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THE PROPAGATING SPECIES IN LIVING CATIONIC POLYMERIZATION: LIVING NATURE AND STERIC STRUCTURE OF POLYMERS

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Abstract: This paper discusses the nature of the living growing species in cationic polymerization from the viewpoint of the steric structure of poly(isobutyl vinyl ether) [poly(IBVE)]. At –78 °C, living polymerization was induced with the HCl–IBVE adduct (**1**)/$ZnCl_2$ system in a $EtNO_2/CH_2Cl_2$ mixture, whereas similar systems with $EtAlCl_2$ led to conventional cationic polymerization. In this polar medium, both systems gave polymers with very similar and low isotacticity (*meso* ≈ 56%), indicating that the propagating reaction is mediated by free ions. Thus, regardless of solvent polarity, or involvement of free ions or ion pairs, living cationic polymerization requires a suitably nucleophilic counteranion. As model reactions of the growing species, **1**/$ZnCl_2$ and **1**/$EtAlCl_2$ were directly analyzed by ^1H NMR spectroscopy.

INTRODUCTION

In cationic polymerization of vinyl monomers, the growing carbocations are highly reactive but unstable and thus living polymerization had been considered difficult for a long time. In the 1980s, we reported for the first time truly living cationic polymerization of vinyl ethers with designed initiating systems (Ref. 1). Ever since, living cationic polymerization has been studied by numerous groups and has become a powerful method to synthesize functional polymers with narrow molecular weight distribution (MWD) and controlled structures (Ref. 2).

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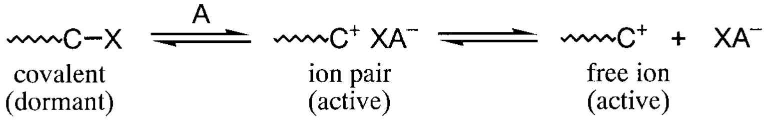
These extensive studies revealed that living cationic polymerization can be achieved only when appropriate initiating systems and reaction conditions are selected. In particular, the involvement of a counterion is important, for which two general explanations have been proposed:

(i) A suitably nucleophilic counteranion in living cationic polymerization stabilizes the growing carbocation which becomes more stable than those in conventional (non-living) counterparts.

(ii) The growing species is the same in nature as that in conventional cationic polymerization, but in living processes the reversible formation of dormant and active species [eq. (1)] lowers the concentration of the latter to prevent undesired side reactions.



(1)

In general, the growing species in cationic polymerization are in an equilibrium among various dissociation states, as illustrated in eq. (1), where X^- represents a counteranion derived from the corresponding initiator (e.g., protonic acid–IBVE adduct), and A is a Lewis acid-type activator (e.g., metal halides) which ionizes the C–X bond of the covalent species. The experimental observations thus far reported have revealed that a key to successful living cationic polymerization is the judicious choice of a counterion for a particular growing end. By employing suitably nucleophilic counterions, for example, living polymerization has been achieved with various initiating systems in less polar media, whereas there are none operable in strongly polar media, where free ions might be involved in the propagating reaction. Equally important, the stereochemistry and its regulation in living cationic polymerization has not been pursued in detail.

The focus of this study is therefore (i) to examine the feasibility of living cationic polymerization mediated by the dissociated species in polar media, and (ii) to discuss the nature of the propagating ends in living and non-living cationic polymerizations as a function of solvent polarity and other related parameters. As mentioned above, there has been no reports of living cationic polymerization mediated by a free ion, because free carbocations are considered too reactive to undergo controlled propagating reactions.

For studies on the growing species, a major problem is the difficulty in obtaining direct evidence for its dissociation state exactly when it attacks a monomer. In fact, dissociation states have yet been totally uncovered so far by kinetic study and/or molecular weight (or MWD) analysis of polymers. It has been reported that the steric structure of polymers in cationic polymerization of some monomers is systematically altered by varying solvent polarity, namely, the dissociation state of the growing ends (Ref.3). This fact suggests that the steric structure may provide evidence for the dissociation state. Thus, we herein discuss the nature of the growing species by employing the steric structure of product poly(vinyl ethers) as a measure of its dissociation state.

