3682 *Macromolecules* **2010**, *43*, 3682–3689
DOI: 10.1021/ma100182b

Macromolecules
ARTICLE

Chain Multiplying Controlled Cationic Polymerization of Isobutyl Vinyl Ether Using Pyrrole: Increment of Propagating Chains by Efficient "Initiator-Like" Transfer Agent

Arihiro Kanazawa, Shokyoku Kanaoka, and Sadahito Aoshima*

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received January 25, 2010; Revised Manuscript Received March 4, 2010

ABSTRACT: Cationic polymerization of isobutyl vinyl ether using pyrrole was examined with a variety of metal chlorides in the presence of a weak Lewis base. In conjunction with oxophilic acids such as $ZrCl_4$, long-lived species were produced to yield polymers with narrow molecular weight distributions (MWDs) and number-average molecular weight (M_n) values based on the used amounts of pyrrole. Acid-trapping experiments using silyl ketene acetal indicated that pyrrole worked not as an initiator but as a transfer agent. The polymerization started from adventitious water, followed by the reactions between the propagating species and the 2- and 5-positions of pyrrole, accompanied by the generation of HCl. In addition to the propagation from the generated HCl, the produced pyrrole-bonded chain-end structures were also activated by the oxophilic chlorides to generate propagating carbocation via the abstraction of the isobutoxy group. As a result, the number of growing chains increased. Such transfer reactions occurred predominantly in the early stage of the polymerization stemming from the highly nucleophilic nature of pyrrole. Thus, the resulting polymers had expected M_n values and narrow MWDs as if pyrrole worked as an initiator.

Introduction

Diversification of the initiating systems for living cationic polymerization of vinyl ethers (VEs) has realized living polymerization of monomers with various functional groups, improvement of polymerization activity, and synthesis of polymers with precise architectures.[1] Recently, our group showed that a variety of metal halides can induce living cationic polymerization of isobutyl VE (IBVE) in combination with suitable types of additives, e.g., a weak Lewis base or an ammonium salt, in conjunction with IBVE−HCl adduct as a cationogen.[2] Furthermore, methanol can be used as an initiator for living polymerization.[3] In contrast to the versatilities of the reactions using IBVE−HCl, initiating systems using methanol as a cationogen showed preferences for particular types of metal halides for achieving living polymerization. Several examples are summarized in Chart 1. Oxophilic Lewis acids such as $NbCl_5$ and $ZrCl_4$ produced long-lived species by exchanging their chlorine atom with the methoxy group of methanol to generate HCl, while chlorophilic ones like $GaCl_3$ and $InCl_3$ induced uncontrolled polymerization and no reaction, respectively. A deeper understanding of such relationships between the nature of the Lewis acids and their polymerization behavior would lead to further development of initiating systems with novel features by utilizing specific interactions of each acid with various heteroatoms.

Pyrrole is a heteroaromatic compound with one nitrogen atom whose lone pair contributes to the 6π system.[4] The pyrrole anion generated by abstracting the proton attached to nitrogen is a common ligand for metal complexes.[5] In addition, the pK_a value of pyrrole in dimethyl sulfoxide (DMSO; Bordwell pK_a)[6] is reported to be 23.0, a more acidic value than that of methanol, 29.0. Thus, the combination of pyrrole and some metal chlorides may induce exchange reactions to generate protic species capable of initiating cationic polymerization of VEs in a similar manner to the system using an alcohol. Pyrrole is also known as a good substrate for electrophilic substitution reactions. Many examples of Friedel−Crafts type reactions using pyrrole derivatives have been reported.[7] Mayr examined the nucleophilicities of various compounds,[8] and nonsubstituted pyrrole is reported to be comparable to nucleophiles such as (2-methylallyl)trimethylsilane and 2-(trimethylsiloxy)propene. These aspects of pyrrole imply its ability to act as a terminator or a transfer agent in cationic polymerization. In fact, *N*-alkylpyrroles are reported to be effective as quencher for living cationic polymerization of isobutene.[9] They react with the propagating carbocation to form pyrrole-end structures, from which no further propagation proceeds. A different situation, however, is anticipated in the case of polymerization of VE. The reaction of pyrrole with the carbocation derived from VE produces a structure having an alkoxy group and a pyrrole ring, in addition to the generation of a protic acid such as HCl. Some Lewis acids may abstract the alkoxy group, generating a carbocation to induce "re-propagation", if the pyrrole moiety is electron-donating enough to stabilize carbocation. Thus, pyrrole may work as an "initiator-like" species, which is actually a transfer agent (Scheme 1), because one reaction between a chain and a pyrrole molecule produces two propagating (initiating) species. Continuous occurrences of such reactions provide propagating chains corresponding to the amounts of the initiator and pyrrole (H−X and HZ in Scheme 1, respectively). A suitable choice of a Lewis acid catalyst is crucial for the abstraction of alkoxy groups to generate carbocation inducing controlled polymerization.

In this study, we investigated cationic polymerization of IBVE using pyrrole as a "cationogen" in conjunction with a variety of metal chlorides. The production of long-lived species was achieved with some Lewis acids such as $ZrCl_4$. Acid-trapping experiments using silyl ketene acetal (SKA) revealed the role of pyrrole not as an initiator but as a transfer agent. The polymerization proceeded

---

*Corresponding author. E-mail: aoshima@chem.sci.osaka-u.ac.jp.

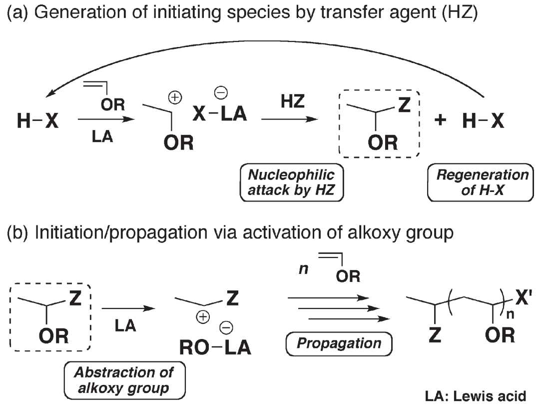
Published on Web 03/16/2010
© 2010 American Chemical Society

Chart 1. Cationic Polymerization Behaviors Using Different Types of Cationogens[a]

cationogen	pK_a in DMSO[b]	$NbCl_5$	$ZrCl_4$	$GaCl_3$	$InCl_3$
IBVE–HCl	1.8 (HCl)	Living[c]	Living	Living	Living
CH_3OH	29.0	Living (C–Cl end)	Living (C–Cl and acetal ends)	Not controlled (acetal end)	No polymn
pyrrole	23.0	*This work – Initiator ? or Transfer agent ?*			

[a] Descriptions in the parentheses of the behaviors using CH_3OH are the structures of the propagating ends confirmed by ^1H NMR analyses. DMSO: dimethyl sulfoxide, IBVE-HCl: isobutyl vinyl ether−HCl adduct. [b] Reference 6. [c] In the presence of a salt (nBu_4NCl); the others are conducted in the presence of an added base (ester or ether).

