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# Effects of monomer and ether structure on metal-free living cationic polymerization of various vinyl ethers using hydrogen chloride with ether

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**Abstract** A highly effective initiating system has been achieved for living cationic polymerization of vinyl ethers consisting of HCl alone without Lewis acid. This system is a facile metal-free living cationic polymerization using no HCl/Lewis acid but the already adopted complex $HCl{\cdot}Et_2O$. In this study, we investigated the effects of a monomer and ether structure on the polymerization behavior. The monomers are classified into three kinds of monomers: alkyl vinyl ether, vinyl ether with electron-donating groups in the pendant, and vinyl ether with bulky group next to the electron-donating substituent in the pendant. The $HCl{\cdot}Et_2O$ systems were applicable for the polymerizations of all vinyl ethers used. However the structure around electron-donating groups in the pendant of monomer affected the polymerizations rate and induction period. The initiation reactions can be successfully achieved using ether effectively dissociating HCl, especially symmetrical ether.

**Keywords** Living cationic polymerization · Metal-free · Vinyl ether · Protonic acid

## Introduction

Metal-free polymerizations are of great importance owing to their low cost as well as low environmental burden. The polymerization system is inherently free from metal catalyst residues thus after-treatment can be easily carried out. The presence of the metal contaminants in the macromolecule can have detrimental effects on the performance of the final polymers. For example, the catalyst residues often degrade the resulting polymer, are responsible for low insulation abilities, and rust out for curing.

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In particular, no metal contaminants are usually required in microelectronics and drug delivery systems.

On the other hand, the synthesis of well-designed polymer with high performance has been demanded for achieving materials used in various fields. An application of living (controlled) polymerization allows to design and synthesize new polymers with controlled architecture such as molecular weight (MW), molecular weight distribution (MWD), and sequence of constitutional repeating units or segments [1, 2].

Metal-free living/controlled polymerization has both above-mentioned properties. Since metal-free is essential to adjust to the biomaterials, these kinds of polymerizations, e.g. living ring-opening polymerizations of lactide and ε-caprolactone, have been investigated much harder quite recently [3–5].

We have recently reported that facile metal-free living cationic polymerization of various vinyl ethers, especially isobutyl vinyl ether, proceeded using hydrogen chloride with diethyl ether ($HCl \cdot Et_2O$) at 0 °C to room temperature and by hydrogen chloride with dioxane (HCl·DO) at 65 °C [6]. The molecular weights of the obtained polymers were controlled with a feed ratio of a monomer and HCl. Contrary to the long held belief [7, 8] that living cationic polymerization does not proceed by HCl, except for a few examples [9, 10], our study brought a new report on metal-free living cationic polymerizations of vinyl ethers using $HCl \cdot Et_2O$. In addition, the $HCl \cdot Et_2O$ initiating system was applicable for various functional vinyl ethers.

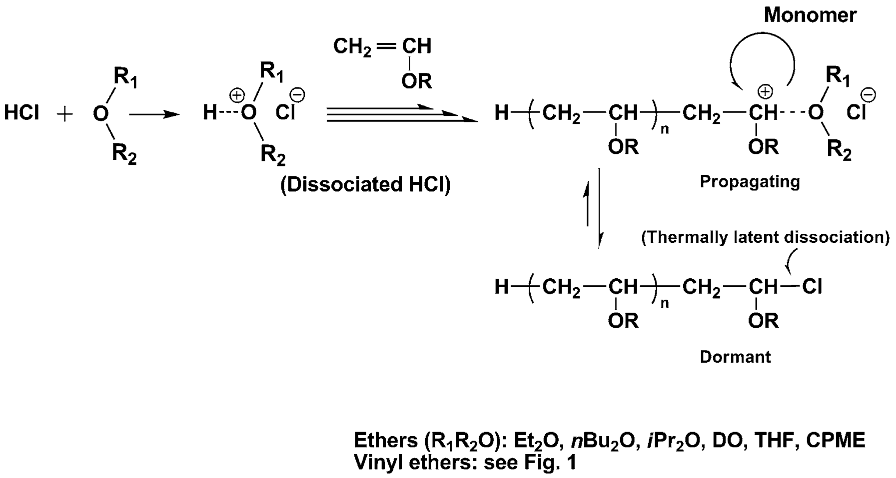
Further investigations showed following features: $Et_2O$ is Lewis base, which is not an activator but an auxiliary agent (like an added base [2, 11]) for HCl dissociation. The amounts of $Et_2O$ have an influence on the polymerization rate and molecular weight distribution. With 1,4-dioxane (DO) instead of $Et_2O$, the polymerization temperature can be changed up to 65 °C. The dissociated HCl, i.e., $HCl \cdot Et_2O$, acts as protonogen and plays both roles as an activator and an initiator. After the $HCl \cdot Et_2O$ induced initiation, thermally latent propagation occurred with a stable carbocation caused by oxygen of $Et_2O$. Thus, the equilibrium between dormant (covalent) and active (carbocation) was displaced toward dormant and no polymerization proceeded at a low temperature ($\leq -40$ °C).

