymerization at lower temperatures, such as -78 °C, was not possible due to the poor solubility of the monomer in toluene.

DSC Measurements

Owing to the rigidity of the naphthyl groups, poly(NpOVE)s are expected to have mechanical properties that differ greatly from those of poly(alkyl VE)s. In fact, DSC measurements revealed that the T_g values of poly(α NpOVE) and the poly(β NpOVE) were 42 °C and 41 °C, respectively (Figure 7). These values are much higher than the T_g of poly(ethyl VE) (−42 °C)⁴³ and poly(PhOVE) (−0.5 °C), a phenyl-containing counterpart, although the values were still lower than that of poly(2-vinylnaphthalene) (127 °C),⁴⁴ in which the rigid naphthyl group is directly linked to the main chain. In addition, the two poly(NpOVE)s showed similar T_g values, which was in contrast to the case of poly(naphthyl methacrylate)s [poly(NpMA)s; T_g = 135 °C for poly(α NpMA), T_g = 119 °C for poly(β NpMA)].⁴⁵ The large flexibility of the oxyethylene spacers of poly(NpOVE)s likely moderates the effect of the substitution position of the naphthyl group on the rigidity of the chains, an effect that does not occur in methacrylates.

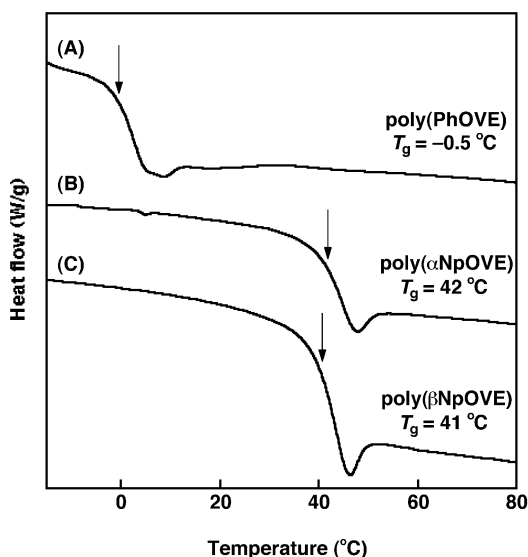


Figure 7. DSC thermograms for (A) poly(PhOVE): $M_n(\text{GPC}) = 2.5 \times 10^4$, $M_w/M_n(\text{GPC}) = 1.05$, (B) poly(α NpOVE): $M_n(\text{GPC}) = 1.3 \times 10^4$, $M_w/M_n(\text{GPC}) = 1.41$, and (C) poly(β NpOVE): $M_n(\text{GPC}) = 2.1 \times 10^4$, $M_w/M_n(\text{GPC}) = 1.10$.

CONCLUSION

The cationic polymerizations of α - and β -substituted naphthoxyethyl VEs were examined using various Lewis acid/added-base initiating systems. The polymerization of β NpOVE proceeded in a living fashion with $\text{Et}_{1.5}\text{AlCl}_{1.5}$ in the presence of 1,4-dioxane or ethyl acetate in toluene at 0 °C. In contrast, frequent side reactions, such as intramolecular Friedel-Crafts reactions, occurred in the polymerization of α NpOVE under similar conditions. The difference in reactivity between the two monomers in electrophilic substitution reactions was attributed to the differences in the HOMO orbital energy and/or in steric hindrance. These results will contribute to monomer design for the precision synthesis of various types of well-defined polymers with naphthalene rings in the side chains. Moreover, because the resultant polymers have T_g values that are higher than room temperature, these polymers can be used as film-forming segments.

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36. The assignment of an end-structure capped by a naphthalene was conducted by comparing to the spectra of alkoxymethylnaphthalene derivatives such as 1,4,5,8-tetrakis(methoxymethyl)naphthalene.³⁷ Peaks of the intervening methine protons between an alkoxy group and a naphthalene ring were observed at 4.9-5.1 ppm.
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40. Living cationic polymerization of PhOVE was carried out using the IBEA/Et_{1.5}AlCl_{1.5} initiating system and an equimolar amount of α MeONp to the monomer was added when the monomer conversion reached 46% (reaction time = 1 h). However, the polymerization

also proceeded in a living fashion without any side reactions even after the addition {polymerization time = 1 h + 6 h, conversion $\sim 100\%$, $M_n(\text{GPC}) = 1.4 \times 10^3$, $M_w/M_n(\text{GPC}) = 1.09$; polymerization condition; $[\text{PhOVE}]_0 = 0.40 \text{ M}$, $[\text{IBEA}]_0 = 4.0 \text{ mM}$, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 20 \text{ mM}$, $[\text{1,4-dioxane}] = 1.2 \text{ M}$, in toluene at 0°C , $[\text{PhOVE}]_0/[\alpha\text{MeONp}]_{\text{add}} = 1/1$ (molar ratio)}.

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Chapter3

Living Cationic Polymerization of Vinylnaphthalene Derivatives

INTRODUCTION

In Chapter 2, the author described the living cationic polymerization of a naphthalene-containing VE. Another type of cationically-polymerizable monomers is a styrene derivative. The controlled cationic polymerizations of certain styrene derivatives is not straightforward because these polymerization reactions have a greater tendency to suffer from Friedel-Crafts reactions, than the polymerization of VEs. Thus, relatively strict reaction conditions are generally required for the living cationic polymerization of styrene derivatives. For styrene or *p*-methylstyrene, for instance, the polymerization must be carried out in the presence of additives at low temperatures, such as $-15\text{ }^{\circ}\text{C}$ or $-80\text{ }^{\circ}\text{C}$.¹⁻³ Based on similar strategies, the living cationic polymerization of various styrene derivatives has been achieved using several initiating systems under appropriate conditions.⁴⁻¹²

Greater difficulties are encountered in the polymerization of styrenic-type monomers such as vinylanthracene,¹³⁻¹⁷ vinylphenanthrene,¹⁸ and vinylnaphthalene derivatives^{14,18-21} because the aromatic rings of these compounds are more susceptible to Friedel-Crafts reactions. This higher susceptibility is due to the high electron densities on the aromatic rings, resulting from the more expanded conjugated systems.²²⁻²⁴ Not only was the controlled polymerization of these monomers achieved, but high molecular weight polymers were obtained in only small amount via a cationic mechanism.

In this chapter, the author examined the cationic polymerization of three vinylnaphthalene derivatives (Chart 1): one with no substituent (2VN), one with an electron-donating substituent (tBOVN), and one with an electron-withdrawing substituent (AcOVN). The pendant groups were expected not only to block side reactions with the naphthalene rings due to the bulkiness of these pendant groups but also to adjust the electron densities of the rings. Our group has reported that the use of an $\text{EtAlCl}_2/\text{SnCl}_4$ combined initiating system is the most effective method for the living cationic polymerization of various styrene derivatives.⁹⁻¹¹ In addition, a variety of metal chlorides have been shown to induce the living cationic polymerization of VEs. Thus, polymerization reactions were first examined

using a single metal chloride or a combined catalyst system. The polymerization behaviors and the polymer properties, such as the T_g , were compared with those of a polymer generated from a corresponding styrene derivative with a *t*BuO group.

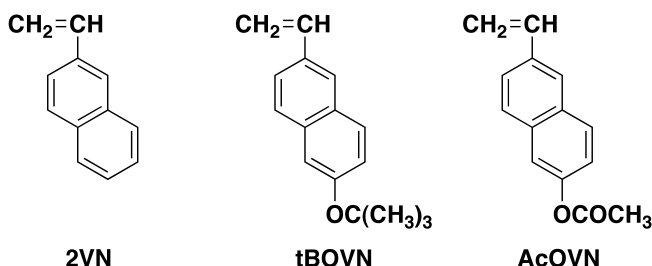


Chart 1. Structures of vinylnaphthalene derivatives

EXPERIMENTAL

Materials

6-*tert*-Butoxy-2-vinylnaphthalene [tBOVN (Tosoh Organic Chemical Co., Ltd.; 99.6%)], 6-acetoxy-2-vinylnaphthalene [AcOVN (Tosoh Organic Chemical Co., Ltd.; 99.6%)], and 2-vinylnaphthalene (2VN; Aldrich; 95%) were dissolved in hexane, washed with 10% aqueous sodium hydroxide and water, and dried thoroughly over NaSO₄ overnight. Subsequently, the monomers were recrystallized from hexane twice and vacuum-dried for over 3 h prior to use. *p*-*tert*-Butoxystyrene (tBOST; Wako; 98.0%) was washed with 10% aqueous sodium hydroxide and water, dried overnight over potassium hydroxide pellets, and distilled twice over calcium hydride before use. Dichloromethane (CH₂Cl₂; Wako; super dehydrated) was dried by passage through a solvent purification column (Glass Contour). Commercially available TiCl₄ (Aldrich; 1.0 M solution in CH₂Cl₂) and EtAlCl₂ (Wako; 1.0 M solution in hexane) were used without further purification. For GaCl₃, a stock solution in hexane was prepared from anhydrous GaCl₃ (Aldrich; > 99.999%). Other materials were prepared and used as described in Chapter 2. All materials except for vinylnaphthalene derivatives and CH₂Cl₂ were stored in brown glass ampules under dry nitrogen.

Polymerization Procedures

Polymerization was carried out under a dry nitrogen atmosphere in a glass tube equipped with a three-way stopcock that had been baked at approximately 400 °C for 10 min before use.

A typical example for the polymerization of tBOVN in CH_2Cl_2 at 0 °C is as follows: A TiCl_4 solution was added to a mixture of IBEA and ethyl acetate in CH_2Cl_2 , and then the solution was kept at room temperature for 30 min to quantitatively produce an initiating species. This solution and SnCl_4 were sequentially added to a tBOVN monomer solution to start the reaction. After a predetermined interval, the polymerization was terminated with methanol containing a small amount of aqueous ammonia (0.1 wt%). The quenched reaction mixture was diluted with CH_2Cl_2 , washed with water to remove the initiator residues, and evaporated to dryness under reduced pressure. The obtained compound was purified by reprecipitation by pouring CH_2Cl_2 polymer solution into methanol to remove residual monomers. The precipitate was vacuum-dried overnight at room temperature to obtain a solid polymer. The percent monomer conversion was determined by gravimetric method or ^1H NMR analysis.

Characterization

The M_n and M_w/M_n of the polymers, and ^1H NMR spectra were measured as described in Chapter 2. Differential scanning calorimetry (DSC) was performed with an EXSTAR6000 DSC6220 instrument in the range of 0 to 80 °C [for poly(tBOS_t)] or 100 to 200 °C [for poly(tBOVN)]. The measurements were conducted under a nitrogen purge (50 mL/min.), and the heating and cooling rates were 10 °C/min. The glass transition temperature (T_g) of the polymers was defined as the temperature corresponding to the midpoint of the heat capacity change during the second heating scan.

RESULTS AND DISCUSSION

Cationic Polymerizations of Vinylnaphthalene Derivatives: the Effect of the Substituent

Cationic polymerization reactions of 2VN, tBOVN, and AcOVN were carried out using SnCl_4 as a Lewis acid catalyst in conjunction with an adduct of isobutyl VE with HCl (IBVE-HCl) as a cationogen in CH_2Cl_2 at 0 °C without any additives. Monomers were consumed quantitatively and the reactions produced polymers under these conditions, but the behavior differed completely among the monomers. The polymerization of tBOVN completed in a few seconds, and yielded a polymer with a broad molecular weight distribution (MWD; polymerization time = 5 sec, conv. ~ 100%, $M_n(\text{GPC}) = 5.5 \times 10^4$, $M_w/M_n(\text{GPC}) = 1.92$). The reactions of 2VN and AcOVN were also not controlled. The frequent occurrence of transfer reactions was indicated by the peaks assignable to the structures derived from not only

β -proton elimination but also intra- or intermolecular Friedel-Crafts alkylation reaction in the ^1H NMR spectra of the resulting polymers. In the ^1H NMR spectrum of the obtained polymer, peaks of the methine protons assignable to the structure derived from Friedel-Crafts alkylations were observed around 4.5–4.8 ppm.²⁵

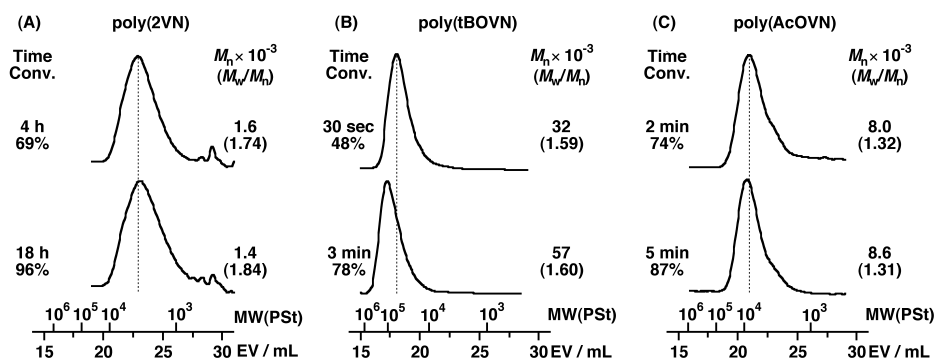


Figure 1. MWD curves for poly(vinylnaphthalene derivative)s obtained using SnCl_4 in CH_2Cl_2 at $0\text{ }^\circ\text{C}$: $[\text{monomer}]_0 = 0.40\text{ M}$, $[\text{IBVE-HCl}]_0 = 4.0\text{ mM}$, $[\text{SnCl}_4]_0 = 10$ (for tBOVN) or 20 (for 2VN and AcOVN) mM, $[\text{ethyl acetate}] = 0.20\text{ M}$ (for 2VN), 1.0 M (for tBOVN), and 0 M (for AcOVN).

To control the reactions of 2VN and tBOVN, ethyl acetate was used as an added base. As shown in Figure 1, the polymerization of 2VN was not controlled, yielding oligomers (Figure 1A), indicative of the frequent occurrence of transfer reactions even in the presence of ethyl acetate. The frequent occurrence of Friedel-Crafts reactions was also supported by the ^1H NMR spectrum, in which some peak signals due to Friedel-Crafts reactions were observed. The polymerization of tBOVN yielded products without oligomeric fractions, and the GPC curve shifted toward the higher molecular weight region as the polymerization proceeded, indicating the existence of long-lived growing species. However, the M_n values were much higher than the theoretical values. These results suggested that tBOVN has a weaker tendency to undergo side reactions such as the Friedel-Crafts reaction, and the initiation reactions were not quantitative. Thus, the polymerization of tBOVN was further examined in detail under various conditions.

Living Cationic Polymerization of tBOVN: The Effects of Initiating Systems and Polymerization Temperatures

Table 1. Cationic Polymerization of tBOVN using various Lewis acids in CH₂Cl₂ at 0 °C ^a

entry	activator	time	conv. (%)	$M_n \times 10^{-4}$ (calcd)	$M_n \times 10^{-4}$ ^b	M_w/M_n ^b
1	SnCl ₄	3 min	78	1.8	5.7	1.60
2	EtAlCl ₂	1 h	68	1.5	2.5	2.13
3	FeCl ₃	10 min	74	1.7	1.9	2.07
4	GaCl ₃	10 min	66	1.5	3.3	1.95
5	TiCl ₄	100 h	48	1.1	0.83	1.53

^a [tBOVN]₀ = 0.40 M, [IBVE–HCl]₀ = 4.0 mM, [Lewis acids]₀ = 10 mM, [ethyl acetate] = 1.0 M.

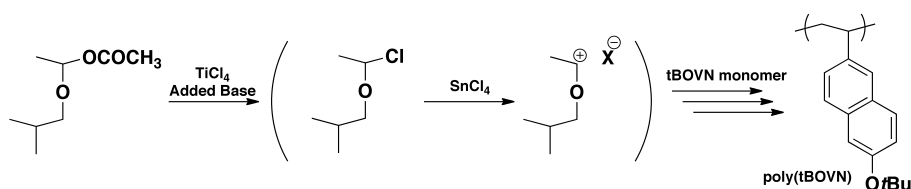
^b Determined by GPC, polystyrene calibration.

