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A User-friendly Living Cationic Polymerization: Degenerative Chain-transfer Polymerization of Vinyl Ethers by Simply Using Mixtures of Weak and Superstrong Protonic Acids

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Abstract Mixtures of a weak protonic acid and a trace amount of superstrong protonic acid were used for the simple control of the cationic polymerization of vinyl ethers *via* a degenerative chain-transfer mechanism, in which the former acid works as a precursor of the chain transfer agent (CTA) or the dormant species and the latter works as a source of the cationic propagating species. The addition of mixtures of phosphoric acid dibutyl ester ((*n*-BuO)₂PO₂H) or 1-octanethiol (*n*-C₈H₁₇SH) and a trace amount of trifluoromethanesulfonic acid (TfOH) to a solution of isobutyl vinyl ether (IBVE) at −78 °C resulted in polymers with controlled molecular weights, which were basically determined by the feed ratio of IBVE to the weak protonic acid, and narrow molecular weight distributions ($M_w/M_n \approx 1.1$). These results were almost the same as those obtained using their prepared adducts of IBVE as CTAs in the presence of a trace amount of TfOH under similar conditions. Methanesulfonic acid (CH₃SO₃H), whose adduct of IBVE has not been isolated due to instability, was similarly used in conjunction with trace TfOH to result in controlled molecular weights but slightly broader MWDs ($M_w/M_n = 1.2$ – 1.8). These results indicate that the sulfoxonium ion is also an effective intermediate in the cationic DT polymerization in addition to the phosphonium and sulfonium intermediates derived from (*n*-BuO)₂PO₂H and *n*-C₈H₁₇SH, respectively. The simple living cationic polymerization was thus achieved by using a combination of a weak protonic acid and a trace amount of TfOH, which are both easily available, low cost, free from metal, and easy to handle, without need for preparation of the initiator.

Keywords Living cationic polymerization; Degenerative chain transfer; RAFT polymerization; Metal free; Vinyl ether

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INTRODUCTION

With ongoing development, living polymerization technologies are now indispensable for the designable construction of various functional polymer materials.^[1] On the other hand, however, a user-friendly living polymerization method based on simple techniques as well as easily available low-cost reagents is greatly desired.

Living cationic polymerization was first reported in 1984 by Higashimura and Sawamoto using a combination of dehydrated hydriodic acid, *i.e.*, anhydrous hydrogen iodide (HI) and molecular iodine (I₂) for vinyl ether.^[2] Here, HI serves as the initiator that results in a polymer chain *via* formation of the dormant C—I bond upon *in situ* electrophilic addition to the monomer, while I₂ serves as the Lewis acid activator that electrophilically activates the C—I bond to reversibly generate the growing carbocationic species. Around the same time, in 1986, Kennedy and Faust reported another

living cationic polymerization using *tert*-alkyl or cumyl acetate (R—OAc) as the initiator and BCl₃ as the activator for isobutylene.^[3]

Since these epoch-making discoveries, living cationic polymerizations have been widely developed for various cationically polymerizable monomers, generally with a combination of a weak protonic acid or an organic halide or ester as an initiator and a metal halide as an activator, and if necessary in the presence of an additive such as a weak Lewis basic compound and an ammonium salt of a halide anion.^[4–9] Living cationic polymerization based on initiator/activator systems is thus established for a wide range of monomers and is highly reliable in terms of the controllability, but it often requires additional processes for the synthesis of the initiator, careful handling of moisture-sensitive metal halides, removal of metal residues from the resulting polymers, use of costly reagents, and complicated procedures, among other challenges.

Recently, we developed another strategy for controlling cationic polymerization *via* degenerative chain-transfer (DT) or reversible chain-transfer mechanisms,^[10–14] which is widely used for controlling radical polymerization, such as in reversible addition-fragmentation chain transfer (RAFT)

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polymerization,^[15–17] iodine transfer radical polymerization (ITP),^[18] tellurium-mediated radical polymerization (TERP),^[19] and organometallic-mediated radical polymerization (OMRP).^[20–22] This living cationic polymerization based on the DT mechanism is attained *via* a combination of a small amount of superstrong protonic acid that acts as a cationogen to generate the growing carbocation *via* electrophilic addition to the monomer and a chain-transfer agent that reversibly reacts with the carbocationic species *via* the transiently stable intermediate to regenerate the dormant polymer chain end. Cationic DT polymerization has now been applied for precision polymer synthesis *via* combination with other controlled polymerizations.^[13,14,23–37] Thus far, the typical initiator is triflic acid (TfOH: CF₃SO₃H), while the chain-transfer agents (CTA) include thiocarbonylthio compounds (R–SC(S)Z),^[10] thioethers (R–SZ),^[11] and phosphoric or phosphinic acid esters (R–OP(O)Z₂).^[12] Therefore, cationic DT or RAFT polymerization can predominantly be free from metals, unlike the former living cationic polymerizations based on the Lewis-acid-catalyzed activation of the dormant species. However, CTA, which bears the dormant covalent bond, has thus far been prepared prior to the polymerization.