However, there are remaining investigations in metal-free living cationic polymerization, which is a precision study on various effects of ethers dissolving HCl and polar monomers on living cationic polymerization. In this study, we provide a research on synthetic approaches to metal-free living cationic polymerization of various vinyl ethers using HCl with ethers, i.e., HCl·ether, as shown in Scheme 1.

## Experimental section

### Materials

For monomers, isobutyl vinyl ether (IBVE, TCI), cyclohexyl vinyl ether (CHVE, TCI) *n*-butyl vinyl ether (NBVE, TCI), *tert*-butyl vinyl ether (TBVE, Aldrich),



**Scheme 1** Reaction mechanism for HCl·ether induced metal-free living cationic polymerization for various vinyl ethers

2-chloroethyl vinyl ether (CEVE, TCI), and 2-methoxyethyl vinyl ether (MOVE, donated by Maruzen Petrochemical) were distilled twice over calcium hydride and were stored in a brown ampoule under dry nitrogen. 2-(*tert*-Butyldimethylsilyloxy)ethyl vinyl ether (SiEVE), 3-(*tert*-butyldimethylsilyloxy)propyl vinyl ether (SiPVE), and 4-(*tert*-butyldimethylsilyloxy)butyl vinyl ether (SiBVE) were prepared and distilled according to the literature method [12]. For HCl in ether (HCl·ether), HCl in $Et_2O$ (HCl·$Et_2O$, Aldrich; 1.0 M), in 1,4-dioxane (HCl·DO Aldrich; 1.0 M), and in cyclopentyl methyl ether (HCl·CPME Watanabe Chemical Industries; 4.0 M) was used as commercially supplied, because there are no differences between them and our prepared dry HCl·ether to prevent water effects. HCl in di-*n*-butyl ether (HCl·$n$$Bu_2O$), in di-isopropyl ether (HCl·$i$$Pr_2O$), and in tetrahydrofuran (HCl·THF) was prepared by bubbling of dry HCl gas into the corresponding dehydrated ether. These concentrations of HCl were estimated by titrimetric determination using 0.1 M NaOH aqueous solution. These dehydrated ethers for adjusting concentrations were obtained as commercially supplied for $Et_2O$ (Wako) and $i$$Pr_2O$ (Kanto Kagaku) or as distilled twice over calcium hydride or sodium for $n$$Bu_2O$, CPME (donated by ZEON), DO, THF. Hexane and toluene were washed by usual methods and were distilled over calcium hydride just before use.

## Polymerization procedures

Polymerization was typically carried out under a dry nitrogen atmosphere in a glass tube equipped with a three-way stopcock baked at 250 °C for 10 min before use. The reaction was initiated by the addition of HCl·ether solution into a mixture of a monomer in hexane or toluene by a dry medical syringe. After quenching the polymerization by methanol containing a small amount (0.1 vol%) of aqueous ammonia, the reaction mixture was washed by water. The product polymer was recovered from the organic layer by evaporation and vaccum-dried. The conversion of a monomer was determined by gravimetry.

### Characterization

The molecular weight distribution of the polymers was measured by size exclusion chromatography (SEC) in tetrahydrofuran at 38 °C on three polystyrene gel columns [TSK gel G-MH$_{HR}$-M $\times$ 2 or $\times$ 3 (exclusion limit $4 \times 10^6$ (polystyrene, PSt)); 7.8 mm i.d. × 300 mm each; flow rate 1.0 mL/min] connected to a Tosoh AS-8020 auto-injector, a CCPM-II dual pump, a UV-8020 UV detector and a RI-8011 refractive detector with a LS-8000 LALLS. The main detector is RI-8011. The number-average molecular weight ($M_n$) and $M_w/M_n$ were calculated from SEC curves on the basis of a PSt calibration. Polymer structure was confirmed by $^1$H NMR (500 MHz) or $^{13}$C NMR (125 MHz) using JEOL JNM-EX500 spectrometer. Molecular mechanics calculations for various ethers were carried out using a modified version of Allinger's MM2 force field, as implemented in the CS Chem3D Pro (CambridgeSoft, Cambridge, MA, USA) molecular modelling software package (version 11.0). The energy was minimized using RMS gradient of 0.10 kcal/mol.