As the first step in the controlled polymerization of tBOVN, reactions using various metal chlorides were performed in the presence of ethyl acetate in CH₂Cl₂ at 0 °C (Table 1). The polymerization reactions proceeded smoothly to reach monomer conversions of 60–80% in 3 min–1 h with EtAlCl₂, SnCl₄, FeCl₃, and GaCl₃ (entries 1–4, Table 1). In contrast, it took more than 100 h with TiCl₄ for half of the charged monomer to be consumed (entry 5, Table 1). The positive shifts in the MWD curves with the consumption of the monomers when using TiCl₄ and SnCl₄ indicate the generation of long-lived species.

Among the Lewis acids examined, SnCl₄ was superior to the others with respect to activity and immunity from side reactions, although the initiation efficiency was low. In contrast, TiCl₄ initiated the reaction with high efficiency but showed very low activity. Thus, the author combined these two catalysts to induce controlled polymerization, i.e., quantitative initiation by TiCl₄ and highly active propagation by SnCl₄. In this initiating system, an adduct of IBVE with acetic acid (IBEA) was used as a cationogen instead of IBVE–HCl because IBEA is more stable, easier to handle, and less toxic than IBVE–HCl. The reaction of IBEA and TiCl₄ produces an initiating species quantitatively through the exchange of the acetoxy and chloride anions (Scheme 1; a peak due to the methine and methylene of IBEA shifted from 5.8 ppm to 5.7 ppm and from 3.17 and 3.37 ppm to 3.21 and 3.63 ppm, respectively. Figure 2), in a manner similar to that in the IBEA–Et_xAlCl_{3–x} ($x = 1$ or 1.5)/SnCl₄ combined system.²⁶ The dual Lewis acid system is effective for the controlled polymerization of VEs and styrene derivatives, including functional monomers, as shown in previous studies by S. Aoshima et al.^{9–11,27}

The polymerization using the IBEA–TiCl₄/SnCl₄ initiating system was examined in the

presence of ethyl acetate in CH_2Cl_2 at 0°C . The reaction proceeded quantitatively without an induction period to give a polymer with a very narrow MWD and an M_n value that agreed with the calculated value {conv. = 52% in 30 sec, $M_n = 0.94 \times 10^4$ [$M_n(\text{calcd.}) = 1.17 \times 10^4$], $M_w/M_n = 1.14$ }. However, a further inspection showed that the MWDs of the products broadened in the higher MW region (Figure 3). This result suggested the occurrence of intermolecular Friedel-Crafts alkylation, which was also supported by the fact that the M_n value of this shoulder peak was twice that of the main peak [$M_n(\text{main}) = 1.8 \times 10^4$, $M_n(\text{shoulder}) = 3.6 \times 10^4$]. In addition, the ^1H NMR spectrum of the polymer contained peaks at approximately 4.6 ppm (peak y in Figure 4) that were assignable to the methine protons between the two naphthyl groups resulting from Friedel-Crafts reactions.²⁵



Scheme 1. IBEA- $\text{TiCl}_4/\text{SnCl}_4$ initiating system.

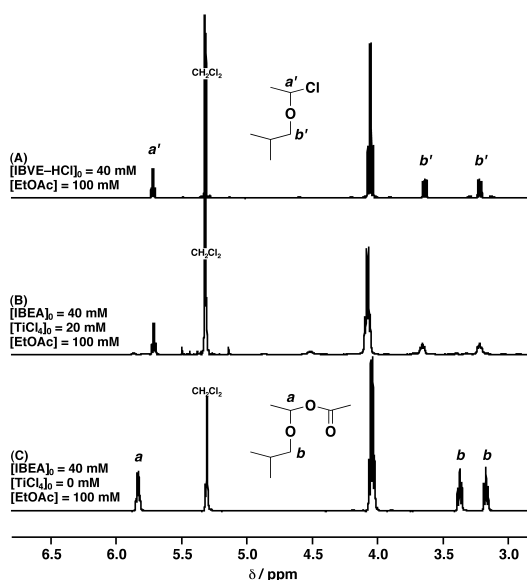


Figure 2. ^1H NMR spectra of (A) IBVE-HCl adduct, (B) the mixture of IBEA and TiCl_4 , (C) IBEA in the presence of ethyl acetate in CD_2Cl_2 at 0°C .

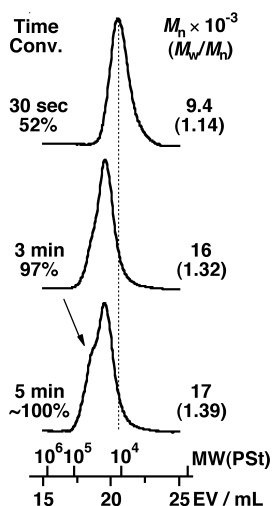


Figure 3. MWD curves for poly(tBOVN) obtained using IBEA–TiCl₄/SnCl₄ initiating system in CH₂Cl₂ in the presence of ethyl acetate at 0 °C: [tBOVN]₀ = 0.40 M, [IBEA]₀/[TiCl₄]₀ = 4.0/2.5, mM, [SnCl₄]₀ = 10 mM, [ethyl acetate] = 0.50 M.

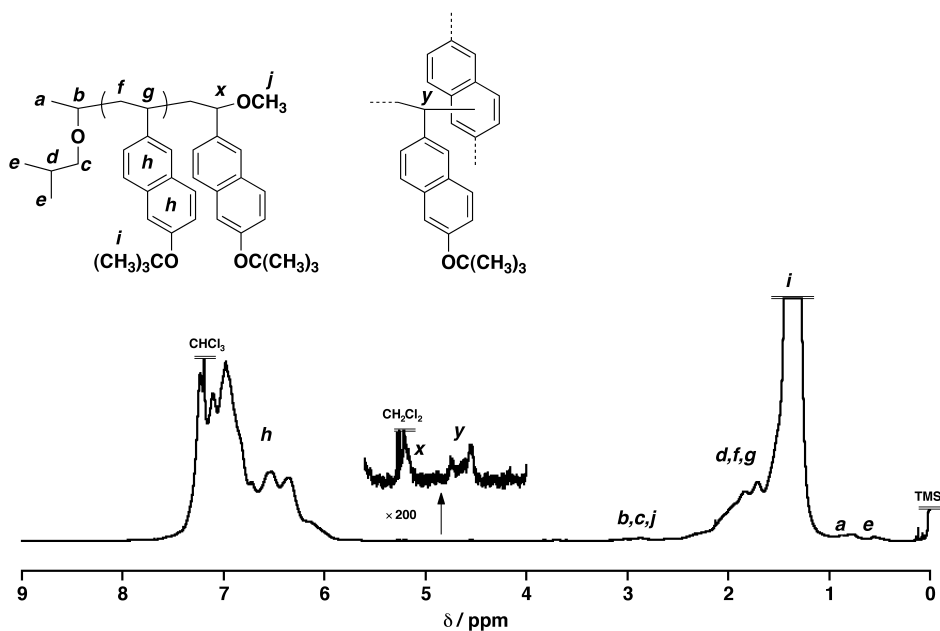


Figure 4. ¹H NMR spectra (500 MHz, CDCl₃, 30 °C) of poly(tBOVN) obtained using IBEA–TiCl₄/SnCl₄ in the presence of ethyl acetate at 0 °C: [tBOVN]₀ = 0.40 M, [IBEA]₀/[TiCl₄]₀ = 4.0/2.5, mM, [SnCl₄]₀ = 10 mM, [ethyl acetate] = 0.50 M. {polymerization time = 3 min, conv = 97%, M_n (GPC) = 1.6×10^4 , M_w/M_n (GPC) = 1.32.}

Table 2. Cationic Polymerizations of tBOVN and tBOS_t using IBEA–TiCl₄/SnCl₄ initiating systems^a

entry	monomer	temp. (°C)	added base	time	conv. (%)	$M_n \times 10^{-4}$ (calcd)	$M_n \times 10^{-4}$ ^b	M_w/M_n ^b
1	tBOVN	0	EtOAc	3 min	97	2.2	1.6	1.32
2		0	DO	3 min	78	1.9	1.8	1.36
3		–15	EtOAc	20 min	97	2.3	2.2	1.40
4		–30	EtOAc	30 min	95	2.0	2.0	1.30
5		–78	EtOAc	5 min	70	1.4	1.6	1.52
6	tBOS _t	0	EtOAc	15 sec	68	1.2	1.4	1.04

^a [tBOVN or tBOS_t]₀ = 0.40 M, [IBEA]₀/[TiCl₄]₀ = 4.0/2.5, mM, [SnCl₄]₀ = 10 mM. [added base] = 1.0 (for EtOAc) or 1.2 (for DO) M in CH₂Cl₂.

^b Determined by GPC, polystyrene calibration.

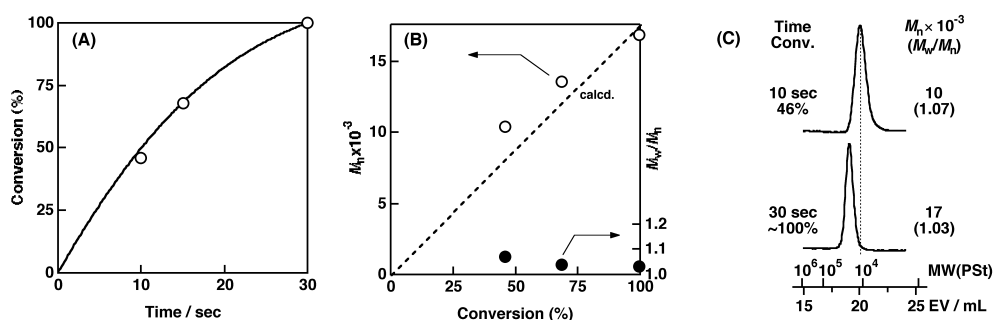


Figure 5. (A) Time–conversion curve, (B) M_n - and M_w/M_n -conversion plots for the polymerization of tBOS_t, and (C) MWD curves of the obtained polymers using IBEA–TiCl₄/SnCl₄ initiating system in CH₂Cl₂ in the presence of ethyl acetate at 0 °C: [tBOS_t]₀ = 0.40 M, [IBEA]₀/[TiCl₄]₀ = 4.0/2.5, mM, [SnCl₄]₀ = 10 mM, [ethyl acetate] = 0.50 M.

In contrast, the cationic polymerization of tBOS_t, a corresponding styrene derivative, proceeded in a living fashion under similar conditions (entry 6, Table 2 and Figure 5). This result suggested that the tBOVN monomer has a higher tendency to engage in side reactions involving the Friedel-Crafts reaction than tBOS_t does, most likely due to the higher nucleophilic nature of the alkoxyⁿaphthyl ring than that of the alkoxyphenyl ring.

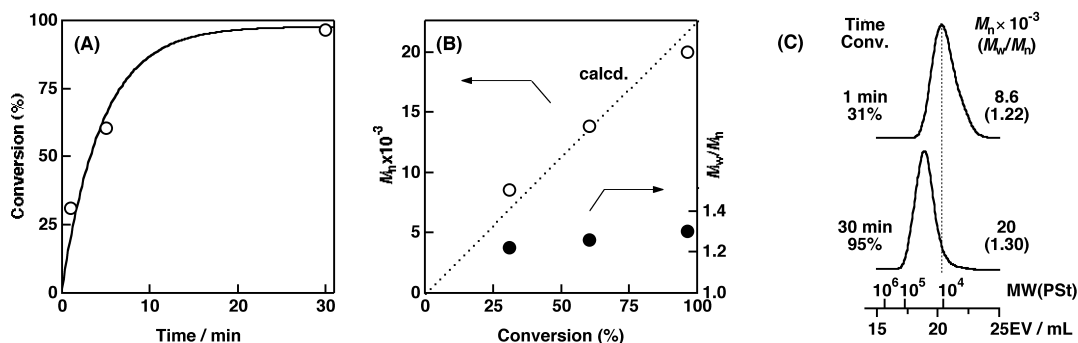


Figure 6. (A) Time-conversion curve, (B) M_n , and (C) M_w/M_n -conversion plots for the polymerization of tBOVN, and (C) MWD curves of the polymers obtained using IBEA- $\text{TiCl}_4/\text{SnCl}_4$ initiating system in CH_2Cl_2 in the presence of ethyl acetate at -30°C : $[\text{tBOVN}]_0 = 0.40\text{ M}$, $[\text{IBEA}]_0/[\text{TiCl}_4]_0 = 4.0/2.5\text{ mM}$, $[\text{SnCl}_4]_0 = 10\text{ mM}$, $[\text{ethyl acetate}] = 0.50\text{ M}$.

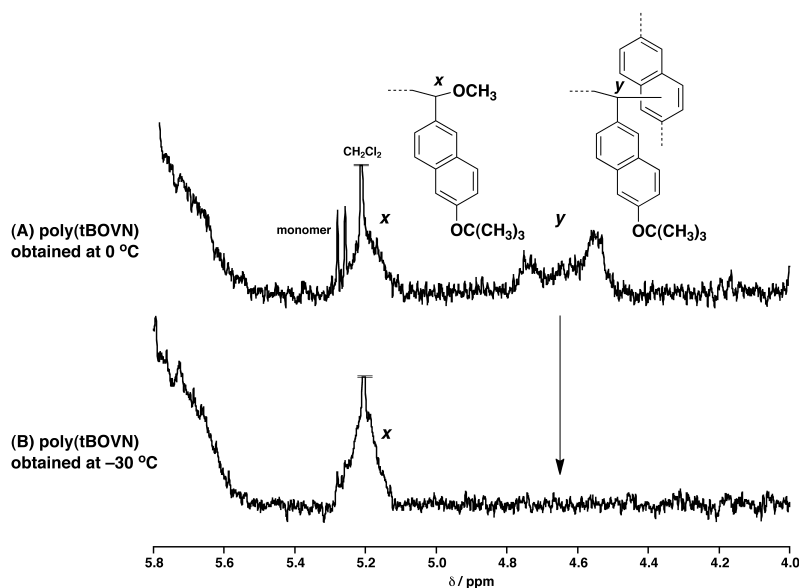


Figure 7. ^1H NMR spectra (500.00 MHz, CDCl_3 , 30°C) of poly(tBOVN)s obtained using IBEA- $\text{TiCl}_4/\text{SnCl}_4$ in the presence of ethyl acetate at (A) 0°C and (B) -30°C : $[\text{tBOVN}]_0 = 0.40\text{ M}$, $[\text{IBEA}]_0/[\text{TiCl}_4]_0 = 4.0/2.5\text{ mM}$, $[\text{SnCl}_4]_0 = 10\text{ mM}$, $[\text{ethyl acetate}] = 0.50\text{ M}$ in CH_2Cl_2 .

Performing reactions at low temperature is known to be one of the most effective methods for suppressing side reactions, such as Friedel-Crafts alkylation, during cationic polymerization. Thus, the polymerization of tBOVN was conducted at lower temperatures (-15°C , -30°C , and -78°C) with the IBEA- $\text{TiCl}_4/\text{SnCl}_4$ initiating system. At -15°C , however, the MWD

curve broadened (entry 3, Table 2) during the later stage, indicating occurrence of side reactions. In contrast, when the polymerization was carried out at $-30\text{ }^{\circ}\text{C}$, quantitative polymerization proceeded, producing polymers with narrow MWDs and M_n values that agreed with the calculated values (entry 4, Table 2). No shoulder peaks appeared, even in the later stage of the reaction. In the ^1H NMR spectrum, peaks corresponding to methine protons at approximately 4.6 ppm resulting from Friedel-Crafts alkylation were not observed (Figure 7B). At $-78\text{ }^{\circ}\text{C}$, the monomer conversion reached a plateau at approximately 70 % in 5 min, and polymers with broad MWDs were produced (entry 5, Table 2).