Scheme 1. Concept of "Initiator-Like" Role of Chain Transfer Agent in Cationic Polymerization of Vinyl Ether



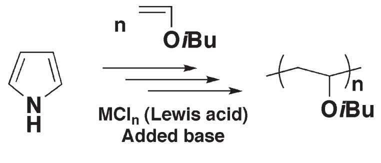
- *The number of propagating chains = $[H\text{-}X]_0 + [HZ]_0$*
- *Z must be highly electron-donating for easy generation of carbocation*
- *Catalyst efficiently abstracting alkoxy group is nessesary*

with the "initiator-like" behavior of pyrrole involving the initiation from adventitious water and subsequent fast alkylation of pyrrole. The resulting chain end is substituted with both a 2-pyrrolyl and an isobutoxy group, and the latter may be abstracted to form a new initiating cation. The 2-pyrrolyl group appended to the chain may be further alkylated at the 5-position to afford branched structures.

Experimental Section

Materials. IBVE (TCI; >99.0%), pyrrole (TCI; >99.0%), *N*-methylpyrrole (TCI; >99.0%), ethyl acetate (Wako; >99.5%), dichloromethane (Nacalai Tesque; 99%), and 1,2-dichloroethane (Wako; >99.5%) were distilled twice over calcium hydride before use. Diethyl ether (Wako; >99.5%), 1,4-dioxane (Wako; >99.5%), and tetrahydrofuran (THF; Wako; >99.5%) were distilled over calcium hydride and then lithium aluminum hydride. Dimethylketene methyl trimethylsilyl acetal (TCI; >95.0%) and 2,5-dimethylpyrrole (TCI; >98.0%) were distilled over calcium hydride under reduced pressure. Anhydrous methanol (Nacalai Tesque; 99.8%; H_2O < 50 ppm) was used for the NMR experiments without further purification. Toluene-d_8 (Wako; 99.6%) was distilled once over sodium. Toluene (Wako; 99.5%) was dried by passage through solvent purification columns (Glass Contour). The adduct of IBVE with HCl (IBVE−HCl) was prepared from the addition reaction of IBVE with HCl.[10] Commercially available $SnCl_4$ (Aldrich; 1.0 M solution in dichloromethane), $ZnCl_2$ (Aldrich; 1.0 M solution in diethyl ether), $EtAlCl_2$ (Wako; 1.0 M solution in hexane), $TiCl_4$ (Aldrich; 1.0 M solution in toluene), and $SiCl_4$ (Aldrich; 1.0 M solution in dichloromethane) were used without further purification. For $FeCl_3$, a stock solution in diethyl ether was prepared from commercial anhydrous $FeCl_3$ (Aldrich; 99.99%). For $GaCl_3$, a stock solution in hexane was prepared from commercial anhydrous $GaCl_3$ (Aldrich; 99.999+%). For $InCl_3$, $AlCl_3$, $HfCl_4$, $ZrCl_4$, $BiCl_3$, and $TaCl_5$, stock solutions in ethyl acetate were prepared from commercial anhydrous $InCl_3$ (Strem; 99.999%), $AlCl_3$ (Aldrich; 99%), $HfCl_4$ (Strem; 99.9+%), $ZrCl_4$ (Aldrich; 99.99%), and $BiCl_3$ (Aldrich; 99.999%), and $TaCl_5$ (Strem; >99.99%). For $GeCl_4$, a stock solution in dichloromethane was prepared from commercial anhydrous $GeCl_4$ (Wako; 99.99%). For $NbCl_5$, a stock solution in the mixture of dichloromethane and ethyl acetate was prepared from commercial anhydrous $NbCl_5$ (Strem; 99.99%). Because pure, solid $MoCl_5$ (Aldrich; 99.99%) and WCl_6 (Strem; 99.9%) did not dissolve completely in 1,2-dichloroethane, the heterogeneous solutions were used for polymerization. All chemicals except for toluene were stored in brown ampules under dry nitrogen.

Scheme 2. Cationic Polymerization of Isobutyl Vinyl Ether Using Pyrrole



[M: Zr, Hf, Ti, Nb, Mo, W, Sn, Al, Fe, Ta, Si, Ge, Ga, Zn, In, Bi]

Characterization. The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with three polystyrene gel columns [Tosoh; TSK gel G-4000H_{XL}, G-3000H_{XL}, and G-2000H_{XL}; exclusion limit molecular weight $= 4 \times 10^5$, 6×10^4, and 1×10^4, respectively; bead size = 5 μm; column size = 7.8 mm (internal diameter) × 300 mm; flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector (wavelength: 254 nm), and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh; M_n = 577 to 1.09×10^6, $M_w/M_n \leq 1.1$). NMR spectra were recorded using JEOL JNM-ECA 500 spectrometer (500.16 MHz for ^1H and 125.77 MHz for ^{13}C). UV−vis spectra were recorded on a JASCO V-550 UV/vis spectrometer with an ETC-505 Peltier-type thermostatic cell holder. A quartz cell with 1.0 cm optical path length was used. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF−MS) spectra were recorded with a Shimadzu/Kratos AXIMA-CFR spectrometer (linear mode; voltage: 20 kV; pressure: $< 1.9 \times 10^{-3}$ Pa) using dithranol as the matrix and sodium trifluoroacetate as the ion source.[11] A solution (2−3 μL) containing a polymer, the matrix, and the ion source (polymer/matrix/ion source = 1 mg/8 mg/1 mg in 1 mL THF) was casted on a stainless steel sample plate (Shimadzu Biotech, DE1580TA) and loaded to the spectrometer. Electrospray ionization mass spectrometry (ESI−MS) spectra were recorded with an Applied Biosystems QSTAR Elite Hybrid LC/MS/MS System (spray voltage: 5500 V, flow rate: 100−300 μL/min) using ethanol as solvent (5 μg/mL).

Polymerization Procedures. The following is a typical polymerization procedure (the $ZrCl_4$ system as an example). A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; the blow temperature ~450 °C) under dry nitrogen. Toluene (3.05 mL), ethyl acetate (0.45 mL; 4.6 mmol), a 50 mM pyrrole solution in toluene (0.50 mL; 2.5×10^{-2} mmol), and a 50 mM $ZrCl_4$ solution in toluene/ethyl acetate (9/1, v/v; 0.50 mL; 2.5×10^{-2} mmol) were added successively into the tube using dry syringes. The polymerization was started by the addition of prechilled IBVE (0.50 mL; 3.8 mmol) at 0 °C. After some period, the reaction was terminated