In this study, we developed a more facile method for the metal-free living cationic DT polymerization of vinyl ethers by simply using a combination of weak and superstrong protonic acids, where the former may generate its adduct of the monomer as a CTA *via in situ* electrophilic addition to the monomer and the proton of the latter adds to the monomer to generate the propagating carbocationic species as a cationo-

gen (Scheme 1). Namely, the roles of the two protonic acids are different. The weak protonic acids used could include phosphoric, sulfonic, and carboxylic acids, alcohol, and thiol, which are all easily available, low cost, and easy to handle, while a trace amount of triflic acid was employed as a superstrong protonic acid to serve as the cationogen.

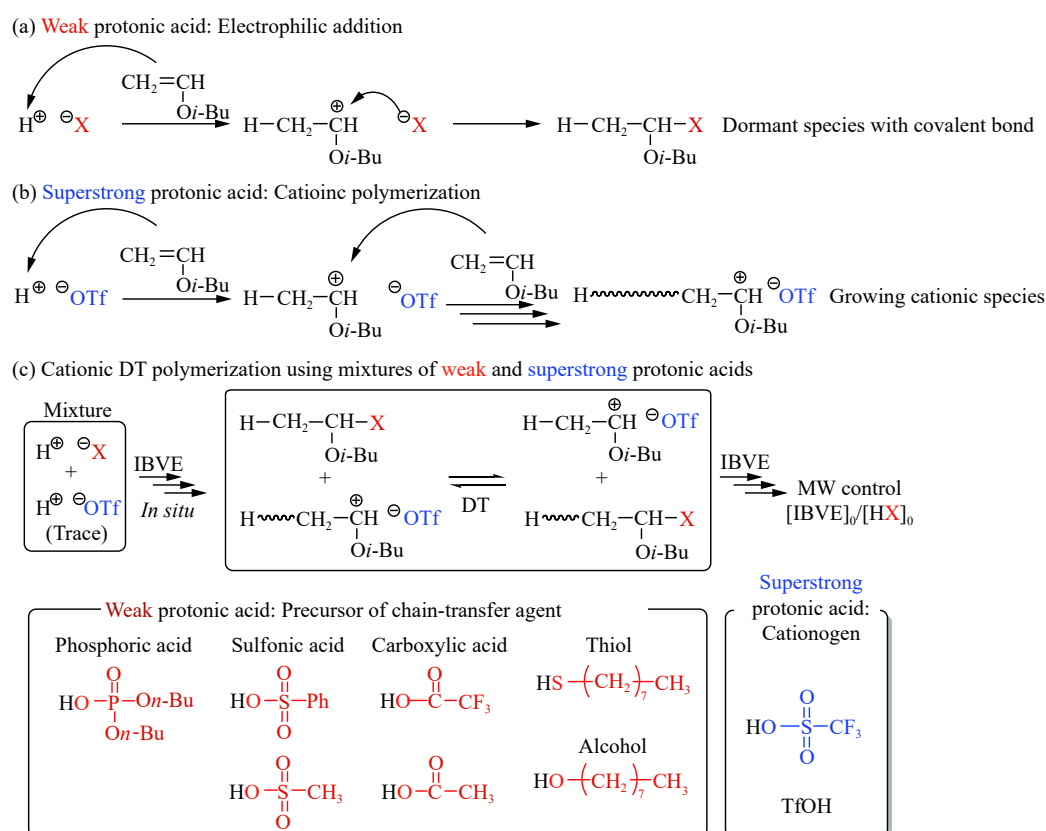
EXPERIMENTAL

Materials

Isobutyl vinyl ether (IBVE) (TCI, 95%) was distilled over calcium hydride under reduced pressure before use. Trifluoromethanesulfonic (triflic) acid (TfOH, TCI, > 98.0%), phosphoric acid dibutyl ester or dibutyl phosphate ((*n*-BuO)₂PO₂H, TCI, > 97.0%), benzenesulfonic acid anhydrous (PhSO₃H, TCI, > 98.0%), methanesulfonic acid (CH₃SO₃H, TCI, > 99.0%), trifluoroacetic acid (CF₃CO₂H, Aldrich, > 99.0%), and acetic acid (CH₃CO₂H, Aldrich, > 99.99%) were used as received. 1-Octanethiol (*n*-C₈H₁₇SH, TCI, > 98.0%) and 1-octanol (*n*-C₈H₁₇OH, TCI, > 99.0%) were used after azeotropic drying with toluene. Toluene (KANTO, > 99.5%; H₂O < 10 ppm), *n*-hexane (KANTO, > 96%; H₂O < 10 ppm), diethyl ether (KANTO, > 99.5%; H₂O < 50 ppm), and dichloromethane (KANTO, > 99.5%; H₂O < 0.005%) were dried and deoxygenized by passage through a Glass Contour Systems column before use.

