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Kyoto University
STEREO- AND REGIOSPECIFIC CATIONIC POLYMERIZATIONS VIA DESIGNED LEWIS ACIDS AND COUNTERANIONS

MAKOTO OUCHI

2001
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GENERAL INTRODUCTION

Background

Specificity in Polymerization. Chain-growth or addition polymerizations of vinyl monomers (CH₂=CHR) give, in most cases, linear polymers where hundreds and sometimes thousands of repeat units (–CH₂–CHR–) are connected with each other in a regular fashion –[CH₂–CHR]ₙ– (Figure 1). Numerous addition polymerizations are now known, readily giving high polymers in quantitative yield simply by mixing a monomer with an initiator, and this very fact might give an impression that they are easy chemical reactions which do not require serious efforts to control. On the contrary, if one carefully inspects the architectures of any seemingly trivial addition polymers, –[CH₂–CHR]ₙ–, one will soon realize that their formation is in fact a result of a chemical process of extremely high specificity and precision.

The linear polymers structure usually consists of a linear chain (or a backbone) of repeat units and terminal groups placed at both ends of the main chain.

![Diagram of polymer structure](image)

Figure 1
For such a regular backbone to form, the following specificities, among others, should be required:

(a) Chemospecificity: The specificity for propagation over any chain-breaking side-reactions, such as chain transfer and termination, which in turn regulates the molecular weight and the molecular weight distribution of the products, along with the structure of the terminal groups. By definition, propagation specificity should be high for high polymers to form, but chain-breaking reactions do occur in most of conventional addition polymerizations. A most important chemospecific chain-growth is generally called as "living polymerization", where the propagation step is free from chain transfer, termination, and any other chain-breaking reactions.1

(b) Stereospecificity: The specificity for the configuration of repeat units along a backbone, resulting from the stereochemistry of propagation reactions; i.e., the specificity for isotactic, syndiotactic, and heterotactic enchainments in the triad expression (Scheme 1).2 A typical example is an isotactic

\[ \text{Isotactic} \]

\[ \text{Syndiotactic} \]

\[ \text{Heterotactic} \]

Scheme 1. Common Polymer Tacticities for Mono-Substituted Polymer.
specific polymerizations.\(^3\)

**(c) Regiospecificity:** The specificity for the way by which repeat units are connected to each other, resulting from which position of a monomer the growing end attacks: e.g., head-to-head versus head-to-tail structures for a monosubstituted alkene monomer (CH\(_2\)=CHR);\(^4\) 1,2- versus 1,4- structures for a linear\(^3\),\(^5\) or cyclic diene\(^6\) monomer (CH\(_2\)=CH–CH=CHR) (Scheme 2).

![Scheme 2. Polymerization of Butadiene](image)

**Butadiene**

**1,2–addition**

**1,4–addition**

**Specificity Control in Cationic Polymerization.** Among chain-growth/addition polymerizations of alkenes and related monomers, cationic polymerization seems interesting to the author, because the acid-catalyzed process still involves uncharted frontiers in terms of the precision control of the specificities discussed above.

In 1984 the first examples of living cationic polymerizations of vinyl monomers were reported (cf. the next section),\(^7\) and since then a series of similar living cationic processes have been developed for almost all of the monomers for carbocationic growth to provide powerful methodologies to synthesize polymers of controlled molecular weights, narrow molecular weight distributions, and well-defined terminal groups.\(^8\) That implies that high chemospecificity can be attained in cationic polymerization.

In contrast, precision control of stereospecificity and regiospecificity has been particularly difficult in cationic polymerization, except that in almost all cases
head-to-tail structures form. The current status of these two areas will be reviewed and discussed in each relevant chapter of this thesis, but a brief general overview will follow herein.

**Stereospecificity in Cationic Polymerization.** In the early phase of research in cationic polymerization, rather accidentally, Schildknecht obtained highly crystalline poly(isobutyl vinyl ether)\(^9\) that, if property analyzed, would have been the first example of stereoregular synthetic polymers. The polymer was synthesized by a heterogeneous polymerization with boron trifluoride etherate at low temperature, and detailed structure analysis by the original authors and also Natta revealed, shortly after the discovery of isotactic polypropylene,\(^{10}\) that the crystalline poly(IBVE) is in fact highly isotactic.\(^{11}\) Since then extensive research was carried out in homogeneous\(^{12}\) and heterogeneous\(^{13}\) cationic polymerizations, in part for attaining high stereospecificity and also in relation to the propagation mechanism.\(^{14}\)

These studies revealed, as in other ionic polymerization,\(^{15}\) that (a) lowering polymerization temperature facilitates stereospecificity;\(^{12}\) and that (b) isotactic propagation is preferred in nonpolar solvent or other systems where ion-pair intermediates are supposed to prevail.\(^{14}\) Despite such general understanding, none of the known cationic polymerization systems can achieve such a high and often exclusive stereospecificity for any monomers as in the most sophisticated olefin\(^{16}\) and anionic polymerizations.\(^{17}\)

**Regiospecificity in Cationic Polymerization.** Because, almost without exception, cationic polymerization gives regular head-to-tail polymers from mono-substituted monomers, regiospecificity control is to be considered primarily in diene polymerization, namely, the specificity for either the 1,2- or the 1,4-main-chain structures originating from a conjugated allylic carbocation as the propagating species (cf. Scheme 2).\(^{18}\) As in the stereospecificity control, the general trend in cationic polymerization is similar to those in other ionic counterparts, and the use of nonpolar media at low temperature leads to a moderate
specification towards the 1,4-structure for 1-phenylbutadiene\textsuperscript{19} and other diene monomers.\textsuperscript{18}

Another area of interest in terms of regiospecificity control is the cationic polymerization of cyclopentadiene (CPD), a cationically polymerizable cyclic diene that gives polymers of potential applications consisting of thermally stable, completely hydrocarbon cyclic repeat units (Scheme 3). Research in cationic CPD polymerization dates back to 1926 when Staudinger and Brusin reported the formation of 1,2- and 1,4-structures.\textsuperscript{20} Subsequently some Lewis acids have been reported to polymerize the cyclic monomer into ill-defined polymers.\textsuperscript{21}

![Scheme 3. Cationic Polymerization of CPD.](image)

Overall, however, for neither linear nor cyclic diene very high 1,2-/1,4-regiospecificity has been achieved in cationic polymerization.

**Precision Control of Cationic Polymerization via Counteranions.** One of the most notable and attractive features in cationic polymerization is the existence of a counteranion accompanying the growing carbocation (Scheme 4). Because the counteranion, by definition, accompanies closely with the growing cationic site, it can affect the course of the propagation reaction, in terms of reactivity (rate), chemospecificity, stereospecificity, and regiospecificity, among other aspects. This, in turn, means that the specificity of propagation reactions can be controlled by designing the counteranions, for example, electronically and sterically.

As illustrated in Scheme 4, a well-defined counteranion can be generated by a combination of a protonic acid (HB; initiator) and a Lewis acid (MX\textsubscript{n};
catalyst). The initiator first adds across the double bond of the monomer to form an adduct carrying a covalently attached anionic part (B) of the acid. This linkage is ionically dissociated by the Lewis acid or the catalyst, and thereby a counteranion (−B-MXₙ) is formed. Thus, the nature of the growing species (~−CH₂−CHR⁺−B-MXₙ) will be governed by the substituent R from the monomer, the anionic part B from the initiator, and the Lewis acid (MXₙ) as the catalyst; note that the last two components give the counteranion −B-MXₙ.

In fact, the fine chemospecificity control, or living cationic polymerization, has been achieved by such two component initiating systems (HB/MXₙ) (see above), and, in these examples, the nucleophilicity of the counteranions is considered the most critical factor for the chemospecificity. Unfortunately, however, none of such general principles have been found for precision control of stereo- and regiospecificity in cationic polymerization.

Objectives: Stereo- and Regiospecific Cationic Polymerizations

From these backgrounds, the author focused his research on the "stereospecific" and "regiospecific" cationic polymerizations. As described above, there have few reports to prepare high-stereoregular polymers or regiospecific
polymers in cationic polymerization. He believed that some particular designed initiating system should be required for the control. In view of these, two-component initiating systems [a protonic acid (HB) and a Lewis acid (MXₙ)] will be suitable to achieve such selectivities via the design of counteranion from steric and electronic viewpoints (Scheme 5).

Therefore, the first object of this study is concerned with stereospecific cationic polymerization of vinyl ethers by a systematic search of the three factors: Lewis acids, monomer substituents, and initiators. Especially, modification of Lewis acid is most interesting, because it can be sterically and electronically designed to give unique environment in the growing end. Thus, the author employed various bulky titanium compounds in place of conventional Lewis acids or metal halides for the cationic polymerization to examine the possibility of stereoregular cationic polymerization. For this purpose, he selected alkyl vinyl ethers (VEs) as monomers, which show high-reactivity in cationic polymerization and then even the weaker designed Lewis acids with some substituents can be used as well. The effects of alkyl group of monomer were also examined due to possibilities of the interaction between oxygen of monomer and central metal of

---

Scheme 5. Environment around Growing Carbocationic Species in Cationic Polymerization of VE and CPD.
Lewis acid. Along with these efforts, he also surveyed the bulky protonic acids as initiators.

Secondly, in connection with regioselectivity, the author noted the cationic polymerization of cyclopentadiene (CPD) because the growing species is most likely a resonating allylic carbocation and thus leads to the regioselectivity, namely 1,2- and 1,4-adduct. To this end, he examined effects of the various factors on regioselectivity. Prior to the examination of the regioselectivity, he decided to develop the living or controlled cationic polymerization of CPD which has never been achieved.

Outline of This Study

The present thesis consists of two parts: Part I (Chapters 1–3) deals with the stereospecific cationic polymerization with designed counteranions derived from a protonic acid (initiator) and a Lewis acid (activator/catalyst). Effects of monomer substituents are also discussed. Part II (Chapters 4–6) discusses the controlled and regiospecific cationic polymerization of cyclopentadiene (CPD) terms of molecular weight and microstructure. The initiating systems were then applied for the syntheses of various CPD-based precision polymers.

Chapter 1 presents the iso-specific cationic polymerization of isobutyl vinyl ether (IBVE) with designed bulky titanium compounds. A series of titanium dichloride [TiCl₂(OAr)₂] were also employed where the metal center carries two substituted phenoxy groups, and a pronounced dependence of isotacticity was observed on the bulkiness, positions, and structure of ring-substituents on OAr (Scheme 6). Overall, isopropyl groups at 2,6-positions on the phenyl group Ar led to the highest isotacticity, whereas bulkier or planer-like groups such as tert-butyl or phenyl were less effective, suggesting that not only bulkiness but three-dimensional shapes of Lewis acids are critical in stereoregulation in cationic
Chapter 2 focuses on the substituents on the vinyl ether monomers with the titanium compounds described in Chapter 1. The tacticities depend on the substituents, where isobutyl and isopropyl vinyl ethers gave highly isotactic polymer ($mm = 83\%$), whereas tert-butyl vinyl ether (TBVE) resulted in a lower isotactic content ($mm = 49\%$) similar to that with a precursor, TiCl$_4$. The statistical analysis revealed that the high isospecificity is achieved not by the chain end but by the catalyst or the counteranion derived therefrom.

In Chapter 3 the author focused on the tacticity control by designed bulky counteranions derived from initiators (HB or B$^-$) for IBVE cationic polymerization. Therefore, phosphoric acid derivatives [(RO)$_2$POOH] coupled with SnCl$_4$ gave

**Scheme 6.** Cationic Polymerization of IBVE with Bulky Lewis Acids.

**Scheme 7.** Cationic Polymerization of IBVE with Bulky Phosphoric Acids.
highly isotactic poly(IBVE)s, where those with bulky substituent (R), $[\text{C}_4\text{H}_9\text{CH(C}_2\text{H}_5\text{CH}_2\text{O)}_2\text{POOH}$ and $(n-\text{C}_{10}\text{H}_{21})_2\text{POOH}$, led to the highest isotacticity ($m = 86\%$) (Scheme 7). In contrast, isospecificity was lower with IBVE–HCl and CF$_3$COOH under the same conditions.

Chapter 4 presents the first example of a precision cationic polymerization of cyclopentadiene (CPD) that forms controlled poly(CPD) with narrow molecular weight distributions (MWDs). With the use of HCl–adduct of CPD or a vinyl ether (initiator), SnCl$_4$ (Lewis acid as catalyst), and n-Bu$_4$NCI (additive), the number-average molecular weights of the polymers increased in direct proportion to monomer conversion, as well as to the monomer-to-initiator mole ratio, and the MWDs were narrow throughout the reactions ($M_w/M_n = 1.2$–$1.3$), clearly narrower than those in the additive-free systems ($M_w/M_n > 2$) (Scheme 8). The prepared poly(CPD) carried the initiator fragment at the α-end (nearly one per chain).

![Scheme 8. Controlled Cationic Polymerization of CPD.](image)

Chapter 5 focuses on the regiospecific polymerization of CPD with the binary initiating systems consisting of a protonic acid and a Lewis acid. The reaction parameters, e.g., solvents, additives, and temperatures, did not dramatically affect regioselectivity, giving 55–60% 1,4–contents almost invariably. On the other hand, a Lewis acid has dramatic effects on the selectivity, where weak
Lewis acids such as ZnX$_2$ ($X = \text{Cl, Br, I}$) gave the highest [1,4]–contents (64, 70, 76%, respectively) (Scheme 9). In particular, the CPD–HCl/ZnBr$_2$ system induced controlled polymerization to give poly(CPD)s with narrow molecular weight distributions (MWDs) ($M_w/M_n = 1.3–1.5$) and relatively high regiospecificity ([1,4] = 70%).

Scheme 9. Regioselectivity of CPD Polymerization with Lewis Acids

Chapter 6 is directed toward the syntheses of a series of CPD-based polymers and copolymers by the controlled systems showed in chapter 4 (Scheme 10). With HCl–adducts of vinyl ethers carrying pendant functional substituents as initiators, end-functionalized poly(CPD) was synthesized in conjunction with SnCl$_4$. The system led to controlled cationic polymerizations of CPD to give controlled α-end-functionalized poly(CPD)s with almost quantitative attachment of the functional groups ($F_n \sim 1$). Additionally, diblock copolymers of 2-chloroethyl vinyl ether (CEVE) and 2-acetoxyethyl vinyl ether with CPD were also synthesized by sequential polymerization of CPD and these vinyl ethers. ABA-Type triblock copolymer of CPD (A) and CEVE (B) was also prepared with the use of a bifunctional initiator.
In conclusion, this thesis presents the control of stereo- and regioselectivity in cationic polymerization by designed counteranions, intensively Lewis acids. Also the controlled polymerization of CPD and its application are discussed. The author hopes that this thesis contributes to further developments in not only cationic polymerization but also novel controlled organic reactions via cationic intermediates.

REFERENCES


PART I

DESIGN OF INITIATING SYSTEMS FOR STEREOSEPECIFIC CATIONIC POLYMERIZATION
Design of Counteranions with Bulky Titanium Lewis Acids as Catalysts

ABSTRACT

Highly isotactic-specific cationic polymerization has been achieved for isobutyl vinyl ether (IBVE) with bis[(2,6-diisopropyl)phenoxy]titanium dichloride [TiCl₂{OC₆H₄(i-Pr)₂(2,6-)}₂ (2)] as a Lewis acid catalyst (activator) to be coupled with the IBVE–HCl adduct (initiator). The polymerization, homogeneous and quantitative, was carried out in n-hexane at −78 °C in the presence of a bulky pyridine (2,6-di-tert-butyl-4-methylpyridine) to give isotactic-rich polymers with a meso dyad \( m = 90–92\% \) \( (M_n \sim 20000) \). Under similar conditions unsubstituted counterparts (TiCl₄, SnCl₄, etc.) gave nearly atactic products \( m = 68\% \). With catalyst 2, the isotactic content \( m \) increased at lower temperature, in less polar solvents, and with the added pyridine \( m = 64–92\% \). To design Lewis acids for stereoregulation, a series of titanium dichloride [TiCl₂(OAr)₂] were also employed where the metal center carries two substituted phenoxy groups, and a pronounced dependence of isotacticity was observed on the bulkiness, positions, and structure of ring-substituents on OAr. Overall, isopropyl groups at 2,6-positions led to the highest isotacticity, whereas bulkier or planer-like groups such as tert-butyl or phenyl were less effective, suggesting that not only bulkiness but three-dimensional shapes of Lewis acids are critical in stereoregulation in cationic polymerization.
**INTRODUCTION**

Stereoregularity is a factor that seriously affects physical properties of polymers. Thus stereospecific polymerizations have extensively been explored and are indeed possible for various monomers. Examples include coordination polymerization of olefins with Ziegler-Natta or metallocene catalysts\(^1\) and anionic polymerization of methacrylates with \(t\)-BuMgBr and \(t\)-BuLi/alkyl aluminum.\(^2\)

In cationic polymerization, however stereoregularity control has been difficult, particularly in homogeneous systems, although nearly complete control of molecular weight has been achieved by various living systems.\(^3\) Effects of catalysts or counteranions, substituents of monomers, solvent polarity, and temperature on tacticity have in fact been investigated rather extensively in cationic polymerization of vinyl ethers (VE), and mechanisms have been proposed for the formation of isotactic and syndiotactic enchainments,\(^4,5\) but very high stereospecificity is still beyond reach thus far.

For example, it has been reported that BF\(_3\)OEt\(_2\),\(^6\) AlEtCl\(_2\),\(^7\) and AlEt\(_2\)Cl\(^7\) give more or less isotactic poly(VE) in less polar solvents at low temperature, but the stereoregularity is not very high \((mm \sim 70\%)\). Vinyl ethers with bulky substituents like benzyl\(^8\) and \textit{tert}-butyl\(^9\) were polymerized with BF\(_3\)OEt\(_2\) to afford polymers of relatively high isotacticity \([mm = 86\% \text{ (benzyl)} \text{ and } 79\% \text{ (\textit{tert}-butyl)})\]. Allyl vinyl ether has also been polymerized by SbCl\(_5\) into isotactic polymer with \(m = 80\%\).\(^10\) In addition, heterogeneous systems with aluminum sulfate and sulfuric acid give crystalline stereoregular poly(VE), where the control of stereoregularity has been made by the orientation and absorption of monomers on the surface of the catalysts.\(^11\) However, the tacticity of the polymers was unknown because of the lack of NMR analysis at that time.