Table 1. Cationic Polymerization of Isobutyl Vinyl Ether (IBVE) Using Pyrrole[a]

entry	metal chloride	$[\text{pyrrole}]_0$ (mM)	time	convn (%)	$M_n \times 10^{-3}$ (calcd)[b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]
1	$ZrCl_4$	5.0	23 h	88	13.4	8.3	1.23
2		10	70 h	83	6.3	4.2	1.31
3	$HfCl_4$	5.0	24 h	88	13.3	8.4	1.38
4		10	30 h	81	6.2	5.3	1.47
5	$TiCl_4$	5.0	122 h	12	1.9	1.5	1.32
6		10	122 h	22	1.6	1.6	1.20
7	$NbCl_5$	5.0	8 h	57	8.6	6.2	1.67
8		10	8.5 h	27	2.1	2.0	1.46
9	$MoCl_5$	5.0	3 h	85	12.8	10.1	1.51
10		10	43 h	75	5.7	5.9 (5.6)[d]	2.64 (1.77)[d]
11	WCl_6	5.0	5 min	98	14.9	5.5	2.82
12		10	2.5 h	89	6.8	6.1	1.62
13	$SnCl_4$	5.0	1 h	78	11.8	10.0	2.02
14		10	6 h	78	5.9	6.6	2.44
15	$AlCl_3$	5.0	53 h	95	14.5	36.6	1.64
16		10	75 h	83	6.3	20.3	1.86
17	$FeCl_3$	5.0	2 h	95	14.4	15.9	2.23
18		10	9 h	66	5.0	6.3	1.98
19	$TaCl_5$	5.0	170 h	90	13.7	6.6	1.62
20		10	170 h	88	6.7	4.5	1.59
21	$SiCl_4$	5.0	123 h	6	–	–	–
22		10	123 h	0	–	–	–
23	$GeCl_4$	5.0	123 h	5	–	–	–
24		10	123 h	3	–	–	–
25	$GaCl_3$	5.0	74 h	2	–	–	–
26		10	74 h	0	–	–	–
27	$ZnCl_2$	5.0	29 h	0	–	–	–
28		10	29 h	0	–	–	–
29	$InCl_3$	5.0	72 h	2	–	–	–
30		10	72 h	1	–	–	–
31	$BiCl_3$	5.0	75 h	3	–	–	–
32		10	75 h	2	–	–	–

[a] $[\text{IBVE}]_0 = 0.76$ M, $[\text{pyrrole}]_0 = 5.0$ or 10 mM, $[\text{metal chloride}]_0 = 5.0$ mM, [added base] = 1.0 M (ethyl acetate for entries 1–16, 19, 20, and 27–32; 1,4-dioxane for entries 17, 18, and 21–24; THF for entries 25 and 26), [heptane] = 5 vol %, in toluene at 0 °C. [b] On the basis of the amounts of pyrrole. [c] M_n: number-average molecular weight, M_w/M_n: polydispersity ratio (weight-average molecular weight/number-average molecular weight), by GPC (polystyrene calibration). [d] For a main peak.

with prechilled methanol containing a small amount of aqueous ammonia solution (0.1%). The quenched mixture was washed with dilute hydrochloric acid, an aqueous NaOH solution, and then water to remove the initiator residues. The volatiles were then removed under reduced pressure to yield a yellowish or reddish, gummy polymer. The monomer conversion was determined by gravimetry or by gas chromatography using heptane (5 vol %) as an internal standard (conversion = 88% for 23 h). The GPC analysis data were as follows: $M_n = 8.3 \times 10^3$, $M_w/M_n = 1.23$.

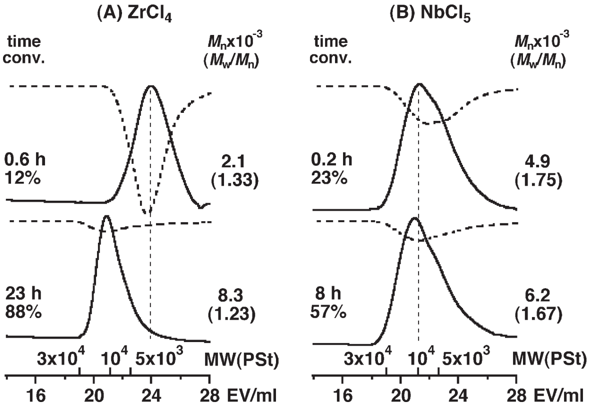


Figure 1. Molecular weight distribution curves for poly(isobutyl vinyl ether)s [poly(IBVE)s] obtained using pyrrole with (A) $ZrCl_4$ or (B) $NbCl_5$ {$[\text{IBVE}]_0 = 0.76$ M, $[\text{pyrrole}]_0 = 5.0$ mM, $[\text{metal chloride}]_0 = 5.0$ mM, [ethyl acetate] = 1.0 M, [heptane] = 5 vol %, in toluene at 0 °C; solid lines: RI, dotted lines: UV; M_n: number-average molecular weight, M_w/M_n: polydispersity ratio (weight-average molecular weight/number-average molecular weight), by GPC (polystyrene calibration)}.

Results and Discussion

Cationic Polymerization of Isobutyl Vinyl Ether Using Pyrrole as a "Cationogen" with a Variety of Metal Chloride Catalysts. Cationic polymerization of IBVE was examined using pyrrole as a "cationogen" in toluene at 0 °C (Scheme 2). Various metal chlorides were used as Lewis acid catalysts in conjunction with a suitable added base, ethyl acetate, 1,4-dioxane, or THF. A suitable base was chosen based on the results of the living cationic polymerization using IBVE–HCl or methanol as a cationogen.[2,3] The reaction was initiated by adding IBVE monomer to a solution of pyrrole, added base, and a Lewis acid. The polymerization results are summarized in Table 1 [also see Figure S1 in the Supporting Information for the time–conversion plots, M_n and M_w/M_n values, and MWD curves]. The Lewis acids fell into three groups in terms of polymerization behavior: long-lived species-mediated (controlled) reactions, uncontrolled polymerization, and no reaction. A typical example of controlled reactions was that using $ZrCl_4$, which induces living polymerization both with IBVE–HCl and with an alcohol. With 5.0 mM of $ZrCl_4$, the polymerization using 5.0 mM of pyrrole proceeded at almost the same rate as that using 5.0 mM of methanol,[3] and produced polymers with unimodal and relatively narrow MWDs (Figures 1A and 2A). The peaks in MWD curves shifted toward the higher molecular weight region with the increase of the monomer conversion, which supports the production of a long-lived species. UV absorptions (254 nm) were also detected almost in accordance with the RI peaks in GPC profiles. The reaction proceeded slower when 10 mM of pyrrole was used (Table 1,

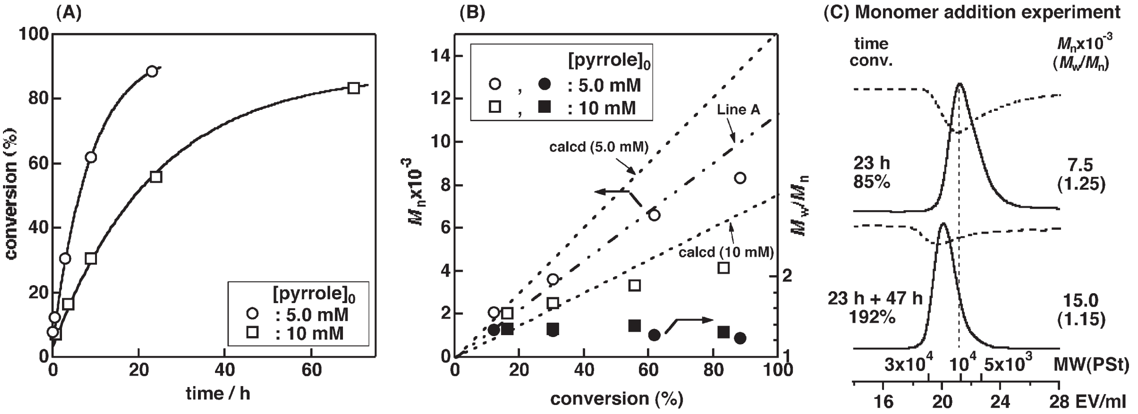
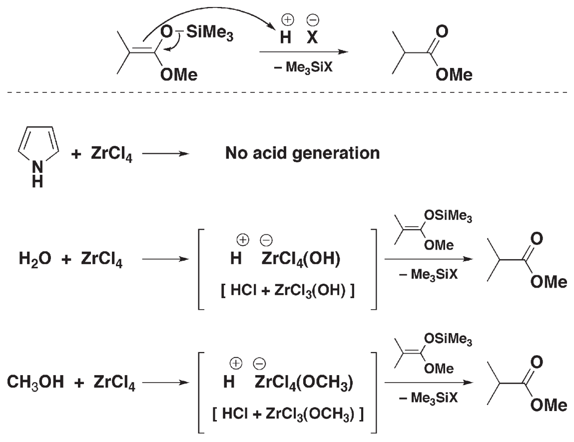