## Results and discussion

### Metal-free living cationic polymerization of various vinyl ethers

To study on effects of a monomer structure on a polymerization behavior, vinyl ether monomers were classified into three categories as shown in Fig. 1 and their polymerizations using HCl·Et$_2$O were investigated. The monomers are grouped as follow: (A) alkyl vinyl ether (B) vinyl ether with electron-donating groups in the pendant, and (C) vinyl ether with bulky group, *tert*-butyldimethylsilyl group, next to the electron-donating substituent in the pendant. The category A includes the monomer for poly(CHVE) with high glass transition [13] and for polyvinyl alcohol precursor, poly(TBVE) [14]. The categories B and C include MOVE and SiBVE,

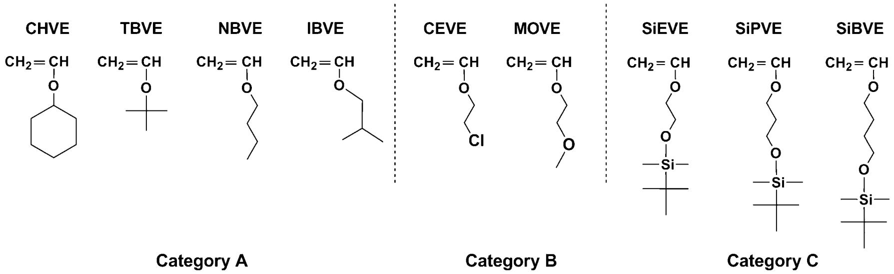


**Fig. 1** Various vinyl ethers

2-hydroxybutyl vinyl ether with protecting group, which are utilized to form thermoresponsive polymers in water [12, 15].

## Polymerization for vinyl ethers in category A and B

The polymerization of alkyl vinyl ethers (category A) were carried out in hexane at 0 °C with $HCl \cdot Et_2O$: $[\text{alkyl vinyl ether}]_0 = 0.76–0.80$ M; $[HCl]_0 = 4.0$ mM; $[Et_2O]_0 = 0.96$ M (this is corresponding to 1/9 volume of solvent). All systems induced homogenous living polymerizations, whereas polymerization rates depended on monomer structures, as reported previously [6]. Irrespective of different structures of alkyl chain, all monomers were consumed quantitatively without an induction period to give quantitative conversion within 45 min (CHVE: $M_n = 17{,}400$, $M_w/M_n = 1.33$ at conv. = 80%; TBVE [16], NBVE [6], and IBVE [6]: $M_w/M_n \leq 1.15$ at conv. >85%).

Next, the polymerizations of vinyl ethers with electron-donating groups in the pendant (category B) were investigated under the same initiator condition as for the alkyl vinyl ether in toluene at 0 °C: $[\text{monomer}]_0 = 0.8$ M; $[HCl]_0 = 4.0$ mM; $[Et_2O]_0 = 0.96$ M. CEVE has a chlorine moiety and MOVE has an ether group (methoxy group) in the pendant. Figure 2 shows time-conversion curves for the polymerizations. For CEVE, the polymerization proceeded smoothly without an induction period and was completed around 50 h. However, different results were obtained for MOVE. This may be due to interaction between $H^+$ and electron donating moiety at the initiation stage. Figure 3a shows the relationship between monomer conversion and $M_n$ or the $M_w/M_n$ ratio of the polymers for poly(CEVE) and poly(MOVE). For the both polymerizations, without a low conversion range, $M_n$ increased in direct proportion to the monomer conversion, and the MWDs of the resulting polymers were quite narrow for poly(CEVE) ($M_w/M_n = 1.16$ at conv. 100%) and were relatively narrow for poly(MOVE) ($M_w/M_n = 1.31$ at conv. 81%) as shown in Fig. 3b.

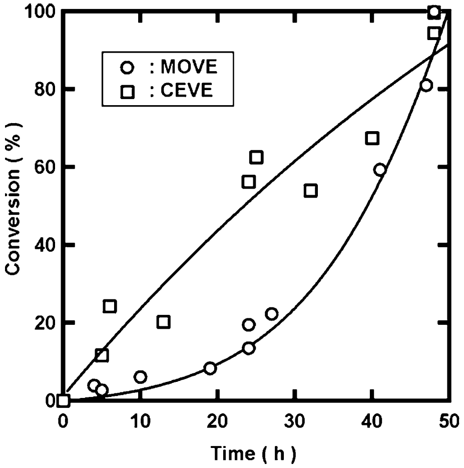


**Fig. 2** Time-conversion curves for the polymerization of CEVE and MOVE by $HCl \cdot Et_2O$ in toluene with 1/9 volume of $Et_2O$ at 0 °C: $[HCl]_0 = 4.0$ mM, $[Et_2O]_0 = 0.96$ M, $[\text{monomer}]_0 = 0.80$ M