Monomer addition experiments were also conducted to confirm the livingness of the polymerization at $-30\text{ }^{\circ}\text{C}$. A fresh tBOVN monomer solution in CH_2Cl_2 was added to the polymerization mixture when the first feed was almost completely consumed (conv. approximately 92%). The molecular weight increased in direct proportion with the monomer conversion, even after the monomer addition, and the peak in the GPC curve shifted to the higher molecular weight region as the polymerization proceeded while retaining a narrow MWD, as shown in Figure 8. These results demonstrated that the living cationic polymerization of a vinylnaphthalene derivative was achieved for the first time.

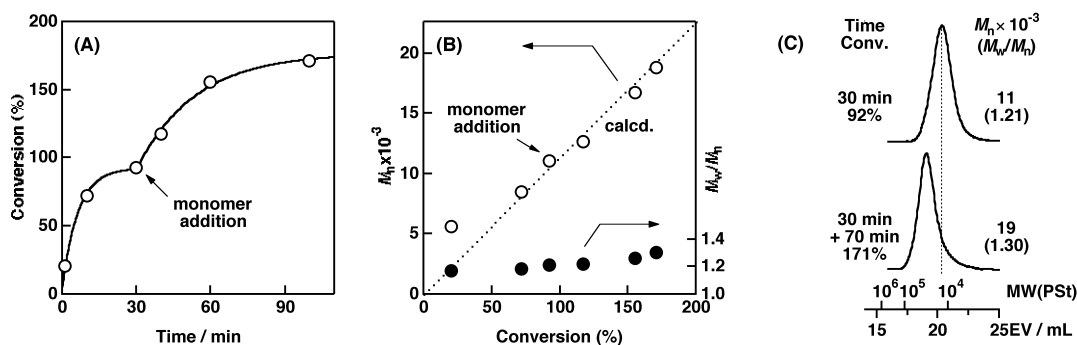


Figure 8. (A) Time-conversion curve, (B) M_n , and (C) M_w/M_n -conversion plots for the polymerization of tBOVN, and (C) MWD curves of the obtained polymers in the monomer addition experiment using $\text{IBEA-TiCl}_4/\text{SnCl}_4$ initiating system in CH_2Cl_2 in the presence of ethyl acetate at $-30\text{ }^{\circ}\text{C}$: $[\text{tBOVN}]_0 = [\text{tBOVN}]_{\text{add}} = 0.20\text{ M}$, $[\text{IBEA}]_0/[\text{TiCl}_4]_0 = 4.0/2.5\text{ mM}$, $[\text{SnCl}_4]_0 = 10\text{ mM}$, $[\text{ethyl acetate}] = 0.50\text{ M}$.

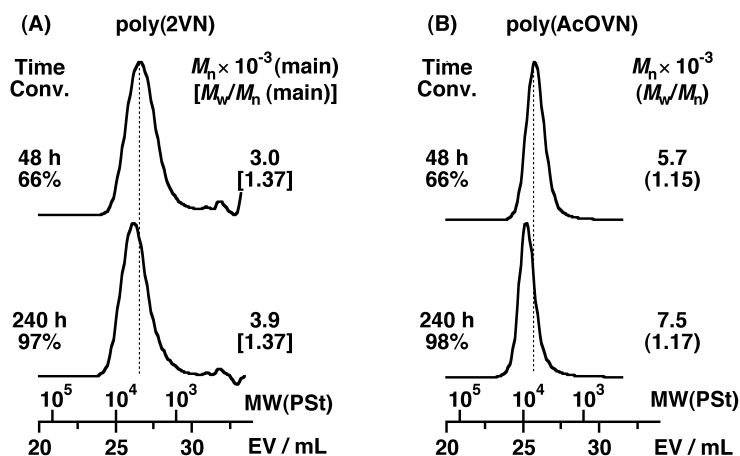
Polymerizations of AcOVN and 2VN Using the IBEA–TiCl₄/SnCl₄ Initiating System

Figure 9. MWD curves for (A) poly(2VN) and (B) poly(AcOVN) obtained using IBEA–TiCl₄/SnCl₄ in the presence of ethyl acetate at –30 °C: [monomer]₀ = 0.40 M, [IBEA]₀/[TiCl₄]₀ = 4.0/2.5, mM, [SnCl₄]₀ = 20 mM, [ethyl acetate] = 0.20 M.

The cationic polymerization reactions of 2VN and AcOVN were examined under conditions similar to those for the living polymerization of tBOVN. With the IBEA–TiCl₄/SnCl₄ combined initiating system, the polymerization of 2VN at –30 °C gave polymers with narrower MWDs and higher molecular weights than did polymerization using SnCl₄ alone at 0 °C (Figure 9A). However, small amounts of oligomers were also produced, indicating the incomplete suppression of chain transfer via Friedel-Crafts reactions. In contrast, the polymerization of AcOVN at –30 °C proceeded in a living fashion and produced well-defined polymers even at the late stage of the polymerization (M_w/M_n = 1.17, Figure 9B). The suppression of Friedel-Crafts reactions was supported by the ¹H NMR spectra of the product.

DSC Measurements

The T_g value of a tBOVN homopolymer (M_n = 1.7×10^4 , M_w/M_n = 1.10) was determined using DSC. The DSC curve is shown in Figure 10, in addition to the DSC curve for poly(tBOST) (M_n = 1.7×10^4 , M_w/M_n = 1.03) for comparison. The T_g s of the polymers are indicated with arrows in Figure 10. The T_g of poly(tBOVN) was 157 °C, higher by 94 °C than that of poly(tBOST), which was 63 °C. This difference is due to the greater rigidity and

bulkiness of the naphthalene rings relative to the benzene rings, restricting the mobility of the polymer chains.

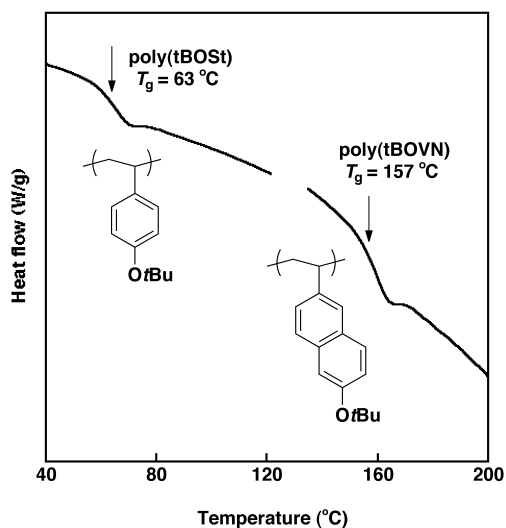


Figure 10. DSC thermograms for poly(tBOVN) ($M_n = 1.7 \times 10^4$, $M_w/M_n = 1.03$) and poly(tBOSt) ($M_n = 1.7 \times 10^4$, $M_w/M_n = 1.10$).

CONCLUSION

The living cationic polymerization of vinylnaphthalene derivatives was first achieved with the IBEA–TiCl₄/SnCl₄ initiating system. Quantitative initiation by TiCl₄ and highly active propagation by SnCl₄ were effective for controlling the polymerization of tBOVN and AcOVN. In addition, low temperature was another key to suppressing side reactions such as Friedel-Crafts alkylation of the naphthyl groups, which are more electrophilic than their Ph counterparts. The homopolymer of tBOVN had a higher T_g by 94 °C than that of tBOSt due to the rigidity and bulkiness of tBOVN. These results will contribute to the application of vinylnaphthalene derivatives as useful products with unique properties.

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Part II

Precision Synthesis of Functional Polymers Based on Reactivity and Property of Naphthalene Ring

Chapter 4

Precision Synthesis of Graft Copolymers via Living Cationic Polymerization of *p*-Acetoxystyrene Followed by Friedel-Crafts-Type Termination Reaction

INTRODUCTION

A straightforward post-polymerization reaction is a powerful method for constructing elaborate polymer architectures. The “click” reaction is among the most effective reactions examined recently. This type of reaction allows the ready and highly efficient synthesis of not only multicomponent linear polymers but also well-defined branched polymers with a controlled three-dimensional sequence arrangement.¹⁻⁴ A Friedel-Crafts alkylation may be another facile post-polymerization reaction because the substrate, an aromatic ring, can survive various types of polymerizations without requiring protection. However this reaction has not been fully developed as a key reaction for the precise synthesis of various polymers.

Friedel-Crafts alkylation could be useful for polymer reactions in cationic polymerizations because an aromatic ring reacts with an electrophile or an electron-deficient species. For example, the use of the electrophilic reactions of aromatic groups has been examined as a novel synthetic tool for producing star-shaped polymers, hyperbranched polymers or end-functional polymers via the cationic polymerization of isobutylene or VEs.⁵⁻¹⁰ More reactive aromatic rings such as a naphthyl group could allow more facile synthesis of well-defined polymers in cationic polymerization. Thus, the author started investigating precision synthesis via cationic polymerization of naphthyl-containing monomers, and have reported the living cationic polymerization of monomers with a naphthyl ring in the previous chapters, despite its high reactivity in the electrophilic substitution reactions owing to more expanded conjugated system than a phenyl ring.^{11,12}

Graft copolymers have received recent attention due to their unique properties,¹³⁻¹⁶ and the synthetic methodologies for preparing these materials are classified according to three general types; (a) “grafting-onto”, (b) “grafting-from”, and (c) “grafting-through” methods. Among these methods, the “grafting-onto” technique, in which the branched chains are formed in advance then attached to the backbone, has the advantage of allowing the full characterization of the product copolymers because the graft density can be easily evaluated

from the molecular weights of the backbone polymer and the branched chains. The grafting-onto method has recently been studied extensively due to the aforementioned “click” chemistry.¹⁻⁴

The use of a Friedel-Crafts reaction in the synthesis of graft copolymers would eliminate one or more steps between the first-stage main chain synthesis and the grafting reaction. Such a simplified synthetic procedure has significant advantages over most conventional “grafting-onto” methods because it eliminates the additional steps necessary for introducing the reactive groups onto the side chains of the backbone polymer and purifying the functionalized polymer.¹⁷⁻²⁰ However, no report has yet described the synthesis of branched polymers via a Friedel-Crafts reaction of more reactive naphthyl groups. Thus, the author focused on the synthesis of graft copolymers using a naphthyl group-containing polymer as a macroterminator. This strategy does not require any functionalization of the side chains because the macroterminator, a well-defined polymer with naphthyl reactive groups, is directly obtained by the base-assisting living cationic polymerization.¹¹

To achieve an efficient reaction of living propagating cations with naphthalene rings, the propagating cations should have high reactivity, which allows the use of less reactive monomers for the synthesis. Highly reactive polyisobutylene or polystyrene carbocations were employed in the above-mentioned synthesis using the Friedel-Crafts reaction.⁵⁻⁹ Another candidate for such less reactive monomers generating highly reactive species is *p*-acetoxystyrene (AcOSt).

In this chapter, the author reports the living cationic polymerization of AcOSt using SnCl_4 as a Lewis acid with the appropriate cationogens and additives. The precision synthesis of various (co)polymers with poly(AcOSt) chains can lead to new materials because poly(AcOSt) can be converted into poly(*p*-hydroxystyrene) (HOSt) via alkali-hydrolysis, which has been utilized for a wide variety of applications from photoresists to adhesives.^{21,22} However, although the cationic polymerization of this monomer has been studied for decades, the living cationic polymerization of AcOSt has not yet been achieved. One somewhat successful example can be found in the study by Storey et al.,^{23,24} which demonstrated the possibility of a controlled cationic polymerization of AcOSt using SnCl_4 as the Lewis acid, and H_2O or AcOSt– H_2O adduct as the cationogen. In addition, a precision synthesis of a well-defined graft copolymer was achieved through a subsequent Friedel-Crafts reaction using a polyVE with a naphthalene ring as the macroterminator in this living system.

EXPERIMENTAL

Materials

p-Methoxystyrene (pMOST; TCI; >95%), *p*-methylstyrene (pMeSt; TCI; >96%), *p*-acetoxystyrene (AcOSt; TCI; >98%), *p*-chlorostyrene (pClSt; TCI; >98%), 2,6-di-*tert*-butylpyridine (DTBP; Aldrich; 97%), and 1-phenylethyl chloride (St-HCl; TCI; >97%) were distilled twice over calcium hydride before use. Methyl chloroacetate (MeClAc; TCI; >98%) was dried overnight over molecular sieves 3A and 4A and distilled twice over calcium hydride before use. For *n*Bu₄NCl, a stock solution in CH₂Cl₂ was prepared from anhydrous *n*Bu₄NCl (Fluka; > 99%). Other materials were prepared and used as described in Chapters 2 and 3. All chemicals and stock solutions except for βNpOVE, toluene and CH₂Cl₂ were stored in brown ampules under dry nitrogen.

Procedures

Synthesis of the Backbone Polymer

Polymerization of NpOVE was employed in a similar manner as described in Chapter 2.

Synthesis of the Graft Copolymer

In the graft copolymerization of poly(AcOSt) (branched chain) with poly(βNpOVE) (backbone polymer), the AcOSt monomer, St-HCl (cationogen) solution in CH₂Cl₂, and ethyl acetate were added successively into a baked tube using dry syringes. The polymerization was initiated by the addition of a SnCl₄ solution in CH₂Cl₂ pre-chilled at 0 °C. After a specific time, a 1.0 mL poly(βNpOVE) solution, which had been previously purified by azeotropic distillation with toluene to remove adventitious water, was added to the reaction mixture (2.5 mL). After another interval, the reaction was quenched with a pre-chilled ammoniacal methanol. The quenched mixture was purified in a manner similar to that described previously.

Alkaline Hydrolysis of the Acetoxy Group

A 1 wt% solution of the graft copolymer with the poly(AcOSt) side chains was prepared in acetone. To this solution, a 3.0 N aqueous NaOH solution (3 equivalents relative to the quantity of acetoxy units in the copolymer) was added to the solution at 0 °C under magnetic stirring. The mixture gradually became cloudy due to the poor solubility of the hydrolyzed units in acetone. After 4 h, deionized water was added to obtain a homogeneous solution, and the stirring was continued for one day. After the mixture was neutralized with 1.0 N aqueous

HCl, the acetone was evaporated, and the polymer product was purified via dialysis against deionized water for at least 2 days, followed by Milli-Q water for another day (the MWCO of dialysis tubes was 12,000).

Characterization

The M_n and M_w/M_n of the polymers, and ^1H NMR spectra were measured as described in Chapters 2 and 3. The absolute weight-average molecular weight was determined using multi-angle laser light scattering coupled with GPC (GPC-MALS) in chloroform at 35 °C on a Dawn HELEOS instrument (Wyatt Technology; Ga–As laser, $\lambda = 658$ nm). The refractive index increment (dn/dc) was measured in chloroform using a differential refractometer (Otsuka Electronics; DRM-3000). The transmittance of the polymer aqueous solutions was measured at 500 nm at various pH values using a JASCO V-550 UV-vis spectrometer equipped with a Peltier-type thermostatic cell holder ETC-505.

RESULT AND DISCUSSION

Living Cationic Polymerization of AcOSt; The Effects of Initiators and Additives

The cationic polymerization of *p*-acetoxy styrene (AcOSt) was first carried out using SnCl_4 as the Lewis acid catalyst in the presence of ethyl acetate or $n\text{Bu}_4\text{NCl}$ as a weak Lewis base²⁵ or an added salt^{26,27} in CH_2Cl_2 at 0 °C (Table 1).²⁸ SnCl_4 was chosen as the catalyst,²⁹ because it is an effective Lewis acid for the living cationic polymerizations of various other styrene derivatives, such as *p*-methoxystyrene (pMOST),^{30,31} *p*-*tert*-butoxystyrene (tBOST),³⁰ *p*-methylstyrene (pMeSt),^{30,32} and *p*-chlorostyrene (pClSt).²⁶ In conjunction with St–HCl as a cationogen, the polymerization of AcOSt proceeded smoothly without an induction period (Figure 1A), yielding polymers with relatively narrow molecular weight distributions (MWDs) ($M_w/M_n = 1.04$ – 1.26). The MWD of the resulting polymer shifted toward the higher molecular weight region over the course of the reaction (Figure 1C). In addition, the M_n value increased linearly with the monomer conversion and was in good agreement with the theoretical values (Figure 1B). A polymerization was conducted using the IBEA– $\text{EtAlCl}_2/\text{SnCl}_4$ system, generating another cationogen in situ and proving efficient for the living polymerization of various styrene derivatives.³⁰ The polymerization of AcOSt proceeded smoothly but slowly with this initiating system, yielding polymers with narrow MWDs ($M_w/M_n = 1.13$; Table 1, entry 4).