Figure 2. (A) Time–conversion curves, (B) M_n and M_w/M_n for the polymerization of isobutyl vinyl ether (IBVE), and (C) molecular weight distribution curves for poly(IBVE)s obtained in the monomer addition experiment using pyrrole/$ZrCl_4$ initiating system {for (A) and (B), $[IBVE]_0$ = 0.76 M, $[pyrrole]_0$ = 5.0 or 10 mM, $[ZrCl_4]_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, [heptane] = 5 vol %, in toluene at 0 °C; for (C), $[IBVE]_0$ = $[IBVE]_{added}$ = 0.76 M, $[pyrrole]_0$ = 5.0 mM, $[ZrCl_4]_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, [heptane] = 5 vol %, in toluene at 0 °C; for (C), solid lines: RI, dotted lines: UV; M_n: number-average molecular weight, M_w/M_n: polydispersity ratio (weight-average molecular weight/number-average molecular weight), by GPC (polystyrene calibration); Line A is the theoretical one assuming that the polymerization proceeded from 5.0 mM of bifunctional initiator and 1.7 mM of protic species (the latter amount is based on the result without any cationogens as shown in Figure 4)}.

entry 2; Figure 2A), different from the case with methanol.[3] The retardation is possibly attributed to the moderation of the Lewis acidity of the metal chloride by the interaction with the basic nitrogen atom of the pyrrole ring. The M_n values of the products increased linearly although they were lower than the calculated ones assuming that just 5.0 or 10 mM of cationogen initiated the polymerization (Figure 2B). Such differences will be discussed later in this article. In addition, a monomer addition experiment was conducted (Figure 2C). The GPC peak shifted to the higher molecular weight region after the addition of a fresh feed of IBVE, which further confirmed the livingness of the propagating species.

Polymerization behaviors using pyrrole with various metal chloride catalysts showed correlation with those using methanol as a cationogen.[3] With methanol, catalysts for living polymerization are divided into two groups depending on the mechanism. Some catalysts such as $HfCl_4$ and $TiCl_4$ induce controlled reactions, in which both carbon–chlorine bond and acetal structure propagating ends are involved, similar to the $ZrCl_4$ case. In contrast, the other group including $NbCl_5$, produces long-lived species with only carbon–chlorine ends. With pyrrole, $HfCl_4$ and $TiCl_4$ also produced long-lived species in polymerization (entries 3–6), although the activity was very low with $TiCl_4$. On the other hand, $NbCl_5$ catalyzed less controlled reactions with pyrrole (entries 7 and 8; Figure 1B). The shifts of the GPC peaks were slight and the procession of the polymerization plateaued around 60% or 30% conversion with 5.0 mM or 10 mM of pyrrole, respectively. Other metal chlorides in the $NbCl_5$ group, $MoCl_5$, $SiCl_4$, and $GeCl_4$, were inferior to $ZrCl_4$, $HfCl_4$, and $TiCl_4$ in reactions using pyrrole. With $MoCl_5$, a long-lived species was produced but considerable tailings in the GPC curves appeared (entries 9 and 10). With $SiCl_4$ and $GeCl_4$, no reaction proceeded possibly because these weak Lewis acids formed inactive complexes with pyrrole (entries 21–24). With $SnCl_4$ and $AlCl_3$, which induce polymerization with low initiator efficiency in reactions using methanol, long-lived species were produced with pyrrole although the MWDs of the product polymers were broad with $SnCl_4$ and the efficiency was also low with $AlCl_3$ (entries 13–16). With chlorophilic and active chlorides, which induced uncontrolled polymerization with methanol mediated by the species consisting only of acetal structures, the reactions with pyrrole were inactive with $GaCl_3$ and uncontrolled with $FeCl_3$ (entries 17, 18, 25, and 26). In contrast, the polymerization using 10 mM of pyrrole produced long-lived species with WCl_6 (entry 12), which cannot mediate controlled reactions with methanol or IBVE–HCl in the presence of a weak Lewis base or an ammonium salt. $ZnCl_2$, $InCl_3$, and $BiCl_3$, which show no activity with methanol, were also inactive in polymerization using pyrrole (entries 27–32).

Scheme 3. Degradation of Silyl Ketene Acetal by Generated Protic Acids



Investigation of the Role of Pyrrole by Acid-Trapping Experiment: Initiator? or Transfer Agent? The role of pyrrole in the cationic polymerization of IBVE was examined in order to determine whether it works as an initiator or a transfer agent. The generation of protic acids, HCl in this case, would be observed if pyrrole reacts with a Lewis acid as methanol does. Thus, an acid-trapping experiment was designed using SKA, dimethylketene methyl trimethylsilyl acetal. If a protic acid is evolved from the mixture of pyrrole and a metal chloride, the SKA should smoothly react with the acid to be degraded to an aliphatic ester as shown in Scheme 3.

The experiments were followed by ^{1}H NMR spectroscopy of the mixture of pyrrole and $ZrCl_4$ in the presence of an added base in toluene-d_8, under conditions similar to those for the polymerization. The results are shown in Figure 3. The spectrum of the equimolar (40 mM) mixtures of SKA, pyrrole, and $ZrCl_4$ (Figure 3B) shows the partial degradation

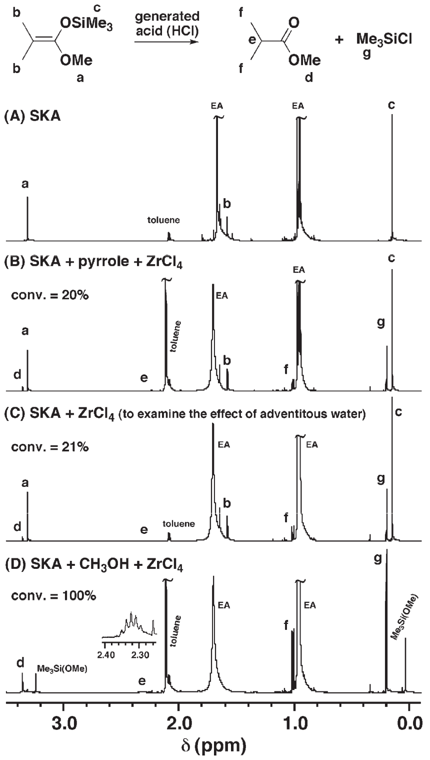


Figure 3. ^{1}H NMR spectra of (A) dimethylketene methyl trimethylsilyl acetal (SKA) and mixtures of (B) SKA, pyrrole, and $ZrCl_4$, (C) SKA and $ZrCl_4$, and (D) SKA, CH_3OH, and $ZrCl_4$, in the presence of ethyl acetate $\{[SKA]_0 = 40$ mM, $[pyrrole]_0 = 0$ or 40 mM, $[CH_3OH]_0 = 0$ or 40 mM, $[ZrCl_4]_0 = 0$ or 40 mM, [ethyl acetate (EA)] = 1.0 M, in toluene-d_8 (nondeuterated toluene was also used for diluting pyrrole and CH_3OH) at 25 °C; time after mixing = (B) 66 min, (C) 45 min, and (D) 7 min; conversions were determined from the integral ratios of peaks **a** and **d**$\}$.