More recently, Sawamoto, Kamigaito, and their co-workers have developed a series of living cationic polymerizations of vinyl ethers, styrene derivatives, and related monomers (eq 1), which are almost invariably initiated by binary systems...
Design of Lewis Acids

Consisting of a protonic acid (HB; initiator) and a Lewis acid (MXₙ). Lewis acid acts as a catalyst/activator that interacts with the terminal covalent bonds (---C--B) derived from initiator HB and thereby induces its reversible dissociation into a growing carbocation. Via this dissociation, in turn, the Lewis acid combines with the anionic part(B) of the terminal to form the counteranion B−MXₙ−, which associates with the growing carbocation, by one way or another, and thus affects the nature of the active species. In the course of these studies, they have in fact noted that the judicious choice of the Lewis acids is crucial in achieving living cationic polymerization, or precise control of the propagation process. In particular, a series of titanium chlorides and alkoxides, Ti(OR)ₙCl₄−ₙ (R = alkyl or aryl) are quite useful in that, by changing the number (n) and the structure of the alkoxyl or aryloxyl substituents (OR), one can systematically control (and thus design) their Lewis acidity and in turn the nucleophilicity of the counteranions.¹² For vinyl ethers, the dichlorides such as TiCl₂(Oi-Pr)₂ and TiCl₂(OPh)₂ proved most efficient and of suitable Lewis acidity to effect living cationic polymerization.

From these findings the author then notes, relative to the stereoregulation of cationic polymerization, that such feature of the HB/MXₙ binary initiating systems would be advantageous, because one could control the stereochemical environment of the growing carbocation through designing the Lewis acid components that
determine the bulkiness, topology, and electronic nature of the associating counteranion. To his knowledge, such a Lewis acid-based approach to the counteranion design is unprecedented, neither in efforts for stereoregulation of cationic polymerization nor in fundamental studies of its stereochemistry. For example, in their now classical work, Higashimura\textsuperscript{4} and Kunitake\textsuperscript{5} were indeed aware of the importance of counteranions in determining, at least in part, the steric course of vinyl ether polymerizations, but their primary attention was apparently directed to the ionic radii and average charge density of counteranions. Therefore, they mostly employed simple spherical counteranions derived from a series of metal halides where the central metals alone were systematically varied. However, these studies led to important knowledge that isotactic propagation is preferred in ion-pair growing ends, i.e., in nonpolar solvent and with suitably bulky counteranions.

In this chapter, first of this thesis, the author therefore examined the possible stereoregulation of cationic polymerization by employing a series of titanium dichlorides [TiCl\textsubscript{2}(OAr)\textsubscript{2}] for which the bulkiness, topology (spatial shape), and electronic nature of counteranions can be manipulated by designing the structure of the aromatic substituents OAr (eq 2). Herein he employed a series of bulky titanium compounds, 2,6-disubstituted TiCl\textsubscript{2}(OAr)\textsubscript{2}, for the cationic polymerization of isobutyl VE (IBVE) in conjunction with adduct 1 (eq 2). His preliminary results show that the tacticity of poly(IBVE) depends on the

\[
\begin{align*}
\text{CH}_3\text{CHCl} & \xrightarrow{\text{TiCl}_2(\text{OAr})_2} \text{CH}_3\text{Cl} \\
1 & \text{(Activator)} \quad \text{O/Bu} \\
& \text{(Initiator)} \\
\rightarrow & \text{IBVE} \\
\text{Counteranion} & \text{Stereoregular Polymer?}
\end{align*}
\]

\textit{eq 2}
substituents of the titanium compounds\textsuperscript{13}. The author reports here that bis(2,6-diisopropylphenoxy) titanium dichloride gives highly isotactic poly(IBVE) ($m = 90-92\%$, $mm = 83\%$) in $n$-hexane at $-78$ °C in the presence of a bulky pyridine additive (2,6-di-tert-butyl-4-methylpyridine: DTBMP).

RESULTS AND DISCUSSIONS

1. Cationic Polymerization of IBVE with Substituted TiCl\textsubscript{2}(OAr\textsubscript{2})

IBVE was polymerized with various 2,6-disubstituted phenoxy titanium(IV) dichlorides [TiCl\textsubscript{2}(OAr\textsubscript{2})] in conjunction with the HCl-adduct of IBVE (1) in toluene at $-78$ °C. The ring substituents have been selected in terms of their bulkiness and shape, along with their electronic nature. Figure 1 shows

![Figure 1](image.png)

Figure 1. Polymerization of IBVE with 1/TiCl\textsubscript{2}(OAr\textsubscript{2}) in toluene at $-78$ °C: $[M]_0 = 0.38$ M; $[I]_0 = 5.0$ mM; $[TiCl\textsubscript{2}(OAr\textsubscript{2})]_0 = 10$ mM. 2,6-substituent (R) on OAr: R = Cl (O); iPr (●); Ph (□).
conversion-time curves of the polymerizations and size-exclusion chromatograms (SEC) of the polymers obtained with various titanium compounds. The polymerization rate depends on the substituents; with the 2,6-dichlorophenoxy titanium compound, which has electron-withdrawing chloro atoms on the phenoxy group, the polymerization occurred very fast and completed in 1 min. On the other hand, the polymerization was very slow with the corresponding 2,6-diphenylphenoxide, which has two bulky substituents on the phenoxy group. These results show that the nature of 2,6-substituents on the phenoxy groups of the titanium compounds has great effects upon the polymerizations.

The number-average molecular weights ($M_n$) were larger than the calculated values, and the molecular weight distributions (MWDs) were broad. These titanium compounds with substituted phenoxide groups were not effective in living polymerization. Such substituents on the phenoxy group near the titanium center may prevent effective interaction between the terminal chloride and the metal due to the steric hindrance, which results in slow interconversion between the dormant and the active species and broad MWDs.

2. Steric Structure of Poly(IBVE) with TiCl$_2$(OAr)$_2$

As shown in the representative $^{13}$C NMR spectrum of a sample obtained with TiCl$_2$[OC$_6$H$_3$i-Pr$_2$(2,6-)]$_2$ (2), the dyad distributions of poly(IBVE) can be determined from the peak intensity ratios of the main-chain methylene carbons [-CH$_2$-CH(O$i$Bu)-] around 39–42 ppm where the meso (m) and racemo (r) dyads are well resolved (Figure 2).$^{14}$ The absorptions of the methylene carbons [-OCH$_2$-CH(CH$_3$)$_2$] around 76–77 ppm can be used for the determination of triad distributions, but the signals of CDCl$_3$ at 77 ppm prevent the precise integrations of these peaks. Spectra of some samples were thus recorded in C$_6$D$_6$ especially for the determination of triad distributions (see below).

Figure 3 compares the partial $^{13}$C NMR spectra for the main-chain methylene signals for a series of poly(IBVE) samples obtained in toluene with
Figure 2. $^{13}$C NMR spectrum (67.9 MHz) of poly(IBVE) in CDCl$_3$ at 55 °C. Polymerization conditions: $[M]_0 = 0.38$ M; $[I]_0 = 5.0$ mM; $[\text{TiCl}_2\text{OC}_6\text{H}_3\text{i-Pr}_2(2,6-)]_0 = 10$ mM, in toluene at $-78$ °C.

Titanium tetrachloride and four TiCl$_2$(OAr)$_2$ derivatives with 2,6-disubstituted phenoxy groups [OAr = O-C$_6$H$_3$Y$_2$(2,6-); Y = C$_6$H$_5$, tert-Bu, Cl, i-Pr]. Except for the difference in Lewis acids, all of the samples were prepared under the same conditions (see Figure 1, caption). The dyad meso/racemo ($m/r$) peak ratios and the peak width clearly changed with the Lewis acids. Namely, in all cases the meso signal is predominant over the racemo counterpart, but meso dyad was rather low (72 %) of the unsubstituted form (TiCl$_4$) and even for the derivatives with very bulky ring-substituents (Y = C$_6$H$_5$, tert-Bu) (Figure 3, A–C). Thus, the introduction of bulky groups on the 2,6-positions of the OAr seems not generally effective, relative to TiCl$_4$, in controlling stereochemistry of the vinyl ether propagation.

In contrast, the isopropyl form (Y = i-Pr; Figure 3, E), whose 2,6-substituents are less bulkier than phenyl or tert-butyl, gave clearly larger and
Figure 3. $^{13}$C NMR spectra (67.9 or 125.8 MHz, CDCl$_3$, 55 °C) around 39–42 ppm of poly(IBVE) obtained with 1/MX$_n$ at -78 °C: (A); [M]$_0$ = 0.38 M, [I]$_0$ = 5.0 mM, [TiCl$_4$]$_0$ = 2.0 mM, in toluene, (B)–(E); [M]$_0$ = 0.38 M, [I]$_0$ = 5.0 mM, [MX$_n$]$_0$ = 10 mM, in toluene.
sharper meso signals to give $m = 83\%$, the highest among the seven $\text{TiCl}_2(\text{OAr})_2$-type Lewis acids employed herein under these conditions (see below also). When compared with those for $\text{TiCl}_4$ and the phenyl or tert-butyl counterparts, the spectral changes are much clearer than that in the rather insensitive numerical meso values: the three meso signals for the isopropyl form are sharper; the $mmm$ peak is particularly predominant; and the racemo peak is very small.

These trends demonstrate that the 2,6-disubstituted phenoxy rings are effective in facilitating the meso propagation but that the bulkiness of the substituent $Y$ [in $\text{-OC}_6\text{H}_3\text{Y}_2(2,6-)$], or the OAr groups in general, is not a primary

Figure 4. Meso dyad contents of poly(IBVE) obtained with $1/\text{MX}_n$ in toluene at $-78 \, ^\circ\text{C}$ and computer-generated molecular models of titanium compounds. Polymerization conditions: $[\text{M}]_0 = 0.38 \, \text{M}$; $[1]_0 = 5.0 \, \text{mM}$; $[\text{TiCl}_2(\text{OAr})_2]_0 = 10 \, \text{mM}$ (2.0 mM only for $\text{TiCl}_4$).
factor. This point can be better illustrated in Figure 4, which shows the computer-generated space-filling molecular models of the seven TiCl$_2$(OAr)$_2$ derivatives and their parent form TiCl$_4$, along with the meso contents of the polymer samples obtained from them (under the same conditions as for those in Figure 3). The models are generated by a molecular mechanics program (MM2) where the conformation is optimized in bond length and bond angle so as to minimize strain energy. In the figure they are shown edge-on in terms of the dihedral plane for the Cl–Ti–Cl bonds; the Ti center is seen behind the two chlorines. In all cases the TiCl$_2$ part is fairly well exposed for the interaction with the terminal chlorine in generating the carbocationic growing species (cf. Scheme 1).

Obviously, the titanium center becomes more sterically hindered with bulkier 2,6-substituents (Y) are attached on the phenoxy groups. Rather unexpectedly, however, the highly bulky forms with Y = phenyl or tert-butyl resulted in rather low meso contents ($m = 72\%$) without appreciable changes from the results for the least bulky parent TiCl$_4$. Along with another bulky derivative with a bridged bisphenoxy group ($m = 70\%$), these crowded Lewis acids appear to form counteranions too bulky for effective stereoregulation. Note that they in fact induced very slow polymerizations only (cf. Scheme 1), probably too bulky to effectively interact with the terminal chlorine, either.

The diisopropyl form (2), which gave the highest meso content among the seven acids, appears less bulky (Figure 4, top left). However, inspection of its molecular model indicates that the isopropyl groups are twisted relative to the aromatic ring, and because of this the space around the titanium center is even more sterically hindered than in the tert-butyl or phenyl derivatives. Apparently similar steric environment can be seen for the 2-tert-butyl-6-methyl form, which also gave relatively high meso value (78%).

These results suggest that stereoregulation is affected by not only overall bulkiness of the Lewis acid or its substituents but other factors, such as the spatial shape and symmetry around the Lewis acid's metal center from which the
counteranion is formed by attaching a chlorine of the dormant terminal. The latter spatial factor is therefore expected to affect the bulkiness and spatial shape of the resulting counteranions, which interact with the cationic growing site and is directly responsible for stereoregulation. Further studies are needed in this line.

3. Highly Isotactic Poly(IBVE): Effects of Reaction Conditions

The steric course of propagation will be affected by interaction of the counteranion with the growing carbocation, and the interaction, in turn, will be a function of not only the counteranion structure but also reaction conditions such as solvent polarity and temperature. The author thus examined the effects of these conditions on the IBVE polymerization with the Lewis acid $2 \left[\text{TiCl}_2\{\text{OC}_6\text{H}_3\text{i-Pr}_2(2,6-)^2\}\right]$ which proved most isotactic-selective among the seven Lewis acids so

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$^a$ [M]$_0$ = 0.38 M; [1]$_0$ = 5.0 mM; [2]$_0$ = 10 mM; [DTBMP]$_0$ = 0 or 2.0 mM.

$^b$ The polymerization was carried out via addition of IBVE into the mixture of 1, 2, and DTBMP in $n$-hexane at -78 °C.
13C NMR spectra (67.9 or 125.8 MHz, CDCl₃, 55 °C) around 39–42 ppm of poly(IBVE) obtained with 1/2 at -78 °C: (A); [M]₀ = 0.38 M, [1]₀ = 5.0 mM, [2]₀ = 10 mM, in CH₂Cl₂, (B); [M]₀ = 0.38 M, [1]₀ = 5.0 mM, [2]₀ = 10 mM, in toluene, (C); [M]₀ = 0.38 M, [1]₀ = 5.0 mM, [2]₀ = 10 mM, in n-hexane, (D); [M]₀ = 0.38 M, [1]₀ = 5.0 mM, [2]₀ = 10 mM, [DTBMP]₀ = 2.0 mM, in n-hexane.

Figure 5.
far discussed. The results are summarized in Figure 5 (\(^{13}\)C NMR; the main-chain methylene region) and Table 1 (meso dyad data).

As in the usual cationic polymerization, the meso contents increased with decreasing solvent polarity (CH\(_2\)Cl\(_2\) < toluene < n-hexane; Figure 5, A–C; Table 1, entries 1–3), and the value for hexane exceeded that for toluene (86% versus 83%). This is due to the suppression of ionic dissociation of the growing carbocation.

Addition of 2,6-di-tert-butyl-4-methylpyridine (DTBMP), known as a hindered base or as a proton trap, increased the meso dyad value, especially 90% in n-hexane (Table 1, entry 5 and Figure 5D). The effects of DTBMP is probably ascribed to the suppression of the initiation from the adventitious water that would generate hydroxide-based less nucleophilic counteranions or to possible interaction between DTBMP and the growing species.

All the polymerizations thus far investigated were initiated by the addition of 2 into the solution of monomer and 1 in n-hexane at -78 °C. To diminish the polar effects of the vinyl ether monomer, the author also examined the polymerization initiated by slow addition of IBVE into the solution of 1 and 2 in n-hexane at -78 °C (Table 1, entry 6). This procedure gave higher meso content (92%). The triad distribution (mm) was 83%, the highest value for poly(IBVE) to our knowledge.

Effects of temperature were investigated where the polymerizations were carried out at -15 °C in the presence of DTBMP (Table 1, entries 7 and 8). The stereoregularity is decreased by increasing the temperature as in usual ionic polymerizations. However, the molecular weight distributions were narrower, and the molecular weight increased with conversion, which suggests occurrence of living polymerization.

4. DSC Analysis of the Isotact-Rich Poly(IBVE)

The formation of isotact-rich poly(IBVE) with \(m \geq 90\%\) promoted him to investigate the thermal property of the polymer by differential scanning calorimetry (DSC). The glass transition temperature (\(T_g\)) of the isotact-rich poly(IBVE) was determined to be -30 °C, which is lower than that of the atactic poly(IBVE) (\(T_g\) ≈ -10 °C). This indicates that the isotact-rich structure causes a decrease in the internal mobility of the polymer chains, leading to a lower \(T_g\).
calorimetry (DSC). The author thus used the isotact-rich polymer (Table 1, entry 6: $m = 90\%$, $M_n = 32100$, $M_w/M_n = 2.12$) and the atactic polymer ($m = 68\%$, $M_n = 33200$, $M_w/M_n = 1.16$) obtained by the living cationic polymerization $1/\text{SnCl}_4/\text{nBu}_4\text{NCI}$ systems at $-15$ °C in CH$_2$Cl$_2$, where both the $M_n$ were about $3 \times 10^4$. Both samples showed an endothermic bias at $-14$ °C due to glass transition, whereas another endothermic peak, probably arising from melting, was different in the two; the isotact-rich poly(IBVE) showed this peak at $131$ °C whereas the atactic poly(IBVE) at 47 °C. There is also difference in appearance, where the former was stiff film and the latter was soft semisolid. These results show that soft and adhesive character of poly(VE) can be changed by tacticity of polymers, which may lead to new character of poly(VE) as materials.

In conclusion, control of stereoregularity in cationic polymerization can be achieved by the Lewis acid-type activators based on their substituents. Especially, bis(2,6-diisopropylphenoxy)titanium dichloride (2) gave isotact-rich ($m \geq 90\%$) poly(IBVE) in n-hexane at $-78$ °C in the presence of DTBMP in conjunction with 1.

**EXPERIMENTAL**

**Materials**

IBVE (Tokyo Kasei; purity $> 99\%$) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide (pellets), and distilled twice over calcium hydride before use. Toluene, n-hexane, and CH$_2$Cl$_2$ (solvents) and carbon tetrachloride (an internal standard for gas chromatography) were purified by the usual methods and distilled twice over calcium hydride before use. TiCl$_4$ (Aldrich, $> 99\%$) was used as received. 2,6-diisopropyl phenol (Tokyo Kasei, $> 98\%$), 2,6-di-tert-butyl phenol (Wako, $> 98\%$),
2,6-dichloro phenol (Aldrich, > 99%), 2,6-diphenyl phenol (Aldrich, > 98%), 2-tert-butyl-6-methyl phenol (Tokyo Kasei, > 95%), and 2,2'-methylene-bis (6-tert-butyl-4-ethyl) phenol (Aldrich, > 90%) were used as received for the preparation of TiCl₂(OAr)₂ as below. All the 2,6-disubstituted phenoxy titanium(IV) dichlorides [TiCl₂(OAr)₂] except TiCl₂(OPh)₂ were prepared as below. TiCl₂(OPh)₂ was prepared and purified as already reported.¹²

Preparation of TiCl₂(OAr)₂

All the procedures were carried out under dry argon in baked glassware equipped with three-way stopcocks. All the solvents were used after purification and distillation. All the 2,6-disubstituted phenoxy titanium(IV) dichlorides [TiCl₂(OAr)₂] were prepared by stirring titanium(IV) chloride and corresponding 2 equivalent 2,6-disubstituted phenol under argon flow to remove the produced HCl gas. For example, 2 was prepared as below. Titanium(IV) chloride (2.6 mL, 23.7 mmol) was added dropwise to a solution of 2,6-diisopropyl phenol (8.8 mL, 47.2 mmol) via a dry syringe in CH₂Cl₂ (30 mL) at -30 °C. On addition of TiCl₄, HCl gas was generated, which was trapped by bubbled into 10% NaOH solution. After stirring at -30 °C for 10 min, the mixture was stirred at room temperature for 1 h. After the solution was evacuated by vacuum pump, the reddish brown liquid remained and then dissolved in toluene. The solution was sealed in brown ampules and stored in the dark in a freezer. 2 was also prepared by another method where equimolar TiCl₄ and Ti(OAr)₄ was mixed together.