Cationic Polymerization Using Two Different Protonic Acids

The cationic polymerization of IBVE was carried out by the



Scheme 1 Roles of weak and strong protonic acids for living cationic polymerization of isobutyl vinyl ether (IBVE) *via* degenerative chain-transfer (DT) mechanism by simply using mixtures of the two acids

syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example of the reaction using $(n\text{-BuO})_2\text{PO}_2\text{H}$ and TfOH is given below. The polymerization reaction was initiated by the addition of mixtures of $(n\text{-BuO})_2\text{PO}_2\text{H}$ (0.05 mmol) and TfOH (2.5 mol) in Et_2O (0.50 mL solution) *via* dry syringe into the monomer solution (4.50 mL) containing IBVE (0.33 mL, 1.53 mmol) in an $n\text{-hexane}/\text{CH}_2\text{Cl}_2$ mixture (80/10, *V/V*) at -78°C . After 24 h, the polymerization was terminated with methanol (2.0 mL) containing a small amount of ammonia. The quenched reaction mixture was washed with aqueous sodium hydrogen carbonate solution to remove the residual TfOH and then with distilled water. The organic layer was evaporated to dryness under reduced pressure and vacuum-dried to give the product polymers ($M_n = 3100$, $M_w/M_n = 1.09$). The monomer conversion was determined by gravimetry (0.25 g, > 99%).

Measurements

^1H -NMR spectra were recorded on a JEOL ECS-400 spectrometer operating at 400 MHz. The number-average molecular weight (M_n) and the molecular weight distribution (MWD, M_w/M_n) of the polymers were determined by size-exclusion chromatography (SEC) in THF at 40°C on two polystyrene gel columns [TSKgel MultiporeHXL-M (7.8 mm i.d. $\times$ 30 cm)] connected to a JASCO PU-2080 precision pump and JASCO RI-2031 detector. The columns were calibrated against 10 standard polystyrene samples (Agilent Technologies; $M_p = 575\text{--}2783000$, $M_w/M_n = 1.02\text{--}1.23$).

RESULTS AND DISCUSSION

Living Cationic Polymerization Using Mixtures of $(n\text{-BuO})_2\text{PO}_2\text{H}$ and TfOH

The cationic polymerization of isobutyl vinyl ether (IBVE) was first examined using phosphoric acid dibutyl ester ($(n\text{-BuO})_2\text{PO}_2\text{H}$) as a weak protonic acid for the precursor of CTA in conjunction with a trace amount (5 mol% of $(n\text{-BuO})_2\text{PO}_2\text{H}$) of TfOH as a cationogen ($[\text{IBVE}]_0/[(n\text{-BuO})_2\text{PO}_2\text{H}]_0/[\text{TfOH}]_0 = 500/10/0.50 \text{ mmol}\cdot\text{L}^{-1}$) in the solvent mixture of $n\text{-hexane}/\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (80/10/10, *V/V/V*) at -78°C . All the polymerizations were conducted by simply adding mixtures of the two protonic acids in Et_2O , which was used to make the solution of TfOH homogeneous, to IBVE in $n\text{-hexane}/\text{CH}_2\text{Cl}_2$ (8/1) at -78°C . As preliminarily reported

for another phosphoric acid diester ($(\text{PhO})_2\text{PO}_2\text{H}$),^[12] the polymerization proceeded with an induction period and was completed within 1 h. However, to further simplify the procedures and analyses, all the polymerizations were run for 24 h to ensure that the monomer conversion was as high as possible. Therefore, no detailed kinetic experiments were conducted in this study.

The combination of $(n\text{-BuO})_2\text{PO}_2\text{H}$ and TfOH resulted in polymers with controlled molecular weights upon the simple addition of the mixture and quenching with methanol after 24 h (entry 1 in Table 1). Fig. 1 compares the SEC curves of the polymers obtained by the specified method in this study (Fig. 1a) and those obtained by using the presynthesized adduct of $(n\text{-BuO})_2\text{PO}_2\text{H}$ and IBVE for cationic RAFT polymerization under the same conditions (Fig. 1b).^[12] There were almost no differences in the SEC curves of the obtained polymers; the MWDs were very narrow ($M_w/M_n < 1.1$), and M_n of the obtained polymers agreed well with the approximate theoretical value assuming that one molecule of $(n\text{-BuO})_2\text{PO}_2\text{H}$ generates one polymer chain (Figs. 2a and 2b). These results indicate that the simple addition of mixtures of $(n\text{-BuO})_2\text{PO}_2\text{H}$ and TfOH ($[(n\text{-BuO})_2\text{PO}_2\text{H}]_0/[\text{TfOH}]_0 = 20/1$) enables the controlled cationic polymerization of IBVE, as in the case of using the presynthesized CTA in the cationic polymerization.^[12]