of SKA, as confirmed by some peaks assigned to the produced ester (peaks **d**, **e**, and **f**; methyl isobutyrate) and to trimethylsilyl chloride (peak **g**). However, the mixture of SKA and $ZrCl_4$ without pyrrole gave similar spectrum (Figure 3C). The conversion values of both mixtures were comparable (~20%). In the latter case, SKA was presumably degraded by the acid produced in the reaction of $ZrCl_4$ and adventitious water. Thus, it is appropriate to conclude that no reaction producing acid occurs between pyrrole and $ZrCl_4$; the observed partial degradation of SKA was brought about by the reaction with adventitious water. The reaction using alcohol was also examined by this method. As shown in Figure 3D, all SKA was decomposed in the mixture of SKA, methanol, and $ZrCl_4$.

These results indicated that pyrrole worked not as an initiator but probably as a transfer agent in the cationic polymerization of IBVE (Scheme 1). The initiation of the reactions is caused by protic impurities such as adventitious water. The ability of $ZrCl_4$ to initiate facile polymerization from such a small amount of protic species is discussed in the following section. In contrast to the case of pyrrole, the result using methanol confirms its role as an initiator, generating acidic species by the reaction with $ZrCl_4$.[3] It is shown here that the mechanisms of polymerization with pyrrole or methanol using $ZrCl_4$ are different, although both systems produce long-lived species.

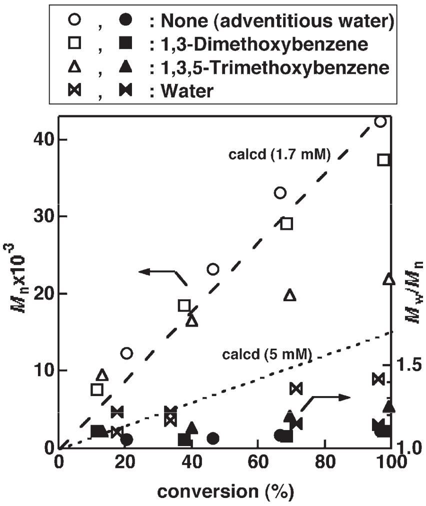


Figure 4. M_n and M_w/M_n for the polymerization of isobutyl vinyl ether (IBVE) using $ZrCl_4$ without cationogen (initiation from adventitious water), or in conjunction with 1,3-dimethoxybenzene, 1,3,5-trimethoxybenzene, and forcibly added water $\{[IBVE]_0 = 0.76$ M, [1,3-dimetoxybenzene, 1,3,5-trimetoxybenzene, or water]$_0$ = 0 or 5.0 mM, $[ZrCl_4]_0 = 5.0$ mM, [ethyl acetate] = 1.0 M, [heptane] = 5 vol %, in toluene at 0 °C; M_n: number-average molecular weight, M_w/M_n: polydispersity ratio (weight-average molecular weight/number-average molecular weight), by GPC (polystyrene calibration)$\}$.

Initiation by Adventitious Water with $ZrCl_4$ and Polymerization Using Other Electron-Rich Aromatic Compounds. The contribution of adventitious water (protic impurities) to the initiation of cationic polymerization using $ZrCl_4$ was examined by conducting the reaction without a cationogen. In the presence of ethyl acetate, polymerization of IBVE smoothly proceeded to produce polymers with very narrow MWDs and the GPC peaks shifted to the higher molecular weight region with the monomer conversion (Figure 4, circle symbols). The M_n values increased linearly along with the line assuming that polymerization was initiated by 1.7 mM of an initiator. This clean reaction is probably brought about by the *in situ* generation of HCl as a result of the reaction between adventitious water and $ZrCl_4$, an oxophilic Lewis acid, similarly to the polymerization using methanol. The ability of water as a cationogen for controlled polymerization with $ZrCl_4$ was also confirmed by the reaction using added water.[12] An equimolar mixture of water and $ZrCl_4$ (5.0 mM) induced polymerization of IBVE to give polymers with narrow MWDs in the presence of ethyl acetate (Figure 4, double-triangle symbols). The results suggest that the mechanisms of the cationic polymerization using pyrrole with $ZrCl_4$ involve initiation from water, followed by transfer reactions by pyrrole, efficiently producing new propagating chains to give polymers with moderate M_n values (Scheme 1).

Cationic polymerization of IBVE using other electron-rich aromatic compounds was also examined for comparison with pyrrole. 1,3-Dimethoxybenzene (DMB) and 1,3,5-trimethoxybenzene (TMB) were used in this study. Both of these were shown to work as transfer agents in the living cationic polymerization of IBVE using IBVE−HCl as a cationogen only when excess amounts were used.[13] Reactions using equimolar DMB or TMB to $ZrCl_4$ were conducted in the presence of ethyl acetate. Their M_n and M_w/M_n are shown in Figure 4. With DMB (square symbols), the polymerization proceeded to give polymers with narrow MWDs but their M_n values increased similarly to those without cationogen. This indicates that almost no reaction occurred with such a small amount of DMB. In contrast, an obvious decrease in the M_n values was observed with TMB (triangle symbols). UV peaks were also detected in the GPC profiles and the peaks had tailings in the lower molecular weight region. These behaviors indicate the occurrence of

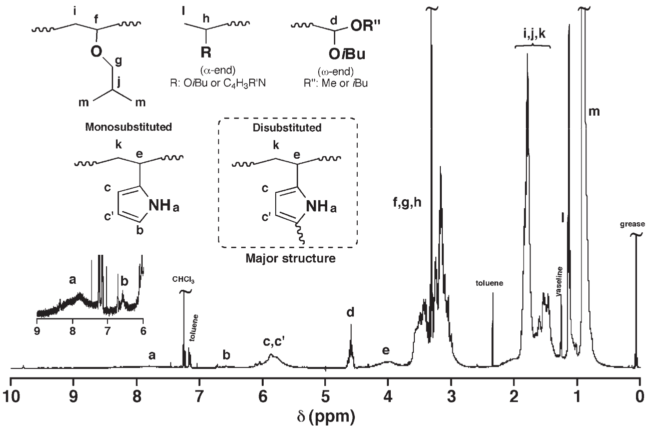


Figure 5. ^{1}H NMR spectrum of poly(isobutyl vinyl ether) [poly(IBVE)] obtained using pyrrole with ZrCl$_4$ {polymerization conditions: $[\mathrm{IBVE}]_0 = 0.76$ M, $[\text{pyrrole}]_0 = 5.0$ mM, $[\mathrm{ZrCl_4}]_0 = 5.0$ mM, [ethyl acetate] = 1.0 M, [heptane] = 5 vol %, in toluene at 0 °C; conversion = 6%, M_n (GPC) = 1.9×10^3; recorded in CDCl$_3$ at 30 °C}.