Synthesis of HCl–IBVE Adduct (1)

The HCl–IBVE adduct 1 was synthesized by bubbling dry HCl gas through a solution of IBVE (9.0 mL IBVE in 60 mL n-hexane; 1.0 M) at -78 °C. The gas was generated by dropping concentrated sulfuric acid into powdery sodium chloride, and dried by passing it through a column packed with calcium chloride. After 30 min, the excess HCl in the reaction mixture was removed by bubbling dry
nitrogen gas at 0 °C for 30 min, and the clean and quantitative formation of adduct 1 was confirmed by $^1$H NMR spectroscopy. The concentration of 1 was determined by titrating the chloride by the Volhard method; the observed value (~1 M) further confirmed the quantitative formation of 1 from IBVE.

**Polymerization Procedures**

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure in toluene is given below: The reaction was initiated by sequential addition of prechilled solutions of 1 (in n-hexane; 0.30 mL) and titanium complex (in toluene, 0.30 mL) via dry syringes into a monomer solution (in toluene; 2.4 mL) containing IBVE (0.15 mL) and CCl₄ (0.15 mL). After predetermined intervals, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl₄ as an internal standard. The polymer yield by gravimetry was in good agreement with the gas-chromatographic conversion of the monomer.

The quenched reaction mixture was washed with dilute hydrochloric acid, aqueous sodium hydroxide solution, and then with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.

**Measurements**

The MWD, $M_n$, and $M_w/M_n$ ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform on three polystyrene gel columns (Shodex K-805L × 3) that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index detector. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemicals; $M_n = 580–1547000; M_w/M_n \leq 1.1$) as well as the monomer. $^1$H and $^{13}$C NMR spectra of the produced polymers...
were recorded in CDCl₃ or CCl₄/C₆D₆(9/1 v/v) at 55 °C on a JEOL LNM-LA500 or a JEOL JNM-GSX270 spectrometer, operating at 500.2 or 270.2 MHz (¹H) and 125.8 or 67.9 MHz (¹³C), respectively. The DSC measurements were performed on a Thermal analyzer system WS002 (MAC Science, Tokyo) equipped with a TAPS1000S control unit and a DSC3100S module. Polymer solid samples (ca. 8 mg) were measured in an aluminum container under a dry nitrogen flow at a heating or cooling rate of 10 °C/min. α-Alumina was used as a standard.

**The Computer-Generated Molecular Models of the Titanium Compounds**

Molecular mechanics were carried out using the CAChe system (CAChe Scientific) to optimize the titanium compounds. MM2 parameters were used as force field parameters, and optimization was done by conjugate gradient method until the convergence energy became less than 0.001 kcal/mol. The molecular model with the lowest energy was determined by generating an exhaustive potential energy map computed from dihedral search labels for all the single bonds searching between −180° and 120° in 5 steps and all the double bonds searching between −180° and 90° in 3 steps, followed by picking up 10 conformers from the one with the lowest energy and further optimization of them.

**REFERENCES AND NOTES**


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(7) Natta, G.; Dall'Asta, G.; Mazzanti, G.; Giannini, U.; Cesca, S. *Angew. Chem.* 1959, 71, 205.


Effects of Monomer Structure on Stereospecificity

ABSTRACT

Stereoregulation in cationic polymerization of various alkyl vinyl ethers was investigated with bis[(2,6-diisopropyl)phenoxy]titanium dichloride [TiCl₂{OC₆H₄(i-Pr)₂(2,6-)}₂] (1; catalyst) in conjunction with the HCl-adduct of isobutyl vinyl ether (IBVE) as an initiator in n-hexane at -78 °C. The tacticities depend on the substituents of the monomers. Isobutyl and isopropyl vinyl ethers gave highly isotactic polymers (mm = 83%), whereas tert-butyl and n-butyl vinyl ethers resulted in lower isotactic contents (mm ∼ 50%) similar to those with TiCl₄, a conventional Lewis acid, thus indicating that the steric bulkiness of the substituents is not the critical factor in stereoregulation. The statistical analysis revealed that the high isospecificity is achieved not by the chain end but by the catalyst 1 or the counteranion derived therefrom.
INTRODUCTION

The synthesis of stereoregular polymers has been one of the most important and attractive objects in polymer chemistry, and near perfect stereoregularity has been achieved in coordination\(^1\) and anionic\(^2\) polymerizations. In cationic polymerization, however, such fine stereoregulation has been difficult in homogeneous systems, partly because of the lack of designed catalysts or counteranions that can control the stereochemistry of carbocation.

Despite these backgrounds, as shown in Chapter 1, the author has found that a designed titanium Lewis acid, bis[(2,6-diisopropyl)phenoxy]titanium dichloride \([\text{TiCl}_2{\text{O}}_C{\text{H}}_4{\text{(i-Pr)}}_2{\text{(2,6)}}_2](1)\), in conjunction with the HCl adduct of isobutyl vinyl ether (HCl–IBVE) (initiator) induces isospecific cationic polymerization of IBVE \((m \geq 90\% ; m \text{ is the content of meso dyad})\) (Scheme 1).\(^3\) Similar 2,6-disubstituted phenoxy derivatives also led to fairly high (~70–80%) isotacticity but cannot exceed the value for 1. Therefore, it has not been revealed why only this titanium compound gives highly isotactic poly(IBVE) among various titanium compounds.

The steric structure of polymers is, in general, determined not only by catalysts but also by the structure of the growing carbocation (i.e., monomers). In cationic polymerization, for example, the tacticity of poly(alkyl vinyl ethers) depends upon the substituent or the alkyl group of the monomers and increases in the following order: alkyl; tert-butyl > isobutyl > methyl > isopropyl > ethyl.\(^4\) On the other hand, Kunitake et al. reported that the size of the counterion (catalyst) or the tightness of the growing ion pair is a critical factor.\(^5\)

In this chapter, the author has therefore investigated the cationic polymerization of various alkyl vinyl ethers with 1 in conjunction with IBVE–HCl in n-hexane at \(-78 \, ^\circ \text{C}\) and discussed the effects of monomer substituent on the tacticity (Scheme 1). Additionally, a mechanism for the isospecific cationic...
polymerization is discussed on the basis of a statistical analysis of their tacticity data.

Results and Discussion

1. Cationic Polymerization of Various Alkyl VE{s with 1.} Cationic polymerization of various alkyl VE{s [alkyl = n-C₄H₉ (NBVE), t-C₄H₉ (TBVE), i-C₃H₇ (IPVE) n-C₃H₇ (NPVE), C₂H₅ (EVE), CH₃ (MVE)] was conducted with 1 in conjunction with the HCl–IBVE as an initiator in the presence of 2,6-di-tert-butyl-4-methylpyridine (DTBMP) in n-hexane at -78 °C, where the highly isotactic poly(IBVE) is obtained.³

As shown in Figure 1, the polymerization rates with 1/IBVE–HCl system depended on the monomers.⁶ For example, the VE{s with a branched substituent (IPVE, TBVE, and IBVE) were polymerized much faster than those with a linear substituent (NPVE and NBVE).} EVE was much less active, and no polymers formed from MVE under the same conditions. These results are probably due to that when the monomer's alkyl group is less bulky, the catalyst 1 can interact (form
Figure 1. Time-conversion curves for the polymerizations of various alkylVEs with IBVE–HCl/I/DTBMP in n-hexane at −78 °C: [M]₀ = 0.38 M; [IBVE–HCl]₀ = 5.0 mM; [I]₀ = 10 mM; [DTBMP]₀ = 2.0 mM. VE: (O) IPVE; (●) TBVE; (●) IBVE; (●) NBVE; (△) NPVE; (▲) EVE; (■) MVE.

a complex) more easily and thus less available for the dissociation of the terminal C–Cl bond into the growing cation. Similar results were also obtained with TiCl₄ in place of 1, where no polymers were formed even from EVE (see Table 1 entry 11). Such reduced rates are also due to the strong interaction between the highly oxophilic titanium metal and oxygen of VE. These results suggest that the Lewis acid catalysts can also interact with the oxygen attached to the substituent and that such interaction may affect the stereoselectivity of the growing species as described below.
2. Steric Structure of Poly(VE)s. The tacticity of the poly(VE)s thus obtained was measured by $^{13}$C NMR spectroscopy in $\text{C}_6\text{D}_6/\text{CCl}_4$ (9/1 v/v) at 55 °C. Regardless of the pendant alkyl groups, the spectra gave well-resolved main-chain methine or methylene signals that are split due to the steric structures (the asterisked carbons in Figure 2). For example, the dyad tacticity of poly(IBVE) was determined from the main-chain methylene carbons $[-\text{CH}_2-\text{CH(Oi-Bu)}-]$ around 39–42 ppm and the pendant methylene carbons $[-\text{OCH}_2-\text{CH(CH}_3)_2]$ around 76–77 ppm (the spectrum not shown) gave the corresponding triad data. For the other poly(alkyl VE)s, the tacticity was determined similarly. Table 1 summarizes these tacticity data along with the number-average molecular weights ($M_n$) and the molecular weight distribution ($M_w/M_n$).

![Figure 2](https://via.placeholder.com/150)

Figure 2. $^{13}$C NMR spectra [67.9 or 125.8 MHz, CDCl$_3$ or CCl$_4$/C$_6$D$_6$ (9/1 v/v), 55 °C] of poly(VE)s obtained with IBVE–HCl/1/DTBMP in $n$-hexane at −78 °C: see Figure 1 for reaction conditions.
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ₐ$[M]₀ = 0.38 \text{ M}; [\text{IBVE–HCl}]₀ = 5.0 \text{ mM}; [1]₀ = 10 \text{ mM}; [\text{DTBMP}]₀ = 2.0 \text{ mM}$ or $[M]₀ = 0.38 \text{ M}; [\text{IBVE–HCl}]₀ = 5.0 \text{ mM}; [\text{TiCl₄}]₀ = 2.0 \text{ mM}$ in $n$-hexane at $-78^\circ \text{C}$.  

ₐCalculated from the triad values: $m = mm + (1/2)mr; r = rr + (1/2)mr$.  

ₐNot determined.
(a) Effects of Pendant Alkyl Groups. The tacticities of the poly(VE)s clearly depended on the alkyl groups in the monomers. IBVE and IPVE, the pendant groups of which are branched near the ether oxygen, gave relatively high isotacticity \( (m = 88-90\%) \), Table 1; entry 1 and 7). In contrast, VE with linear (NBVE, NPVE, and EVE) or highly bulky (TBVE) substituents gave less isotactic contents (Table 1; entry 3, 9, 10, and 5). Especially, the poly(EVE) and poly(TBVE) had lower isotacticity \( (m = 64 \text{ and } 69\%) \), respectively. The tacticity is thus determined not by the stereo bulkiness but the structure (or branching) of the alkyl substituents, in contrast to the results for the conventional cationic polymerization with BF\(_3\)OEt\(_2\), where the bulkiest \( \text{t-butyl} \) derivative (TBVE) gave the highest isotacticity.\(^8,9\) When combined with our previous results with different Lewis acids,\(^3\) the observed trend implies that the factor determining the tacticity with the 1/HCl–IBVE initiating system is not only the bulkiness of the counteranion from Lewis acid but also the structure of the pendant groups, or the interaction between the Lewis acid and the pendant ether oxygen of VE.

(b) Effects of Lewis Acids (Catalysts). Some of the samples showed \(^{13}\)C NMR signals of the carbons adjacent to the ether oxygen, from which triad tacticity can be determined, and these resonances depended on the Lewis acids, as well as the alkyl groups. Figure 3 compares these peaks for poly(IBVE), poly(NBVE), poly(TBVE), and poly(IPVE) samples obtained with 1 and TiCl\(_4\) (see also Table 1). In all four systems, 1 led to higher isotacticity than TiCl\(_4\) did. In particular, the difference is distinct \((83\% \text{ vs } 46\%)\) in poly(IBVE) and poly(IPVE). Though less pronounced, a similar difference is found for poly(NBVE) and poly(TBVE). Note that, with TiCl\(_4\), isotacticity is almost independent for the those butyl polymers, in contrast to the clear dependence with bulkier 1 as a catalyst. Such a high dependence suggests some interaction between 1 and the substituents. As for poly(IPVE), a relative high isotacticity was obtained with TiCl\(_4\), though still lower than that with 1 \((69\% \text{ vs } 83\%)\).
Figure 3. $^{13}$C NMR spectra [67.9 or 125.8 MHz, CDCl$_3$ or CCl$_4$/C$_6$D$_6$ (9/1 v/v), 55 °C] of poly(VE)s obtained with IBVE–HCl/I/DTBMP or IBVE–HCl/TiCl$_4$ in n-hexane at −78 °C: (A), (C), (E), and (G) [M]$_0$ = 0.38 M; [IBVE–HCl]$_0$ = 5.0 mM; [I]$_0$ = 10 mM; [DTBMP]$_0$ = 2.0 mM, (B), (D), (F), and (H) [M]$_0$ = 0.38 M; [IBVE–HCl]$_0$ = 5.0 mM; [TiCl$_4$]$_0$ = 2.0 mM.

(c) Tacticity Statistics. To elucidate the polymerization mechanism or the transition state of the growing carbocation, the author further examined the statistics of the triad distributions. First, if he assumes the chain end model, namely the one-parameter model proposed by Bovey, the triad distribution [I (isotactic; $mm$), H (heterotactic; $mr$), S (syndiotactic; $rr$)] is expressed as:

\[
I = \sigma_1^2 \quad (1)
\]
\[
H = 2(\sigma_1 - \sigma_1^2) \quad (2)
\]
\[
S = (1 - \sigma_1)^2 \quad (3)
\]

where the parameter $\sigma_1$ is the probability that a monomer adds a polymer chain to give the isotactic (dyad meso) configuration as that of the preceding unit. In
Figure 4, the probability (P, %) of each tacticity is plotted against $\sigma_1$ obtained by eq 1. The solid lines are theoretical (the Bovey plot, eq 1–3) for the chain-end control. The plots of $H$ and $S$ for NBVE/TiCl$_4$ (■) and TBVE/TiCl$_4$ (♦), which gave the lower isotacticity (Table 1), seem to follow this model. In contrast, the plots for IBVE/1 (○), and IPVE/1 (△), and IPVE/TiCl$_4$ (▲), which gave the higher $I$ value, clearly deviate from the calculated lines. This suggests that the stereochemistry of these systems follows some statistics other than chain-end control.

Figure 4. Relationship between $\sigma_1$ and triad tacticity of poly(VE)s with IBVE–HCl/I/DTBMP or IBVE–HCl/TiCl$_4$ in n-hexane at −78 °C; (O) IBVE/1; (♦) IBVE/TiCl$_4$; (△) IPVE/1; (▲) IPVE/TiCl$_4$; (□) NBVE/1; (■) NBVE/TiCl$_4$; (◇) TBVE/1; (♦) TBVE/TiCl$_4$. The curves indicate the theoretical values calculated from the Bovey’s model.
On the other hand, for a system if tacticity is controlled by the catalyst; i.e.,
the so-called enantiomorphic-site control, the following equations hold:

\[ I = 1 - 3(\sigma - \sigma^2) \]  \hspace{1cm} (4)
\[ H = 2(\sigma - \sigma^2) \]  \hspace{1cm} (5)
\[ S = \sigma - \sigma^2 \]  \hspace{1cm} (6)

where the parameter \( \sigma \) represents the persistence probability that a monomer adds
a polymer chain in either configuration determined by the catalyst (or the

\[ \text{Figure 5. Relationship between } \sigma \text{ and triad tacticity of poly(VE)s with IBVE–HCl/1/DTBMP or IBVE–HCl/TiCl}_4 \text{ in } n\text{-hexane at } -78 \, ^\circ \text{C; (O) IBVE/1; (●) IBVE/TiCl}_4; (\triangle) \text{ IPVE/1; (▲) IPVE/TiCl}_4; (□) \text{ NBVE/1; (■) NBVE/TiCl}_4; (◇) \text{ TBVE/1; (●) TBVE/TiCl}_4. The curves indicate the theoretical values calculated from the enantiomorphic catalyst sites model.} \]
counteranion therefrom). Figure 5 shows the plots for the observed probability (P, %) against σ₂ as defined by eq 4. The solid lines are drawn according to the equations 4–6. In contrast to Figure 4, the plots of H and S for IBVE/1 (O), IPVE/1 (Δ), and IPVE/1 (▲) agree well with the calculated lines, whereas the plots for NBVE and TBVE seem inconsistent with the calculated lines.

These results show that the high isospecificity (m ~ 90%) in the polymerizations of IBVE and IPVE with IBVE–HCl/1 is due to not the chain-end control but the catalyst control, most probably originated from 1 or the counteranion therefrom. Although the enantiomeric site control has already been applied to the cationic polymerization of methyl vinyl ether with heterogeneous catalysts, there have been no examples for homogeneous systems even for isospecific cationic polymerization of BF₃OEt₂. However, 1 is not effective for all the alkyl vinyl ethers for example, the TBVE system seems to follow the chain-end control (◇ in Figure 4) even with the use of 1, probably due to the bulky t-butyl substituent. The polymerization of NBVE with TiCl₄ is controlled by chain end (■ in Figure 4), but one with 1 can involve the enantiomeric-site (catalyst) control (□ in Figure 5). Thus, the Lewis acid, 1 can effectively control the tacticity in the cationic polymerization of alkyl vinyl ethers, although the controllability also depends on the substituents of monomer.

Considering these results, the author proposes a new transition state [(A) in Scheme 2] for the IBVE–HCl/1 system, where the Lewis acid interacts with the anion from the initiator chloride and most probably with the ether oxygen of the incoming monomer. When this monomer-counteranion interaction operates, 1 can effectively control the direction of the incoming monomer’s approach to the growing cation to result in stereoregulation. Other transition states for conventional cationic polymerization have been proposed elsewhere [(B) and (C) in Scheme 2], which do not involve interaction between the counteranion and the incoming monomer. Apparently, these two transition states cannot be applied for our systems with high isospecificity.
In conclusion, 1 proved effective in isospecific cationic polymerization of IBVE and IPVE in conjunction with IBVE–HCl, to give relatively high isotactic content ($m_m = 83\%$ or $m ~ 90\%$) that has not been attained by other cationic catalysts. The author proposed that this is most probably due to the effective interaction between 1 and the incoming monomer via the enantiomorphically-site control.