In this study, cationic polymerization of isobutyl vinyl ether (IBVE) was examined with HCl–IBVE adduct (**1**)/$ZnCl_2$, **1**/$EtAlCl_2$, and AcOH–IBVE adduct (**2**)/$EtAlCl_2$ initiating systems at –78 °C in solvents of various polarity. Toluene, dichloromethane (CH_2Cl_2), and a mixture of nitroethane and dichloromethane (1:1 v/v) ($EtNO_2/CH_2Cl_2$) were employed as polymerization solvents. IBVE was selected as a monomer because the isotacticity of its polymers is known to continuously decrease as solvent polarity increases (Ref.3) and because various types of initiating systems can induce its living polymerization (Ref.2). To compare living and non-living systems, **1**/$ZnCl_2$ and **1** or **2**/$EtAlCl_2$ were employed as initiating systems that induce living and non-living cationic polymerization, respectively. Polymerization was carried out at a low temperature (–78 °C) to suppress side reactions of the growing ends and to regulate the steric structure.

RESULTS AND DISCUSSION

Effects of Solvent Polarity on Living Nature

IBVE–HCl Adduct (1)/$ZnCl_2$ Initiating System

Effects of solvent polarity on the IBVE polymerization at low temperature were examined with

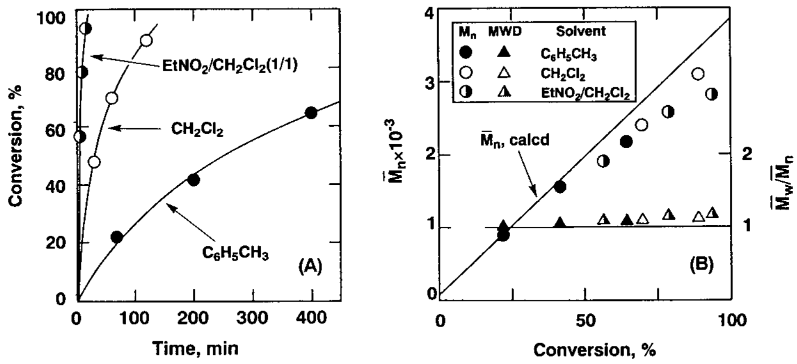


Fig. 1. Time-conversion curves (A) and M_n and M_w/M_n of poly(IBVE) (B) obtained with **1**/$ZnCl_2$ at –78 °C: $[M]_0$ = 0.38 M, $[1]_0$ = 10 mM, $[ZnCl_2]_0$ = 5.0 mM. The diagonal solid line in (B) indicates the M_n calculated from the feed ratio of IBVE to **1** and monomer conversion.

1/$ZnCl_2$, which induces living polymerization even at room temperature in nonpolar solvent. As shown in Fig. 1, polymerization rate sharply increased with solvent polarity and, in $EtNO_2/CH_2Cl_2$, became 50-60 times as large as that in toluene. Independent of solvent polarity, in contrast, the product polymers had very narrow MWD (M_w/M_n = 1.03–1.19), and the M_n increased proportionally to monomer conversion, which agreed with the calculated values assuming that one polymer chain forms per **1** molecule.

To confirm the living nature in this polar medium, a fresh feed of IBVE ($[IBVE]_0 = [IBVE]_{add}$ = 0.38 M) was added to the reaction mixture when monomer conversion reached ca. 90%. On the addition of the monomer, the second phase polymerization occurred without an induction phase in a rate similar to that of the first-stage. The MWD of the polymers remained narrow ($M_w/M_n < 1.1$), and the relationship between conversion and the M_n values were linear (Fig. 2). Polymers with narrow MWD, however, did not form after the conversion of the second charge of the monomer had reached ca. 70%, where they started precipitating. Thus, **1**/$ZnCl_2$ induces living cationic polymerization of IBVE at low temperature even in a strongly polar $EtNO_2/CH_2Cl_2$ mixture.

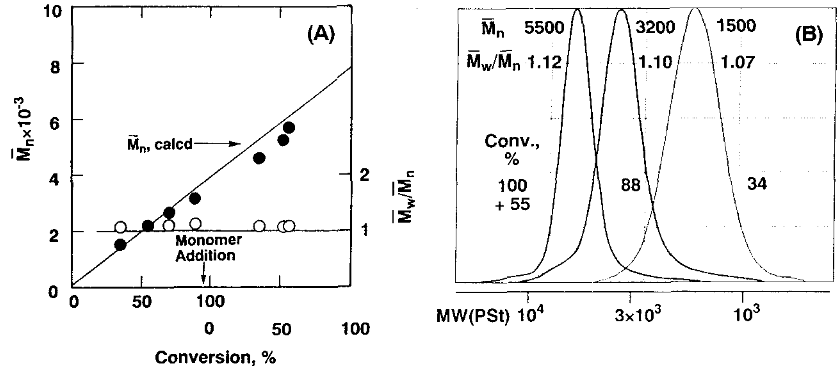


Fig. 2. M_n, M_w/M_n (A), and MWD curves (B) in a monomer-addition experiment in the polymerization with **1**/$ZnCl_2$ in $EtNO_2/CH_2Cl_2$ at −78 °C: $[M]_0 = [M]_{add}$ = 0.38 M, $[\mathbf{1}]_0$ = 10.0 mM, $[ZnCl_2]_0$ = 5.0 mM. The diagonal solid line in (A) indicates the M_n calculated from the feed ratio of IBVE to **1** and monomer conversion.