The obtained polymer was then analyzed by ^1H -NMR spectroscopy (Fig. 3A). The obtained polymers showed large absorptions of repeating IBVE units (a–e) and small absorptions that can be attributed to the methyl group (a'; 1.1 ppm) at the α -end initiated from protonic acid and the methine proton (b'; 4.6 ppm) of the ω -end acetal generated upon quenching the polymerization with methanol.^[12] Both the dormant phosphoric chain end and the cationic propagating terminal reacted with methanol to be changed into the acetal chain end as obtained. The molecular weight ($M_{n,\text{NMR}}$) calculated from the integration ratio of the ω -terminal methine (b') to the repeating monomer unit (e) was close to that determined by SEC ($M_{n,\text{SEC}}$).

These results indicate that the simple mixing of $(n\text{-BuO})_2\text{PO}_2\text{H}$ as a precursor of CTA and TfOH as a cationogen, which are both commercially available, low cost, and easily handle, and of course free from metal, induced the cationic DT polymerization of IBVE *via in situ* formation of the CTA from $(n\text{-BuO})_2\text{PO}_2\text{H}$, followed by cationic propagation

Table 1 Cationic polymerization of IBVE using mixtures of weak (HX) and superstrong (TfOH) protonic acids ^a

Entry	HX	$[\text{M}]_0/[\text{HX}]_0$	Conv. ^b (%)	$M_{n,\text{SEC}}$ ^c	$M_{n,\text{Calcd}}$ ^d	M_w/M_n ^c
1	$(n\text{-BuO})_2\text{PO}_2\text{H}$	50	> 99	5000	5000	1.09
2	$(n\text{-BuO})_2\text{PO}_2\text{H}$	25	> 99	3100	2500	1.09
3	$(n\text{-BuO})_2\text{PO}_2\text{H}$	100	> 99	10500	10000	1.08
4	PhSO_3H	50	> 99	5600	5000	2.51
5	$\text{CH}_3\text{SO}_3\text{H}$	50	97	5500	4800	1.51
6	$\text{CH}_3\text{SO}_3\text{H}$	25	> 99	3000	2500	1.19
7	$\text{CH}_3\text{SO}_3\text{H}$	100	> 99	11500	11500	1.93
8	$\text{CF}_3\text{CO}_2\text{H}$	50	97	16900	4900	3.36
9	$\text{CH}_3\text{CO}_2\text{H}$	50	> 99	11900	4800	2.60
10	$n\text{-C}_8\text{H}_{17}\text{SH}$	50	> 99	5600	5000	1.12
11	$n\text{-C}_8\text{H}_{17}\text{OH}$	50	> 99	10800	5000	2.83

^a Conditions: $[\text{IBVE}]_0/[\text{HX}]_0/[\text{TfOH}]_0 = 500/10/0.50 \text{ mmol}\cdot\text{L}^{-1}$ in $n\text{-hexane}/\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (80/10/10, *V/V/V*) at -78°C for 24 h; ^b Determined by a gravimetric method; ^c The M_n and M_w/M_n were determined by SEC; ^d $M_{n,\text{Calcd}} = \text{MW}(\text{IBVE}) \times ([\text{IBVE}]_0/[\text{HX}]_0) \times \text{Conv.} + \text{MW}(\text{chain end})$

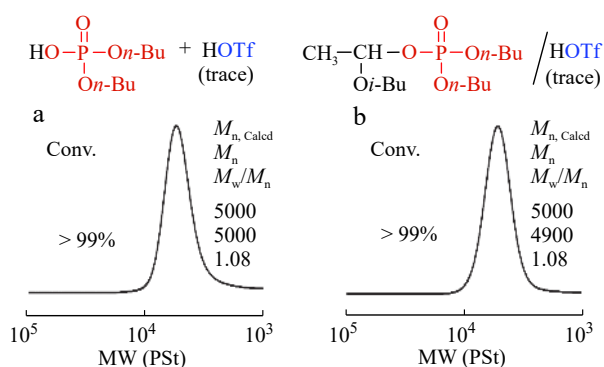


Fig. 1 SEC curves of polymers obtained by using mixtures of (*n*-BuO)₂PO₂H (a) or its adduct of IBVE (b) with a trace amount of TfOH for cationic polymerization of IBVE in *n*-hexane/CH₂Cl₂/Et₂O (80/10/10, *V/V/V*) at -78°C : [IBVE]₀/[(*n*-BuO)₂PO₂H]₀/[TfOH]₀ = 500/10/0.50 mmol·L⁻¹ in *n*-hexane/CH₂Cl₂/Et₂O (80/10/10, *V/V/V*) at -78°C

triggered by TfOH, to result in well-defined poly(IBVE) with controlled molecular weights, as in the case of using the presynthesized CTA in conjunction with TfOH.^[12]