Table 1. Cationic Polymerizations of AcOST^a

entry	initiator	additive ^b	[M] ₀ /[I] ₀	time / h	conv. (%)	$M_n \times 10^{-3}$ ^c	M_w/M_n ^c
1	St-HCl	EtOAc	100	24	97	13	1.13
2		EtOAc	50	18	97	7.2	1.17
3		EtOAc	20	5	91	3.0	1.26
4	IBEA-EtAlCl ₂	EtOAc	160	130	98	16	1.13
5	St-HCl	<i>n</i> Bu ₄ NCl	100	4	94	13	1.04

^a [AcOST]₀ = 0.65 (for entry 4) or 1.0 (for entries 1–3, 5) M, [initiator]₀ = 4.0 (for entry 4), 10 (for entries 1 and 5), 20 (for entry 2) or 50 (for entry 3) mM, [SnCl₄]₀ = 20 (for entry 4) or 100 (for entries 1–3, 5) mM. [additive] = 0.20 M (for entry 4), 1.0 M (for entries 1–3) or 40 mM (for entry 5), in CH₂Cl₂ at 0 °C.

^b EtOAc = ethyl acetate

^c Determined by GPC with polystyrene calibration.

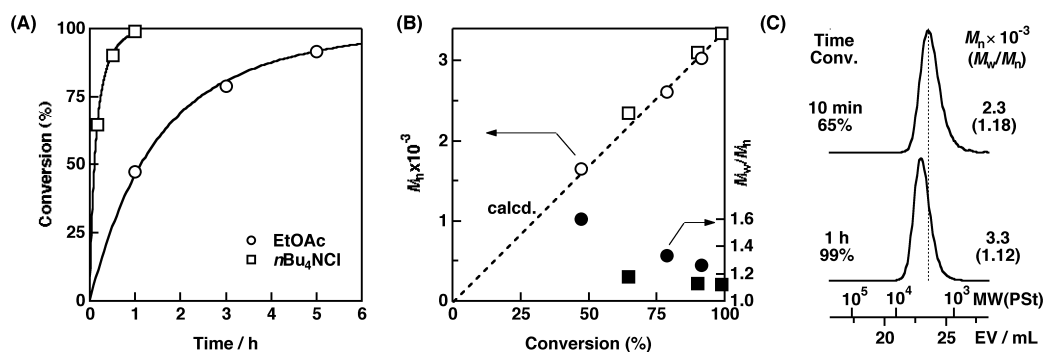


Figure 1. (A) Time–conversion curves, (B) M_n -, and M_w/M_n -conversion plots, and (C) MWD curves of the obtained poly(AcOST)s using St-HCl/SnCl₄ initiating system in the presence of ethyl acetate or *n*Bu₄NCl in CH₂Cl₂ at 0 °C; polymerization conditions: [AcOST]₀ = 1.0 M, [St-HCl]₀ = 50 mM, [SnCl₄]₀ = 100 mM, and [ethyl acetate] = 1.0 M (circles) or [*n*Bu₄NCl] = 40 mM [squares and (C)].

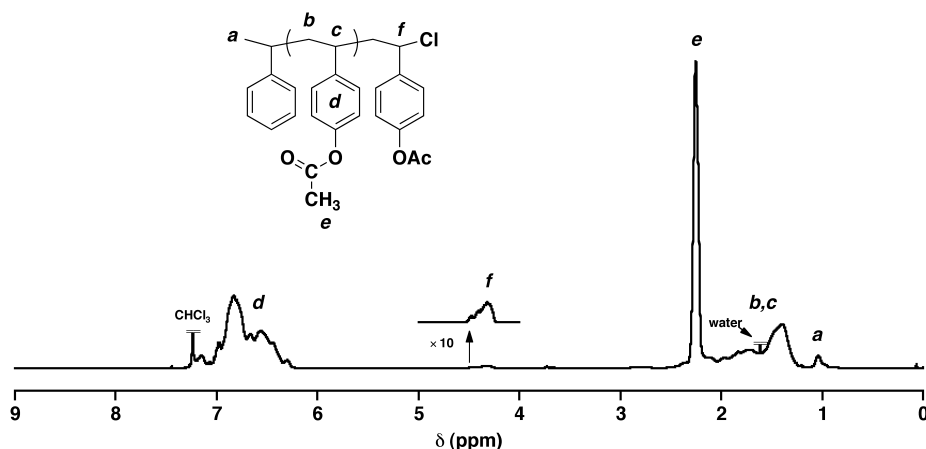


Figure 2. ^1H NMR (500 MHz, CDCl_3 , 30 $^\circ\text{C}$) spectrum of poly(AcOSt) ($M_n = 3.0 \times 10^3$, $M_w/M_n = 1.26$) obtained using St-HCl/ SnCl_4 initiating system in CH_2Cl_2 at 0 $^\circ\text{C}$; polymerization conditions: $[\text{AcOSt}]_0 = 1.0$ M, $[\text{St-HCl}]_0 = 50$ mM, $[\text{SnCl}_4]_0 = 100$ mM, $[\text{ethyl acetate}]_0 = 1.0$ M.

The ^1H NMR analysis of the resulting polymer revealed a well-defined polymer structure with an initiator fragment at the α -end (Figure 2; peak *a*) and a carbon-chlorine bond at the ω -end (peak *f*). The end-functionality (F_n) was determined to be 0.93 based on the integral ratio of the chain-end peaks ($F_n = 3f/a$). No peaks were observed for side reaction products such as β -proton elimination and Friedel-Crafts-type reactions, which indicates the quantitative formation of one polymer chain per one St-HCl. These results confirmed that the polymerization of AcOSt proceeded in a highly controlled manner.

The living nature of the polymerization using a St-HCl/ SnCl_4 initiating system was confirmed by the monomer addition experiment. A fresh AcOSt solution was fed to the reaction mixture when the initial feed was nearly consumed. The added monomer was polymerized smoothly and consumed nearly quantitatively in 6 h [Figure 3(A)]. The resulting polymer exhibited a unimodal and narrow molecular weight distribution, irrespective of the monomer conversion. In addition, the M_n increased in direct proportion with the degree of monomer conversion [Figure 3(B)]. The ^1H NMR spectrum revealed that the resulting polymer exhibited a quantitative end-functionality ($F_n = 0.99$). These results demonstrated that the St-HCl/ SnCl_4 initiating system induced the living cationic polymerization of AcOSt in the presence of an appropriate additive.

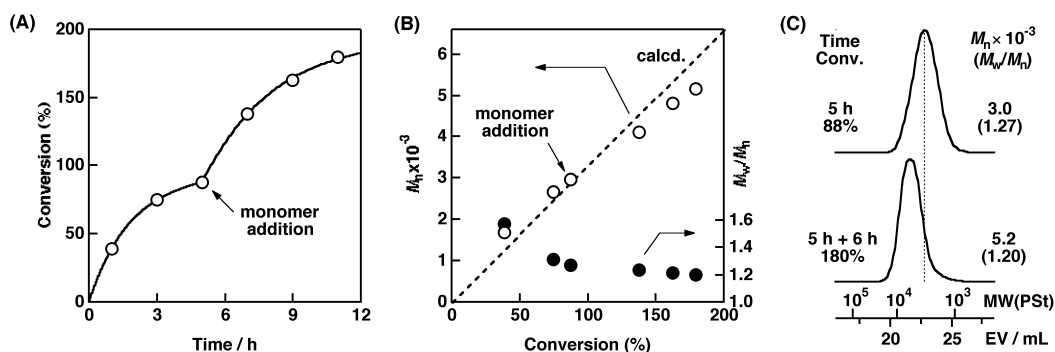
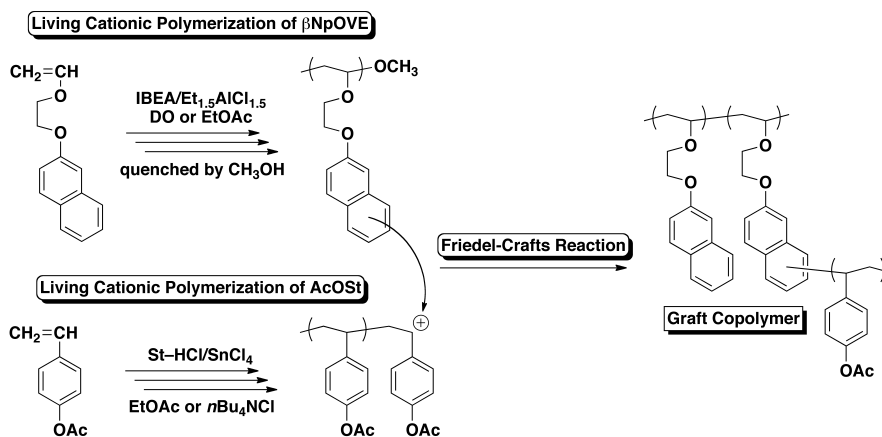


Figure 3. (A) Time–conversion curves, (B) M_n - and M_w/M_n -conversion plots for the polymerization of AcOSt, and (C) MWD curves of the obtained polymers using St–HCl/SnCl₄ initiating system in the presence of ethyl acetate in CH₂Cl₂ at 0 °C; polymerization conditions: [AcOSt]₀ = 1.0 M, [St–HCl]₀ = 50 mM, [SnCl₄]₀ = 100 mM, and [ethyl acetate] = 1.0 M, [AcOSt]₀/[AcOSt]_{add} = 1/1 (molar ratio).

Precision Synthesis of Graft Copolymer Branched Poly(AcOSt)s via the Subsequent Friedel-Crafts Reaction

The synthesis of graft copolymers was examined using poly[2-(2-naphthoxy)ethyl VE] [poly(βNpOVE)] as a multifunctional terminator for the living cationic polymerization of AcOSt as illustrated in Scheme 1. The naphthyl group was expected to function as a Friedel-Crafts-type quencher because of its high nucleophilicity. The author have demonstrated that a well-defined poly(βNpOVE) was synthesized by a base-assisting living cationic polymerization with the IBEA/Et_{1.5}AlCl_{1.5} initiating system described in Chapter 2.¹¹



Scheme 1. A synthetic route of the graft copolymers via living cationic polymerization of AcOSt and subsequent Friedel-Crafts reaction with poly(βNpOVE)

Table 2. Synthesis of graft copolymers with various poly(Sts) ^a

entry	branch	[cationogen] ₀ / [Np units] _{add}	$M_n \times 10^{-4}$ (GPC) ^c	M_w/M_n (GPC) ^c	NB ^f	grafting reaction efficiency (%) ^g
1 ^b	AcOSt	1/10	5.1	1.24	18	95
2 ^b		1/5	5.6	1.20	29	31
3 ^b		1/1	6.4	1.14	41	22
4 ^c	pClSt	1/10	4.2	1.24	18	96
5 ^c		1/1	6.2	1.17	66	35
6 ^d	pMeSt	1/10	2.7	1.14	2	11
7 ^d		1/1	4.3	1.14	17	8.9

^a Added poly(β NpOVE): M_n (GPC) = 2.5×10^4 , M_w/M_n (GPC) = 1.10. Degree of polymerization = 190. The reactions were conducted in CH₂Cl₂ at 0 °C for 40 h.

^b [AcOSt]₀ = 1.0 M, [St–HCl]₀ = 50 mM, [SnCl₄]₀ = 100 mM, [ethyl acetate] = 1.0 M.

^c [pClSt]₀ = 1.0 M, [St–HCl]₀ = 50 mM, [SnCl₄]₀ = 100 mM, [*n*Bu₄NCl] = 40 mM.

^d [pMeSt]₀ = 1.0 M, [IBVEeHCl]₀ = 50 mM, [SnCl₄]₀ = 10 mM, [2,6-di-*tert*-butylpyridine] = 10 mM.

^e Determined by GPC for main peaks, polystyrene calibration.

^f The number of branches. Estimated by ¹H NMR integral ratios.

^g Calculated by the following equation; $100 \times [\text{estimated number of branches}]/[\text{theoretical number of branches}]$.

A poly(β NpOVE) solution in CH₂Cl₂ was added to the AcOSt polymerization mixture at 96% AcOSt conversion. Using a [St–HCl]₀/[naphthalene units in the poly(β NpOVE)] ratio of 1/10 (entry 1 in Table 2 and Figure 4), the GPC curve shifted toward the higher molecular weight region after adding the polymer solution while maintaining a narrow MWD. The grafting reaction was nearly quantitative (95%), although a small quantity of poly(AcOSt)s remained. The incomplete of the grafting reaction likely stemmed from a small quantity of dead AcOSt chains that formed indanyl end structures due to an intramolecular Friedel-Crafts-type reaction. In addition, the grafting efficiency decreased with the increasing [St–HCl]₀/[naphthalene units in the poly(β NpOVE)] ratios (1/5 and 1/1, entries 2 and 3 in Table 2), an effect that is likely due to a steric hindrance among the grafted branches, which prevented further reactions between the living polymers to the unreacted naphthyl groups.

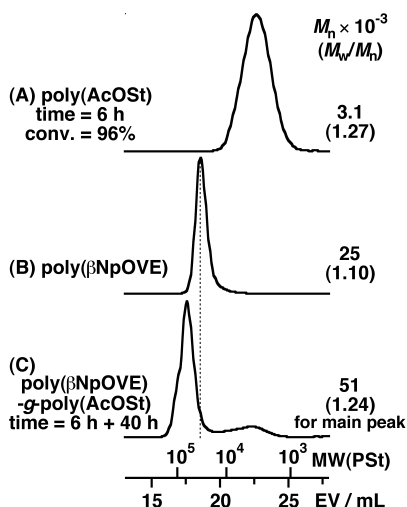


Figure 4. MWD curves for the synthesis of (A) poly(AcOSt), (B) poly(βNpOVE) and (C) the product after the addition of poly(βNpOVE): $[\text{AcOSt}]_0 = 1.0 \text{ M}$, $[\text{St-HCl}]_0 = 50 \text{ mM}$, $[\text{SnCl}_4]_0 = 100 \text{ mM}$, $[\text{ethyl acetate}] = 1.0 \text{ M}$, in CH_2Cl_2 at 0°C . $[\text{St-HCl}]_0/[\text{Np units}]_{\text{add}} = 1/10$ (molar ratio).

The absolute molecular weight of the graft copolymer (entry 3 in Table 2) was determined using GPC–MALS analysis. The obtained value $[M_w(\text{MALS}) = 2.0 \times 10^5]$ was larger than that obtained by simple GPC analysis with polystyrene standards $[M_w(\text{GPC}) = 6.4 \times 10^4]$, which supports the formation of a branched and compact structure. The number of branched polymers was calculated to be 43 using the following equation;

$$\text{number of branches} = \frac{(M_w \text{ of graft copolymer}) - (M_w \text{ of backbone polymer})}{M_w \text{ of branched polymer}}$$

in which the M_w s were determined via GPC–MALS measurements.

The high efficiency of the grafting reaction was also confirmed by the ^1H NMR spectrum (Figure 5) of the resulting graft copolymer, poly(βNpOVE)-*graft*-poly(AcOSt), after the fractionation via GPC. The spectrum presents a new peak (*f* in Figure 5) that is not derived from the VE backbone or the poly(AcOSt). The signal is assignable to the methine proton adjacent to the naphthyl and phenyl rings. The presence of this structure confirms that the proposed Friedel-Crafts-type termination reaction took place between the naphthyl groups and the living AcOSt polymer.³³ The number of branches calculated by the ratio of the backbone peak integral (peaks *b*, *c*, and *d*) with that of the aromatic peaks (peaks *e*, *i*, and *k*) was 41,³⁵ which is in good agreement with the value of 43 estimated by GPC–MALS.