1/$EtAlCl_2$ and IBVE–CH_3CO_2H Adduct (2)/$EtAlCl_2$ Initiating Systems

Polymerization was also examined with **1** or **2** in conjunction with $EtAlCl_2$ which is a stronger Lewis acid than $ZnCl_2$. Since polymerization rate is large with this aluminum compound, polymerization was carried out at a low $EtAlCl_2$ concentration for **1**/$EtAlCl_2$, and a small amount of dioxane was added with **2**/$EtAlCl_2$ to render the polymerization controllable (Ref. 2). With both initiating systems, however, the polymerization rate was large and not reproducible, while the steric structure of the polymers showed good reproducibility.

The results of the polymerization are summarized in Table 1. Irrespective of initiating system and solvent polarity, the polymers had unimodal MWD and the M_n much larger than the calculated values assuming that one **1** or **2** molecule generates one polymer chain. In contrast to **1**/$ZnCl_2$, thus, **1**/$EtAlCl_2$ and **2**/$EtAlCl_2$ induced non-living (conventional) cationic polymerization even at low temperature.

Table 1. Cationic Polymerization of IBVE with HCl–IBVE (**1**)/$EtAlCl_2$ and CH_3CO_2H–IBVE (**2**)/$EtAlCl_2$ in Various Solvents ([IBVE]$_0$ = 0.38 M, −78 °C)

Initiating System		Solvent		
		Toluene	CH_2Cl_2	$EtNO_2/CH_2Cl_2$ (1:1)
	Conv., %	67	12	7
HCl–IBVE (**1**) / $EtAlCl_2$	M_n(obs)	34,000	20,600	14,500
(10 / 0.50 mM)	M_n(calcd)	2550	460	270
	M_w/M_n	2.57	1.68	1.67
CH_3CO_2H–IBVE (**2**)/	Conv., %	70	100	100
$EtAlCl_2$	M_n(obs)	12,500	28,600	27,700
(10 / 20 mM)	M_n(calcd)	2660	3800	3800
Dioxane (20 mM)	M_w/M_n	2.59	1.63	1.36

When **2** was mixed with $EtAlCl_2$, a chlorine terminal group [~$CH_2CH(O\textit{i}Bu)Cl$] was observed by ^1H NMR, and the steric structure (isotacticity) was very similar to those obtained with **1**/$EtAlCl_2$ (*meso* content: in toluene 78.9% for both **1** and **2**; in $EtNO_2/CH_2Cl_2$, 54.7 for **1** and 56.6% for **2**). These results suggest that the acetate terminal derived from **2** was converted into the chlorine counterpart during the polymerization. Such an exchange of counteranions is now under investigation with **1**/$EtAlCl_2$ and **2**/$EtAlCl_2$.

Effects of Solvent Polarity and Common Ion Salts on Steric Structure

Solvent Polarity

Fig. 3. shows the *meso* content (diad) of the product polymers obtained in various solvents. The *meso* content with **1**/$ZnCl_2$ is lower by 10% than those with **1** or **2**/$EtAlCl_2$ in toluene and decreased as solvent polarity increased. Note that, in $EtNO_2/CH_2Cl_2$, both $ZnCl_2$- and $EtAlCl_2$-based initiating systems gave very similar isotacticity (*meso* ≈ 56%).

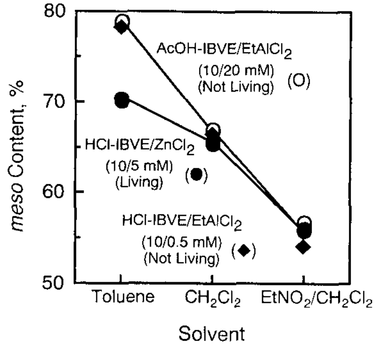


Fig. 3. Effects of solvent polarity on the steric structure of poly(IBVE) obtained with **1**/$ZnCl_2$, **1**/$EtAlCl_2$, and **2**/$EtAlCl_2$ at −78 °C. See Fig. 1. and Table 1 for the reaction conditions.