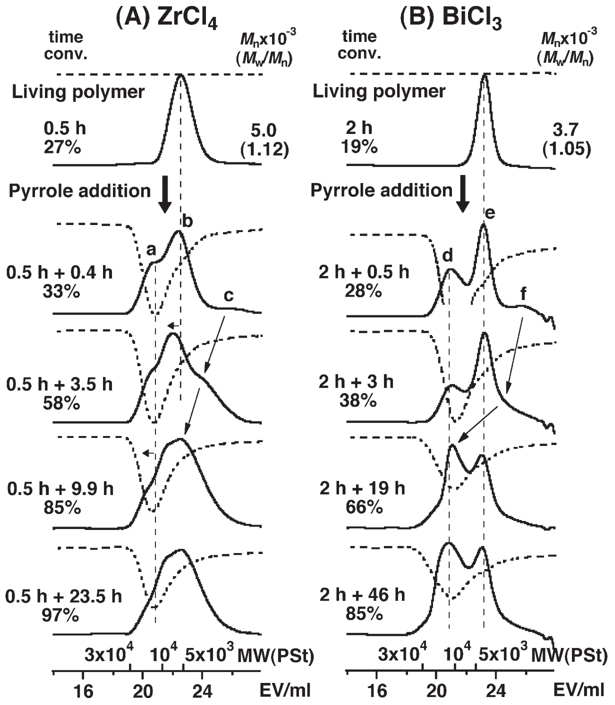


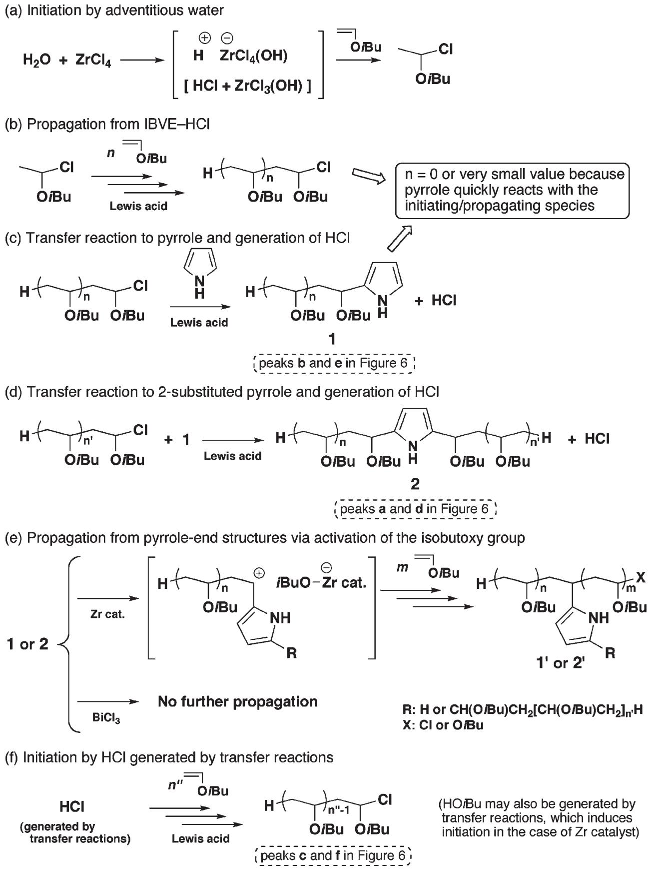
Figure 6. Molecular weight distribution curves for poly(isobutyl vinyl ether)s [poly(IBVE)s] obtained before and after adding pyrrole toward the living polymerization systems with (A) IBVE−HCl/ZrCl$_4$ and (B) IBVE−HCl/BiCl$_3$ {$[\mathrm{IBVE}]_0 = 0.76$ M, $[\mathrm{IBVE{-}HCl}]_0 = 5.0$ mM, $[\text{metal chloride}]_0 = 5.0$ mM, $[\text{pyrrole}]_{\text{added}} = 10$ mM, [ethyl acetate] = 1.0 M, [heptane] = 5 vol %, in toluene at 0 °C; solid lines: RI, dotted lines: UV; see Scheme 4 for the symbols **a**−**f**; M_n: number-average molecular weight, M_w/M_n: polydispersity ratio (weight-average molecular weight/number-average molecular weight), by GPC (polystyrene calibration)}.

transfer reactions by TMB as is the case with pyrrole, although the efficiency is low. The low reactivities of the methoxybenzenes are possibly due to their low nucleophilicity.[14] Nucleophilicity parameter *N*, which is investigated by Mayr et al., can be a good measure for the comparison. The *N* value of DMB is reported to be 2.48, which is much smaller than that of pyrrole (4.65; that of TMB is not reported).[8] Other nucleophilic compounds such as furan derivatives may also function as good transfer agents. In those cases, the degree of the nucleophilicity should be very important for the efficient reactions. In the present study, polymerization using more nucleophilic pyrrole derivatives was performed to investigate the effect of nucleophilicity (Supporting Information; Figure S2). With *N*-methylpyrrole (*N*: 5.85),[8] a more nucleophilic derivative, controlled polymerization proceeded to produce polymers with narrow MWDs in a similar manner. However, the rate was smaller than that using pyrrole. This is possibly because of the stronger interaction of the Lewis acid with the more basic nitrogen atom. Such an effect was further supported by the polymerization using 2,5-dimethylpyrrole (*N*: 8.01),[8] in which the reaction was extremely slow.[15] The results demonstrated that the appropriate nucleophilicity of pyrrole is good for the controlled polymerization with moderate activity.

Analysis of Product Polymer Obtained with Pyrrole. The product polymer obtained with pyrrole using ZrCl$_4$ was analyzed by NMR spectroscopy. Peaks characteristic to the polymer obtained by this initiating system appeared around 7.8, 6.6, 5.8, and 4.0 ppm (**a**, **b**, **c**, **c**′, and **e**), where no peak are present in poly(IBVE) produced using IBVE−HCl or methanol, as shown in Figure 5. These signals are assigned to the protons of the 1- (*N*-attached), 5-, and 3,4-positions of pyrrole rings, and methine protons of the main chain bonded to pyrrole, respectively. The notable feature of the spectrum is the small integral ratio of peak **b** compared to those of **a**, **c**, **c**′, and **e** [**a**: **b**: (**c**, **c**′): **e** ∼ 0.87: 0.15: 2.13: 1.00]. Since both 2- and 5-positions of pyrrole are reactive in substitution reactions,[7] the small ratio suggests the frequent occurrence of the disubstitution by propagating carbocations.[16]