**EXPERIMENTAL**

**Materials**

IBVE, NBVE, EVE (Tokyo Kasei; purity >99\%), TBVE (Aldrich; 99\%), IPVE, and NPVE (Nippon Carbide Ind. 99\%) were washed with 10\% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide (pellets), and distilled twice from calcium hydride before use. The initiator (HCl–IBVE)$^{14}$ and the catalyst, TiCl$_2$[OC$_6$H$_3$i-Pr$_2$(2,6-)]$_2$ (I),$^3$ were prepared as reported. Toluene (Wako; >99\%) as solvent was dried overnight over calcium chloride, distilled from sodium benzophenone ketyl. Carbon tetrachloride (internal standard for gas chromatography; >99\%) were dried overnight over
calcium chloride, distilled twice from calcium hydride. TiCl₄ (Aldrich; >99%) and DTBMP (Aldrich; 98%) was used as received.

**Polymerization Procedures**

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure of IBVE is given below: The reaction was initiated by sequential addition of prechilled solutions of IBVE–HCl (in n-hexane; 0.30 mL) and mixture of 1 and DTBMP (in toluene, 0.30 mL) via dry syringes into a monomer solution (in toluene; 2.4 mL) containing IBVE (0.15 mL) and CCl₄ (0.15 mL). After predetermined intervals, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl₄ as an internal standard. The polymer yield by gravimetry was in good agreement with the gas-chromatographic conversion of the monomer.

The quenched reaction mixture was washed with dilute hydrochloric acid, aqueous sodium hydroxide solution, and then with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.

**Measurements**

The MWD of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: 20–1000 Å; 8.0 nm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index detector. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemicals; $M_n = 580–1547000$; $M_w/M_n ≤ 1.1$) as well as the styrene monomer. $^1$H NMR and $^{13}$C NMR spectra of the produced polymers were recorded in CDCl₃ or CCl₄/C₆D₆ (9/1 v/v) at 55 °C on a JEOL.
LNM–LA500 or a JEOL JNM–GSX270 spectrometer, operating at 500.2 or 270.2 MHz (\(^1\text{H}\)) and 125.8 or 67.9 MHz (\(^{13}\text{C}\)), respectively.

REFERENCES AND NOTES


Chapter 3

Design of Counteranions with Bulky Phosphoric Acids as Initiators

ABSTRACT

In cationic polymerization of isobutyl vinyl ether (IBVE) with binary initiating systems consisting of a protonic acid as an initiator and a Lewis acid as an activator/catalyst, phosphoric acid derivatives [(RO)₂POOH] coupled with SnCl₄ gave highly isotactic poly(IBVE)s, where those with a bulky substituent (R), [C₄H₉CH(C₂H₅)CH₂O]₂POOH (7) and (n-C₁₀H₂₁)₂POOH (8), led to the highest isotacticity [meso dyad (m) = 86%]. In contrast, isospecificity was lower with IBVE-HCl and CF₃COOH under the same conditions. From the effects of polymerization temperature (−78 to 0 °C), it was concluded that the high isospecificity with 7 and 8 is due to an enthalpic factor.
Chapter 3

INTRODUCTION

For high stereoregulation in cationic polymerization, which has been difficult,\textsuperscript{1-5} the author has recently employed a binary system\textsuperscript{6} consisting of a protonic acid (HB) as an initiator and a Lewis acid (MX\textsubscript{n}) as an activator.\textsuperscript{7} Obviously, not only stability or reactivity but also the stereochemistry of the growing species can be affected by steric and electronic interaction with the counteranion (BMX\textsubscript{n}\textsuperscript{-}) to be generated from the anionic part (B\textsuperscript{-}) of HB and the catalyst MX\textsubscript{n}. This implies that design of the initiator HB or the catalyst MX\textsubscript{n} (or both) might lead to stereospecific cationic polymerization. For example, the combination of a bulky Lewis acid, bis[(2,6-diisopropyl)phenoxy]titanium dichloride [TiCl\textsubscript{2}(OC\textsubscript{6}H\textsubscript{4}(i-Pr)\textsubscript{2}(2,6-))\textsubscript{2} (1)], with the HCl-adduct of isobutyl vinyl ether (HCl-IBVE; 2) leads to highly isotactic poly(IBVE) (m $\geq$ 90%; $m = \text{meso}$ dyad) (Scheme 1).\textsuperscript{7} Alternatively, aromatic acetals with sterically hindered substituents as initiators also give fairly high isospecificity ($m \sim 81\%$).\textsuperscript{8} Similar approaches have been reported by Aoshima\textsuperscript{9a} and Hashimoto,\textsuperscript{9b} who employed hindered esters (as additives; $m = 62-66\%$) and hindered carboxylic acids (initiators; $m = 66-69\%$), respectively.

From these backgrounds, the author focused our attention on the tacticity control by designed bulky counteranions derived from initiators (HB or B\textsuperscript{-}) for

\begin{equation}
\text{CH}_3\text{C-CH-Cl O-i-Bu} \quad \text{TiCl}_2\quad \text{O} \quad \text{CH}_2=\text{CH} \quad \text{O-i-Bu} \quad \text{IBVE} \quad \text{Toluene or n-Hexane, \text{-78} °C} \quad \text{Isotactic poly(IBVE)} \quad m \geq 90\%
\end{equation}

Scheme 1
IBVE cationic polymerization (Scheme 2). This approach is considered complementary with the previous one, as presented in Chapter 1, via sterically designed Lewis acids $[\text{TiCl}_2(\text{OAr})_2; \text{Ar} = \text{substituted phenyl}]$. The protonic acids include $\text{HCl}$, $\text{CF}_3\text{COOH}$, and a series of phosphoric acids $[(\text{RO})_2\text{POOH}]$ with bulky substituents $R$ (4–8). The author reports herein new highly isospecific cationic polymerization of IBVE with selected $(\text{RO})_2\text{POOH}$ (7 and 8).

**Results and Discussion**

1. Various Combinations of HB and MX$_n$. (a) Effects of Acid Anions (B$^-$). IBVE was polymerized in toluene at $-78^\circ$C with three protonic acids (initiators) 2–4 carrying simple but different anions in conjunction with various MX$_n$, ZnCl$_2$, SnCl$_4$, EtAlCl$_2$, TiCl$_4$, and 1; in the latter, the first four are conventional metal halides for cationic polymerization, whereas 4 is a designed
Lewis acid to give high isospecificity with Cl\(^-\) anion \((m > 90\%)\).\(^7a\) The results are summarized in Table 1.

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\(^a\) [M\(_0\)] = 0.38 M; [HB\(_0\)] = 5.0 mM; [MX\(_n\)]\(_0\) = 5.0 mM (10 mM only for ZnCl\(_2\)); in toluene at \(-78\ ^\circ\text{C}\).

In addition to variation of polymerization rate and polymer molecular weight, the stereoregularity of the products depended on the combination of HB and \(\text{MX}_n\). Figure 1 shows some \(^{13}\text{C}\) NMR spectra of the main-chain methylene
Design of Initiators

Figure 1. $^{13}$C NMR spectra [125.8 MHz, CCl$_4$/C$_6$D$_6$ (9/1 v/v), 55 °C] around 39–42 ppm of poly(IBVE)s obtained with HB/MX$_n$ in toluene at -78 °C: [M]$_0$ = 0.38 M; [HB]$_0$ = 5.0 mM; [MX$_n$]$_0$ = 5.0 and 10 (only for ZnCl$_2$) mM.

region [-CH$_2$-CH(Oi-Bu)] for poly(IBVE)s obtained with some specific combination, and the meso (m) and the racemo (r) dyad contents were calculated from the integration ratios (see also Table 1). Although all these polymers are more or less isotactic, the signal patterns and the isospecificity (m) therefrom clearly depended on the HB/MX$_n$ combinations. For example, ZnCl$_2$ led to a lower isotactic content (m ~ 70%) irrespective of the acids anions (Table 1, entry 1–3; Figure 1A–1C), probably due to the smaller size of the counteranion. With SnCl$_4$, TiCl$_4$, and 4, the meso content was higher and dependent on the initiators (Table 1, entry 4–6, 10–12, and 13–15; Figure 1D–1I). Thus, the tacticity of poly(IBVE) obtained with the binary system was influenced with not only Lewis acid but also the anionic part of the initiator. In particular, a phosphoric acid derivative, 4, gave a high isotacticity (m = 80%) in conjunction with SnCl$_4$, which
is comparable to that for the 2/1 pair ($m = 82\%$; entry 13 in Table 1). Namely, a bulky protonic acid (4) seems as effective as a bulky Lewis acid (1) for high isospecificity. However, the combination of bulky two components, 4 (initiator) and 1 ($\text{MX}_n$) resulted in a lower $m$ content ($m = 76\%$; entry 15 in Table 1). Thus, bulkiness is not a single factor for stereoregulation and some shape or structural factor should also be considered, and phosphoric acids seem interesting initiators.

(b) Effects of SnCl$_4$ Concentration. A factor critical in the stereoregulation in ionic polymerization is the ionic dissociation of the growing carbocation,$^{14}$ and this can be modulated not only by the structural variation of the cations (monomers) and the counteranions (initiating systems) but also by the concentration of the carbocationic species. For the HB/$\text{MX}_n$ systems, the latter factor is in part controlled by the concentration of the MX$_n$ catalyst. Thus, effects

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$^{a}[\text{M}]_0 = 0.38 \text{ M}; [\text{HB}]_0 = 5.0 \text{ mM in toluene at } -78 ^\circ$C.
of SnCl₄ concentration were examined on polymerization with the three initiators (2–4), where the [SnCl₄]₀ was varied in the range 1.0–10 mM (Table 2). The number-average molecular weights (M_n) and molecular weight distributions (MWDs) were clearly dependent on the combination and the concentration. Controlled M_n and narrow MWDs were obtained with 1 irrespective of [SnCl₄]₀. On the other hand, 2 and 3 resulted in less controlled molecular weights and MWDs even at low [SnCl₄]₀, probably due to slow initiation and interconversion between the dormant and the active species.

Figure 2 shows ¹³C NMR spectra of the poly(IBVE)s obtained at 10 and 1.0 mM of SnCl₄ (see also Figure 1D–F for 5.0 mM SnCl₄). With all initiators, the lower [SnCl₄]₀ is, the stronger the meso signals, and therefore the m values monotonously increased at lower catalyst concentration (Figure 3). Similar effects were observed in the cationic polymerization of tert-butyl VE with H₂O/BF₃OEt₂ system.¹⁵ Because the lower [SnCl₄]₀ concentration means

**Figure 2.** ¹³C NMR spectra [125.8 MHz, CCl₄/C₆D₆ (9/1 v/v), 55 °C] around 39–43 ppm of poly(IBVE)s obtained with HB/SnCl₄ in toluene at −78 °C: [M]₀ = 0.38 M; [HB]₀ = 5.0 mM; [SnCl₄]₀ = 10 and 1.0 mM.
dilution of a weak electrolyte solution, which in turn facilitates the ionic dissociation of the growing cation, the enhanced isospecificity seems inconsistent with the notion that less dissociated or ion pair species is favorable for isotactic propagation. The author suspects that the rather complicated action of SnCl₄ upon interaction of cationogen (initiator like 2) might be responsible for this opposite trend in stereoregulation (see below).¹⁶

![Graph](image)

**Figure 3.** Relationship between [SnCl₄]₀ and meso content (m, %) of poly(IBVE) with HB/SnCl₄ in toluene at -78 °C: [M]₀ = 0.38 M; [HB]₀ = 5.0 mM; [SnCl₄]₀ = 10, 5.0 and 1.0 mM.

Perhaps more important, the phosphoric acid 3 proved more effective in affording isotactic poly(IBVE) than 1 and 2, to give 84% meso dyad at the lowest SnCl₄ concentration.
2. Phosphoric Acid/SnCl₄ Systems: Isospecific Bulky Anions. (a) Polymerizations. The formation of iso-rich poly(IBVE) with 4/SnCl₄ system promoted him to investigate a series of phosphoric acids [(RO)₂POOH] (4–8) with bulky substituents as initiators in conjunction with SnCl₄ at a low concentration (1.0 mM) (Scheme 1).

Figure 4 shows time–conversion curves of the polymerizations and the MWDs of the obtained poly(IBVE)s. All the polymerizations proceeded quantitatively, and the rates were dependent on the initiators, in contrast to that with similar systems coupled with ZnCl₂ at –15 °C, where they were almost independent of the substituents.¹² This may be due to an anion exchange reaction between the acid and SnCl₄, as considered later.

![Figure 4](image-url)

**Figure 4.** Time-conversion curves and MWD curves for the polymerizations of IBVE with (RO)₂POOH/SnCl₄ in toluene at –78 °C: [M]₀ = 0.38 M; [(RO)₂POOH]₀ = 5.0 mM; [SnCl₄]₀ = 1.0 mM. (RO)₂POOH: (●) 5; (○) 6; (▲) 7; (●) 4; (◆) 8.

*Design of Initiators*
Figure 5. $^{13}$C NMR spectra [125.8 MHz, CCl$_4$/C$_6$D$_6$ (9/1 v/v), 55 °C] around 39–43 ppm of poly(IBVE)s obtained with (RO)$_2$POOH/SnCl$_4$ in toluene at -78 °C: [M]$_0$ = 0.38 M; [(RO)$_2$POOH]$_0$ = 5.0 mM; [SnCl$_4$]$_0$ = 1.0 mM. The spectrum (F) with 2/1 is from ref 8a.
(b) Stereoregularity. The meso dyad of the poly(IBVE)s with 5–8 were examined by $^{13}$C NMR (Figure 5). All of those initiators gave high isotacticity, among which the phosphates with a long and bulky alkyl group (7 and 8) induced the highest isotacticity ($m = 86\%$; Figure 5D and E). These isotactic polymers formed hard films similar to those obtained with the bulky Lewis acid 1 ($m = 90\%$; see also Figure 5F).$^{7a}$

Table 3. Effects of Temperature on Cationic Polymerization of IBVE with HB/SnCl$_4^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>HB</th>
<th>temperature, °C</th>
<th>time</th>
<th>conv, %</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>$m$ (dyad), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>-78</td>
<td>2 h</td>
<td>98</td>
<td>27,900</td>
<td>3.04</td>
<td>86</td>
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<tr>
<td>2</td>
<td>7</td>
<td>-60</td>
<td>30 sec</td>
<td>98</td>
<td>26,800</td>
<td>2.39</td>
<td>81</td>
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<tr>
<td>3</td>
<td>7</td>
<td>-40</td>
<td>1 min</td>
<td>99</td>
<td>32,700</td>
<td>2.64</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>-20</td>
<td>3 min</td>
<td>99</td>
<td>14,000</td>
<td>2.64</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0</td>
<td>10 min</td>
<td>92</td>
<td>6,600</td>
<td>2.50</td>
<td>70</td>
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<td>7</td>
<td>-78</td>
<td>3 min</td>
<td>94</td>
<td>8,700</td>
<td>1.11</td>
<td>77</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>-60</td>
<td>1 min</td>
<td>99</td>
<td>9,300</td>
<td>1.08</td>
<td>76</td>
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<td>1 min</td>
<td>100</td>
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<td>1.11</td>
<td>73</td>
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<tr>
<td>9</td>
<td>2</td>
<td>-20</td>
<td>1 min</td>
<td>100</td>
<td>7,400</td>
<td>1.43</td>
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<td>1 min</td>
<td>100</td>
<td>7,300</td>
<td>3.74</td>
<td>68</td>
</tr>
</tbody>
</table>

$^a$ [M]$_0 = 0.38$ M; [HB]$_0 = 5.0$ mM; [SnCl$_4$]$_0 = 1.0$ mM in toluene.

(c) Effects of Polymerization Temperature. Finally, effects of polymerization temperature were examined in the polymerization with 7 coupled with SnCl$_4$; the same set of experiments were carried out with the chloride 2 for comparison (Table 3). Unexpectedly, polymerization rate with the 7/SnCl$_4$ system showed a complicated temperature dependence: $-60$ °C $\sim -40$ °C $> -20$ °C.
> 0 °C > −78 °C. In contrast, the polymerization rate with 2/SnCl₄ simply increased at higher temperature.

Figure 6 shows the temperature dependence of the poly(IBVE) tacticity, according to the Fordham equation:

$$\ln(m/r) = (\Delta S_{m}^{\ddagger} - \Delta S_{r}^{\ddagger})/R - (\Delta H_{m}^{\ddagger} - \Delta H_{r}^{\ddagger})/RT$$

where $\Delta S_{m}^{\ddagger} - \Delta S_{r}^{\ddagger}$ is the difference in activation entropy and $\Delta H_{m}^{\ddagger} - \Delta H_{r}^{\ddagger}$ is the difference in activation enthalpy between isotactic ($m$) and syndiotactic ($r$) enchainment, $R$ is the gas constant (8.3145 J/mol·K), and $T$ is the absolute temperature. In both systems, a good linear relationship holds between the $\ln(m/r)$ and the reciprocal of the temperature, whereas the slope and the intercept were quite different between

Figure 6. Relationship between $1/T$ and $\ln(m/r)$ of poly(IBVE)s obtained with 2/SnCl₄ and 7/SnCl₄ in toluene at −78, −60, −40, −20, or 0 °C: [M]₀ = 0.38 M; [HB]₀ = 5.0 mM; [SnCl₄]₀ = 1.0 mM. System: 2/SnCl₄ (△); 7/SnCl₄ (●).
the two systems. The phosphoric acid system obviously involves a high enthalpy difference, consistent with its high isospecificity.

The high isoselectivity by the phosphoric acids is probably due to exchange reaction with SnCl₄ to generate a bulkier Lewis acid e.g., SnCl₃[OP(O)(OR)₂], as previously reported for similar systems.¹² The tin metal has higher coordination number, and hence a bulkier counteranion can be formed to induce isospecificity. The new bulkier Lewis acid might further interact with the phosphate-capped dormant end ——C—OP(O)(OR)₂ to form a bulkier counteranion carrying two bulky phosphates. In contrast, with the use of a series of acetic acids as an initiator, such an exchange reaction does not occur and resulted in lower isospecificity.¹⁸

In Part I, the author demonstrates an effective isospecificity enchainment by a bulky protonic acid and/or a bulky Lewis acid from which the counteranion forms.

EXPERIMENTAL

Materials

IBVE (Tokyo Kasei; >99%) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide (pellets), and distilled twice from calcium hydride before use. Toluene (Wako; >99%) were dried overnight over calcium chloride, distilled from sodium benzophenone ketyl. Carbon tetrachloride (internal standard for gas chromatography; >99%) were dried overnight over calcium chloride, distilled twice from calcium hydride. The protonic acids (initiators) and the Lewis acids except for 1 were obtained commercially and used without further purification: CF₃COOH (3; Wako; >99%), (n-BuO)₂POOH (4; Tokyo Kasei; >97%), (PhO)₂POOH (5; Aldrich; 99%),
Chapter 3

(PhCH₂O)₂POOH (6; Tokyo Kasei; >98%), [C₄H₉CH(C₂H₅)CH₂O]₂POOH (7; Tokyo Kasei; >97%), (n-C₁₀H₂₁)₂POOH (8; Tokyo Kasei; >95%), ZnCl₂ (Aldrich; 1.0 M solution in Et₂O), SnCl₄ (Aldrich; 1.0 M solution in CH₂Cl₂), EtAlCl₂ (Kanto Chemicals; 1.0 M solution in n-hexane), TiCl₄ (Aldrich; >99%). The titanium compound 17 and the HCl–IBVE adduct 2¹⁹ were synthesized as already reported.