In the conventional cationic polymerization of IBVE with various metal halides such as BF_3, it has been reported that the isotacticity decreased with increasing solvent polarity because the counterion can hardly interact with the growing end in polar media (Ref.3). Thus, the above-mentioned similar isotacticity suggests that the propagating reactions with both $ZnCl_2$ and $EtAlCl_2$ are mediated by a free ion in a polar solvent, whether or not the polymerization is living. Equally important, the free ionic growing species from **1**/$ZnCl_2$ in $EtNO_2/CH_2Cl_2$ exhibits the living nature, although living cationic polymerization has been considered to occur only when the growing carbocation is not a free ion so as to be stabilized by a counteranion.

Common Ion Salts

To confirm the occurrence of living polymerization by the dissociated free ionic species, the effects of common ion salts on the steric structure of polymers were examined with the **1**/$ZnCl_2$-initiated polymerization. The *meso* content may increase if a common ion salt shifts the equilibrium to the covalent or ion pair side. IBVE was thus polymerized with **1** in the presence of *n*Bu_4NCl, 1.5 equivalent to **1**/$ZnCl_2$, in various solvents (Fig. 4).

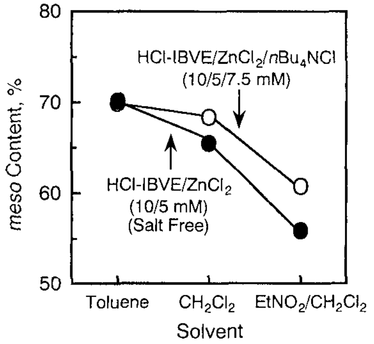
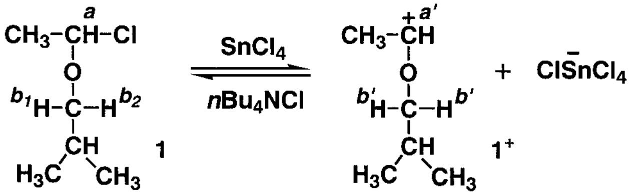


Fig. 4. Effects of common ion salts on the steric structure of poly(IBVE) obtained with **1**/$ZnCl_2$ at −78 °C. $[nBu_4NCl]_0$ = 7.5 mM, see Fig. 1. for other reaction conditions.

Neither polymerization rate nor polymer steric structure was affected by the addition of the salt in toluene. In polar solvents, on the other hand, the added salt retarded the polymerization and enhanced the isotacticity of the product polymers (Fig. 4). These results also support that a part of the propagating species are free ions in CH_2Cl_2 and $EtNO_2/CH_2Cl_2$, where living cationic polymerization does occur.

^{1}H NMR Analysis of Model Reactions of the Growing End

As a model reaction of the growing species, the interaction of **1** with metal halides was directly analyzed by ^{1}H NMR spectroscopy. We have already reported the dissociation states of **1** in the presence of metal halides in CD_2Cl_2 at –78 °C monitored by ^{1}H NMR (Ref.4) and ^{13}C NMR (Ref.5). For example, on addition of $SnCl_4$, **1** dissociates into carbocation $\mathbf{1}^+$ ($\mathbf{1}/SnCl_4$ = 100/20 mM) and non-living polymerization occurs under these conditions. A common ion salt (nBu$_4$NCl) suppresses the dissociation of the growing end whose NMR spectrum shows the signal due to the covalent species, and in turn living polymerization occurs. The signals of the methylene protons (b_1 and b_2) are, however, broader than the corresponding peak of **1**. The broadening shows the inversion of the configuration of the chiral carbon C^a via an ionic intermediate that exists at a concentration below the NMR detection limit. These results demonstrated that the equilibrium was far shifted to the covalent species, namely a concentration of $\mathbf{1}^+$ is very low in this system.



(2)

The results obtained from ^{1}H NMR analysis and polymerization in our previous study can be summarized as follows. When **1** is activated by a strong Lewis acid such as $SnCl_4$, $\mathbf{1}^+$ is observed by NMR analysis, and non-living polymerization occurs. By contrast, in conjunction with a weak Lewis acid for which only the covalent species is observed, living polymers are obtained (Ref.4). Unfortunately, all these studies invariably employed a single, relatively polar solvent, CD_2Cl_2.

In this study, however, the results of the steric structure of the polymers showed that the propagating species includes the dissociated ionic species in the IBVE polymerization with $\mathbf{1}/ZnCl_2$ in $EtNO_2/CH_2Cl_2$. Thus, the relationships between the existence of $\mathbf{1}^+$ (monitored by NMR) and the living nature were examined with $\mathbf{1}/ZnCl_2$ and $\mathbf{1}/EtAlCl_2$ in relation to solvent polarity.