Polymerization Using Sulfonic and Carboxylic Acids in Conjunction with TfOH

As it was proven that (*n*-BuO)₂PO₂H itself was sufficiently effective in place of the prepared CTA for the living cationic polymerization of IBVE in conjunction with a trace amount of TfOH, other relatively weak protonic acids, such as sulfonic (PhSO₃H and CH₃SO₃H) and carboxylic (CF₃CO₂H and CH₃CO₂H) acids, were similarly employed under the same conditions. Whereas adducts of the carboxylic acids (CF₃CO₂H and CH₃CO₂H) and IBVE have been prepared^[38,39] and used as possible CTAs in the cationic RAFT polymerization of IBVE,^[10] those of sulfonic acids (PhSO₃H and CH₃SO₃H) are too unstable to be isolated and have not been used as CTAs.

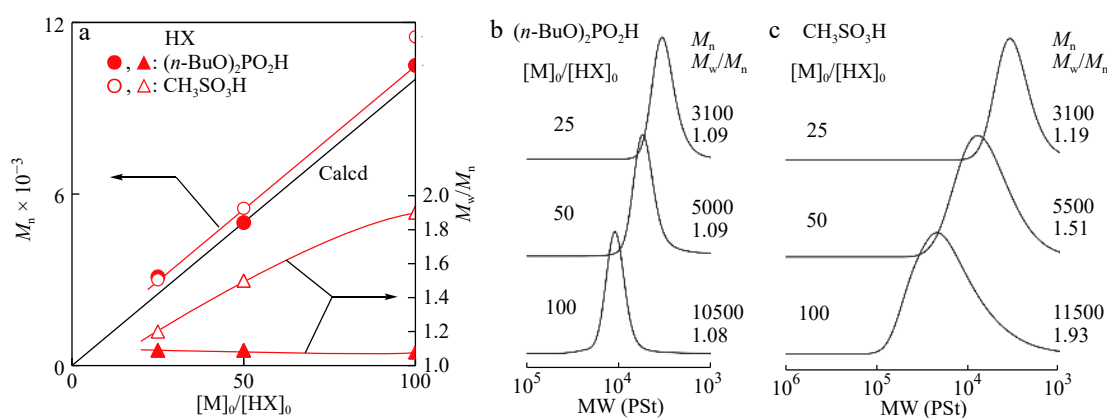


Fig. 2 (a) M_n and M_w/M_n , SEC curves of polymers obtained by using mixtures of (b) (*n*-BuO)₂PO₂H or (c) CH₃SO₃H with a trace amount of TfOH for cationic polymerization of IBVE at varying the feed ratio of IBVE to HX in *n*-hexane/CH₂Cl₂/Et₂O (80/10/10, *V/V/V*) at -78°C : [IBVE]₀/[HX]₀/[TfOH]₀ = 500/5, 10, or 20/0.50 mmol·L⁻¹

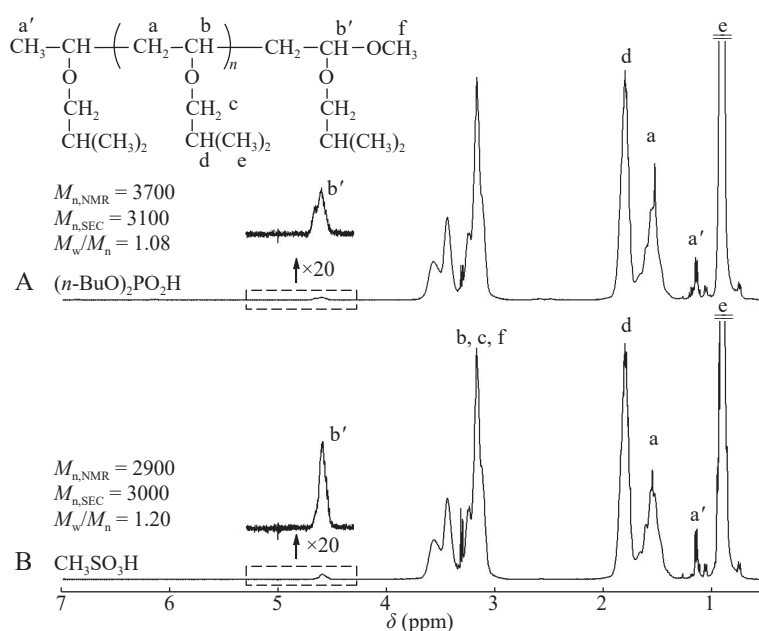


Fig. 3 ¹H-NMR spectra (in CDCl₃ at 55°C) of polymers obtained by using mixtures of (A) (*n*-BuO)₂PO₂H or (B) CH₃SO₃H with a trace amount of TfOH for cationic polymerization of IBVE in *n*-hexane/CH₂Cl₂/Et₂O (80/10/10, *V/V/V*) at -78°C upon quenching the polymerization with methanol: [IBVE]₀/[HX]₀/[TfOH]₀ = 500/10/0.50 mmol·L⁻¹