Polymerization Procedures

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure is given below: The reaction was initiated by sequential addition of prechilled solutions of HB (0.015 mmol; 0.30 mL of 0.050 M in toluene) and MXₙ (0.015 mmol; 0.30 mL of 0.050 M in toluene) via dry syringes into a monomer solution (in toluene; 2.4 mL) containing IBVE (1.14 mmol; 0.15 mL) and CCl₄ (0.15 mL). The total volume of the reaction mixture was thus 3.0 mL. After predetermined intervals, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl₄ as an internal standard. The polymer yield by gravimetry was in good agreement with the gas-chromatographic conversion of the monomer.

The quenched reaction mixture was washed with dilute hydrochloric acid, aqueous sodium hydroxide solution, and then with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.

Measurements

The MWD of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: 20–1000 Å; 8.0 nm i.d. × 30 cm) × 3; flow rate 1.0
mL/min] that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index detector. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemicals; $M_n = 580-1547000$; $M_w/M_n \leq 1.1$) as well as the styrene monomer. $^{13}$C NMR spectra of the produced polymers were recorded in CCl$_4$/C$_6$D$_6$ (9/1 v/v) at 55 °C on a JEOL LNM–LA500 spectrometer, operating at 500.2 MHz ($^1$H) and 125.8 MHz ($^{13}$C), respectively.

REFERENCES AND NOTES

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PART II

PRECISION CATIONIC POLYMERIZATION OF CYCLOPENTADIENE: CONTROL OF MOLECULAR WEIGHT AND REGIOSPECIFICITY
Chapter 4

Design of Initiating Systems for Control of Molecular Weight of Poly(CPD)

ABSTRACT

Precise control of molecular weights and their distributions (MWD) in cationic polymerization of cyclopentadiene (CPD) has first been achieved with three-component initiating system, the HCl-adduct of CPD or a vinyl ether (initiator), SnCl₄ (Lewis acid as catalyst), and n-Bu₄NCl (additive), in dichloromethane at −78 °C. The number-average molecular weights of the polymers increased in direct proportion to monomer conversion, as well as to the monomer-to-initiator mole ratio (up to 200), and the MWDs were narrow throughout the reactions ($M_w/M_n = 1.2−1.3$), clearly narrower than those in the additive-free systems ($M_w/M_n > 2$). Weak bases such as diethyl ether and ethyl acetate also proved effective as additives, whereas THF inhibited CPD polymerization. The poly(CPD) carried the initiator fragment at the α-end (nearly one per chain), and consisted of nearly the same contents of the 1,2- and 1,4-repeat units; free from other enchainments.
INTRODUCTION

Hydrocarbon polymers with rigid cyclic repeat units have attracted much attention as new materials of attractive thermal, mechanical, and electronic properties such as high glass-transition temperature and low dielectric constant. A majority of such polymers have been obtained via addition (vinyl) polymerization of cyclic olefins,\textsuperscript{1,2} cyclopolymerization of α,ω-dienes,\textsuperscript{2} and ring-opening metathesis polymerization of bicyclic olefins.\textsuperscript{3} Among the three methods, the first gives the most rigid backbones where cyclic units are directly connected each other without spacers, whereas the second and the third methods generate polymers with one and two spacer carbons, respectively, in the main chain. The monomers for the addition polymerization include cyclic dienes, which afford rigid main chains of directly linked, unsaturated rings that may be hydrogenated into more stable saturated structures.\textsuperscript{4}

Cyclopentadiene (CPD) is a representative cyclic diene that is easily obtained by the retro Diels-Alder reaction of dicyclopentadiene, and can be polymerized via cationic addition mechanism with conventional Lewis acids (metal halides) and stable carbocation salts (eq 1).\textsuperscript{5} The growing species therein is most likely a relatively stable allylic carbocation and thus leads to 1,2- and 1,4-enchainments in the main-chain cyclic units. Despite its long history of research dating back to the 1920s,\textsuperscript{6–10} the precise control of CPD cationic polymerization has not been attained, in terms of molecular weights, main-chain microstructure (1,2- vs. 1,4-); occasional formation of insoluble products renders research more difficult. The poor controllability is also seen in the transition metal-catalyzed coordination polymerizations developed more recently.\textsuperscript{11,12}
Controlled Polymerization of CPD

One of the most effective techniques to control polymer molecular weight and structures is living polymerization. Living cationic polymerization\(^{13}\) has been achieved for various vinyl monomers, such as vinyl ethers, styrene derivatives, isobutene, indene, \(N\)-vinylcarbazole, and \(\beta\)-pinene, where the obtained polymers have controlled molecular weights and narrow molecular weight distributions (MWDs).\(^{14}\) Most of living cationic polymerizations can be achieved by binary system that consists of a protonic acid (HB) or its derivative as an initiator and a Lewis acid (\(MX_n\)) as an activator (eq 2). The Lewis acid activates the C–B bond in the initiator and polymer terminals to give a growing cationic species (\(--\text{C}^+\)) accompanied by a counteranion (\(\text{BMX}_n^-\)). The choice of initiators, Lewis acids, and additives is crucial in achievement of living polymerization.\(^{14}\)

![Initiator](image)

\begin{equation}
\begin{array}{c}
\text{Initiator} \\
\text{Activator} \\
\text{Living Polymer}
\end{array}
\end{equation}

Given these backgrounds, the author became interested in precision control of CPD cationic polymerization for at least two reasons: There are few or no living cationic polymerizations of linear and cyclic aliphatic dienes; no general methods are available for controlling the 1,2- and 1,4-structures in the CPD main chain, despite that the selective formation of such units would be important in the chemistry of allylic-type growing carbocations and would also give interesting materials (see above). This study was thus to develop living cationic polymerization of CPD with HB/Lewis acid initiating systems; the effects of additives and solvent polarity were also examined for optimization of reaction control. This chapter reports the first example, to his knowledge, precise control of polymer molecular weights and MWDs in cationic CPD polymerization, with use of the HCl–CPD adduct (1)/SnCl\(_4\) initiating system in the presence of an additive such as \(n\)-Bu\(_4\)NCl, diethyl ether, and ethyl acetate.

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RESULTS AND DISCUSSIONS

1. Search of Initiators

As potential initiators for living cationic polymerizations of CPD, we first examined hydrogen chloride adducts of CPD (1), 2-chloroethyl vinyl ether (2), α-
methylstyrene (3), and styrene (4). The use of these adducts means that, in eq 2, the anion $B^-$ is invariably the chloride, while the carbocationic parts differ in structure and reactivity. The polymerizations were carried out in toluene at $-78 \, ^\circ C$ with SnCl$_4$ as the activator ($MX_n$) in eq 2: [CPD]$_0$/[Initiator]$_0$/[SnCl$_4$]$_0 = 500/5.0/50$ mM. All systems induced polymerization, whereas the rate depended upon the initiators (Figure 1). The CPD adduct 1 induced a fast and quantitative polymerization. The polymerizations with 2 and 3 proceeded at nearly the same rate as with 1 at the initial stage but slowed down subsequently. In contrast, 4 resulted in a much slower and incomplete polymerization.

![MWD curves of poly(CPD) obtained with R–Cl/SnCl$_4$ in toluene at $-78 \, ^\circ C$: [M]$_0 = 0.50$ M; [R–Cl]$_0 = 5.0$ mM; [SnCl$_4$]$_0 = 50$ mM. R–Cl: (A) 1; (B) 2; (C) 3; (D) 4.](image)

**Figure 2.** MWD curves of poly(CPD) obtained with R–Cl/SnCl$_4$ in toluene at $-78 \, ^\circ C$: [M]$_0 = 0.50$ M; [R–Cl]$_0 = 5.0$ mM; [SnCl$_4$]$_0 = 50$ mM. R–Cl: (A) 1; (B) 2; (C) 3; (D) 4.
Figure 2 shows the MWDs of the obtained polymers, as measured by size-exclusion chromatography (SEC) with a polystyrene calibration. The SEC curves with 1 were relatively narrow and shifted to higher molecular weights with increasing CPD conversion. The adducts 2 and 3 also gave relatively narrow MWDs until ~50% conversion, however, they became broader at higher conversion. The MWDs with 4 were much broader due to slow initiation from 4, which has a stronger and less active C–Cl bond than the others. Thus, 1 proved most suitable for controlling cationic polymerization of CPD with SnCl₄.

2. Effects of Solvents

In general, cationic polymerization is affected by solvent polarity and the effects of solvents were then examined in the CPD polymerization with 1/SnCl₄ at −78 °C. As shown in Figure 3, the higher the polarity of solvent is, the faster the
rate of polymerization. Addition of CH$_2$Cl$_2$ to toluene (toluene/CH$_2$Cl$_2$ = 3/1 v/v) made the polymerization faster, where conversion reached 96% in 15 min. The polymerization in CH$_2$Cl$_2$ was very fast and completed within 1 min to give products of multimodal SEC curves. On the other hand, the polymerization in methylcyclohexane (MCH), a less polar solvent, was much slower even with 10 times more SnCl$_4$ (50 mM) than in CH$_2$Cl$_2$. These results show that the polymerization of CPD highly depends on solvent polarity. The MWDs of the polymers were fairly narrow in toluene or its mixture with CH$_2$Cl$_2$. The multimodal MWD in CH$_2$Cl$_2$ is probably due to a highly active, dissociated growing carbocation, which can attack a double bond in another polymer chain to generate comb-like and partially cross-linked polymers. In contrast to the polymerization with SnCl$_4$ alone in CH$_2$Cl$_2$ reported previously, no insoluble gels formed with the 1/SnCl$_4$ system. Overall, therefore, less polar media are better suited for control of CPD polymerization.

3. Effects of Additives: Control of CPD Polymerization

Control of polymerization in polar media like CH$_2$Cl$_2$ may be possible by addition of an ammonium salt or a base, as demonstrated in cationic polymerizations of vinyl ethers$^{15-17}$, styrene derivatives$^{18}$, and isobutene$^{19,20}$. These additives are expected to affect the nature of the growing carbocation by suppressing ionic dissociation or stabilizing the growing carbocation. As shown in Figure 4, addition of a chloride, n-Bu$_4$NCl, retarded the polymerization in CH$_2$Cl$_2$ and gave poly(CPD)s with much narrower MWDs ($M_w/M_n \sim 1.2$) than those in the salt free systems.

The number-average molecular weights ($M_n$) of the polymers increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one polymer chain forms per CPD-HCl adduct molecule, although they were based on a polystyrene calibration (Figure 5). Therefore, n-Bu$_4$NCl proved an effective additive for control of molecular weights and MWDs.
Figure 4. Effects of added n-Bu₄NCI on CPD polymerization with 1/SnCl₄ in CH₂Cl₂ at -78 °C: [CPD]₀ = 500 mM; [1]₀ = 5.0 mM; [SnCl₄]₀ = 5.0 mM; [n-Bu₄NCI]₀ = 5.0 mM. Additive: (O) none; (●) n-Bu₄NCI.

Figure 5. $M_n$, $M_w/M_n$, and MWD curves of poly(CPD) obtained with 1 (●, △) or 2 (O, Δ)/SnCl₄ in the presence of n-Bu₄NCI in CH₂Cl₂ at -78 °C: [CPD]₀ = 500 mM; [1 or 2]₀ = 5.0 mM; [SnCl₄]₀ = 5.0 mM; [n-Bu₄NCI]₀ = 5.0 mM. The diagonal bold line indicates the calculated $M_n$ assuming the formation of one polymer chain per 1 molecule.
in cationic polymerization of CPD. Another initiator 2, also gave polymers with controlled molecular weights and narrow MWDs in conjunction with n-Bu4NCl. To his knowledge, these are the first examples of control molecular weights and MWDs of poly(CPD).

A series of oxygen-based nucleophiles such as diethyl ether (Et2O), isopropyl ether (i-Pr2O), ethyl acetate (EA), and tetrahydrofuran (THF) were also employed for the control of the polymerization with 1/SnCl4 in CH2Cl2 at -78 °C (Figure 6).16,17 Addition of Et2O and EA retarded the polymerization moderately, where the conversion reached 95% in 2 h and 93% in 16 h, respectively. With both additives, the MWDs were as narrow as those obtained with n-Bu4NCl. The Mn increased linearly with conversion and agreed with the

![Figure 6](image-url)

**Figure 6.** Time-conversion and MWD curves of poly(CPD) obtained with 1/SnCl4 in the presence of additives in CH2Cl2 at -78 °C: [CPD]0 = 500 mM; [1]0 = 5.0 mM; [SnCl4]0 = 10 mM, Additive 1 vol% ([Et2O]0 = 96 mM, [EA]0 = 100 mM, [i-Pr2O]0 = 71 mM, [THF]0 = 120 mM). Additive: (O) Et2O; (●) EA; (♦) i-Pr2O; (■) THF.
calculated values. The polymerization with i-Pr2O, a weaker and hindered base, was fast and uncontrolled, similar to that in the absence of additives. In contrast, no polymers were obtained with THF, a stronger base. Thus, the 1/SnCl4 initiating system afforded poly(CPD) with controlled molecular weight and narrow MWDs in the presence of bases such as n-Bu4NCl, Et2O, and EA.

Figure 7 is to demonstrate further control of molecular weights and the distributions by the ratio of monomer to initiator ([M]₀/[Initiator]₀). Thus, in the 1/SnCl4/n-Bu4NCl initiating system, the amount of 1 was fixed ([I]₀ = 5.0 mM), whereas the initial monomer concentration was varied ([M]₀ = 250, 500, and 1000

![Figure 7.](image)

Figure 7. $M_n$, $M_w/M_n$, and MWD curves of poly(CPD) obtained with 1/SnCl4 in the presence of n-Bu4NCl in CH2Cl2 at -78 °C: [CPD]₀ = 1000 (◯), 500 (●), 250 (▲) mM; [I]₀ = 5.0 mM; [SnCl4]₀ = 5.0 mM; [n-Bu4NCl]₀ = 5.0 mM. The diagonal bold line indicates the calculated $M_n$ assuming the formation of one polymer chain per 1 molecule.
Controlled Polymerization of CPD

mM; DPₙ = 50, 100, and 200, respectively) (Figure 7). The Mₙ increased linearly to monomer conversion and agreed well with the respective calculated values. These results also show that 1 in fact serves as an initiator to form polymer with controlled molecular weights.

The living nature of the polymerization with the 1/SnCl₄ initiating system in the presence of n-Bu₄NCl or Et₂O was then examined in monomer-addition experiments; thus CPD was polymerized with these systems and a fresh feed of CPD was added to the reaction mixture when the initial charge had almost been consumed. Although a second-phase polymerization proceeded, it was slower than the first and terminated at 50–70% conversion of the added CPD, to give products of a bimodal SEC curve with a small shoulder of lower molecular weights. This indicates that a part of the growing carbocations reacts with the double bond of a polymer chain, not that of monomer, to be inactivated at the latter stage of the first-phase polymerization where most of the monomer has been consumed. Thus, the cationic polymerizations of CPD with these systems can not be defined as “living polymerization”, despite that the observed molecular weight increase and the narrow MWDs show a long lifetime of the intermediate and the near absence of side-reactions.

5. Polymer Analysis

The structure of the poly(CPD) obtained with 2/SnCl₄/n-Bu₄NCl in CH₂Cl₂ was examined by 1H NMR spectroscopy (Figure 8). The vinyl ether adduct 2 was used herein for easy detection of the initiator fragment. The poly(CPD) shows large characteristic signals of main chain repeat units, i.e., olefinic (e) and aliphatic protons (f-i). The aliphatic protons consist of roughly four parts due to 1,2- and 1,4-structures, as known in conventional cationic polymerization of CPD. The 1,2-unit content was 46% based on peak areas [(1 – f/e) × 100]. The stereoselectivity was almost the same in both salt-present and salt-free systems. This point is discussed in Chapter 5 in detail.
In addition to these major peaks, there appeared minor absorptions assignable to the initiator fragment (a–d). The $M_n$ (NMR) was determined from the relative peak area of the main-chain repeat units (e) to the initiator moiety (b–d), and was very close to that by SEC [$M_n$(NMR) = 3000, $M_n$(SEC) = 2900]. This also suggests that 2 serves as the initiator that forms one living polymer chain per molecule.

The poly(CPD) obtained with 1/SnCl$_4$/n- Bu$_4$NCl and 2/SnCl$_4$/n-Bu$_4$NCl was further analyzed by matrix-assisted laser-desorption-ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) (Figure 9). Both spectra consist of a series of sharp peaks separated by a 66 Da interval each, corresponding to the molecular weight of CPD monomer. These indicate the virtual absence of
Figure 9. MALDI-TOF-MS spectrum of poly(CPD) obtained with 1/SnCl₄ (A) and 2/SnCl₄ (B) in the presence of n-Bu₄NCl in CH₂Cl₂ at −78 °C: [CPD]₀ = 500 mM; [1 or 2]₀ = 5.0 mM; [SnCl₄]₀ = 5.0 mM; [n-Bu₄NCl]₀ = 5.0 mM. (A): $M_n = 3700$, $M_w/M_n = 1.14$ (B): $M_n = 2900$, $M_w/M_n = 1.15$.

significant side reactions such as chain-transfer. Furthermore, there is 41 Da difference between the sharp peaks in the two spectra, which agrees with the mass difference between 1 and 2. This result also indicates that one initiator generates one polymer chain and that every polymer chains contains the initiator moiety at the α-end. The terminal structure predicted from the absolute mass was olefin structure, which is due to chlorine elimination induced by laser similar to the Cl-terminated polymers obtained with transition metal-catalyzed living radical polymerization or due to hydrogen chloride elimination during the work-up process.22

In conclusion, the author has demonstrated the synthesis of poly(CPD) with controlled molecular weights and narrow MWDs via cationic polymerization of
Chapter 4

CPD with the 1 or 2/SnCl₄ initiating system in the presence of n-Bu₄NCI, Et₂O or EA in CH₂Cl₂ at −78 °C. To his knowledge, this is the first example of precise control of molecular weights and the distributions in cationic polymerization of CPD.