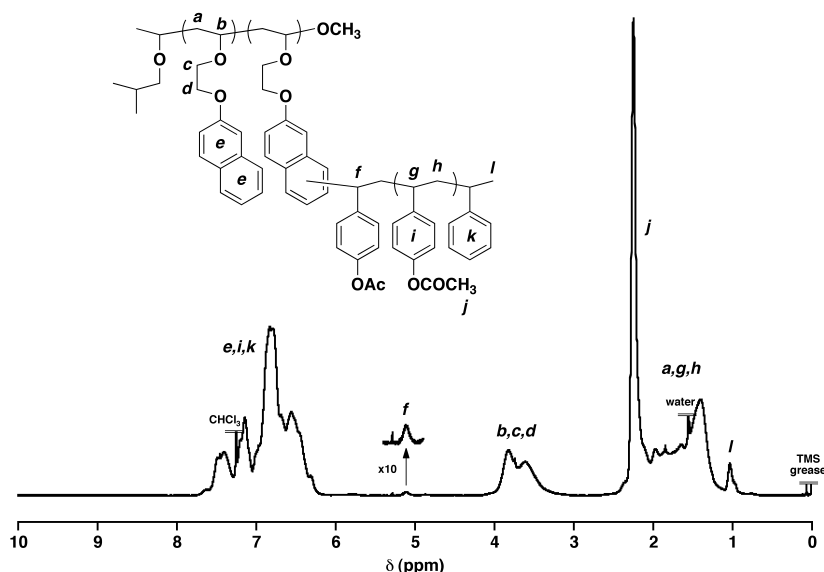


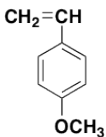
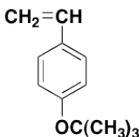
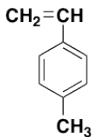
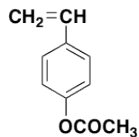
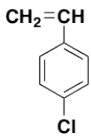
Figure 5. ^1H NMR spectrum (500 MHz, in CDCl_3 , 30 $^\circ\text{C}$) of poly(βNpOVE)-*graft*-poly(AcOSt) {polymerization conditions: $[\text{AcOSt}]_0 = 1.0$ M, $[\text{St-HCl}]_0 = 50$ mM, $[\text{SnCl}_4]_0 = 100$ mM, [ethyl acetate] = 1.0 M, in CH_2Cl_2 at 0 $^\circ\text{C}$. $[\text{St-HCl}]_0/[\text{Np units}]_{\text{add}} = 1/1$ (molar ratio).}

Synthesis of Graft Copolymers with Branches of Various Poly(styrene) Derivatives

Motivated by the successful synthesis of the graft copolymer with the poly(AcOSt) living polymer, the author focused his attention on the Friedel-Crafts-type grafting of poly(βNpOVE) side-chains with the living propagating carbocations of other styrene derivatives, such as pMOST, tBOST, pMeSt, and pClSt. Prior to these experiments, the author investigated the possibility of a reaction between the growing carbocations and the naphthyl side chains of poly(βNpOVE). Only highly reactive carbocations, which are generated from monomers with lower reactivity, were predicted to react with the naphthyl groups. The reactivity of the styrene derivatives is related to the ^{13}C NMR chemical shifts of the β -carbon.³⁶ The order summarized in Table 3 is in relatively good agreement with that of the reactivity in cationic polymerizations.³⁷ Using 2-methoxynaphthalene (βMeONp) as an alternative for poly(βNpOVE), model experiments were performed to determine whether the propagating species of these styrene derivatives react with βMeONp during their living cationic polymerizations. The polymerizations of pMOST or tBOST remained living despite the presence of a large quantity of βMeONp . In contrast, βMeONp retarded the polymerizations of pMeSt and AcOSt, causing frequent Friedel-Crafts reactions. Especially, in the case of pClSt, side

reactions were induced by toluene, a common solvent for cationic polymerization. Based on these results, the author explored the synthesis of the graft copolymers with poly(pMeSt) and poly(pClSt) branches.

Table 3. Friedel-Crafts-type termination reactions of various poly(styrene derivatives) with β MeONp

styrene derivatives					
	pMOSSt	tBOSSt	pMeSt	AcOSSt	pClSt
$\delta(\beta\text{C})$ ppm ^a	111.1	112.1	112.5	113.8	114.4
β MeONp addition ^b	undisturbed	undisturbed	F-C reaction	F-C reaction	F-C reaction

^a ^{13}C NMR chemical shifts for β -carbons of various styrene derivatives

^b undisturbed; β MeONp did not disturb the living polymerization; F-C reaction: β MeONp induced the Friedel-Crafts reactions in the living polymerization.

Grafting reactions were performed by adding the poly(β NpOVE) solution to each living polymerization system.^{26,32} The ratio of the $[\text{cationogen}]_0/[\text{naphthalene units in the poly}(\beta\text{NpOVE})]$ were 1/1 and 1/10. In every cases, the GPC profiles of the products revealed the appearance of a new fraction with a narrow MWD, which was in a higher molecular weight region than the original poly(β NpOVE) backbone (entries 4-7 in Table 2). These results indicate that well-defined graft copolymers with poly(pMeSt) and poly(pClSt) branches were successfully obtained using this methodology, although a certain quantity of unreacted branches remained (Figure 6). The numbers of the branches were determined to be 16 for pMeSt (entry 5 in Table 2) and 64 for pClSt (entry 7 in Table 2) via GPC-MALS analysis [$M_w(\text{MALS}) = 9.9 \times 10^4$ for pMeSt and 3.0×10^5 for pClSt], and these values agreed with those of 16 and 66 estimated by ^1H NMR analysis, respectively. The numbers of branches followed the order pMeSt < AcOSSt < pClSt, which is in good agreement with the reactivity order of their carbocations for a Friedel-Crafts reaction.

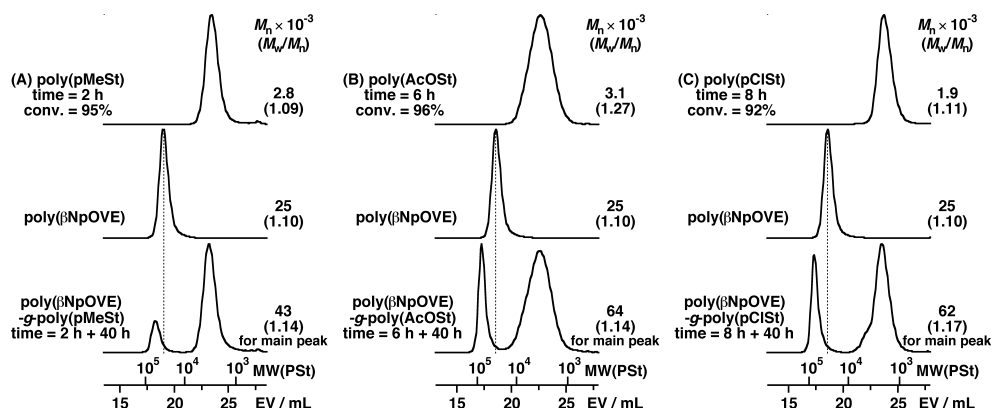


Figure 6. MWD curves of various resulting polymers obtained before and after the addition experiment of β MeONp for living polymerization of (A) poly(pMeSt), (B) poly(AcOSt) and (C) poly(pClSt), in CH_2Cl_2 at 0 °C: (A) $[\text{pMeSt}]_0 = 1.0$ M, $[\text{IBVE-HCl}]_0 = 50$ mM, $[\text{SnCl}_4]_0 = 10$ mM, $[\text{2,6-di-tert-butylpyridine}] = 10$ mM, (B) $[\text{AcOSt}]_0 = 1.0$ M, $[\text{St-HCl}]_0 = 50$ mM, $[\text{SnCl}_4]_0 = 100$ mM, $[\text{ethyl acetate}] = 1.0$ M (C) $[\text{pClSt}]_0 = 1.0$ M, $[\text{St-HCl}]_0 = 50$ mM, $[\text{SnCl}_4]_0 = 100$ mM, $[\text{nBu}_4\text{NCl}] = 40$ M. $[\text{initiator}]_0/[\text{Np units}]_{\text{add}} = 1/1$ (molar ratio). M_n values were calculated by GPC measurements.

Solubilities of the Graft Copolymers

The author investigated the solubility of the resulting graft copolymers in various solvents at room temperature. The solubility characteristics of the graft copolymers and backbone poly(β NpOVE) were summarized in Table 4. For example, poly(β NpOVE)-*graft*-poly(pClSt) was readily dissolved in ethyl acetate, which dissolves poly(pClSt) but not poly(β NpOVE). In contrast, the poly(β NpOVE)-*graft*-poly(pClSt) was insoluble in DMSO, in which poly(β NpOVE) is soluble and poly(pClSt) is not. Thus, the solubility of the graft copolymer is likely governed largely by the nature of branches.

Furthermore, poly(β NpOVE)-*graft*-poly(AcOSt) was converted into poly(β NpOVE)-*graft*-poly(HOST) by the alkaline hydrolysis of the acetoxy groups of the poly(AcOSt) branches, and its solubility characteristics were examined in various solvents. The poly(AcOSt) branches was quantitatively converted into poly(HOST), as confirmed by ^1H NMR analysis. The solubility of the poly(β NpOVE)-*graft*-poly(HOST) in methanol and in alkaline water changed upon hydrolysis.

Table 4. Solubility of various graft copolymers and their branches at room temperature (1 wt%) ^a

entry	polymer	EtOAc	acetone	DMSO	MeOH	H ₂ O
1	β NpOVE ₁₉₀	I	I	S	I	I
2	AcOSt ₁₀₀	S	S	S	I	I
3	β NpOVE ₁₉₀ -g-(AcOSt ₂₀) ₄₀	S	S	S	I	I
4	HOS _t ₁₀₀	S	S	S	S	I
5	β NpOVE ₁₉₀ -g-(HOS _t ₂₀) ₄₀	S	S	S	S	I
6	pClSt ₁₀₀	S	I	I	I	I
7	β NpOVE ₁₉₀ -g-(pClSt ₂₀) ₆₆	S	I	I	I	I
8	pMeSt ₁₀₀	S	I	I	I	I
9	β NpOVE ₁₉₀ -g-(pMeSt ₂₀) ₁₈	S	I	I	I	I

^a S: soluble, I: insoluble.

Furthermore, the aqueous solution of this graft copolymer exhibited a pH-responsive phase separation behavior with high sensitivity (Figure 7). When the pH was decreased, the transparent solution became opaque at a critical pH of 11.3. In addition, the transmittance was somewhat reduced at the alkaline region possibly due to the formation of micellar aggregates with a hydrophobic β NpOVE core and hydrophilic HOS_t coronas. The author propose that the pH-responsive phase separation occurred through the protonation of the hydroxy groups, which was accompanied by a reduction in the hydrophilicity of the polymer side chains.

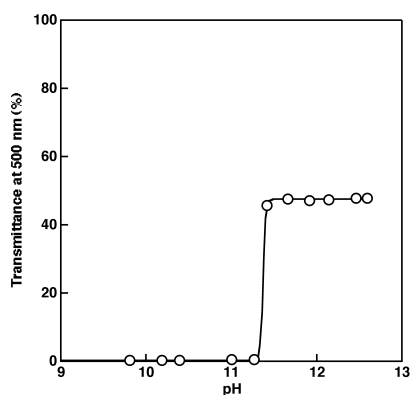


Figure 7. Transmittance at 500 nm for an aqueous solution of poly(β NpOVE)-*graft*-poly(HOS_t): [phenolic units]₀ = 20 mM, [added NaCl]₀ = 0.10 M, at 30 °C.

CONCLUSION

A Friedel-Crafts-type termination reaction of naphthyl groups was shown to be highly effective for synthesizing graft copolymers using a cationic polymerization. The simple addition of a naphthyl-carrying VE polymer into a living polymerization system involving a less reactive styrene derivative yielded well-defined graft copolymers. The reactivity of the growing carbocation was a decisive factor for achieving an efficient grafting reaction. Moreover, HOS_t-branched graft copolymers were prepared and exhibited a pH-responsive behavior in water. In addition, various grafted side chains were synthesized with other styrene derivatives. This new synthetic method based on a Friedel-Crafts-type termination reaction on a naphthalene-containing polymer would allow for the synthesis of various functional polymers with unique architectures. Furthermore, the living cationic polymerization of AcOS_t was achieved for the first time using a St–HCl/SnCl₄ initiating system in the presence of an appropriate additive such as ethyl acetate or *n*Bu₄NCl.

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28. The reaction was uncontrolled in the presence of a weaker Lewis base, methyl chloroacetate (MeClAc), because it lacked the ability to sufficiently stabilize the propagating carbocations and moderate the Lewis acidity of the SnCl₄. {polymerization conditions: [AcOSt]₀ = 1.0 M, [St-HCl]₀ = 50 mM, [SnCl₄]₀ = 100 mM, [MeClAc] = 1.0 M, in CH₂Cl₂ at 0 °C. polymerization time = 5 min., conv. = 77%, M_n (GPC) = 2.8×10^3 , M_w/M_n (GPC) = 2.21.}
29. The polymerization was also examined using other Lewis acid catalysts in conjunction with another cationogen, IBEA. Among the catalysts used (SnCl₄, FeCl₃, GaCl₃, EtAlCl₂, and ZnCl₂), SnCl₄ was superior to the others in terms of controllability.
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33. The highest probability of HOMO electron densities was calculated to be on the 1-position of β MeONp by a quantum chemical calculation in Chapter 2,¹¹ indicating that a carbon at this position is most likely to be attacked electrophilically. Thus, the assignment of a connected-structure produced by a Friedel-Crafts-type reaction was conducted by comparing with the spectrum of 2-methoxy-1-(1-phenylethyl)naphthalene, which is a structure of β MeONp substituted with a styryl group at the 1-position of the naphthyl ring. A peak of Ph-CH-Np was observed at 5.26 ppm.³⁴
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35. Peaks *b*, *c*, and *d* were assignable to poly(β NpOVE) chains, and peaks *e*, *i*, and *k* were derived from aromatic protons in the graft copolymer in Figure 5. Therefore, the integral ratio of those peaks corresponds to the composition ratio of β NpOVE units (*n*) and AcOSt units (*m*) (*n/m* determined to be 0.23). The degree of polymerization (DP) of each polymer was determined via NMR analysis of the prepolymer obtained before grafting reaction [DP of poly(β NpOVE) = 190, and DP of poly(AcOSt) = 20]. In this case, because *n/m* and *n* are 0.23 and 190, respectively, the number of AcOSt units (*m*) was determined to be 820. Thus, the number of branched poly(AcOSt), which is obtained from the value *m*/[DP of AcOSt (= 20)], was determined to be 41.
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Chapter 5

Precise Synthesis of pH-Responsive Copolymers with Naphthoic Acid Side Groups via Living Cationic Polymerization

INTRODUCTION

Among the various types of stimuli-responsive polymers,¹⁻¹³ pH-responsive anionic polymers are of great importance in various applications, such as drug and gene delivery,¹⁴⁻¹⁷ metal-ion scavenging,¹⁸ and controlled biomineralization.¹⁹ An important advantage of anionic pH-responsive polymers is their pH-dependent ionic complexation with cationic compounds, such as amines and metal ions, hydrogen atoms bonded to oxygen atoms, and hydrophobic materials.²⁰⁻²³ These various interactions are critical to reversible microphase separations or self-organization phenomena, such as protein folding and the formation of lipid bilayers and a DNA double helices.²⁴⁻²⁷ The growing diversity of these materials can be attributed to the availability of various anionic acid groups, such as carboxy, phenolic hydroxy, and sulfo groups. Thus, pH-responsive polymers enable the construction of novel functional materials. A specific, critical pH range may be required for certain applications. For example, a polymer with a transition near neutral pH is required for physiological uses. However, the critical pH for the phase transition of widely investigated homopolyacids such as poly(acrylic acid) and poly(methacrylic acid) ranges from 4 to 6.²⁸⁻³¹

The key to precisely controlling the pH response of a homopolymer chain is the introduction of an appropriate hydrophobic group, which preferably shows strong interaction in water under certain conditions at the position adjacent to a carboxy group. This strategy was recently shown to be feasible by our group. A homopolyVE containing carboxyphenyl groups prepared via a living cationic polymerization induced a pH-sensitive phase separation in water with a pH of 6.5.⁴ In addition to the hydrophobicity of the polymer, the aromatic group was expected to substantially change the relationship between the pH-responsiveness and the degree of ionization. Even though a naphthyl ring is a good hydrophobic candidate, the cationic polymerization of naphthyl-containing monomers suffers from inevitable Friedel-Crafts side reactions with the naphthyl rings, as observed during the cationic polymerization of vinylnaphthalene derivatives.^{32,33}

In Chapter 2, the author demonstrated that the living cationic polymerization of β -substituted naphthoxyethyl VE (NpOVE in Chart 1) occurred under appropriate reaction conditions. The substituted position on the naphthyl ring is critical to this living polymerization. In fact, frequent intramolecular Friedel-Crafts reactions occurred during the cationic polymerization of the α -substituted counterpart, whereas the phenyl-substituted analog underwent a living polymerization under similar conditions.³⁴ In addition, the introduction of a carboxy ester to the aromatic ring is expected to further suppress any side reactions due to its electron-withdrawing nature and steric hindrance.