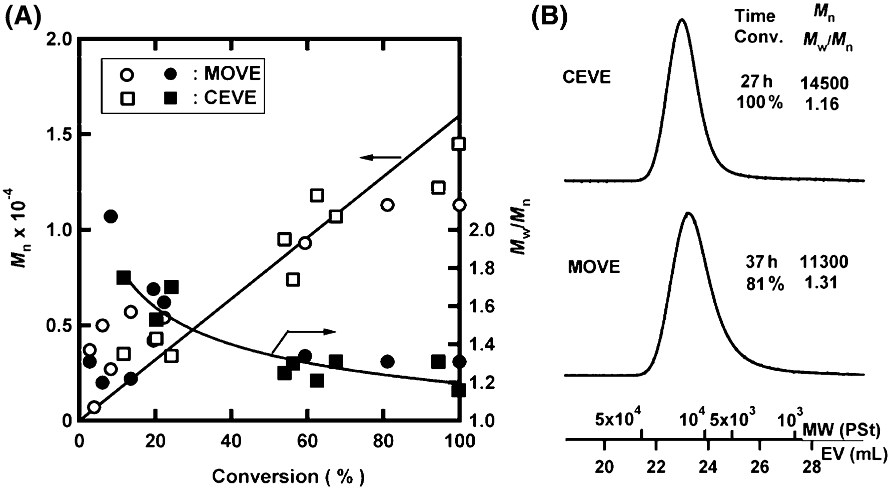


**Fig. 3** **a** $M_n$ and $M_w/M_n$ for the polymerization of CEVE and MOVE by HCl·Et$_2$O in toluene with 1/9 volume of Et$_2$O at 0 °C: $[HCl]_0 = 4.0$ mM, $[Et_2O]_0 = 0.96$ M, $[monomer]_0 = 0.80$ M. **b** The MWD curves for PCEVE and PMOVE

## Polymerization for vinyl ethers in category C

On the basis of polymerization for MOVE, the polymerizations of vinyl ethers with bulky group next to the electron-donating substituent in the pendant (category C) were performed under the same condition in toluene at 0 °C with HCl·Et$_2$O. These monomers have the same ether oxygen but different spacer lengths. Alternatively, degrees of interaction between $H^+$ and ether oxygen in the pendant are smaller than that of MOVE due to bulky *tert*-butyldimethylsilyloxy group, which interactions should be stronger with increasing the length of spacer alkyl groups. Figure 4 shows time-conversion curves for these polymerizations. In a similar fashion for MOVE, all polymerizations have an induction period during 30 min. However, after the induction period, smooth polymerization occurred and all monomers were consumed quantitatively to give quantitative conversion within 2 h. No effects of steric hindrance on polymerization were observed because the induction period was still present in all monomers in category C. However, the polymerization rate decreased with the length of the alkyl chain between vinyl ether and *tert*-butyldimethylsilyloxy group. This is an inverse result from the polymerization using metal Lewis acids such as $Et_{1.5}AlCl_{1.5}$ [12], may be unique for the HCl·Et$_2$O polymerization system. Figure 5a shows the relationship between monomer conversion and $M_n$ or the $M_w/M_n$ ratio of the polymers. Although all monomers polymerized with induction period, $M_n$ increased in direct proportion to the monomer conversion. The MWDs of the resulting polymers were monodispersal during polymerization and relatively narrow as shown in Fig. 5b. These results for monomers suggested that HCl·Et$_2$O system is applicable for the polymerization of various vinyl ethers as shown in Fig. 1, however, the structure around electron-donating groups such as isolated ether oxygen contributes the polymerizations rate and induction period.

## Effects of structure of ether dissolving HCl

In order to investigate the effects of structure of ether dissolving HCl on polymerization system, we have examined a series of oxygen based nucleophiles (ethers) such as *n*$Bu_2O$, *i*$Pr_2O$, $Et_2O$, CPME, DO, and THF. Herein, only IBVE was used as a monomer for comparisons. In Fig. 6, these ether structures are represented as the most stable computer-generated models calculated by MM2 and $pK_a$ values [17] are also shown.

The previous research [6] revealed that $Et_2O$ could control both $M_n$ and $M_w/M_n$ as increasing the concentration of $Et_2O$ though the polymerization rate was slow. Alternatively, $Et_2O$ solely as a solvent without toluene and hexane can be polymerized in living fashion. On the basis of these results, the HCl·ether induced living cationic polymerizations of IBVE which were demonstrated using various ether concentrations and temperatures. Figure 7 shows the polymerization results utilizing *n*$Bu_2O$, *i*$Pr_2O$, and $Et_2O$ using HCl at 0 °C ($[IBVE]_0 = 0.76$ M, $[HCl]_0 = 4.0$ mM) in conjugation with HCl initiating system. Figure 7a shows time-conversion curves, Fig. 7b indicates the relationship between monomer conversion and $M_n$ or the $M_w/M_n$ ratio of the polymers, Fig. 7c summarizes all MWDs. Each polymerization proceeded smoothly in living fashion. For example, *n*$Bu_2O$ has the lowest $pK_a$ value as shown in Fig. 6. In spite of the lowest $pK_a$ value, polymerization proceeded without induction period as well as the case of $Et_2O$ and completed about 20 min, though *n*$Bu_2O$ was used as a solvent. The $M_w/M_n$ of the final polymer has relatively narrow MWD, which is slightly larger than that of $Et_2O$ ($M_w/M_n = 1.26$ at conv. 95.9%). In using *i*$Pr_2O$ as an added base with metal Lewis acid for polymerization of IBVE, non-living polymerization usually occurred [18]. Thus, this is a small effect as an added base for living cationic polymerization. However, the application of the *i*$Pr_2O$ provided "living" polymerization (with slightly broad MWDs) as shown in Fig. 7b and c. The $M_n$ increased in