Addition of Pyrrole during Living Polymerization Initiated by IBVE−HCl. Addition experiments of pyrrole during living polymerization of IBVE initiated by IBVE−HCl were conducted to investigate the modes of the reaction between pyrrole and the propagating carbocation. ZrCl$_4$ and BiCl$_3$ were used as catalysts for the reactions. Combined with pyrrole or methanol, the former can induce polymerization, whereas the latter is inactive. Twice molar amounts of pyrrole (10 mM) to the propagating chains were added when the monomer conversion reached 20 to 30% in living polymerization using 5.0 mM of IBVE−HCl as a cationogen. The changes in the MWD curves are shown in Figure 6. After the addition of pyrrole, three kinds of peaks were observed in both cases. The peaks with higher molecular weight, **a** and **d**, appeared with strong UV absorption. The molecular weights were about twice as large as those before the addition. These are assigned to polymers with a disubstituted pyrrole ring, obtained from the reaction between one pyrrole molecule and two living propagating species [structure **2**; the plausible mechanism for the pyrrole addition experiment is explained by (b)−(f) in Scheme 4, in which value "*n*" is not small for this experiment]. The peaks in almost the same region to those present before the addition, **b** and **e**, are due to monosubstituted products (structure **1**). A clear difference between the two catalysts was confirmed in the changes of these peaks. The peaks shifted toward the higher molecular weight region with the conversion in the case of ZrCl$_4$, while almost no shift was observed with BiCl$_3$. This is because oxophilic ZrCl$_4$ could activate the end structure produced by the reaction with pyrrole by abstracting the isobutoxy group (Scheme 4e). The propagation reaction of IBVE proceeded from the generated carbocation to yield polymers into which the pyrrole ring was incorporated as the side chain (structure **1**′). Similar reactions also occurred with the disubstituted species (structure **2**′), although the shift of the peaks was subtle. The third peaks, **c** and **f**, were observed in the lower molecular weight

Scheme 4. Plausible Polymerization Mechanisms for the Cationic Polymerization with the Pyrrole/$ZrCl_4$ Initiating System [for the Pyrrole Addition Experiment Shown in Figure 6, Only Pathways b−f Are Involved and the Value of "*n*" Is Not Small]



region. These newly appearing propagating chains were produced via the initiation from HCl generated by the transfer reactions.

The pyrrole addition experiments provided meaningful information about the mechanism of polymerization using pyrrole. The disubstitution of pyrrole by two propagating chains agrees with the small integral ratio of the protons of the 5-position in the ^{1}H NMR spectrum (Figure 5). The propagation from the pyrrole-bonded ends by the abstraction of the isobutoxy group with oxophilic Lewis acids explains the increment of the propagating chains as described in Scheme 1. The involvement of the effective alkoxy abstraction by an oxophilic Lewis acid in the propagation step is responsible for similar patterns of polymerization behaviors among Lewis acids using alcohol and pyrrole. The high efficiency of pyrrole as a transfer agent is also a notable feature.

Polymerization Mechanism Using Pyrrole. Possible mechanistic pathways for the polymerization using pyrrole with $ZrCl_4$ are shown in Scheme 4. The polymerization is initiated by adventitious water, via the reaction with $ZrCl_4$ generating HCl, followed by the formation of IBVE−HCl (Scheme 4a). Subsequent propagation from IBVE−HCl occurs (Scheme 4b), but pyrrole reacts with the propagating species to give the end structure with a pyrrole ring and an isobutoxy group (structure **1**) in addition to the generation of HCl (Scheme 4c). The reaction between the monosubstituted species (**1**) and another propagating chain produces disubstituted ones (structure **2**) as shown in Scheme 4d. After these reactions with pyrrole rings, the isobutoxy groups of structures **1** and **2** can be abstracted by a Zr catalyst (not expressed as $ZrCl_4$ here because some of the initial chloride ligands have been replaced by hydroxide and isobutoxide ligands due to initiation by adventitious water and re-initiation of pyrrole-terminated chains) to generate carbocationic species and to induce the subsequent propagation (Scheme 4e).[17] The pyrrole-attached carbocation is stabilized by the strong electron-donating ability of the pyrrole ring. Here, because of the high nucleophilicity of pyrrole, the number of IBVE units extended should be very small when pyrrole reacts with the growing ends. Under the most efficient conditions (*n* and $n' = 0$ in Scheme 4), structures **1** and **2** can be assumed to be very simple mono- and bifunctional initiators, respectively. In the overall reaction pathways, the HCl (or HO*i*Bu in some cases) generated by the transfer reactions plays a significant role in increasing polymer chains, which similarly reacts with pyrrole rings to generate HCl again. Since the number of reactions with the pyrrole rings corresponds to that of the generated HCl molecules, the polymerization proceeds as if pyrrole functions as an "initiator" as a result of the highly efficient transfer reactions.[18] Polymerization with a larger amount of pyrrole (50 mM), which produced structures with many pyrrole rings by frequent substitution reactions (Supporting Information; Figure S7 and Scheme S1), also indicated the high nucleophilicity of pyrrole. Line A in Figure 2 is the calculated one assuming that 1.7 mM of protic impurities (derived from the reaction without cationogen; Figure 4) and 5.0 mM of a bifunctional initiator work as cationogens (the calculated M_n values correspond to those for the initiation from 6.7 mM of a monofunctional initiator although the distribution of chain length is different). Relatively good agreement of the experimental results with the calculated values, in addition to the unimodal and narrow MWDs of the products, supports the occurrence of clean and efficient reactions as described here. The coloration of the product polymers (yellowish to reddish) implies occurrence of undesired reactions such as the formation of conjugated structures by dealcoholization as shown in Scheme S2 (Supporting Information).[20] A rough estimation by the UV−vis spectrum of the product (Supporting Information; Figure S8) indicates 2 to 3% of all chains formed such structures.[21]

The effectiveness of some catalysts, e.g., $ZrCl_4$ and $HfCl_4$, is attributed to their high oxophilicity and moderate chlorophilicity, as expected from the polymerization using alcohol as a cationogen.[3] The initiation of controlled polymerization was accompanied by the reaction between adventitious water and an oxophilic Lewis acid. Other chlorides such as $MoCl_5$ can also produce long-lived species both from water and alcohols. These acids mediate controlled polymerization only with the propagating species having carbon−chlorine bonds in the reactions using methanol, in contrast to the case with $ZrCl_4$. However, different phenomena were observed between these catalysts when surplus amounts of methanol were used. Excess methanol induce undesired reactions with $MoCl_5$, because $MoCl_5$ reacts with only an equimolar amount of alcohol. In contrast, $ZrCl_4$ can activate multiple alkoxy species. The limited ability to abstract alkoxy groups by $MoCl_5$ likely resulted in the less controlled behavior in the polymerization using pyrrole. The ineffectiveness of the chlorophilic chlorides, e.g., $FeCl_3$ and $InCl_3$, which induce uncontrolled polymerization and no reaction with alcohol, respectively, is attributed to their poor activity both in the initiation from water and in the abstraction of alkoxy groups for controlled polymerization. These studies on the metal chloride catalysts indicate that good balances between oxo- and chlorophilicity for $ZrCl_4$ and $HfCl_4$ permit the controlled polymerization of IBVE with pyrrole as an "initiator-like" transfer agent.

Conclusions

Precise cationic polymerization of IBVE using pyrrole as an "initiator-like" transfer agent was achieved by combination with suitable types of oxophilic Lewis acids such as $ZrCl_4$ in the presence of a weak Lewis base. The polymerization was initiated by a small amount of adventitious water, followed by the highly efficient reactions between the propagating species and the 2- and 5-positions of pyrrole, accompanied by the generation of HCl. The pyrrole-bonded end structures were also activated to form carbocations by the abstraction of the isobutoxy groups. Thus, the number of growing chains increased during the reaction since polymerization proceeds both from the generated HCl and the pyrrole-end structures. Oxophilic Lewis acids like $ZrCl_4$ showed excellent abilities in abstracting the isobutoxy groups. Frequent transfer reactions in the early stage of the polymerization stemmed from the highly nucleophilic nature of pyrrole. This gave polymers with narrow MWDs and M_n values agreeing with the calculated ones, assuming that pyrrole functioned as an initiator. This unprecedented reaction introduces a novel and unique method to synthesize polymers with various architectures.