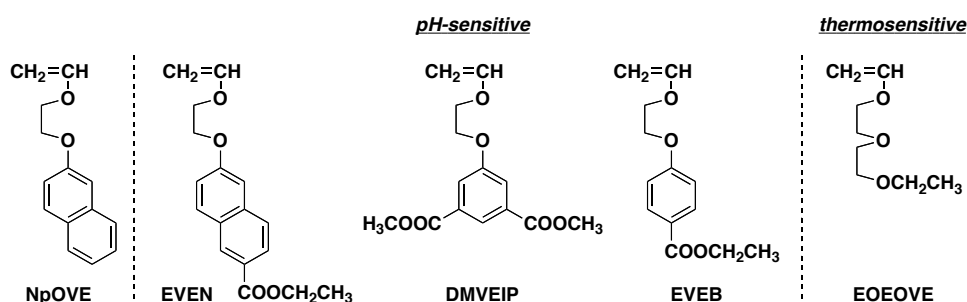


Chart 1. Structures of vinyl monomers related to this Chapter

Therefore, in this Chapter, the author focused on synthesizing pH-responsive block or random copolymers via the cationic polymerization of the naphthyl carboxylate-containing monomer ethyl 6-[2-(vinylloxy)ethoxy]-2-naphthoate (EVEN in Chart 1). Thus, the author first examined the feasibility of a living cationic polymerization using EVEN with various Lewis acids in the presence of a base. Next, living cationic copolymerizations were performed using the various functional monomers depicted in Chart 1. Furthermore, various carboxy-containing block and random copolymers were prepared via the hydrolysis of side esters, and their pH-responsive behaviors were investigated using ^1H NMR, transmittance change, and DLS analyses in aqueous solutions.

EXPERIMENTAL

Materials

Ethyl 6-[2-(vinylloxy)ethoxy]-2-naphthoate (EVEN; > 99.5%), dimethyl 5-[2-(vinylloxy)ethoxy]isophthalate (DMVEIP; > 99.5%), and ethyl 4-(2-(vinylloxy)ethoxy)benzoate (EVEB; > 99.5%) were supplied by Canon. These VEs were

recrystallized twice from ethyl acetate for EVEN or dry hexane for DMVEIP and EVEB and then vacuum-dried for more than 3 h prior to use. Other materials were prepared and used as described in Chapters 2 and 3. All materials except the solvents were stored in brown ampules under dry nitrogen.

Procedures

Polymerization

Polymerizations were performed in a similar manner as described in Chapters 2 and 3.

Alkaline Hydrolysis of Pendant Carboxy Ester Groups

The ester pendant was converted into the carboxy group as described below.⁴ Poly(EVEN) was dissolved in DMSO to prepare a 1 wt% solution, and 3.0 M sodium hydroxide (five equivalents relative to the ester unit in the polymer) was added. The mixture was magnetically stirred at room temperature. The originally transparent mixture gradually became cloudy because even the partially hydrolyzed polymer was insoluble in DMSO. After 4 h, water was added to homogenize the mixture, and the resulting transparent solution was stirred for an additional day. The obtained sodium salt was neutralized with 1.0 M aqueous hydrochloric acid, and the polymer product was purified by dialysis first against distilled water for at least 2 days and then against Milli-Q water for another day. Evaporation of the water under reduced pressure yielded poly{6-[2-(vinylloxy)ethoxy]-2-naphthoic acid} [poly(VEN)].

Potentiometric Titration and Turbidity Measurement

For potentiometric titrations, polymer samples were dissolved into Milli-Q water to give a monomeric unit concentration of 20 mM, and NaCl of 0.10 M was added. With rapid stirring, aliquots of a standardized 0.10 N hydrogen chloride solution were injected using a burette. The solution was allowed to chemically and thermally equilibrate for 5 min after each addition and pH of the sample was measured with a HORIBA/pH ION METER F-23 equipped with HORIBA pH Electrode 9610-10D at 30 °C. The pH meter was calibrated before titration with standardized phosphate buffer solutions at pH 4, 7, and 9.

Characterization

The M_n and M_w/M_n of the polymers, ^1H NMR spectra, MALDI-TOF-MS spectra, and transmittance of the polymer aqueous solutions were measured as described in Chapters 2, 3,

and 4. The pH values of aqueous solutions were measured by using a F-52 digital pH meter (HORIBA). The hydrodynamic diameter (D_h) was determined by dynamic light scattering (DLS) [FPAR-1000HG (Otsuka Electronics); $\lambda = 632.8$ nm, scattering angle = 90 °].

RESULTS AND DISCUSSION

Living Cationic Polymerization of an Ester-Containing Vinyl Ether with a Naphthyl Ring: Effects of the Ester Substituent

Table 1. Cationic polymerizations of EVEN, DMVEIP, and NpOVE ^a

entry	monomer	initiator/activator	added base ^b	time	conv. (%)	$M_n \times 10^{-4}$ ^c	M_w/M_n ^c
1	EVEN	IBEA / Et _{1.5} AlCl _{1.5}	–	2.3 h	86	1.3	1.26
2		IBEA / Et _{1.5} AlCl _{1.5}	EtOAc	18 h	83	1.8	1.16
3		IBEA / Et _{1.5} AlCl _{1.5}	DO	6 h	91	1.9	1.09
4		IBVE–HCl / ZnCl ₂	DO	30 min	99	0.92	1.72
5		IBVE–HCl / FeCl ₃	DO	5 sec	100	0.84	1.60
6	DMVEIP	IBEA / Et _{1.5} AlCl _{1.5}	DO	5 h	98	1.7	1.09
7	NpOVE	IBEA / Et _{1.5} AlCl _{1.5}	DO	2 h	92	0.96	1.38

^a [monomer]₀ = 0.40 M, [initiator]₀ = 4.0 mM, [Lewis acid]₀ = 20 (for entries 4, 5, 7) or 40 (for entries 1–3, 6) mM, [added base] = 1.0 M (for EtOAc) or 1.2 M (for DO), in CH₂Cl₂ at 0 °C.

^b DO = 1,4-dioxane, EtOAc = ethyl acetate.

^c Determined by GPC, polystyrene calibration.

The cationic polymerization of ethyl 6-[2-(vinylloxy)ethoxy]-2-naphthoate (EVEN in Chart 1) was performed using a variety of Lewis acids in CH₂Cl₂ at 0 °C in the presence of either 1,4-dioxane or ethyl acetate as an added base. The adducts of isobutyl VE (IBVE) with HCl [IBVE–HCl; CH₃CH(O*t*Bu)Cl] or acetic acid [IBEA; CH₃CH(O*t*Bu)OCOCH₃] were employed as the cationogen. All of the catalysts used induced a quantitative polymerization, producing polymers with high molecular weights (Table 1). Among the investigated catalysts, Et_{1.5}AlCl_{1.5} induced the most controlled polymerization [time = 6 h, conv. = 91%, M_n (GPC) = 1.9×10^4 ,³⁵ M_w/M_n = 1.09 (entry 3 in Table 1)]. The M_n values increased linearly with the monomer conversions and the product polymers exhibited very narrow MWDs as shown in Figure 1. The polymerization of EVEN in the absence of any additives proceeded faster

relative to the base-assisting system. The reaction produced a well-controlled polymer with a relatively narrow MWD (time = 2.3 h, conv. = 86%, $M_w/M_n = 1.26$, entry 1), indicating that the pendant ester group played a role as an added base. In contrast, the polymerizations of EVEN using $ZnCl_2$ and $FeCl_3$ yielded polymers with broad molecular weight distributions (MWDs) containing oligomeric acetal byproducts with low molecular weights (entries 4 and 5, respectively).³⁶

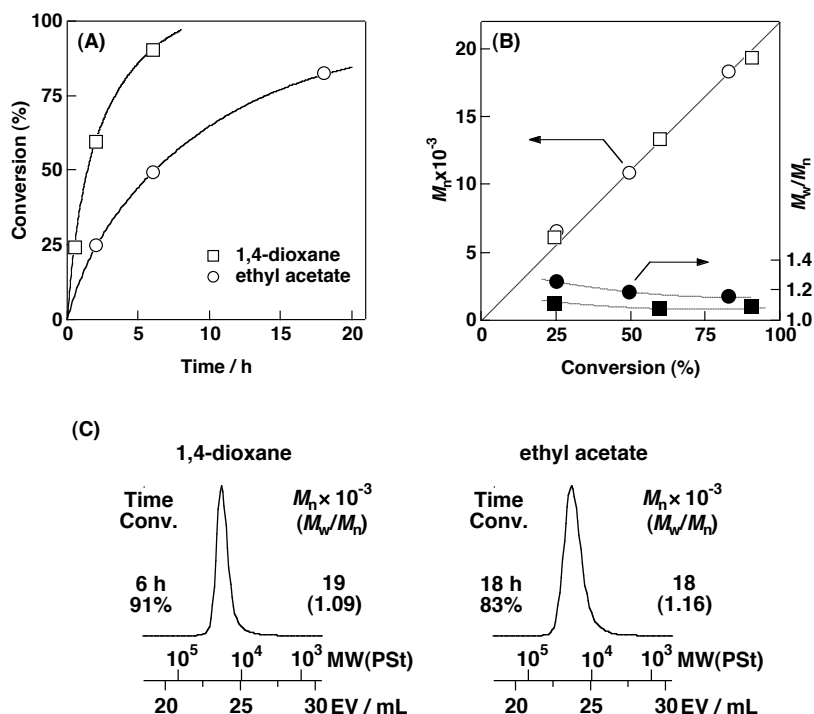


Figure 1. (A) Time-conversion curve, (B) M_n - and M_w/M_n -conversion plots for the polymerization of EVEN, and (C) MWD curves of the obtained polymers using IBEA/ $Et_{1.5}AlCl_{1.5}$ initiating system in CH_2Cl_2 in the presence of 1,4-dioxane (squares) or ethyl acetate (circles) at 0 °C: $[EVEN]_0 = 0.40$ M, $[IBEA]_0 = 4.0$ mM, $[Et_{1.5}AlCl_{1.5}]_0 = 40$ mM, $[added\ base] = 1.2$ M (for 1,4-dioxane) or 1.0 M (for ethyl acetate).

The cationic polymerization of dimethyl 5-(2-(vinylloxy)ethoxy)isophthalate (DMVEIP in Chart 1) also proceeded via a living mechanism with almost the same polymerization rates despite its two ester groups ($M_w/M_n = 1.09$, entry 6). The inclusion of an additional ester group in the monomer pendant had no or a little effect on the rate and controllability of the polymerization for the same initiating systems under similar reaction conditions. In contrast to the successful polymerizations of EVEN and DMVEIP, the non-substituted analog, NpOVE,

underwent an ill-defined polymerization in CH_2Cl_2 because of frequent side reactions, as indicated by the broad MWD curves of the products ($M_w/M_n = 1.38$, entry 7). The ^1H NMR and MALDI-TOF-MS results also indicated frequent side reactions.^{40,46} The different behavior was observed when toluene was used, where a well-controlled polymerization of NpOVE was achieved, as previously reported.³⁴

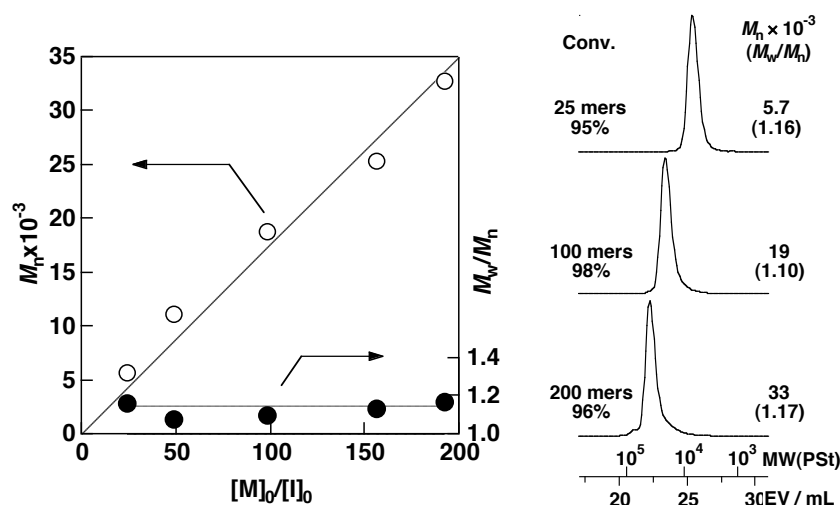


Figure 2. M_n and M_w/M_n versus $[M]_0/[I]_0$ ratio for the polymerization of EVEN using IBEA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ in CH_2Cl_2 at 0°C : $[\text{EVEN}]_0 = 0.10\text{--}0.80\text{ M}$, $[\text{IBEA}]_0 = 4.0\text{ mM}$, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 40\text{ mM}$, $[1,4\text{-dioxane}] = 1.2\text{ M}$, in CH_2Cl_2 at 0°C .

To further confirm the living nature of the EVEN polymerization using the IBEA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ initiation system, the reactions were examined using monomer/initiator ratios that ranged from 25 to 200 (Figure 2). For all of these ratios, the MWDs of the obtained poly(EVEN)s were narrow ($M_w/M_n \leq 1.17$), and the molecular weight increased linearly with the monomer/initiator ratio. These results clearly indicate that the combination of an Al-based Lewis acid with an added base is a highly effective initiating system for the living cationic polymerization of EVEN. The complete absence of side reactions was further confirmed by ^1H NMR and MALDI-TOF-MS (Figures 3 and 4) analyses of the poly(EVEN) obtained using the IBEA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ initiating system in CH_2Cl_2 . The ^1H NMR spectrum indicated that the polymer had uniform chain ends, i.e., an α -end derived from IBEA (peaks *a* and *b*) and an ω -end derived from the quencher (peaks *o* and *p*). None of the peaks observed in the spectrum were assignable to Friedel-Crafts side-reaction products despite the general tendency for

naphthalene rings to easily react with electron-deficient species such as carbocations. In addition, the MW calculated from the ratio of the aromatic protons (peak *j* in Figure 3) to the methyl protons (peak *b* in Figure 3) of the α -end group derived from IBEA was in good agreement with the theoretical value [conv. = 84%, $M_n(\text{GPC}) = 1.8 \times 10^4$, $M_n(\text{NMR}) = 2.3 \times 10^4$, and $M_n(\text{calcd.}) = 2.4 \times 10^4$, $M_w/M_n = 1.15$].³⁵ For the MALDI-TOF-MS spectrum, only a single peak series was detected with an interval of 286.3, which corresponds to the EVEN monomer. The obtained mass value of 5595.4 is very close to the calculated value of 5595.3 for the structure with the ideal α - and ω -end groups derived from IBEA (cationogen) and methanol (quencher), respectively [$\text{CH}_3\text{CH}(\text{OiBu})-(\text{EVEN})_{19}-\text{OCH}_3/\text{Na}^+$].