EXPERIMENTAL

Materials

Unless otherwise specified, all of the chemicals were purchased from Wako company, Japan. CPD was obtained by the retro Diels-Alder reaction of dicyclopentadiene (Tokyo Kasei; >95%) at 165 °C over calcium hydride and distilled from calcium hydride. It was stored at −84 °C and used within one month. The purity and the absence of dicyclopentadiene in CPD was confirmed by NMR before use (purity >99%). CH₂Cl₂ (>99%) was dried overnight over calcium chloride, distilled from phosphorous pentoxide and then from calcium hydride before use. Methylcyclohexane (MCH) (Tokyo Kasei; >99%), carbon tetrachloride (internal standard for gas chromatography; >99%), ethyl acetate (EA) (>99%) and 1-phenylethyl chloride (4; >97%) were dried overnight over calcium chloride, distilled twice from calcium hydride. Toluene (>99%), diethyl ether (Et₂O) (>99%), and tetrahydrofuran (THF) (>99%) were dried overnight over calcium chloride, distilled from sodium benzophenone ketyl. SnCl₄ (Aldrich; 1.0 M solution in CH₂Cl₂), n-Bu₄NCI (Tokyo Kasei; >98%) and isopropyl ether (i-Pr₂O) (Aldrich; anhydrous; 99%) were used as received.

Synthesis of HCl Adduct 1–3

The HCl adducts 1–3 were synthesized by bubbling dry HCl gas into a solution of the respective vinyl compounds (CPD, CEVE, and αMeSt). The
synthesis of HCl–CPD adduct 1 as a typical example was done below. Dry HCl gas was bubbled into 1.0 M toluene solution (36 mL) of CPD (3.0 mL; 0.036 mol) at –78 ºC. The gas was generated by dropping concentrated sulfuric acid into powdery sodium chloride, and dried by passing it through a column packed with calcium chloride. After 30 min, the excess HCl in the reaction mixture was removed by bubbling dry nitrogen gas at 0 ºC for 30 min, and the clean and quantitative formation of adduct 1 was confirmed by 1H NMR spectroscopy. The concentration of 1 was determined by titrating the chloride by the Volhard method. The observed value (0.89 M) further confirmed the quantitative formation of 1 from CPD.

**Polymerization Procedures**

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure in CH2Cl2 is given below: The reaction was initiated by sequential addition of prechilled solutions of 1 (0.02 mmol; 0.40 mL of 0.050 M in CH2Cl2) and SnCl4 (0.02 mmol; 0.40 mL of 0.050 M in CH2Cl2) via dry syringes into a monomer solution (in CH2Cl2; 3.2 mL) containing CPD (2.0 mmol; 0.165 mL) and CCl4 (0.165 mL). The total volume of the reaction mixture was thus 4.0 mL. For polymerization in the presence of additives, these were dissolved in SnCl4 solution prior to initiation. After predetermined intervals, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia. 3-tert-Butyl-4-hydroxy-5-methylphenyl sulfide (0.014 mmol; 0.005 g) was then added as an antioxidant immediately after quenching reaction. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl4 as an internal standard. The polymer yield by gravimetry was in good agreement with the gas-chromatographic conversion of the monomer. The quenched reaction mixture was washed with dilute hydrochloric
acid and with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.

**Measurements**

The MWD of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: 20–1000 Å; 8.0 nm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] that were connected to a Jasco PU–980 precision pump and a Jasco 930-RI refractive index detector. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemicals; $M_n = 580–1547000$; $M_w/M_n ≤ 1.1$) as well as the styrene monomer. $^1$H NMR spectra of the produced polymers were recorded in CDCl$_3$ on a JEOL LNM-LA500 spectrometer, operating at 500.2 MHz. MALDI-TOF-MS spectra were measured on a Perseptive Biosystems Voyager-DE STR equipped with a 2-m linear flight tubes and a 337-nm nitrogen laser (pulse width, 3 ns), along with a delayed extraction capability. All experiments were carried out at an accelerating potential of 20 kV. In general, mass spectra from 256 laser shots were accumulated summed to produce a final spectrum. Angiotensin I (human; MW = 1296.5) (BACHEM) and insulin (bovine pancreas 28.3; MW = 5733.50) (nacalai) were used as internal standards to calibrate the mass scale. Samples for MALDI-TOF-MS analysis were prepared by mixing the poly(CPD), a matrix (1,8-dihydroxy-9(10H)-anthracenone; dithranol), and a cationizing agent (silver trifluoroacetate) in THF. For example, a poly(CPD) sample (approximately 10 mg/mL) was dissolved in THF. The matrix and the cationizing agent were also dissolved separately in THF (30 mg/mL and 10 mg/mL, respectively). A 30 μL portion of the poly(CPD) solution, 90 μL of the matrix solution, and 30 μL of the cationizing agent were mixed in a glass vial. Then 0.5 μL portions of the mixture were deposited onto 10–20 wells of the gold-coated sample plate and dried in air at room temperature.
REFERENCES AND NOTES


(13) Miyamoto, M.; Sawamoto, M; Higashimura, T. Macromolecules 1984, 17, 265.


Design of Initiating Systems for Control of Regiospecificity in CPD Polymerization

ABSTRACT

The control of regioselectivity in cationic polymerization of cyclopentadiene (CPD) was examined with initiating systems consisting of HCl-adduct of CPD (I; initiator) and a Lewis acid (activator/catalyst), and among a series of metal halides as catalysts, weak Lewis acids such as ZnX$_2$ (X = Cl, Br, I) gave the highest [1,4]–contents (64, 70, 76%, respectively). In particular, the 1/ZnBr$_2$ system induced controlled polymerization to give poly(CPD)s with narrow molecular weight distributions (MWDs) ($M_w/M_n = 1.3$–1.5) and relatively high regiospecificity ([1,4] = 70%). In contrast, SnCl$_4$, TiCl$_4$, and other strong Lewis acids resulted in less controlled microstructures ([1,4] = 45–50%). Other reaction parameters, e.g., solvents, additives, and temperatures, did not dramatically affect regioselectivity, giving 55–60% 1,4–contents almost invariably.
INTRODUCTION

Cyclopentadiene (CPD) is one of the most representative and inexpensive cyclic dienes, and its polymer is a candidate for new hydrocarbon-polymeric materials with rigid cyclic repeat units. CPD can be polymerized by cationic catalysts to give two rigid main-chain cyclic units, 1,2- and 1,4-enchainments, due to the allylic growing carbocation.\(^1\) Despite the long research history that dates back to 1920s,\(^2\)-\(^6\) fine control of molecular weights and microstructures of the polymers is difficult, and the products thus far reported are invariably of low molecular weights and poorly controlled architectures.

As shown in Chapter 4, however, the author has succeeded in controlling molecular weights and molecular weight distributions (MWDs) in cationic polymerization of CPD by using an initiating system consisting of an HCl-adduct (1 or 2; initiator) and SnCl\(_4\) (activator/catalyst) in the presence of an additive such as \(n\)-Bu\(_4\)NCl, diethyl ether, or ethyl acetate (eq 1).\(^7\) These polymerizations are considered to proceed via the allylic carbocation (3) reversibly generated from its dormant, chlorine-capped species, to give polymers with controlled molecular weights and narrow MWDs (\(M_w/M_n = 1.2-1.3\)).

\[
\begin{align*}
\text{Initiator} & \quad \xrightarrow{\text{SnCl}_4} \quad \underset{\text{Activator}}{\text{R-Cl}} \quad \underset{\text{R-ClSiSnCl}_4}{\text{ClSiSnCl}_4} \\
\text{CPD} & \quad \underset{\text{Additive}}{\text{ClSiSnCl}_4} \\
\text{R-Cl: } & \quad \begin{array}{c}
\text{Cl} \\
\text{1}
\end{array} \quad \begin{array}{c}
\text{CH}_3\text{CH-Cl} \\
\text{2}
\end{array}
\end{align*}
\]
However, even these systems failed to control another critical factor of CPD
cationic polymerization, the regioselectivity for the main chain, giving nearly equal
amounts of 1,2- and 1,4-units as do conventional systems. Another problem in
cationic CPD polymerization is the formation of irregular main-chain structures
due to cation rearrangement) and insoluble products (due to the in-chain double
bonds). Thus, the regiospecific cationic polymerization of CPD has not
been attained yet, which is in contrast to that some metal-catalyzed coordination
polymerizations of cyclopentene generate crystalline, highly isotactic cis-1,3-
polymers.

Thus, this chapter is directed to develop regiospecific cationic polymerization
of CPD with the binary initiating systems [1/MXₙ (Lewis acid)], in relation to the
effects of reaction conditions such as solvents, temperatures, additives, and Lewis
acids (Scheme 1). As with other vinyl monomers, these reaction parameters
may affect the nature of the growing CPD (allylic) carbocation and, in turn, the
regiospecificity in propagation. For example, in cationic polymerization of
isobutyl vinyl ether, the meso dyad contents (isotacticity) can be varied between 60

Regioselectivity:

![Regioselectivity Diagram](image)

Solvent: toluene, CH₂Cl₂, methylcyclohexane (MCH)
Additive: n-Bu₄NCl, Et₂O, CH₃CO₂Et₂, i-Pr₂O, Ph₃CCl, TiCl₄(O-Pr)₂, AlBr₃, BCl₃, ZnX₂ (X = Cl, Br, I)

MXₙ: SnX₄ (X = Cl, Br), TiX₄ (X = Cl, Br), TiCl₂(O-Pr)₂, AlBr₃, BCl₃, ZnX₂ (X = Cl, Br, I)

Scheme 1
and 90% with designed Lewis acids (see Chapter 1). None of such stereochemical control via catalyst design, however, are found in cationic polymerization of CPD and related cyclic or linear conjugated dienes.

In this chapter, the author reports that 1,4-enchainment can be varied between 51 and 76% with the use of various catalysts and that especially 1/ZnBr$_2$-system induces controlled cationic polymerization to give poly(CPD)s with controlled molecular weights, narrow MWDs ($M_w/M_n = 1.2–1.3$), and relatively high regiospecificity ([1,4] = 70%).

RESULTS AND DISCUSSIONS

1. Effects of Solvents, Additives, and Temperature.

(a) Solvents. In cationic polymerization of vinyl monomers, the steric structure of its polymers depends on solvent polarity, which affects the ionic dissociation of the growing carbocation. Therefore, CPD polymerization

![Figure 1. Effects of solvents on the MWD curves of poly(CPD) obtained with 1/SnCl$_4$ at -78 °C: See Table 1 for reaction conditions.](image)
was carried out with the 1/SnCl₄ initiating system at −78 °C in various solvents, toluene, methylcyclohexane (MCH), and CH₂Cl₂ (Table 1, entry 1–3 and Figure 1, A–C). The higher the solvent polarity, the faster the polymerization, and the molecular weight and MWDs of the polymers depended on the solvents.

The microstructures of the obtained poly(CPD) was analyzed by ¹H NMR spectroscopy. Figure 2 shows the representative ¹H NMR spectrum of a sample obtained with 1/SnCl₄ in toluene at −78 °C (for entry 3, Table 1). Characteristic signals appear in two regions, one for the olefinic proton (D; a¹,2 and a¹,4) around 5.5−6.0 ppm and the other for the aliphatic protons (b¹,2, c¹,2, d¹,2, b¹,4, and c¹,4) around 1.5−3.0 ppm. The latters consist of well-resolved three parts; i.e., 1.4−1.8

Figure 2. ¹H NMR spectra (500 MHz, CDCl₃) of poly(CPD)s (Mₙ = 7500, Mₘ/Mₙ = 1.62, [1,2]/[1,4] = 45/55) obtained with 1/SnCl₄ in toluene at −78 °C: [CPD]₀ = 0.50 M; [1]₀ = 5.0 mM; [SnCl₄]₀ = 5.0 mM; entry 3, Table 1.
ppm (A; $c^1$, $d^1$), 1.8–2.2 ppm (B; $d^1$, $l^1$), and 2.2–2.8 ppm (C; $c^1$, $b^1$, $l^1$, and $b^1$). The 1,2- and 1,4-contents (hereafter, [1,2] and [1,4], respectively) can be calculated from their integrated signal intensities by the following two methods:\(^3\)

**Method 1:** $[1,2]$, % = \[
\frac{(B + C - A)}{(A + B + C)} \times 100
\]

**Method 2:** $[1,2]$, % = \[
\left[1 - \frac{A}{D}\right] \times 100
\]

where A, B, C, and D represent the peak intensities of the four signals.

If a poly(CPD) sample consists of the two “regular” main-chain units, 1,2- and 1,4-units, olefinic/aliphatic protons ratio $D/(A+B+C)$ should be 0.5. If the ratio deviates from 0.5, the polymer contains other structures, such as those from the isomerization of the growing carbocation and saturated units via chain transfer or termination. The observed ratios for all of the poly(CPD) are close to 0.50, which indicates the absence of such side reactions under our reaction conditions with 1/SnCl$_4$. The regioselectivity did not depend on the solvents, either, where the [1,2] contents were around 45%.

**Additives.** The effects of additives, which would interact with growing carbocation\(^2\) or Lewis acid activator\(^2\) were also examined with use of the 1/SnCl$_4$ system in CH$_2$Cl$_2$ at $-78$ °C (Table 1, entry 4–11 and Figure 3, A–H). In addition to $n$-Bu$_4$NCI\(^7\), weak Lewis bases including diethyl ether, and ethyl acetate, Ph$_3$CCl and 2,6-di-tert-butyl-4-methylpyridine proved effective in controlling molecular weights and MWDs ($M_w/M_n = 1.3–1.4$) (Figure 3, A–E). However, diisopropyl ether, 2,4,6-trimethylpyridine, and 1-butylimidazole gave broader and multimodal MWDs (Figure 3, F–H), though some of them were effective in living cationic polymerization of styrene. In contrast, none of the additives affected the regiospecificity; i.e., all polymers showed about 45%–[1,2] and 55%–[1,4] contents (Table 1). Thus, control of stereospecificity in cationic polymerization with 1/SnCl$_4$ was difficult by changing solvent polarity or by adding salts and Lewis bases.

**Temperature.** The regiospecificity was not affected by polymerization temperature (0 to $-78$ °C), either. Rather unusual in cationic polymerization, the
Table 1. Effects of Solvent and Additive on CPD Polymerization with $1/$SnCl$_4$ at $-78 \, ^\circ$C$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>[SnCl$_4$]$_0$, mM</th>
<th>solvent</th>
<th>[additive]$_0$, mM</th>
<th>time, min</th>
<th>conv, %</th>
<th>$M_n$ ($M_w/M_n$)</th>
<th>[1,2]/[1,4], %</th>
<th>Meth. 1</th>
<th>Meth. 2</th>
<th>$D/(A+B+C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.0</td>
<td>toluene</td>
<td>none</td>
<td>0</td>
<td>120</td>
<td>7,500 (1.62)</td>
<td>46 / 54</td>
<td>45 / 55</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>MCH$^b$</td>
<td>none</td>
<td>0</td>
<td>2940</td>
<td>4,300 (2.17)</td>
<td>46 / 54</td>
<td>45 / 55</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
<td>CH$_2$Cl$_2$</td>
<td>none</td>
<td>0</td>
<td>1</td>
<td>8,600 (3.33)</td>
<td>47 / 53</td>
<td>45 / 55</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>CH$_2$Cl$_2$</td>
<td>$n$-Bu$_4$NCl</td>
<td>5.0</td>
<td>2</td>
<td>6,500 (1.29)</td>
<td>46 / 54</td>
<td>46 / 54</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>CH$_2$Cl$_2$</td>
<td>Et$_2$O</td>
<td>96</td>
<td>120</td>
<td>7,100 (1.33)</td>
<td>44 / 56</td>
<td>45 / 55</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>CH$_2$Cl$_2$</td>
<td>EA$^c$</td>
<td>100</td>
<td>960</td>
<td>6,600 (1.30)</td>
<td>46 / 54</td>
<td>46 / 54</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5.0</td>
<td>CH$_2$Cl$_2$</td>
<td>Ph$_3$CCl</td>
<td>5.0</td>
<td>3</td>
<td>5,500 (1.29)</td>
<td>46 / 54</td>
<td>46 / 54</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5.0</td>
<td>CH$_2$Cl$_2$</td>
<td>DTBMP$^d$</td>
<td>4.5</td>
<td>1</td>
<td>7,700 (1.41)</td>
<td>48 / 52</td>
<td>47 / 53</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>CH$_2$Cl$_2$</td>
<td>$i$-Pr$_2$O</td>
<td>71</td>
<td>1</td>
<td>6,600 (3.67)</td>
<td>47 / 53</td>
<td>45 / 55</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>CH$_2$Cl$_2$</td>
<td>TMP$^e$</td>
<td>4.5</td>
<td>1</td>
<td>5,800 (2.54)</td>
<td>48 / 52</td>
<td>47 / 53</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>5.0</td>
<td>CH$_2$Cl$_2$</td>
<td>BIZ$^f$</td>
<td>4.5</td>
<td>1</td>
<td>8,000 (2.44)</td>
<td>47 / 53</td>
<td>46 / 54</td>
<td>0.49</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ [CPD]$_0$ = 500 mM; [1]$_0$ = 5.0 mM; [SnCl$_4$]$_0$ = 5.0 – 50 mM; [Additive]$_0$ = 0 – 100 mM. $^b$ methylcyclohexane. $^c$ ethyl acetate. $^d$ 2,6-di-tert-butyl-4-methylpyridine. $^e$ 2,4,6-trimethylpyridine. $^f$ 1-butylimidazole.
Chapter 5

Figure 3. Effects of various additives on the MWD curves of poly(CPD) obtained with 1/SnCl\(_4\) in CH\(_2\)Cl\(_2\) at \(-78^\circ\)C: See Table 1 for reaction conditions.

Overall polymerization rate with 1/SnCl\(_4\) in toluene did not clearly depend on temperature (conversion: 50% in 15 min; 80–100% in 120 min), though there were some differences in time-conversion profiles for the temperatures. The olefinic/aliphatic protons ratios was also close to 0.50; a slight decrease at 0 °C (47%) might indicate some side reaction at higher temperature, however the regioselectivity also unchanged, 55–60% [1,4] units.

2. Effects of Lewis Acids. Apart from external reaction parameters like solvent and temperature, the author employed various Lewis acids (MX\(_n\)) in conjunction with 1 in toluene or CH\(_2\)Cl\(_2\) at \(-78^\circ\)C. The Lewis acids were: SnX\(_4\) (X = Cl, Br), TiX\(_4\) (X = Cl, Br), TiCl\(_2\)(Oi-Pr)\(_2\), AlBr\(_3\), BCl\(_3\), and ZnX\(_2\) (X = Cl, Br, I). The results are summarized in detail in Table 2.
(a) **Molecular Weight Control.** Entry 1–5, Table 2, show the data for the polymerization in nonpolar toluene solvent. Strong Lewis acids such as TiX₄ (X = Cl, Br) and AlBr₃ induced rapid polymerizations (90% conversion within 10 min) to give broad MWDs. On the other hand, with a weak Lewis acid (BCl₃), a slower polymerization occurred (75% in 30 min, 100% in 5 h) and resulted in broader MWDs. Other weak Lewis acids such as SnBr₄, TiCl₂(Oi-Pr)₂, and ZnX₂ (X = Cl, Br, I) were not active enough in toluene.