For benzenesulfonic and methanesulfonic acids, M_n values of the obtained polymers were both close to the calculated values, assuming that one molecule of PhSO_3H or $\text{CH}_3\text{SO}_3\text{H}$ generates one polymer chain (entries 4 and 5 in Table 1). As also shown in Fig. 4, the MWD of the polymers obtained with $\text{CH}_3\text{SO}_3\text{H}$ was relatively narrow ($M_w/M_n \approx 1.5$) in comparison to that obtained with PhSO_3H ($M_w/M_n \approx 2.5$), suggesting that a more electron-donating methyl group on the sulfonic acid enables faster interconversion between the dormant and cationic propagating species *via* a better stabilized intermediate.^[10,12] In addition, when the feed ratio of monomer to $\text{CH}_3\text{SO}_3\text{H}$ was varied between 25 and 100, the M_n increased in direct proportion to the feed ratio and was close to the calculated value (open circles in Fig. 2a). The SEC curves also shifted toward higher molecular weight, retaining the unimodal peak along with an increase in the feed ratio (Fig. 2c).

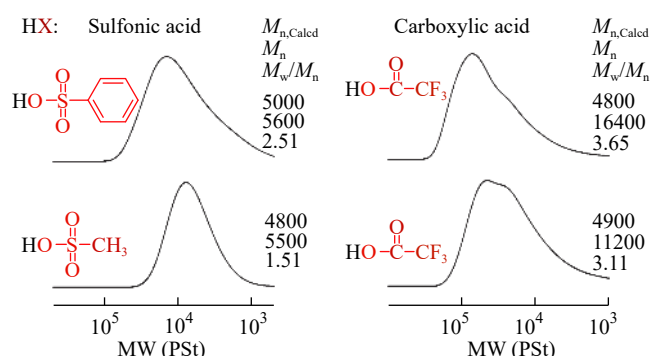


Fig. 4 SEC curves of polymers obtained by using mixtures of sulfonic or carboxylic acid with a trace amount of TfOH for cationic polymerization of IBVE in *n*-hexane/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (80/10/10, *V/V/V*) at -78°C : $[\text{IBVE}]_0/[\text{HX}]_0/[\text{TfOH}]_0 = 500/10/0.50 \text{ mmol}\cdot\text{L}^{-1}$

The ^1H -NMR spectrum of the polymers obtained with $\text{CH}_3\text{SO}_3\text{H}$ in the presence of a trace amount of TfOH was almost the same as that obtained with $(n\text{-BuO})_2\text{PO}_2\text{H}$ under the same conditions. The ω -terminal was an acetal upon quenching with CH_3OH , and the $M_{n,\text{NMR}}$ based on the ω -terminal was close to that determined by SEC ($M_{n,\text{SEC}}$). These results revealed for the first time that the sulfoxonium intermediate is also effective for controlling the cationic DT polymerization of vinyl ether, although the CTA is difficult to isolate due to its instability. In addition, the simple mixing of a protonic acid, which may form the dormant species *in situ*, and a trace amount of a superstrong protonic acid is an effective method to develop new initiating systems for controlling cationic polymerization.

In contrast to the sulfonic acids, carboxylic acids, such as trifluoroacetic ($\text{CF}_3\text{CO}_2\text{H}$) and acetic acid ($\text{CH}_3\text{CO}_2\text{H}$), resulted in polymers with higher molecular weights ($M_n > 10000$) than the calculated values and broad MWDs ($M_w/M_n > 3.0$) (Fig. 4). These results were similar to those obtained using their adducts of IBVE as CTAs,^[10,12] which suggests that the experimental data obtained by simply mixing a weak protonic acid and a small amount of TfOH can predict the effectiveness of its adduct as the CTA in cationic DT polymerization and that these carboxylic acids are not effective precursors of CTAs for controlling cationic polymerization.

Polymerization Using Thiol and Alcohol in Conjunction with TfOH

Although the acidity of thiol and alcohol is much lower than that of phosphoric, sulfonic, and carboxylic acids,^[40] they may form adducts *in situ* in the presence of TfOH to serve as CTA precursors.^[11] Indeed, the adduct of *n*-butanethiol and IBVE has been prepared in the presence of a catalytic amount of *p*-toluenesulfonic acid and proved to be effective for the cationic DT polymerization of IBVE in the presence of a trace amount of TfOH.^[11,12]

Here, 1-octanethiol, which has a longer alkyl chain and a relatively high boiling temperature (200°C) and is easier to handle due to having less odor than *n*-butanethiol,^[41] and 1-octanol were employed as protonic compounds for CTA precursors in conjunction with a trace amount of TfOH (entries 10 and 11 in Table 1). The polymerizations similarly occurred and completed within 24 h in both cases. However, the molecular weights of the products were quite different for thiol and alcohol. 1-Octanethiol afforded polymers with very narrow MWDs ($M_w/M_n \approx 1.1$) and a controlled M_n that agreed well with the calculated value (Fig. 5). These results were almost the same as those obtained using the isolated adduct of *n*-butanethiol, which is a similar primary thiol, and IBVE as CTA.^[11,12] By contrast, 1-octanol resulted in polymers with broad MWDs ($M_w/M_n \approx 3$) and higher molecular weights ($M_n > 10000$) than the calculated values, as in the polymerization with carboxylic acid.