Fig. 5 shows ^1H NMR spectra of mixtures of **1** and Lewis acids at −78 °C in toluene-d_8 and CD_2Cl_2, where the ratio of **1** and a Lewis acid was set the same as that in the polymerization. Upon the addition of both Lewis acids in toluene, the signals assigned to the methine (H^a) and methylene protons (H^{b_1}, H^{b_2}) are the same in shape and position as those of **1** alone (Fig. 5A–C). In CD_2Cl_2, the same spectrum was also observed with a small amount of a Lewis acid (Fig. 5F), whereas in the presence of its large amount, the split signals of the methylene protons are the same in position but become broader than those of **1** (Fig. 5E and G). Under these conditions, therefore, the dissociation state observed by ^1H NMR did not correspond to the living nature as observed before; the $ZnCl_2$ system induced living polymerization, while non-living polymerization occurred with the $EtAlCl_2$ version.

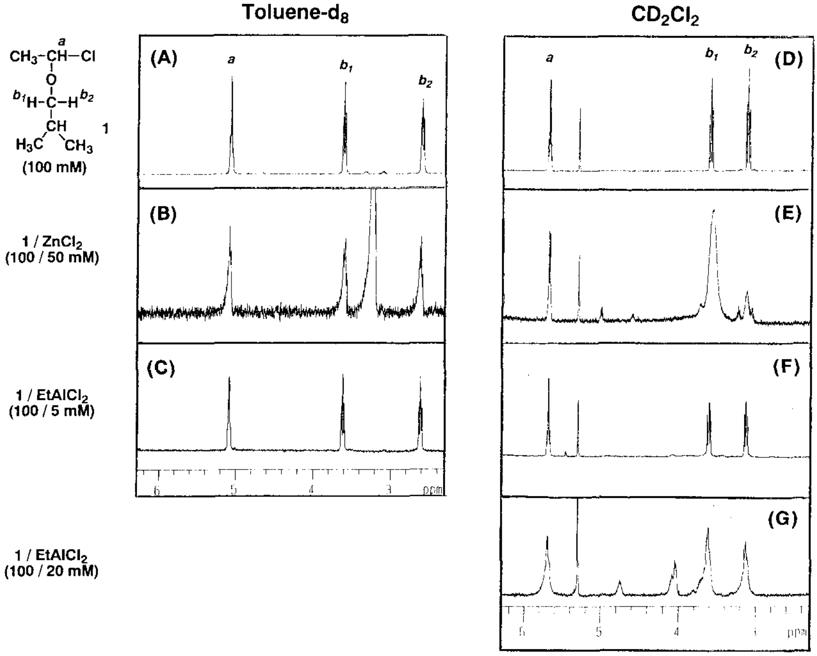


Fig. 5. ^1H NMR spectra of **1**, and the mixture of **1**/MX_n at −78 °C in toluene-d_8 (A–C) and CD_2Cl_2 (D–G): $[\mathbf{1}]_0$ = 100 mM. MX_n and $[MX_n]_0$: (B and E) $ZnCl_2$, 50 mM; (C and F) $EtAlCl_2$, 5 mM; (G) $EtAlCl_2$, 20 mM.

CONCLUDING REMARKS

In this study, cationic polymerization of IBVE was examined at low temperature. The major finding of this study may be summarized as follows:

(1) Living polymerization was induced with **1**/$ZnCl_2$ even in such polar solvents as CH_2Cl_2 or $EtNO_2/CH_2Cl_2$, whereas **1**/$EtAlCl_2$ led to conventional cationic polymerization even in nonpolar media (toluene).

(2) The steric structure of the polymers suggested that the free ionic growing species was involved in the living polymerization with **1**/$ZnCl_2$ in polar media.

(3) The results of model reactions of the growing end by ^1H NMR revealed that the living nature does not totally correspond to the observation of free carbocations in the system.

It should be noted that the free ionic growing end led to living cationic polymerization. This also indicates that reversible formation of dormant and covalent species from the ionic counterpart plays a key role in realizing living cationic polymerization. Even under the conditions where the ionic species is free ionic, however, carbocations cannot be observed in a certain system. For examples, **1**/$ZnCl_2$ gave living polymers, whereas **1**/$EtAlCl_2$ induced non-living cationic polymerization, although both systems led to essentially the same results in the NMR analysis of the model reactions (Fig. 5). With the nature of the living growing end, therefore, the dissociation state still remains uncovered. We are investigating the nature of the growing species and are also developing new initiating systems and reaction conditions for living cationic polymerization.

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