Marked effects of Lewis acids were observed in polar CH₂Cl₂ solvent (Figure 4 and entry 6–12, Table 2). Strong Lewis acids like TiX₄ (X = Cl, Br) and AlBr₃ gave insoluble gels due to crosslinking as previously reported for cationic polymerization with them in the absence of 1. In contrast, weaker Lewis acids such as SnBr₄, TiCl₂(Oi-Pr)₂, and ZnX₂ (X = Cl, Br, I), which were not active in

![Figure 4](image_url)

**Figure 4.** MWD curves of poly(CPD) obtained with 1/MXₙ in CH₂Cl₂ at -78 °C: [CPD]₀ = 0.50 M; [1]₀ = 5.0 mM; [MXₙ]₀ = 5.0 mM or 100 mM (for ZnX₂).
Table 2. Effects of Lewis Acids on CPD Polymerization with 1 (initiator) at −78 °C<sup>a</sup>

<table>
<thead>
<tr>
<th>entry</th>
<th>MX&lt;sub&gt;n&lt;/sub&gt;</th>
<th>[MX&lt;sub&gt;n&lt;/sub&gt;]&lt;sub&gt;0&lt;/sub&gt;, mM</th>
<th>solvent</th>
<th>time, h</th>
<th>conv, %</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;)</th>
<th>[1,2] / [1,4], %</th>
<th>D/(A+B+C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SnCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>5.0</td>
<td>toluene</td>
<td>2</td>
<td>91</td>
<td>7,500 (1.62)</td>
<td>46 / 54</td>
<td>45 / 55</td>
</tr>
<tr>
<td>2</td>
<td>TiCl&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.0</td>
<td>toluene</td>
<td>1</td>
<td>98</td>
<td>7,700 (3.25)</td>
<td>44 / 56</td>
<td>43 / 57</td>
</tr>
<tr>
<td>3</td>
<td>TiBr&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.0</td>
<td>toluene</td>
<td>10</td>
<td>95</td>
<td>4,700 (2.34)</td>
<td>49 / 51</td>
<td>48 / 52</td>
</tr>
<tr>
<td>4</td>
<td>AlBr&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>0.5</td>
<td>toluene</td>
<td>5</td>
<td>93</td>
<td>6,700 (2.94)</td>
<td>45 / 55</td>
<td>43 / 57</td>
</tr>
<tr>
<td>5</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>5.0</td>
<td>toluene</td>
<td>5</td>
<td>100</td>
<td>9,200 (2.49)</td>
<td>42 / 58</td>
<td>41 / 59</td>
</tr>
<tr>
<td>6</td>
<td>SnCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>5.0</td>
<td>CH₂Cl₂</td>
<td>1</td>
<td>100</td>
<td>8,600 (3.33)</td>
<td>47 / 53</td>
<td>45 / 55</td>
</tr>
<tr>
<td>7</td>
<td>SnBr&lt;sub&gt;4&lt;/sub&gt;</td>
<td>5.0</td>
<td>CH₂Cl₂</td>
<td>15</td>
<td>70</td>
<td>8,700 (24.4)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>47 / 53</td>
<td>46 / 54</td>
</tr>
<tr>
<td>8</td>
<td>TiCl&lt;sub&gt;2&lt;/sub&gt;(Oi-Pr)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.0</td>
<td>CH₂Cl₂</td>
<td>1 day</td>
<td>87</td>
<td>8,700 (1.99)</td>
<td>41 / 59</td>
<td>41 / 59</td>
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<tr>
<td>9</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>5.0</td>
<td>CH₂Cl₂</td>
<td>4</td>
<td>77</td>
<td>3,100 (4.93)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>45 / 55</td>
<td>44 / 56</td>
</tr>
<tr>
<td>10</td>
<td>ZnCl&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>100</td>
<td>CH₂Cl₂</td>
<td>26 days</td>
<td>63</td>
<td>4,800 (1.37)</td>
<td>36 / 64</td>
<td>36 / 64</td>
</tr>
<tr>
<td>11</td>
<td>ZnBr&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>100</td>
<td>CH₂Cl₂</td>
<td>5 days</td>
<td>92</td>
<td>8,700 (1.37)</td>
<td>31 / 69</td>
<td>30 / 70</td>
</tr>
<tr>
<td>12</td>
<td>ZnI&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>100</td>
<td>CH₂Cl₂</td>
<td>14 days</td>
<td>86</td>
<td>11,200 (15.3)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>26 / 74</td>
<td>24 / 76</td>
</tr>
</tbody>
</table>

<sup>a</sup> [CPD]<sub>0</sub> = 500 mM; [Initiator]<sub>0</sub> = 5.0 mM; [MX<sub>n</sub>]<sub>0</sub> = 0.5–100 mM.  
<sup>b</sup> These Lewis acids gave insoluble polymers in CH₂Cl₂.  
<sup>c</sup> Dissolved in n-hexane.  
<sup>d</sup> Dissolved in Et₂O.  
<sup>e</sup> Bimodal MWD; see Figure 4.
Figure 5. $M_n$, $M_w/M_n$, and MWD curves of poly(CPD) obtained with 1/ZnBr$_2$ in CH$_2$Cl$_2$ at -78 °C: [CPD]$_0$ = 0.50 M; [1]$_0$ = 5.0 mM; [ZnBr$_2$]$_0$ = 100 mM.

toluene, induced polymerizations in CH$_2$Cl$_2$, despite the still low activity with some systems. Most of the Lewis acids gave bimodal or multimodal SEC curves, but ZnCl$_2$ and ZnBr$_2$ led to narrow MWDs that are similar to that for the controlled CPD polymers with 1/SnCl$_4$/n-Bu$_4$NCl system (Figure 3, trace A)

Especially with ZnBr$_2$, a quantitative polymerization occurred to give polymers with narrow MWDs ($M_w/M_n = 1.3$–$1.5$) (Figure 5). Also, the $M_n$ increased in direct proportion to monomer conversion, as in the polymerization with 1/SnCl$_4$/n-Bu$_4$NCl in CH$_2$Cl$_2$ at -78 °C. Thus, 1/ZnBr$_2$ proved effective in controlling molecular weights in cationic polymerization of CPD in a salt/additive free solvent.

(b) Regiospecificity with Lewis Acids. Table 2 also summarizes the 1,2- and 1,4-microstructures of poly(CPD) samples obtained with a series of Lewis acids at -78 °C. The olefinic/aliphatic protons ratios $[D/(A+B+C)]$ are nearly
Figure 6. $^1$H NMR spectra (500 MHz, CDCl$_3$) around 1.3–3.2 ppm of poly(CPD) obtained with various Lewis acids coupled with 1 in CH$_2$Cl$_2$ at $-78$ °C. See Table 2 for reaction conditions.
independent of the catalysts and close to 0.50, as expected for the main chains exclusively with the regular 1,2- and 1,4-units.

In sharp contrast, Lewis acids clearly and markedly affected the regiospecificity ([1,4] content) in both toluene and in CH$_2$Cl$_2$. For example, Figure 6 shows the main-chain aliphatic proton regions of $^1$H NMR spectra of poly(CPD) obtained in CH$_2$Cl$_2$ (see also Table 2, entry 6–12); a similar trend can be seen for the samples in toluene solvent (Table 2, entry 1–5). The 1,4-unit contents for CH$_2$Cl$_2$, determined from these spectra, are compared more visually in

![Figure 7. 1,4-contents of poly(CPD) obtained under various conditions. See Table 1 and Table 2 for reaction conditions.](image)
Chapter 5

Figure 7 as a function of Lewis acids.

As already discussed, strong Lewis acids such as SnCl₄ and TiCl₄ give more or less conventional poor regioselectivity around 55%, irrespective of solvent polarity, additives, and molecular weight control (the so-called living nature of the relevant polymerizations). A similarly low 1,4-content (51%) can be found with CH₃SO₃H, a protonic acid sometimes employed for CPD cationic polymerization.²⁴

With weaker Lewis acids (the bottom 4 entries in Figure 6 and Table 2), importantly, the signals of the 1,2-units clearly weaken and, in turn, those of the 1,4-units increasingly become sharper and stronger in the order of (SnCl₄ < TiCl₄ < TiCl₂(Oi-Pr)₂ < ZnCl₂ < ZnBr₂ < ZnI₂). In particular, ZnI₂ led to a 76% 1,4-content, perhaps the highest, to his knowledge, reported thus far for cationically prepared poly(CPD). Another finding of interest is that ZnBr₂ gives a relatively high 1,4-content (70%), the second highest just below the iodide version, and that the bromide also allows a fine molecular weight control in salt-free CH₂Cl₂ solvent (see the previous section). Thus, given these dual controllability in both MWD and 1,4-content, the 1/ZnBr₂ initiating system might lead to a regiospecific and living cationic polymerization of CPD, though optimum reaction conditions have not yet specified. The regiospecificity with weak Lewis acids is most probably due to formation of tight ion pairs in comparison to strong Lewis acids. However, it is not still clarified why the 1,4-enchainment is predominant with their catalysts.

4. DSC Analyses of Poly(CPD)s. The success in the controlled polymerization of CPD in terms of molecular weight and main-chain microstructure promoted him to investigate the thermal property of the polymers by differential scanning calorimetry (DSC) (Figure 7). The author employed three poly(CPD) samples with controlled molecular weights and narrow MWDs but low regiospecificity (Mₙ = 2700, 6600, 10100; [1,4] = 55% each) obtained with
Figure 8. Dependence of molecular weight and main-chain microstructure on $T_g$ of poly(CPD). The three samples (●: $M_n = 2700$, $M_w/M_n = 1.17$; $M_n = 6600$, $M_w/M_n = 1.26$; $M_n = 10100$, $M_w/M_n = 1.33$) with 45%-[1,2] and 55%-[1,4] were obtained with 1/SnCl$_4$/n-Bu$_4$NCl in CH$_2$Cl$_2$ at $-78$ °C: [CPD]$_0 = 0.25$, 0.50, or 1.00 M; [1]$_0 = 5.0$ mM; [SnCl$_4$]$_0 = 5.0$ mM; [n-Bu$_4$NCl]$_0 = 5.0$ mM. The sample (▲: $M_n = 5100$, $M_w/M_n = 1.35$) with 30%-[1,2] and 70%-[1,4] were obtained with 1/ZnBr$_2$ in CH$_2$Cl$_2$ at $-78$ °C: [CPD]$_0 = 0.50$ M; [1]$_0 = 5.0$ mM; [ZnBr$_2$]$_0 = 100$ mM.

1/SnCl$_4$/n-Bu$_4$NCl, and another sample ($M_n = 5100$; [1,4] = 70%) with a higher regiospecificity with 1/ZnBr$_2$ in CH$_2$Cl$_2$ at $-78$ °C.

Every sample showed an endothermic bias due to glass transition, and the glass transition temperature ($T_g$) was dependent on $M_n$ and microstructure (Figure
7). The larger the $M_n$, the higher the $T_g$ for the three samples with the same 1,4-content. When the molecular weights are similar (6100 vs 5100), $T_g$ decreased sharply with increasing 1,4-content, most likely due to a increase in the more flexible five-membered ring in the main chain.

In conclusion, enchainments in cationic polymerization of CPD with the 1/Lewis acid system can be affected not by solvents, additives, and temperatures but dramatically by Lewis acids. Specifically, weak Lewis acids such as TiCl$_2$(Oi-Pr)$_2$ and ZnX$_2$ ($X = $ Cl, Br, I) induced regiospecific polymerization with relatively high 1,4-contents, among which the highest content was obtained with ZnI$_2$ ([1,4] = 76%).

**EXPERIMENTAL**

**Materials**

Unless otherwise specified, all of the chemicals were purchased from Aldrich. CPD was obtained by the retro Diels-Alder reaction of dicyclopentadiene (Tokyo Kasei; >95%) over calcium hydride and distilled from calcium hydride. It was stored at -84 °C and used within one month. The purity and the absence of dicyclopentadiene in CPD was confirmed by NMR before use (purity >99%). CH$_2$Cl$_2$ (Wako; >99%) was dried overnight over calcium chloride, distilled from phosphorous pentoxide and then from calcium hydride before use. Methylcyclohexane (Tokyo Kasei; >99%), carbon tetrachloride (Wako; internal standard for gas chromatography; >99%), ethyl acetate (Wako; >99%) and 1-butylimidazole (98%) were dried overnight over calcium chloride, distilled twice from calcium hydride. Toluene (Wako; >99%) and diethyl ether (Wako; >99%) were dried overnight over calcium chloride, distilled from sodium benzophenone.
The following materials were used as received: SnCl₄, SnBr₄ and BCl₃ (all 1.0 M solution in CH₂Cl₂); TiCl₄ (>99.9%); TiBr₄ and AlBr₃ (both >99.99%); ZnCl₂ (1.0 M solution in Et₂O); ZnBr₂ and ZnI₂ (both >99.999%); CH₃SO₃H (Nacalai Tesque; 99%); n-Bu₄NCl and Ph₃CCl (both Tokyo Kasei; >98%); 2,6-di-tert-butyl-4-methylpyridine (98%); 2,4,6-trimethylpyridine (99%); and isopropyl ether (anhydrous; 99%). TiCl₂(Oi-Pr)₂ was prepared and purified as already reported.²⁵ The HCl adduct 1 was synthesized by bubbling dry HCl gas into a solution of CPD as already reported.⁷²⁶

**Polymerization Procedures**

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure with the 1/ZnBr₂ system is given below: The reaction was initiated by sequential addition of prechilled solutions of 1 (0.015 mmol; 0.30 mL of 0.050 M in CH₂Cl₂) and ZnBr₂ (0.3 mmol; 0.30 mL of 1.0 M in Et₂O) via dry syringes into a monomer solution (in CH₂Cl₂; 2.4 mL) containing CPD (1.5 mmol; 0.124 mL) and CCl₄ (0.124 mL). The total volume of the reaction mixture was thus 3.0 mL. For polymerization in the presence of an additive, it was dissolved in the Lewis acid solution prior to initiation. After predetermined intervals, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia. 3-tert-Butyl-4-hydroxy-5-methylphenyl sulfide (0.014 mmol; 0.005 g) was then added as an antioxidant immediately after quenching reaction. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl₄ as an internal standard. The polymer yield by gravimetry was in good agreement with the gas-chromatographic conversion of the monomer. The quenched reaction mixture was washed with dilute hydrochloric acid and with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.
Measurements

The MWD of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: 20–1000 Å; 8.0 nm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] that were connected to a Jasco PU-980 precision pump and a Jasco 930-R1 refractive index detector. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemicals; $M_n = 580$–$1547000$; $M_w/M_n \leq 1.1$) as well as the styrene monomer. $^1$H NMR spectra of the produced polymers were recorded in CDCl$_3$ on a JEOL LNM-LA500 spectrometer, operating at 500.2 MHz. The DSC measurements were performed on a Thermo Plus 2 Series (Rigaku, Tokyo) equipped with a DSC8230L module. Polymer solid samples (ca. 6 mg) were measured in an aluminum container under a dry nitrogen flow at a heating or cooling rate of 10 deg/min. α-Alumina was used as a standard.

REFERENCES AND NOTES

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(7) Chapter 4 of this thesis; Ouchi, M.; Kamigaito, M.; Sawamoto, M. Macromolecules, in press.


(24) Polymerization conditions (the same as those in Table 2, footnote a): [CPD]₀ = 500 mM; [CH₃SO₃H]₀ = 5.0 mM; at -78 °C in CH₂Cl₂; time 20 min; conversion = 78 %; $M_n$ = 37,000; $M_w/M_n$ = 4.20 (bimodal); [1,4] = 51%; $D/(A+B+C) = 0.49$.


Chapter 6

Synthesis of End-Functionalized CPD Polymers and Copolymers of CPD

ABSTRACT

A series of cyclopentadiene (CPD)-based polymers and copolymers were synthesized by a controlled cationic polymerization of CPD. End-functionalized poly(CPD) was synthesized with the HCl-adducts [initiator: CH$_3$CH(OCH$_2$CH$_2$X)Cl; X = Cl (2a), acetate (2b), methacrylate (2c)] of vinyl ethers carrying pendant functional substituents X in conjunction with SnCl$_4$ (Lewis acid as catalyst) and n-Bu$_4$NCl (additive) in dichloromethane at -78 °C. The system led to controlled cationic polymerizations of CPD to give controlled α-end-functionalized poly(CPD)s with almost quantitative attachment of the functional groups ($F_n \sim 1$). With the 2a or 2b/SnCl$_4$/n-Bu$_4$NCl initiating systems, diblock copolymers of 2-chloroethyl vinyl ether (CEVE) and 2-acetoxyethyl vinyl ether (AcOVE) with CPD were also synthesized by sequential polymerization of CPD and these vinyl ethers. ABA-Type triblock copolymer of CPD (A) and CEVE (B) was also prepared with the use of a bifunctional initiator. Copolymerization of CPD and CEVE with 2a/SnCl$_4$/n-Bu$_4$NCl afforded random copolymers with controlled molecular weights and narrow molecular weight distributions ($M_w/M_n = 1.3–1.4$).
INTRODUCTION

As discussed in Chapter 4, the author has succeeded in controlling polymer molecular weight and its distribution in cationic polymerization of cyclopentadiene (CPD),\(^1\) even though conventional cationic systems for CPD usually result in oligomers of ill-defined molecular weights and structures. CPD is an inexpensive and attractive monomer that gives rigid polymers of cyclic hydrocarbon repeat units with attractive thermal, mechanical, and electronic properties such as high glass-transition temperature and low dielectric constant. The new CPD polymerization is achieved with an initiating system consisting of an initiator, an activator (catalyst), and an additive (eq 1). The initiator may be the HCl-adduct of CPD (1) or 2-chloroethyl vinyl ether (CEVE) (2a) (initiator); the catalyst is a Lewis acid such as SnCl\(_4\); typical additives include \(n\)-Bu\(_4\)NCl, diethyl ether, and ethyl acetate. As in living polymerization, one initiator generates one polymer chain where the initiator moiety is attached to the \(\alpha\)-end (eq 1).

\[
\begin{align*}
\text{Activator} & \quad \text{SnCl}_4 \\
\text{Initiator} & \quad \text{R–Cl} \quad \overset{\text{ClSnCl}_4}{\text{Cl}} \\
\text{CPD} & \quad \overset{\text{ClSnCl}_4}{\text{R–Cl}} \\
\text{Additive} & \quad \text{n-Bu}_4\text{NCl, Et}_2\text{O, Ethyl Acetate}
\end{align*}
\]

This chapter is directed to demonstrate the synthetic capability of the new CPD polymerization. The first purpose was thus the synthesis of end-functionalized poly(CPD)s (3) with the use of the HCl-adducts (2b and 2c) of functional vinyl ethers as initiators (eq 2). These adducts are effective functional initiators in living cationic polymerization of vinyl ethers\(^2\), styrene derivatives\(^3\) and \(\beta\)-pinene\(^4\) to give \(\alpha\)-end-functionalized polymers. Specifically, 2b can be converted into the corresponding hydroxy group by deprotection of the acetoxy group. Macromonomers with a methacryloxy group can be obtained from 2c.
The second objective was to synthesize block and random copolymers of CPD with vinyl ethers. For this pair of monomers, the CPD unit can be regarded as a hard segment, whereas the vinyl ether segment as a soft segment with polar ether substituents. Structural formulae 4–7 illustrate the target polymers. AB-block polymers (4 and 5) involve 2-chloroethyl vinyl ether (CEVE) and 2-acetoxyethyl vinyl ether (AcOVE). Upon hydrolysis, the acetoxyethyl moiety in 5 may lead to new amphiphilic block copolymers of CPD. The ABA-type triblock copolymer (6), consisting of hard and soft segments, is also obtained from a bifunctional initiator. In addition, the controlled random copolymerization of CPD and CEVE was investigated (cf. Formula 7).