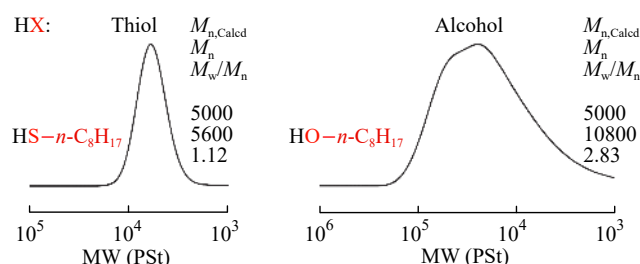


Fig. 5 SEC curves of polymers obtained by using mixtures of thiol or alcohol with a trace amount of TfOH for cationic polymerization of IBVE in *n*-hexane/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (80/10/10, *V/V/V*) at -78°C : $[\text{IBVE}]_0/[\text{HX}]_0/[\text{TfOH}]_0 = 500/10/0.50 \text{ mmol}\cdot\text{L}^{-1}$

The obtained polymers were also analyzed by ^1H -NMR spectroscopy (Fig. 6). In contrast to the polymers obtained with phosphoric and sulfonic acids (Fig. 3), there were no methoxy acetal protons attributed to the ω -terminal originating from methanol as the quencher. However, the polymer obtained with 1-octanethiol showed the ω -end thioacetal methine proton (b') at 4.7 ppm, which was slightly shifted downfield compared with that of the methoxy acetal proton at 4.6 ppm, and the characteristic methylene proton (f) adjacent to the sulfur atom at 2.5 ppm (Fig. 6A). The $M_{n,\text{NMR}}$ calculated using the peaks of the terminal thioacetal (b') and pendent methyl protons (e) of the repeating IBVE units was close to that determined by SEC ($M_{n,\text{SEC}}$). These results obtained by the SEC and NMR analyses indicate that 1-octanethiol formed the thioacetal CTA *in situ* almost quantitatively in the presence of a trace amount of TfOH prior to polymerization and that the formed thioacetal worked as an effective reversible CTA as in the polymerization using the presyn-

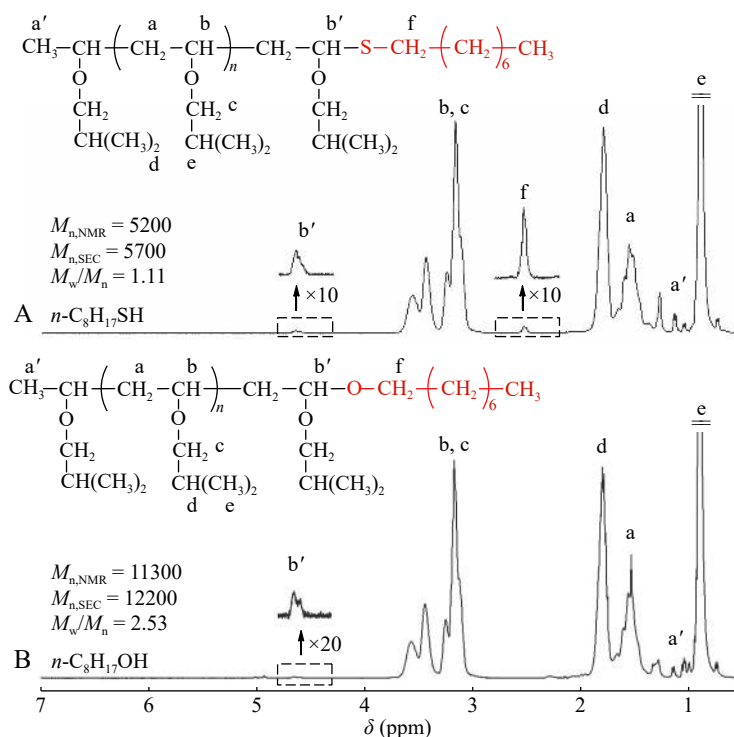


Fig. 6 ^1H -NMR spectra (in CDCl_3 at 55°C) of polymers obtained by using mixtures of (A) $n\text{-C}_8\text{H}_{17}\text{SH}$ or (B) $n\text{-C}_8\text{H}_{17}\text{OH}$ with a trace amount of TfOH for cationic polymerization of IBVE in $n\text{-hexane}/\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (80/10/10, $V/V/V$) at -78°C upon quenching the polymerization with methanol: $[\text{IBVE}]_0/[\text{HX}]_0/[\text{TfOH}]_0 = 500/10/0.50 \text{ mmol}\cdot\text{L}^{-1}$

thesized thioacetal.^[11,12]