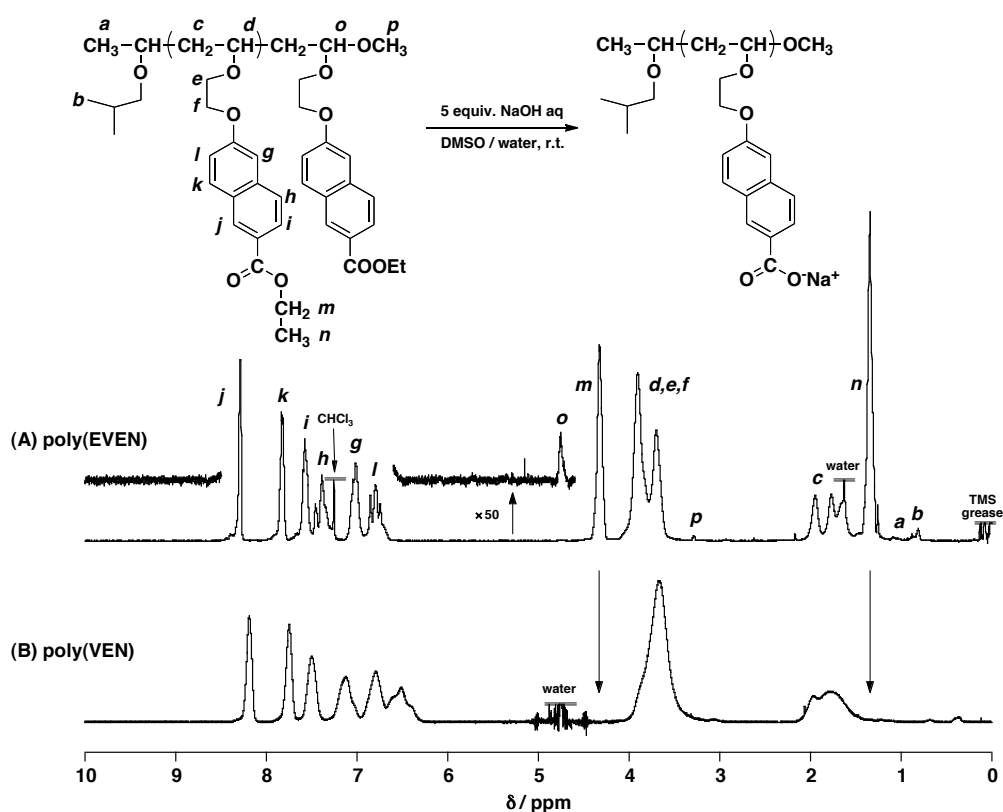


Figure 3. ^1H NMR spectra [500 MHz, CDCl_3 (upper) at 30 °C or D_2O (lower) at 50 °C] of (A) poly(EVEN) obtained using IBEA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ in the presence of ethyl acetate at 0 °C (polymerization conditions: $[\text{EVEN}]_0 = 0.40$ M, $[\text{IBEA}]_0 = 4.0$ mM, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 40$ mM, $[\text{ethyl acetate}] = 1.0$ M.) and (B) poly(VEN) obtained by the alkaline hydrolysis of poly(EVEN) in DMSO/water at room temperature.

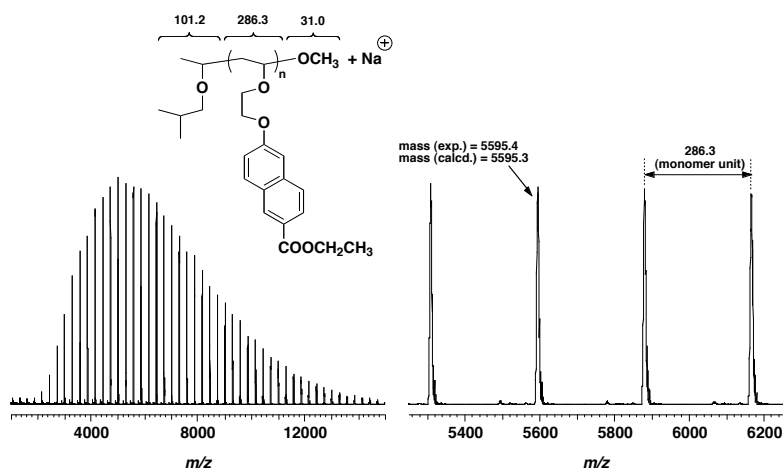


Figure 4. MALDI-TOF-MS spectra of poly(EVEN) $\{M_n(\text{NMR}) = 1.1 \times 10^4$, $M_n(\text{GPC}) = 0.97 \times 10^4$, $M_w/M_n = 1.20$; polymerization conditions: $[\text{EVEN}]_0 = 0.40$ M, $[\text{IBEA}]_0 = 4.0$ mM, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 40$ mM, $[\text{ethyl acetate}] = 1.0$ M, in CH_2Cl_2 at 0°C .}

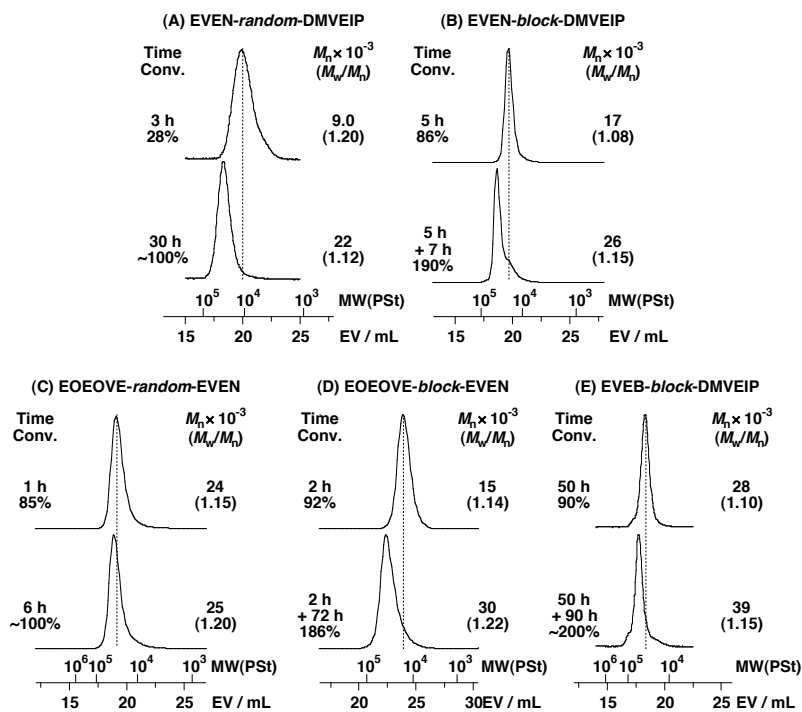


Figure 5. MWD curves for obtained using base assisting initiating systems in CH_2Cl_2 (A)–(D) or toluene (E) at 0°C : (A)–(D) $[\text{EVEN}]_0 = 0.40$ M, $[\text{IBEA}]_0 = 4.0$ mM, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 40$ mM, $[\text{added base}] = 1.2$ M (for 1,4-dioxane) or 1.0 M (for ethyl acetate). $[\text{EVEN}]_0/[\text{DMVEIP or EOEOVE}]_0 \text{ or add} = 1/1$ (molar ratio). (E) $[\text{EVEB}]_0 = 0.80$ M, $[\text{IBEA}]_0 = 4.0$ mM, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 40$ mM, $[\text{ethyl acetate}] = 1.0$ M. $[\text{EVEB}]_0/[\text{DMVEIP}]_{\text{add}} = 4/1$ (molar ratio).

Furthermore, various random and block copolymerizations of EVEN with other functional monomers, such as DMVEIP, EVEN, and EOEOVE, were examined using the IBEA/Et_{1.5}AlCl_{1.5} initiating system in the presence of an added base. DMVEIP and EVEN both have carboxy groups protected as esters, and EOEOVE has an oxyethylene unit, which induces thermoresponsivity. All of the monomers employed can be homopolymerized in a living fashion using the IBEA/Et_{1.5}AlCl_{1.5} initiating system. Successful random and block copolymerizations also proceeded with this initiating system and yielded well-defined random and block copolymers (Figure 5).

pH-Responsive Behaviors of the Carboxy-Containing Homopolymers in Water

The ester groups in the side chains were hydrolyzed to carboxy groups to yield a pH-responsive polymer. The quantitative transformation of poly(EVEN) into poly[6-(2-(vinylloxy)ethoxy)-2-naphthoic acid (VEN)] was confirmed by ¹H NMR analysis of the product, as shown in Figure 3B. The methyl and methylene peaks from the ethoxy group at 1.34 and 4.33 ppm, respectively, disappeared completely after hydrolysis. Other homo- and co-polymers containing carboxy groups were prepared in a similar manner [poly(DMVEIP) → poly(VEIP), poly(EVEB) → poly(VEB)^{4,47}].

The transmittances of the aqueous solutions of the obtained carboxy homopolymers at 500 nm at various pH levels were measured at 30 °C.⁴⁸ Rapid changes in the turbidity were observed at pH 7.0 for poly(VEN) and pH 4.8 for poly(VEIP) (Figure 6); these polymers were soluble in aqueous solutions with pH levels greater than these critical pH levels but precipitated under more acidic conditions. Poly(VEN) was pH-sensitive at a higher pH (7.0) than was poly(VEB) (pH 6.5). To investigate the role of polymer ionization in determining the critical pH, the homopolymers were titrated, and the apparent degree of ionization was estimated.^{49,50} An apparent degree of ionization was defined as α_{app} . On the titration measurements, the polymer ionization was calculated from a charge neutrality condition:

$$\alpha_{app} = \frac{[H^+] + [Na^+] - [OH^-] - [Cl^-]}{[\text{carboxylic acid}]}$$

where [carboxylic units] is the concentration of carboxylic groups in the polymer. However, the α_{app} values would be incorrect because the aggregation occurred during the titration experiments. Poly(VEN) began to aggregate after only a small amount of the carboxy anions were protonated ($\alpha_{app} \sim 0.8$), because of the hydrophobicity of a naphthyl group. In contrast, for poly(VEIP), the estimated α_{app} value was 0.4–0.5 at the critical pH of 4.8, which indicated that

the phase separation began when almost half of the total carboxy units in the polymer chain were protonated.

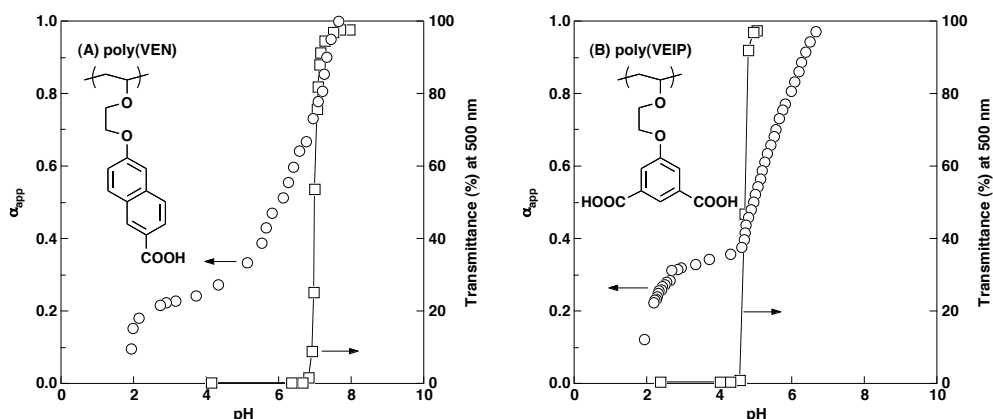


Figure 6. Apparent degrees of ionization (α_{app}) plots (circles) and temperature dependence of transmittance at 500 nm light for aqueous solutions of (A) poly(VEN) [precursor poly(EVEN): M_n (GPC) = 1.7×10^4 , M_w/M_n (GPC) = 1.11] and (B) poly(VEIP) [precursor poly(DMVEIP): M_n (GPC) = 1.7×10^4 , M_w/M_n (GPC) = 1.12] as a function of pH. [monomeric units] $_0$ = 20 mM, [added NaCl] $_0$ = 0.10 M.

Various Stimuli-Responsive Behaviors of Naphthalene- and Carboxy-Containing Copolymers with Other Functional Segments

1. Double pH-responsive behavior

The author also investigated the solution behavior of random and diblock copolymers—VEN₁₀₀-*random*-VEIP₁₀₀, VEN₁₀₀-*block*-VEIP₁₀₀, and VEB₂₀₀-*block*-VEIP₅₀—that consisted of two pH-sensitive segments according to turbidity and dynamic light scattering (DLS) measurements of their aqueous solutions at various pH values at 30 °C. The random copolymer VEN₁₀₀-*random*-VEIP₁₀₀ exhibited a drastic turbidity change at pH 5.2. This pH value was between the critical values of the corresponding homopolymers [Figure 7(A)]. Thus, the phase-separation pH value was controlled by combining two different pH-responsive segments. Figure 7(B) shows the pH-dependent transmittance for the solution of the block copolymer VEN₁₀₀-*block*-VEIP₁₀₀. A two-step transmittance change was observed at pH 7.0 and 4.9, which correspond to each segment's individual critical pH. The transmittance of the aqueous solution decreased slightly at pH 7.0, which suggests the formation of aggregates, and the polymer precipitated at pH 4.9. To examine the formations at each pH region, DLS measurements of the diblock copolymers were conducted (measurement conditions: 0.01wt% solution, [added NaCl] $_0$ = 0.10 M at 30 °C, CONTIN; 90 °). For VEN₁₀₀-*block*-VEIP₁₀₀, the

hydrodynamic diameter D_h at pH 11 was 10 nm, which indicates that the copolymer dissolved as a unimer; this result is consistent with the fact that both segments behave as hydrophilic chains in water at this pH. When pH values decreased, the VEN segment became hydrophobic at pH 7.0 due to protonation, and this diblock copolymer formed a micelle through hydrophobic interactions with a hydrophobic VEN core and a hydrophilic VEIP corona ($D_h = 57$ nm at pH 6.5). Moreover, a block copolymer with another carboxy unit, benzoic acid, $\text{VEB}_{200}\text{-block-VEIP}_{50}$ also exhibited a two-step phase separation when the pH was changed [Figure 7(C)]. In this way, various double pH-sensitive block copolymers were prepared via base-assisting living cationic polymerization.