Formulae 4–7
RESULTS AND DISCUSSIONS

1. End-Functionalized Poly(CPD)s

As shown in eq 2, end-functionalized poly(CPD)s (3b and 3c) were prepared with 2b and 2c, respectively, in CH$_2$Cl$_2$ at -78 °C. Initiators 2b and 2c induced slow and incomplete polymerizations under the conditions ([SnCl$_4$]$_0$ = [n-Bu$_4$NCl]$_0$ = 5.0 mM) suitable for the controlled polymerization with 2a. This is probably due to the ester groups in 2b and 2c, which may interact with SnCl$_4$ and weaken its Lewis acidity. However, a lower concentration of n-Bu$_4$NCl (4.0 mM) permitted quantitative polymerizations, though slower than that with 2a (Figure 1).

Figure 1. Time-conversion curves for the polymerization of CPD with R–Cl/SnCl$_4$/n-Bu$_4$NCl in CH$_2$Cl$_2$ at -78 °C: [M]$_0$ = 0.50 M; [R–Cl]$_0$ = 5.0 mM; [SnCl$_4$]$_0$ = 5.0 mM; [n-Bu$_4$NCl]$_0$ = 4.0 mM. R–Cl: (♦) 2a; (●) 2b; (▲) 2c.

Figure 2 shows the number-average molecular weight ($M_n$) and molecular weight distributions (MWDs) of the obtained polymers obtained from 2b and 2c, as
Figure 2. \( M_n \), \( M_w/M_n \), and MWD curves of poly(CPD) obtained with R–Cl/SnCl\(_4\)/n-Bu\(_4\)NCl in \( \text{CH}_2\text{Cl}_2 \) at \(-78 \, ^\circ \text{C} \): \([\text{M}]_0 = 0.50 \, \text{M}; \) \([\text{R–Cl}]_0 = 5.0 \, \text{mM}; \) \([\text{SnCl}_4]_0 = 5.0 \, \text{mM}; \) \([\text{n-Bu}_4\text{NCl}]_0 = 4.0 \, \text{mM}. \) R–Cl: (●, O) 2b; (△, Δ) 2c.

measured by size-exclusion chromatography (SEC) with a polystyrene calibration. The \( M_n \) increased in direct proportion to monomer conversion, and the MWDs were narrow throughout the reactions \( (M_w/M_n = 1.2–1.5) \). Thus, both the acetoxy and methacryloxy-functionalized initiators led to CPD polymers with controlled molecular weights and narrow MWDs.

The end-groups of these polymers were analyzed by \(^1\text{H} \) NMR spectroscopy. Figure 3A shows the spectrum of the poly(CPD) (3b) obtained from initiator 2b. The sample shows large characteristic signals of the main chain olefinic \((d \text{ and } h)\) and aliphatic protons \((a-c \text{ and } e-g)\). Additionally, small absorptions appeared, assignable to the initiator fragment \((i-m)\). The \( M_n \) (NMR) was thus determined from the relative peak area of the main-chain repeat units \((d \text{ and } h)\) to the initiator moiety \((l)\). The value for the sample was close to that by SEC \([M_n(\text{NMR}) = 2100, M_n(\text{SEC}) = 2600]\), indicating that 2b forms one polymer chain per molecule.

Figure 3B shows the \(^1\text{H} \) NMR spectrum of the methacryloxy-end poly(CPD) (3c) from 2c. The spectrum is very similar to Figure 3A except for the
Figure 3. $^1$H NMR spectra (500 MHz, CDCl$_3$) of poly(CPD)s [(A) $M_n = 2600$, $M_w/M_n = 1.18$, (B) $M_n = 2500$, $M_w/M_n = 1.20$] obtained with 2b (A) and 2c (B). See Figure 2 for reaction conditions.

Absorptions of the methyl ($n$) and the vinyl proton ($o$) of the methacryloxy group. The $M_n$ (NMR) was also close to that by SEC [$M_n$(NMR) = 2400, $M_n$(SEC) = 2500]. Thus, the functionalized initiators derived from the corresponding vinyl ethers proved effective in the synthesis of end-functionalized poly(CPD)s.

2. Block Copolymerization of CPD with Vinyl Ethers

2-1. Diblock Copolymers

The AB-block copolymer 4 was synthesized by sequential polymerization of VE and CPD with the HCl–vinyl ether adduct/SnCl$_4$/n-Bu$_4$NCl system. The first step was the living cationic polymerization of CEVE with 2a in CH$_2$Cl$_2$ at $-78$ °C. CPD equimolar to the CEVE was then added. In this system, the living CEVE polymer can be regarded as a macrorinitiator with a C–Cl terminal, similar to 2a.
The polymerization of CEVE proceeded in a living fashion to form a poly(CEVE) prepolymer with a very narrow MWD ($M_w/M_n = 1.07$) (Figure 4A). The subsequent polymerization of CPD proceeded smoothly and the SEC curve of the product shifted to higher molecular weight relative to the CEVE prepolymer and
Figure 5. $^1$H NMR spectra (500 MHz, CDCl$_3$) of (A) poly(CEVE) ($M_n = 10600$, $M_w/M_n = 1.08$), (B) CEVE–CPD block copolymer ($M_n = 19500$, $M_w/M_n = 1.20$), (C) poly(AcOVE) ($M_n = 12800$, $M_w/M_n = 1.06$), and (D) AcOVE–CPD block copolymer ($M_n = 20100$, $M_w/M_n = 1.23$).
the MWD curves stayed narrow \((M_w/M_n = 1.20)\) (Figure 4B). These indicate the formation of an AB-block copolymer of CEVE and CPD.

Block copolymer (5) of AcOVE and CPD was also synthesized in a similar way. AcOVE was first polymerized with initiator 2b. The polymerization was living even in the absence of an additive (Figure 4C), because of the ester moiety in the monomer. This in turn requires a higher concentration of SnCl\(_4\) (20 mM) for quantitative polymerizations. In the second step, CPD polymerized in a controlled fashion from the living AcOVE and under the additive free condition, to give a block copolymer with a narrow MWD \((M_w/M_n = 1.17)\). Thus, the ester group in AcOVE unit serves as an effective basic additive for controlling the polymerization of CPD as well.

Figure 5A shows the \(^1\)H NMR spectrum of the prepolymer of CEVE after quenching with methanol, where small absorptions originating from the \(\alpha\)- (a) and \(\omega\)-end groups (f and g) are observed in addition to signals of the main chain repeat units (b–e). The spectrum of the final product (Figure 5B) exhibits the typical signals of CPD repeat units, olefinic (k and o) and aliphatic protons (h-j and l-n), along with the absorptions of poly(CEVE) prepolymer. The terminal methine proton (f) of CEVE prepolymer is absent in the spectrum of 4 (Figure 5B). These indicate that every CEVE polymer chain initiated the intended block copolymer. The ratio of CEVE and CPD units \([n/(m+1)]\) in 4 was 100/84 [by NMR; \((c+d+e)/(k+o)\)], in good agreement with the calculated value 100/89, based on the initial feed ratio and conversion.

A similar NMR analysis also confirmed the formation of the AcOVE–CPD block polymers (Figure 5C and 5D). The AcOVE/CPD units ratio \(n/(m+1)\) \([= e/(l+p)\) by NMR\] was 97/85 close to the calculated 97/94.

2-2. Synthesis of Triblock Copolymer

The clean formation of AB-type diblock copolymers of VE and CPD was then extended to ABA-type triblock copolymers. In particular, CPD–VE–CPD
Scheme 1. Synthesis of CPD–CEVE–CPD Triblock Copolymer with a Bifunctional Initiator

Figure 6. MWD curves of (A) poly(CEVE) and (B) CPD–CEVE–CPD triblock copolymer (6) obtained with 8/SnCl$_4$/n-Bu$_4$NCl in CH$_2$Cl$_2$ at $-78\,^\circ$C: [CEVE]$_0$ = 0.50 M; [CPD]$_{add}$ = 1.0 M; [8]$_0$ = 5.0 mM; [SnCl$_4$]$_0$ = 20 mM; [n-Bu$_4$NCl]$_0$ = 18 mM.
triblock copolymer can be a thermoplastic elastomer. The author examined the synthesis by sequential polymerization from VE to CPD via a bifunctional initiator (8) (Scheme 1).

The polymerization of CEVE with 8 gave a bifunctional living prepolymer of CEVE with a narrow MWD ($M_w/M_n = 1.20$) (Figure 6A). After the consumption of CEVE, a double molar amount of CPD to that of CEVE was added to the reaction mixture. CPD was smoothly polymerized (93% conversion in 5 h), and the SEC curve of the product shifted to higher molecular weight ($M_w/M_n = 1.34$), and the prepolymer seems absent (Figure 6B).

Figure 7A shows the $^1$H NMR spectrum of the two-armed prepolymer of CEVE before the CPD addition. Key signals include those of the aromatic protons ($b$ and $c$) from 8 and the terminal methine ($l$) and methoxy ($m$) protons. The arm number ($F_n$) of the polymer was 2.0, calculated from the peak intensity

Figure 7. $^1$H NMR spectra (500 MHz, CDCl$_3$) of (A) poly(CEVE) (M$_n$ = 9700, $M_w/M_n = 1.22$) and (B) CPD–CEVE–CPD triblock copolymer (6) (M$_n$ = 28900, $M_w/M_n = 1.32$). See Figure 6 for reaction conditions.
ratio of the terminal methine \((l)\) to the aromatic protons \((b\) and \(c)\). This result shows that the initiator 8 gave two-armed living poly(CEVE).

The final product (Figure 7B) after the CPD addition exhibit the signals of olefinic \((q\) and \(u)\) and aliphatic protons \((n-p\) and \(r-t)\), characteristic to CPD, and the terminal methine \((l)\) disappeared. The CEVE/CPD units ratio \([n/(m+1) = (i+j+k)/(q+u)]\) was 100/180 (calcd., 100/186). These results demonstrated the formation of the CPD–CEVE–CPD triblock copolymer (6). The product was sticky like an uncrosslinked rubber and different from the respective homopolymers and the CEVE–CPD diblock copolymer (4).

3. Random Copolymerization of CPD and CEVE

An equimolar mixture of CPD and CEVE was polymerized with 2a/SnCl\(_4\)/n-Bu\(_4\)NCl in CH\(_2\)Cl\(_2\) at \(-78\) °C (Scheme 2). As seen in Figure 8, both monomers were consumed almost simultaneously, more slowly than in the respective homopolymerizations.

\[
\text{Scheme 2}
\]

The \(M_n\) of the products increased with the yield. The MWDs were unimodal and relatively narrow throughout the reactions \((M_w/M_n = 1.3-1.4)\). Thus, the controlled random copolymerization of CPD and CEVE proved possible with 2a/SnCl\(_4\)/n-Bu\(_4\)NCl, where copolymer composition is nearly close to the initial mole ratio of the monomers, even at low conversion.

The copolymer was apparently random as examined by \(^1\)H NMR (Figure 9). The spectrum of the product (Figure 9C) was different from those of the
Figure 8. Copolymerization of CPD (▲) and CEVE (●) and homopolymerization of CPD (■) and CEVE (♦) with 2a/SnCl₄/n-Bu₄NCl in CH₂Cl₂ at -78 °C: [CPD]₀ = [CEVE]₀ = 0.50 M; [2a]₀ = 5.0 mM; [SnCl₄]₀ = 10 mM; [n-Bu₄NCl]₀ = 9.0 mM.

homopolymers (Figure 9A and 9B), their blend (Figure 9D), and the CEVE–CPD block copolymer (Figure 5B). The peaks of the copolymer (7) were broader than those of the others for both CPD and CEVE units, which supports the random sequence of the two units. The ratio of CPD and CEVE units [(n+m)/l)] was 44/36 (calculated 44/42).
Figure 9. $^1$H NMR spectra (500 MHz, CDCl$_3$) of (A) poly(CPD) ($M_n = 7000$, $M_w/M_n = 1.44$), (B) poly(CEVE) ($M_n = 8600$, $M_w/M_n = 1.07$), (C) CPD–CEVE random copolymer ($M_n = 12600$, $M_w/M_n = 1.41$), and (D) blend of poly(CPD) and poly(CEVE).

EXPERIMENTAL

Materials

Unless otherwise specified, all of the chemicals were purchased from Wako company, Japan. CPD was obtained by the retro Diels-Alder reaction of
dicyclopentadiene (Tokyo Kasei; >95%) over calcium hydride and distilled from calcium hydride. It was stored at -84 °C and used within one month. The purity and the absence of dicyclopentadiene in CPD was confirmed by NMR before use (purity >99%). 2-chloroethyl vinyl ether (CEVE) (Nisso Maruzen Chemical; > 99%) was washed with 10% aqueous sodium hydroxide and then water, dried overnight with anhydrous sodium sulfate, and distilled twice under reduced pressure from calcium hydride before use. 2-Acetoxy vinyl ether (AcOVE)\(^7\) and 2-vinylxyethyl methacrylate (VEM)\(^8\) (precursor for 2c) were prepared by the reaction of CEVE with sodium acetate and sodium methacrylate respectively, dried overnight with anhydrous sodium sulfate, and distilled twice under reduced pressure from calcium hydride before use. CH\(_2\)Cl\(_2\) (>99%) was dried overnight over calcium chloride, distilled from phosphorous pentoxide and then from calcium hydride before use. Carbon tetrachloride (internal standard for gas chromatography; >99%) was dried overnight over calcium chloride, distilled twice from calcium hydride. SnCl\(_4\) (Aldrich; 1.0 M solution in CH\(_2\)Cl\(_2\)), n-Bu\(_4\)NCl (Tokyo Kasei; >98%), and bisphenol A divinylxyethyl ether (BPA–DEVE) (Nisso Maruzen Chemical; > 99%; precursor for 3) were used as received.

**Synthesis of HCl Adduct 2a–2c and 8**

The HCl adducts 2a–2c and 8 were synthesized by bubbling dry HCl gas into a solution of the respective vinyl compounds (CEVE, AcOVE, VEM and BPA–DEVE).\(^9\) The synthesis of HCl–CPD adduct 2a was carried out as follows. Dry HCl gas was bubbled into 1.0 M CH\(_2\)Cl\(_2\) solution (35 mL) of CEVE (4.0 mL; 0.039 mol) at -78 °C. The gas was generated by dropping concentrated sulfuric acid into powdery sodium chloride, and dried by passing it through a column packed with calcium chloride. After 30 min, the excess HCl in the reaction mixture was removed by bubbling dry nitrogen gas at 0 °C for 30 min, and the clean and quantitative formation of adduct 2a was confirmed by \(^1\)H NMR.
spectroscopy. The concentration of 2a was determined by titrating the chloride by the Volhard method. The observed value (1.03 M) further confirmed the quantitative formation of 2a from CEVE.

**Polymerization Procedures**

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure for α-end-functionalyzed polymer is given below: The reaction was initiated by sequential addition of prechilled solutions of 2b (0.015 mmol; 0.30 mL of 0.050 M in CH₂Cl₂) and a mixture of SnCl₄ (0.015 mmol; 0.30 mL of 0.050 M in CH₂Cl₂) and n-Bu₄NCl (0.012 mmol; 0.30 mL of 0.040 M in CH₂Cl₂) via dry syringes into a monomer solution (in CH₂Cl₂; 2.4 mL) containing CPD (1.5 mmol; 0.124 mL) and CCl₄ (0.124 mL). The total volume of the reaction mixture was thus 3.0 mL. After predetermined intervals, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia. Another typical example for the block copolymerization of CEVE-CPD is given below: The reaction was initiated by sequential addition of prechilled solutions of 2a (0.015 mmol; 0.30 mL of 0.050 M in CH₂Cl₂) and a mixture of SnCl₄ (0.015 mmol; 0.30 mL of 0.050 M in CH₂Cl₂) and n-Bu₄NCl (0.015 mmol; 0.30 mL of 0.050 M in CH₂Cl₂) via dry syringes into a monomer solution (in CH₂Cl₂; 2.4 mL) containing CEVE (1.5 mmol; 0.153 mL) and CCl₄ (0.153 mL). The total volume of the reaction mixture was thus 3.0 mL. The reaction was run for 1 min, where CEVE conversion reached 100%. CPD (1.5 mmol; 0.124 mL) was then added to the preformed living poly(CEVE) solution. 3-tert-Butyl-4-hydroxy-5-methylphenyl sulfide (0.014 mmol; 0.005 g) was then added as an antioxidant immediately after quenching reaction containing poly(CPD) or copolymer with CPD units. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl₄ as an internal standard. The polymer yield by gravimetry was in good agreement with the gas-chromatographic
conversion of the monomer. The quenched reaction mixture was washed with dilute hydrochloric acid and with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.

**Measurements**

The MWD of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: 20–1000 Å; 8.0 nm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] that were connected to a Jasco PU–980 precision pump and a Jasco 930-RI refractive index detector. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemicals; \( M_n = 580–1547000; M_w/M_n \leq 1.1 \)) as well as the styrene monomer. \(^1\)H NMR spectra of the produced polymers were recorded in CDCl₃ on a JEOL LNM–LA500 spectrometer, operating at 500.2 MHz.

**REFERENCES AND NOTES**

(1) Chapter 4 of this thesis; Ouchi, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules*, in press.


LIST OF PUBLICATIONS

Chapter 1  

Chapter 2  

Chapter 3  

Chapter 4  
Macromolecules, in press.

Chapter 5  
Macromolecules, submitted.

Chapter 6  

Other Publications

“Amphiphilic 3-Arm Star Block polymers by Living Cationic Polymerization”

“MALDI-TOF-MS Analysis of Ru(II)-Mediated Living Radical Polymerizations of Methyl Methacrylate, Methyl Acrylate, and Styrene”
Nonaka, H.; Ouchi, M.; Kamigaito, M.; Sawamoto, M. Macromolecules, in press.
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