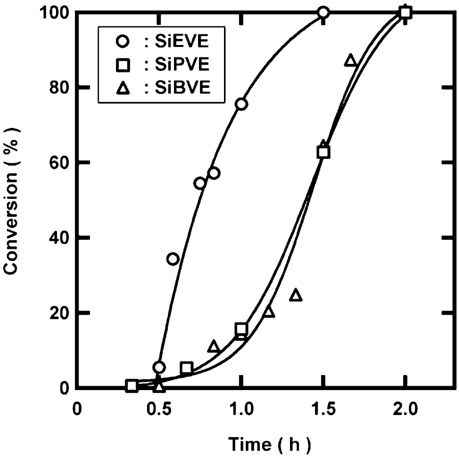


**Fig. 4** Time-conversion curves for the polymerization of SiEVE, SiPVE, and SiBVE by HCl·$Et_2O$ in toluene with 1/9 volume of $Et_2O$ at 0 °C: $[HCl]_0 = 4.0$ mM, $[Et_2O]_0 = 0.96$ M, $[monomer]_0 = 0.80$ M

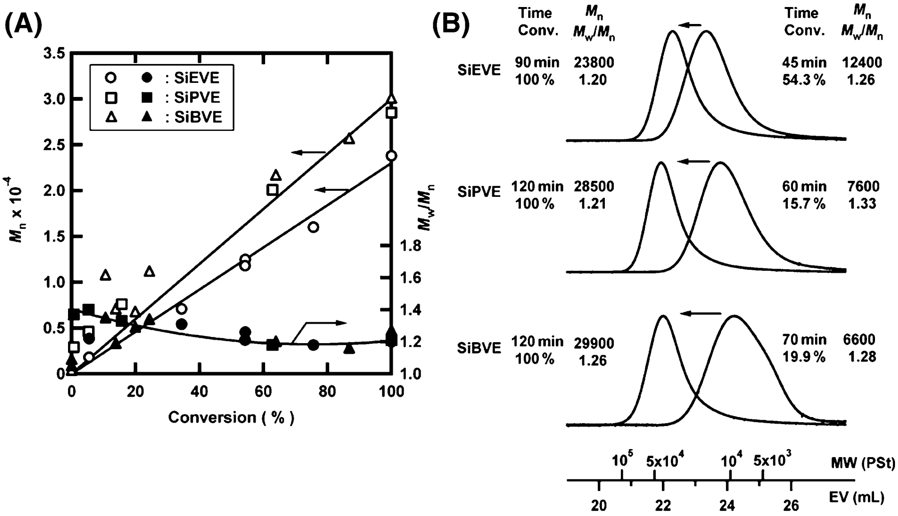


**Fig. 5** **a** $M_n$ and $M_w/M_n$ for the polymerization of SiEVE, SiPVE, and SiBVE by HCl·Et$_2$O in toluene with 1/9 volume of Et$_2$O at 0 °C: $[HCl]_0 = 4.0$ mM, $[Et_2O]_0 = 0.96$ M, $[monomer]_0 = 0.80$ M. **b** The MWD curves for the obtained polymers at the 100% and lower conversion