Acknowledgment. A.K. expresses his special thanks to JSPS Research Fellowships for Young Scientists and The Global COE Program "Global Education and Research Center for Bio-Environmental Chemistry" of Osaka University.

Supporting Information Available: Figures showing time−conversion curves and M_n−conversion plots of polymerization, MWD curves, NMR spectra, MALDI−TOF−MS spectra, ESI−MS spectra, UV−vis spectra, and some polymerization data and schemes showing reaction mechanisms. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For reviews: (a) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111–172. (b) Kennedy, J. P.; Ivan, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser: New York, 1992. (c) Matyjaszewski, K.; Sawamoto, M. In *Cationic Polymerizations*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; Chapter 4. (d) Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2285–2293. (e) Puskas, J. E.; Kaszas, G. *Prog. Polym. Sci.* **2000**, *25*, 403–452. (f) De, P.; Faust, R. In *Macromolecular Engineering. Precise Synthesis, Materials Properties, Applications.*; Matyjaszewski, K.; Gnanou, Y.; Leibler, L., Eds.; WILEY-VCH GmbH & Co. KGaA: Weinheim, Germany, 2007; Chapter 3. (g) Goethals, E. J.; Prez, F. D. *Prog. Polym. Sci.* **2007**, *32*, 220–246. (h) Aoshima, S.; Yoshida, T.; Kanazawa, A.; Kanaoka, S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1801–1813. (i) Aoshima, S.; Kanaoka, S. *Chem. Rev.* **2009**, *109*, 5245–5287.

(2) Kanazawa, A.; Kanaoka, S.; Aoshima, S. *Macromolecules* **2009**, *42*, 3965–3972.

(3) Kanazawa, A.; Kanaoka, S.; Aoshima, S. *Macromolecules* **2010**, *43*, ASAP article.

(4) Jones, R. A.; Bean, G. P. *The Chemistry of Pyrroles*; Academic Press: New York, 1977.

(5) (a) Bynum, R. V.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368–2374. (b) Fischer, P. J.; Young, V. G., Jr.; Ellis, J. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 189–191. (c) Saeed, I.; Katao, S.; Nomura, K. *Organometallics* **2009**, *28*, 111–122.

(6) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.

(7) (a) Jorapur, Y. R.; Lee, C. H.; Chi, D. Y. *Org. Lett.* **2005**, *7*, 1231–1234. (b) Palomo, C.; Oiarbide, M.; Kardak, B. G.; Garcia, J. M.; Linden, A. *J. Am. Chem. Soc.* **2005**, *127*, 4154–4155.

(8) (a) Nigst, T. A.; Westermaier, M.; Ofial, A. R.; Mayr, H. *Eur. J. Org. Chem.* **2008**, 2369–2374. (b) Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66–77.

(9) (a) Storey, R. F.; Stokes, C. D.; Harrison, J. J. *Macromolecules* **2005**, *38*, 4618–4624. (b) Martinez-Castro, N.; Morgan, D. L.; Storey, R. F. *Macromolecules* **2009**, *42*, 4963–4971. (c) Morgan, D. L.; Storey, R. F. *Macromolecules* **2010**, *43*, 1329–1340.

(10) Higashimura, T.; Kamigaito, M.; Kato, M.; Hasebe, T.; Sawamoto, M. *Macromolecules* **1993**, *26*, 2670–2673.

(11) Katayama, H.; Kitaguchi, H.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4023–4031.

(12) Water was introduced to the system by using water-saturated toluene.

(13) Tachikawa, E.; Nishizaki, H.; Kanaoka, S.; Aoshima, S. *Polym. Prepr. Jpn.* **2007**, *56*, 259.

(14) The steric hindrance of TMB may also be another reason for the low efficiency. However, TMB can effectively function as a transfer agent when a large amount is used,[13] which implies that the steric effect is not critical.

(15) Another purpose for the polymerization using 2,5-dimethylpyrrole was to confirm the reaction of the propagating chains with non-substituted pyrrole at the 2- and 5-positions as described in the later sections. The reaction should proceed in similar rate to that without any cationogens or transfer agents (Figure 4) even if the 1-, 3-, and 4-positions of 2,5-dimethylpyrrole were inert [reactions at the 3- and 4-positions were implied by the ^{1}H NMR spectrum of the product polymer; Supporting Information (Figure S4)]. Thus, the extremely low activity of the polymerization supports the strong acid−base interaction of 2,5-dimethylpyrrole with $ZrCl_4$.

(16) In contrast to the NMR analysis, both MALDI−TOF−MS and ESI−MS could not prove the involvement of pyrrole to the polymer chains, possibly because of the much lower ionization efficiency of pyrrole-involved structures compared to the chains without pyrrole. Only peaks corresponding to poly(IBVE)s with the proton α-ends and the methoxy or the isobutoxy ω-ends were detected in the MALDI−TOF−MS spectrum (Supporting Information; Figure S5). Small amounts of chains with the aldehyde ω-ends produced by the unintended hydrolysis of the acetal ends in the purification process using acid was also confirmed by the ESI−MS spectra (Supporting Information; Figure S6), which showed sharper peaks than the MALDI−TOF−MS spectrum. The masses of the observed peaks were smaller than those expected from the GPC analysis, in which the value $M_n = 1.9 \times 10^3$ was obtained. Thus, pyrrole-involved structures were likely to exist in larger molecular weight region than those of the observed peaks.

(17) The present cationic system may be specific for VEs. No propagation from pyrrole-terminated species would be induced with other monomers such as styrenes and *N*-vinylcarbazole, since a carbon−aryl (C−C) or the carbon−carbazole ring (C−N) bond is difficult to cleave, yielding carbocation, with any Lewis acid.

(18) Another living polymerization system with chain transfer reaction is the immortal polymerization using an aluminum-porphyrin catalyst,[19] which is conducted in the presence of a transfer agent such as alcohol. The exchange of alcohol (e.g., methanol) with an active polymer chain on the porphyrin occurs frequently in the early stage, yielding a dormant chain. In the propagating reaction, dormant polymer chains (e.g., a polymer with a terminal hydroxy group) and porphyrin-bonded active chains exchange rapidly, in other words, chain transfer occurs continuously throughout the reaction, to realize living polymerization.

(19) (a) Asano, S.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1148–1149. (b) Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2861–2871.

(20) Aoshima, S.; Higashimura, T. *Polym. J.* **1984**, *16*, 249–258.

(21) The ratio of the chains with conjugated structures was estimated by comparing with pyrrole derivatives having a diene or a triene substituent at the 2-position reported in ref 22. Those compounds have absorption around 300−400 nm whose molar coefficient values are $(3.0-4.0) \times 10^4$. The absorbance of the product polymer at 300 nm was used to compare with these values.

(22) Ahmed, F. R.; Toube, T. P. *J. Chem. Soc. Perkin Trans. I* **1984**, 1577–1579.