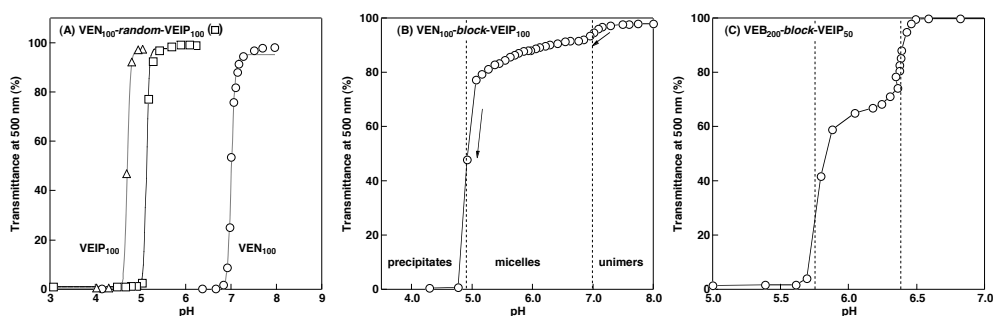
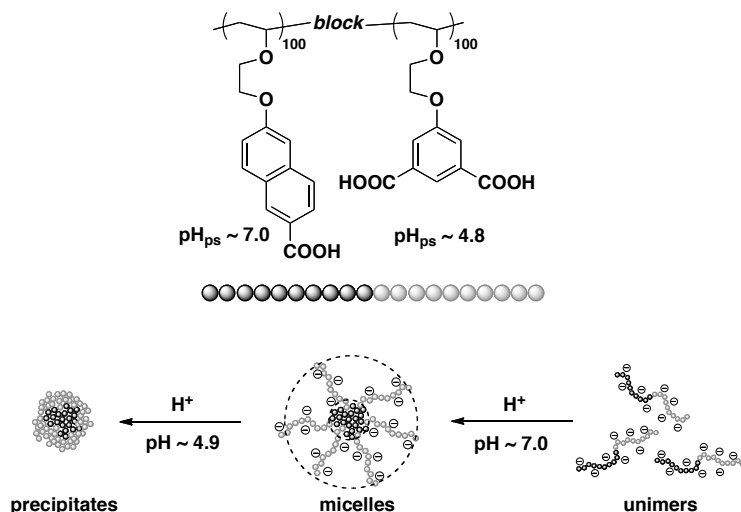


Figure 7. pH dependence of transmittance at 500 nm light for aqueous solutions of (A) $\text{VEN}_{100}\text{-random-VEIP}_{100}$, (B) $\text{VEN}_{100}\text{-block-VEIP}_{100}$, and (C) $\text{VEB}_{200}\text{-block-VEIP}_{50}$; $[\text{carboxy units}]_0 = 20$ mM, $[\text{added NaCl}]_0 = 0.10$ M.



Scheme 1. Conceptual illustration of the double pH-responsive behavior for the aqueous solution of $\text{VEN}_{100}\text{-block-VEIP}_{100}$

2. Dual stimuli-responsiveness

The pH/temperature-sensitive behavior of block copolymer solutions of VEN and 2-(2-ethoxy)ethoxyethyl VE (EOEOVE) was examined at different pH values. Poly(EOEOVE) underwent phase separation at its lower critical solution temperature (LCST) in aqueous solution, which were driven by the dehydration of the polymer side chains.

In Figure 8, the correlation between temperature and transmittance for a 0.5 wt% aqueous solution of the random copolymer, EOEOVE₁₆₀-*random*-VEN₄₀, were plotted at various pH. The phase separation temperature of the copolymer increased with increasing pH values, and thermoresponsive behavior was not observed over pH 7.0. Because almost all carboxy groups were deprotonated at pH 7.0, judging from the titration curve of poly(VEN) (Figure 6), the random copolymer was highly hydrophilic owing to a hydration and an electric repulsion of carboxylic anions and dissolved at in the whole temperature regime examined. However, when a tiny amount of carboxylic groups were protonated below pH 7.0, the random copolymer easily aggregated through a hydrophobic interaction and π - π stacking interaction of the naphthyl groups. Thus, the phase-separation temperature was altered by varying the ratio of hydrophobic segments with the protonation of carboxylic groups.

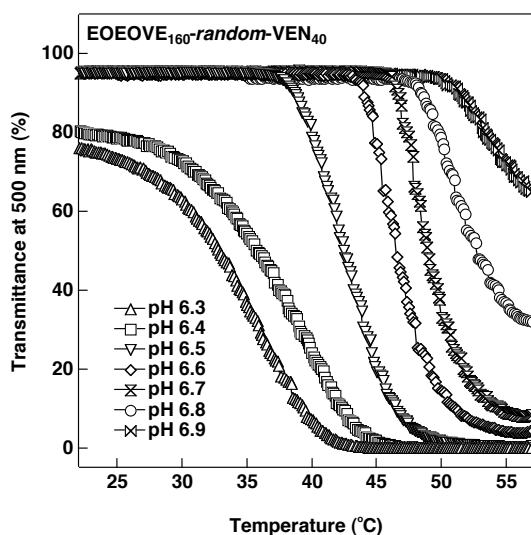


Figure 8. Temperature dependence of transmittance at 500 nm light for 0.5wt% aqueous solutions of EOEOVE₁₆₀-*random*-VEN₄₀ at various pH values: [added NaCl]₀ = 0.10 M (scanning rate; 1.0 °C/min.).

An aqueous solution of the block copolymer exhibited thermosensitive phase separation at pH 11, i.e., at a pH greater than the pK_a value of poly(VEN) [Figure 9]. At higher temperatures, the transmittance decreased relative to that at lower temperatures, and the copolymer was thought to form micelle-like structures because the EOEOVE segments became hydrophobic due to dehydration. To confirm this hypothesis, DLS measurements of the 0.05 wt% aqueous solution were conducted at pH 11 (circles, Figure 9). The measurements revealed that almost all of the block copolymer chains existed as approximately 5 nm unimers at 50 °C.⁵¹ When the solution temperature was increased, the block copolymer formed a larger aggregate with a D_h of approximately 100 nm at approximately 54 °C. However, A solution of this polymer underwent precipitation at pH 6.0 in the whole temperature regime examined. This precipitation most likely results from the copolymer aggregating via hydrophobic interaction due to the formation of hydrogen bonds between the oxyethylene side chains of the EOEOVE segments and the protonated carboxy groups of the VEN segments in the acidic region. This precipitation^{21,54}

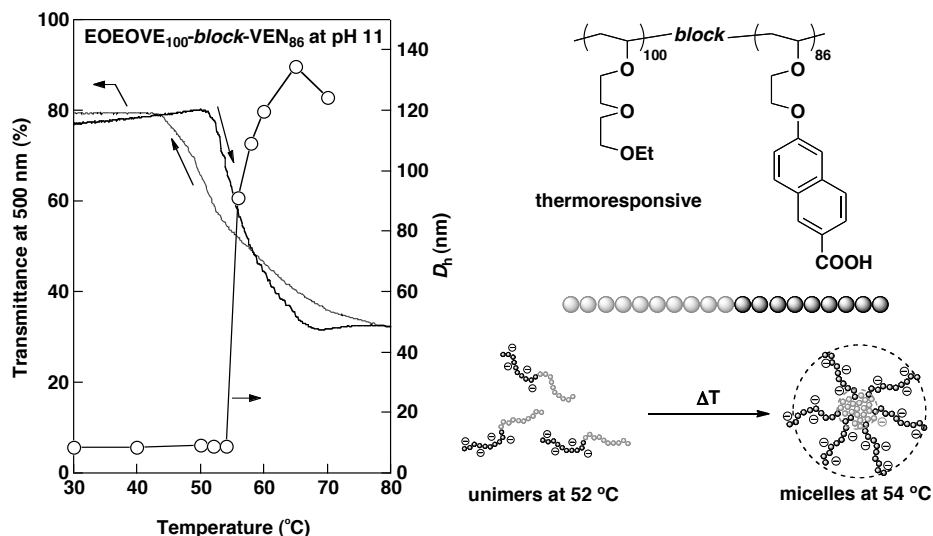


Figure 9. Temperature dependence of transmittance at 500 nm light for a 0.5 wt% aqueous solution (scanning rate; 1.0 °C/min) and DLS measurement for 0.05 wt% aqueous solution (circles, 90 °, CONTIN method.) of EOEVE₁₀₀-block-VEN₈₆ at various pH values: [added NaCl]₀ = 0.10 M, and schematic illustration of the self-assemble behavior for the aqueous solution of EOEVE₁₀₀-block-VEN₈₆.

CONCLUSIONS

The IBEA/Et_{1.5}AlCl_{1.5} initiating system induced the living cationic polymerization of a VE with a carboxy ester and a naphthyl group (EVEN) in CH₂Cl₂ in the presence of an added base at 0 °C. The ester groups on the naphthyl ring played an important role in suppressing the Friedel-Crafts side reactions that are typical of a naphthalene ring. In addition, the subsequent alkaline hydrolysis quantitatively produced a polymer that contained carboxy groups. The aqueous solutions of the obtained polymer showed pH-responsive phase-separation behavior with a high sensitivity. Block copolymers consisting of the two different carboxy segments exhibited a two-step polymer morphology change. Furthermore, a block copolymer with a pH-sensitive carboxy segment and a thermosensitive segment exhibited dual stimuli-responsiveness in water.

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35. The measured M_n values were smaller than the theoretical values despite the instrument being calibrated against polystyrene standards. The MWs calculated from the ^1H NMR peak intensity ratios agreed well with the theoretical values, as described in a later section.
36. Previously, Hashimoto et al.^{37,38} reported that oligomeric acetal compounds consisting of two alkoxy groups derived from monomer side chains were formed from methyl 4-[2-(vinyl-ethoxy)ethoxy]benzoate or 2-vinyl-ethoxyethyl phthalimide by protic impurities during the cationic polymerizations of these VEs using ZnCl_2 . Similar oligomers were produced in

the polymerizations where ZnCl_2 and FeCl_3 were used, as confirmed by ^1H NMR analysis of the resulting polymers.³⁹

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39. Methine proton peaks of oligomeric acetal compounds were observed at 4.9 ppm in ^1H NMR spectra of product polymers obtained using ZnCl_2 and FeCl_3 .
40. The ^1H NMR spectrum of poly(NpOVE) obtained in CH_2Cl_2 contained some small peaks at 4.5–6.5 and 8.0–10.0 ppm. These peaks were assigned to the protons of the structures resulting from Friedel-Crafts-type reactions, aldehyde protons at ω -end, the olefin protons stemming from β -proton elimination and mid-chain alcohol abstraction.⁴¹⁻⁴⁴ Various substituted naphthalene structures were formed by Friedel-Crafts-type reactions between a side chain naphthyl ring and a growing carbocation at the ω -end of the polymer. The assignments were conducted by comparing with 2-methoxy-1-(methoxymethyl)naphthalene.⁴⁵
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Chapter 6

SUMMARY

This thesis study demonstrated the first examples of successful precision synthesis of naphthalene-containing polymers with various architectures from both VEs and styryl-type analogs in cationic polymerization. A naphthalene derivative moiety, much more nucleophilically reactive than a phenyl counterpart, has been considered an obstacle to achieving controlled polymer synthesis in cationic polymerization because of the high susceptibility to cationic species, leading to Friedel-Crafts-type side reactions, although numerous examples of living polymerization of styrene derivatives using various initiating systems. This great difficulty was first overcome by performing cationic polymerization of naphthalene-containing monomers using the base-assisting cationic initiating systems. The key to controlling polymerization of naphthalene-containing monomers is the choice of initiating systems, polymerization conditions, and monomer structures. The high reactivity of a naphthalene moiety, in turn, was shown to be useful for achieving a ready polymer reaction. The author devised a new way to synthesize graft copolymers via the coupling reaction of pendant naphthalene moieties of cationically prepared polymers with another type of living cationic polymers. Another motivation for this study was the potential of more condensed aromatic rings in polymer chains to lead to unprecedented functions derived from their unique and excellent properties, such as thermal, optical, and mechanical properties. The author next targeted the design and creation of well-defined materials based on the specific properties of naphthyl rings. As a result, sensitive pH-responsive polymers were obtained, which showed pH-driven phase transition around a neutral pH.

Part I described the living cationic polymerizations of various naphthalene-containing monomers using a Lewis acid catalyst in the presence of an added base.

In Chapter 2, the author designed two VE monomers with naphthyl groups at different substituted positions and investigated their cationic polymerization using base-containing initiating systems. Living polymerization of 2-(2-naphthoxy)ethyl VE (β NpOVE) proceeded, whereas appreciable Friedel-Crafts-type side reactions occurred in the polymerization of 1-(2-naphthoxy)ethyl VE (α NpOVE) under conditions similar to those for β NpOVE. This

difference in the polymerization behavior is attributed to the difference between the HOMO orbital energies of naphthalene rings, supported by quantum chemical calculations of model compounds. This research could serve as a guideline for the design of naphthalene-containing monomers to yield well-defined polymers via a cationic mechanism.

Chapter 3 presented living cationic polymerizations of vinylnaphthalene derivatives. Side reactions related with naphthyl rings occurred frequently under the suitable conditions for the living cationic polymerization of a corresponding styrene derivative. The polymerization was controlled as a result of the author's thorough screening of various reaction conditions in the cationic polymerization. In particular, the side reactions were suppressed by setting polymerization temperature appropriately. Moreover, the obtained polymer had a much higher T_g value than that of the corresponding styrene derivative polymer.

Part II presented the development of a new methodology for well-defined graft copolymers and the synthesis of novel stimuli-responsive block and random copolymers by utilizing the high reactivity and hydrophobicity of naphthyl rings.

Chapter 4 described a novel effective strategy for the precision synthesis of graft copolymers using a potential of naphthalenes to readily react with carbocations. The pendant alkoxynaphthyl groups of a polyVE were shown to efficiently terminate the living cationic polymerization of various styrene derivatives, such as *p*-acetoxystyrene (AcOSt), *p*-methylstyrene, and *p*-chlorostyrene. The branches of poly(AcOSt) were converted into poly(*p*-hydroxystyrene)s by alkaline hydrolysis and an aqueous solution of the resulting graft copolymer exhibited a sensitive pH-responsive phase separation.

In Chapter 5, the author achieved the living cationic polymerization of a naphthyl-containing VE with a carboxy ester on the ring. The ester substituent is likely to elicit an effect to suppress side reactions by naphthyl rings due to the electron-withdrawing property and the steric hindrance. Moreover, the obtained polymer was converted into a naphthoic-acid-containing homopolymer by alkaline hydrolysis. An aqueous solution of the resulting homopolymer showed a pH-driven phase separation at pH 7.0, which was a higher value than that of a phenyl counterpart due to the highly hydrophobicity of naphthyl rings. Random or block copolymers with other functional segments, such as other polyacids or thermoresponsive segments, were also prepared quantitatively as well as homopolymers. The copolymers were found to form various aggregation structures under appropriate conditions. The self-assembly systems were established through the hydrophobic interaction and hydrogen

bonding under mild conditions.

Naphthalene-containing monomers can be within the scope of monomers for living cationic polymerization as demonstrated in this research, and these results will encourage further development of living polymerizations of vinyl monomers with more condensed rings, such as anthracene or pyrene rings as mentioned in General Introduction. Moreover, the author believes that the naphthalene-containing polymers will contribute to the construction of novel stimuli-responsive materials and will be employed for the industrial materials utilizing their mechanical and optical properties.

LIST OF PUBLICATIONS

Chapter 2

“Living Cationic Polymerization of Vinylnaphthalene Derivatives”

Yu Shinke, Arihiro Kanazawa, Shokyoku, Kanaoka, and Sadahito Aoshima
J. Polym. Sci., Part A: Polym. Chem. submitted.

Chapter 3

“Living Cationic Polymerization of Vinyl Ethers with a Naphthyl Group: Decisive Effect of the Substituted Position on Naphthalene Ring”

Yu Shinke, Arihiro Kanazawa, Shokyoku, Kanaoka, and Sadahito Aoshima
J. Polym. Sci., Part A: Polym. Chem. **2012**, 50, 5041-5048.

Chapter 4

“Precision Synthesis of Graft Copolymers via Living Cationic Polymerization of *p*-Acetoxystyrene and Subsequent Friedel-Crafts-Type Termination Reaction”

Yu Shinke, Hidehiro Yamamoto, Arihiro Kanazawa, Shokyoku, Kanaoka, and Sadahito Aoshima
J. Polym. Sci., Part A: Polym. Chem. submitted.

Chapter 5

“Precise Synthesis of pH-Responsive Copolymers with Naphthoic Acid Side Groups via Living Cationic Polymerization”

Yu Shinke, Arihiro Kanazawa, Shokyoku, Kanaoka, and Sadahito Aoshima
J. Polym. Sci., Part A: Polym. Chem. submitted.