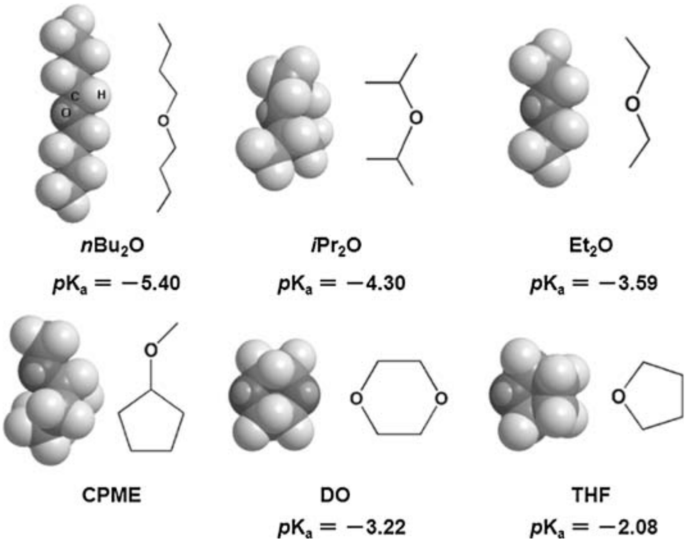


**Fig. 6** Ether structures as the most stable computer-generated model (MM2) and p$K_a$ values

direct proportion to the monomer conversion. The living polymerization is characteristic for HCl·ether inducing living cationic polymerizations and may be occurred due to fast dissociation of HCl, because oxygen atom is protruding from ethers as shown in Fig. 6.

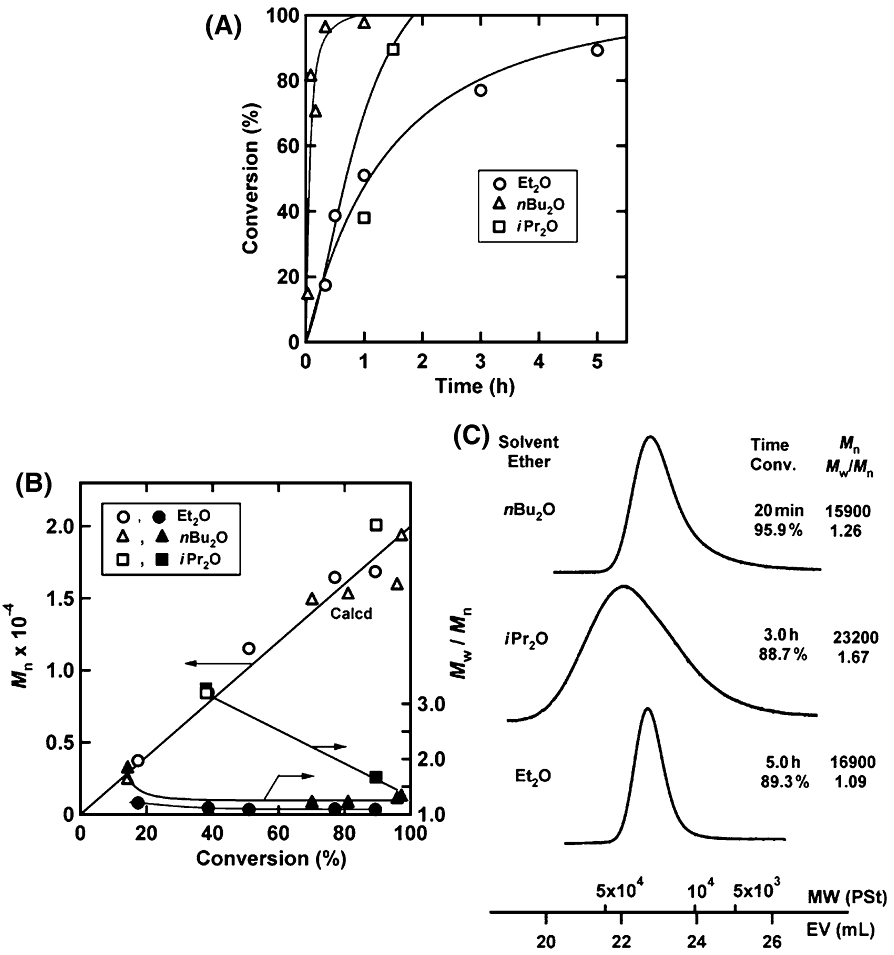


**Fig. 7** **a** Time-conversion curves, **b** $M_n$ and $M_w/M_n$ for the polymerization of IBVE by HCl in various ether ($Et_2O$, $n\text{Bu}_2O$, and $i\text{Pr}_2O$) at 0 °C: $[HCl]_0 = 4.0$ mM, $[IBVE]_0 = 0.76$ M. **c** The MWD curves for the obtained polymers at the highest conversion

For CPME, DO, and THF, cationic polymerization was demonstrated at 0 or 30 °C in consideration of their melting points. In the case of HCl·CPME, polymerization was carried out under various conditions such as $[CPME]_0 = 9.44$ mM, 0.21 M and as a solvent at 0 or 30 °C, even though could not be controlled perfectly at the region of low conversion. Figure 8 shows the polymerization results complying with following conditions: $[IBVE]_0 = 0.76$ M, $[HCl]_0 = 4.0$ mM, $[CPME]_0 = 0.21$ M in toluene at 0 °C. As shown in Fig. 8b, initial polymerization could not be controlled. The cause may be due to non-perfect dissociation of HCl in CPME, because CPME has a steric hinderance of cyclopentyl moiety next to oxygen atom of the ether, which can be explained using the structure shown in Fig. 6. In the case of HCl·DO and HCl·THF, living cationic polymerization has been achieved at a slower rate than that of $Et_2O$ because of their high p$K_a$ values. These results for additive ethers suggested that cationic initiation can be successfully achieved using ether effectively dissociating HCl, especially symmetrical ether. Furthermore, propagation can be successfully occurred in living fashion.

## Polymer structure

The structure of poly(IBVE) obtained using HCl·ether was examined by $^1$H NMR and $^{13}$C NMR. From the $^1$H NMR results (not shown) for all polymerizations of IBVE, we concluded that the end group of poly(IBVE) have been transformed from

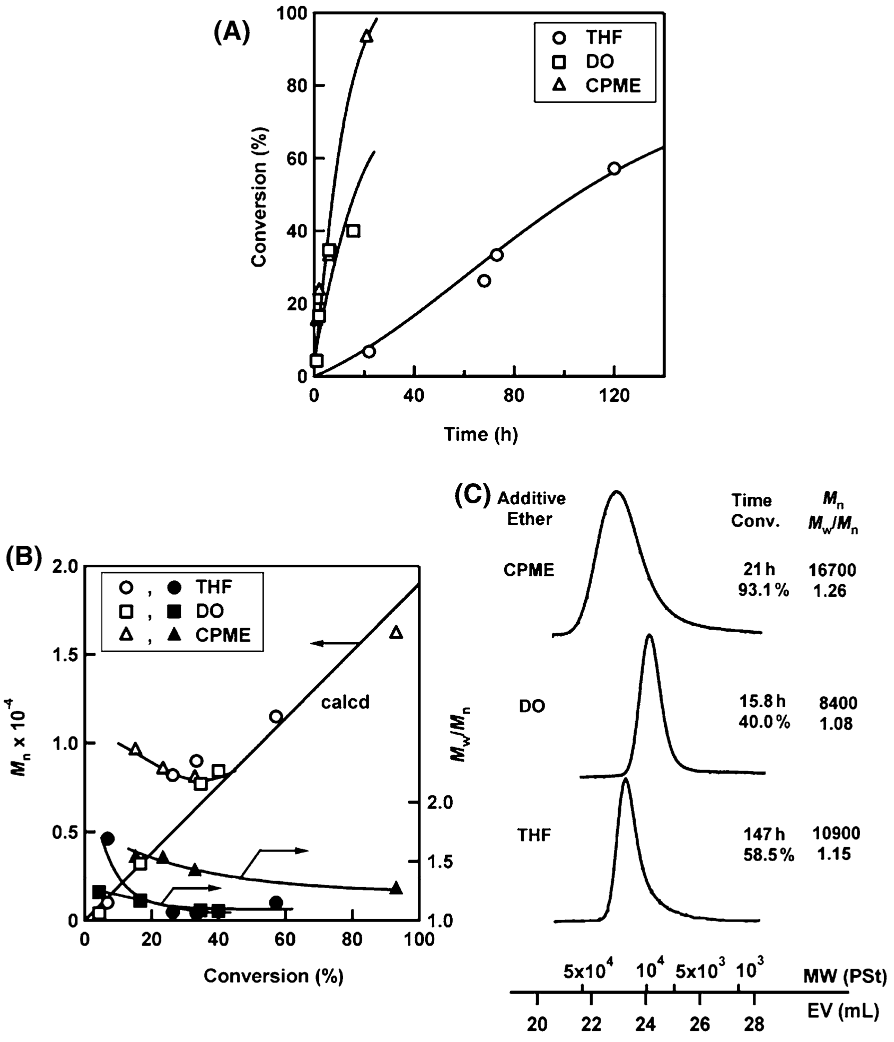


**Fig. 8** **a** Time-conversion curves, **b** $M_n$ and $M_w/M_n$ for the polymerization of IBVE by HCl·ether in hexane at 0 °C for CPME or 30 °C for THF and DO: $[HCl]_0 = 4.0$ mM, $[IBVE]_0 = 0.76$ M, $[ether]_0 = 0.21$ M. **c** The MWD curves for the obtained polymers at the highest conversion

carbocation or –Cl from dormant to $-OCH_3$ after quenching the polymerization by methanol. From $^{13}C$ NMR, the steric structure (dyad) of various poly(vinyl ether)s were examined, which were obtained by $HCl\cdot Et_2O$ ($[Et_2O]_0 = 0.96$ M). These structures were relatively meso rich; the meso/raceme ratios were 63/37, 64/36, 58/42, 68/32, and 68/32, for poly(IBVE), poly(TBVE), poly(SiEVE), poly(SiPVE), and poly(SiBVE), respectively (conv. $\geq$ 89.3%, samples obtained at the highest conversion). These results were almost the same as that of usual cationic polymerization [12, 19].

## Conclusion

We were able to investigate the effects of the monomer and ether structures on HCl·ether induced polymerization system. The monomer structure around electron-donating groups in the pendant of monomer affected the polymerization rate and induction period. The initiation reactions can be successfully achieved using ether effectively dissociating HCl, especially symmetrical ether. The HCl·ether inducing system can be widely applied for polymerization of various vinyl ethers in living fashion.

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## References

1. Jagur-Grodzinski J (ed) (2005) Living and contorolled polymerization: synthesis, characterization and properties of the respective polymers and copolymers. Nova, New York
2. Aoshima S, Kanaoka S (2008) Synthesis of stimuli-responsive polymers by living polymerization: poly(*N*-Isopropylacrylamide) and poly(vinyl ether)s. Adv Polym Sci 210:169–208
3. Lohmeijer BGG, Pratt RC, Leibfarth F, Logan JW, Long DA, Dove AP, Nederberg F, Choi J, Wade C, Waymouth RM, Hedrick JL (2006) Guanidine and amidine organocatalysts for ring-opening polymerization of cyclic esters. Macromolecules 39:8574–8583
4. Dove AP (2008) Controlled ring-opening polymerisation of cyclic esters: polymer blocks in self-assembled nanostructures. Chem Commun 48:6446–6470
5. Lee H, Zeng F, Dunne M, Allen C (2005) Methoxy poly(ethylene glycol)-*block*-poly($\delta$-valerolactone) copolymer micelles for formulation of hydrophobic drugs. Biomacromolecules 6:3119–3128
6. Sugihara S, Tanabe Y, Kitagawa M, Ikeda I (2008) Facile metal-free living cationic polymerization of various vinyl ethers by hydrogen chloride with ether. J Polym Sci Part A Polym Chem 46:1913–1918
7. Sawamoto M, Fujimori J, Higashimura T (1987) Living cationic polymerization of *N*-vinylcarbazole initiated by hydrogen iodide. Macromolecules 20:916–920
8. Sawamoto M (1991) Modern cationic vinyl polymerization. Prog Polym Sci 16:111–172
9. Nuyken O, Kroner H (1990) Living cationic polymerization of isobutyl vinyl ether, 1. Initiation by hydrogen iodide/tetraalkylammonium salts. Macromol Chem 191:1–16
10. Cho CG, Feit BA, Webster OW (1990) Cationic polymerization of isobutyl vinyl ether: livingness enhancement by dialkyl sulfides. Macromolecules 23:1918–1923
11. Aoshima S, Kobayashi E (1995) Living cationic polymerization of vinyl ethers in the presence of added bases: recent advances. Macromol Symp 95:91–102
12. Sugihara S, Hashimoto K, Matsumoto Y, Kanaoka S, Aoshima S (2003) Thermosensitive polyalcohols: synthesis via living cationic polymerization of vinyl ethers with a silyloxy group. J Polym Sci Part A Polym Chem 41:3300–3312

13. Zhou Y, Faust R (2005) Syntheses and characterization of poly(cyclohexyl vinyl ether-*stat*-vinyl alcohol)-*b*-polyisobutylene-*b*-poly(cyclohexyl vinyl ether-*stat*-vinyl alcohol) triblock copolymers and their Application as coatings to deliver paclitaxel from coronary stents. Macromolecules 38:8183–8191
14. Ohgi T, Sato T (1993) Preparation of highly isotactic poly(vinyl alcohol). Macromolecules 26:559–560
15. Sugihara S, Ohashi M, Ikeda I (2007) Synthesis of fine hydrogel microspheres and capsules from thermoresponsive coacervate. Macromolecules 40:3394–3401
16. Zaleska IM, Kitagawa M, Sugihara S, Ikeda I (2009) Synthesis of biocompatible and biodegradable block copolymers of polyvinyl alcohol-*block*-poly(ε-caprolactone) using metal-free living cationic polymerization. J Polym Sci Part A Polym Chem (in press)
17. Arnett EM (1963) Quantitative comparisons of weak organic bases. In: Cohen SG, Streitwieser A Jr, Taft RW (eds) Progress in physical organic chemistry, vol. 1. Interscience, New York, pp 223–403
18. Kishimoto Y, Aoshima S, Higashimura T (1989) Living cationic polymerization of vinyl monomers by organoaluminum halides. 4. Polymerization of isobutyl vinyl ether by ethylaluminum dichloride ($EtAlCl_2$) in the presence of ether additives. Macromolecules 22:3877–3882
19. Ouchi M, Kamigaito M, Sawamoto M (2001) Stereoregulation in cationic polymerization by designed Lewis acids. II. Effects of alkyl vinyl ether structure. J Polym Sci Part A Polym Chem 39:1060–1066