The polymer obtained with 1-octanol also showed the octanol-derived acetal methine proton (b') at 4.7 ppm (Fig. 6B), which was downfield from that of the methanol-derived acetal proton at 4.6 ppm. In addition, $M_{n,\text{NMR}}$ based on the octanol-derived acetal terminal methine (b') and the repeating IBVE methylene protons (e) was close to $M_{n,\text{SEC}}$, although they were both higher ($M_n \approx 10000$) than the theoretical value ($M_{n,\text{Calcd}} = 5000$). These results indicate that most of the generated polymer chains came from 1-octanol, whereas the chain-transfer process and/or the formation of the acetal chain end was slower than the propagation process, resulting in polymers with higher molecular weights and broader MWDs.

CONCLUSIONS

In summary, we developed simple metal-free living cationic polymerization using a combination of weak and superstrong protonic acids, which is based on the *in situ* formation of a chain-transfer agent and subsequent cationic polymerization via a degenerative chain-transfer mechanism. A user-friendly living cationic polymerization was achieved by simply adding mixtures of the two types of protonic acids, i.e., a weak protonic compound as the precursor of CTA and a trace amount of superstrong acid as the cationogen, to the monomer solution with no need for the synthesis and purification of CTA. In the cationic DT polymerization of isobutyl vinyl ether using TfOH as the cationogen, not only phosphoric acid but also sulfonic acid and thiol are efficient protonic compounds for use as the CTA precursor. We hope

that this simple method will become popular for synthesizing well-defined functional polymer materials in addition to other methods.^[4–9,42]

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REFERENCES

- Matyjaszewski, K.; Müller, A. H. E. *Controlled and living polymerizations; From mechanisms to applications*, Wiley-VCH, Weinheim, **2010**.
- Miyamoto, M.; Sawamoto, M.; Higashimura, T. Living polymerization of isobutyl vinyl ether with hydrogen iodide/iodine initiating system. *Macromolecules* **1984**, *17*, 265–268.
- Faust, R.; Kennedy, J. P. Living carbocationic polymerization III demonstration of the living polymerization of isobutylene. *Polym. Bull.* **1986**, *15*, 317–323.
- Sawamoto, M. Modern cationic vinyl polymerization. *Prog. Polym. Sci.* **1991**, *16*, 111–172.
- Kennedy, J. P.; Iván, B. *Designed polymers by carbocationic macromolecular engineering: Theory and practice*, Hanser Publishers, New York, **1992**.
- Matyjaszewski, K. *Cationic polymerizations: Mechanisms, synthesis & applications*, Marcel Dekker, New York, **1996**.
- Puskas, J. E.; Kaszas, G. Living carbocationic polymerization of resonance-stabilized monomers. *Prog. Polym. Sci.* **2000**, *25*, 403–452.

- 8 Goethals, E. J.; Du Prez, F. Carbocationic polymerizations. *Prog. Polym. Sci.* **2007**, *32*, 220–246.
- 9 Aoshima, S.; Kanaoka, S. A Renaissance in living cationic polymerization. *Chem. Rev.* **2009**, *109*, 5245–5287.
- 10 Uchiyama, M.; Satoh, K.; Kamigaito, M. Cationic RAFT polymerization using ppm concentrations of organic acid. *Angew. Chem. Int. Ed.* **2015**, *54*, 1924–1928.
- 11 Uchiyama, M.; Satoh, K.; Kamigaito, M. Thioether-mediated degenerative chain-transfer cationic polymerization: A simple metal-free system for living cationic polymerization. *Macromolecules* **2015**, *48*, 5533–5542.
- 12 Uchiyama, M.; Satoh, K.; Kamigaito, M. A phosphonium intermediate for cationic RAFT polymerization. *Polym. Chem.* **2016**, *7*, 1387–1396.
- 13 McKenzie, T. G.; Fu, Q.; Uchiyama, M.; Satoh, K.; Xu, J.; Boyer, C.; Kamigaito, M.; Qiao, G. G. Beyond traditional RAFT: Alternative activation of thiocarbonylthio compounds for controlled polymerization. *Adv. Sci.* **2016**, *3*, 1500394.
- 14 Kamigaito, M.; Satoh, K.; Uchiyama, M. Degenerative chain-transfer process: Controlling all chain-growth polymerizations and enabling novel monomer sequences. *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57*, 243–254.
- 15 Moad, G.; Rizzardo, E.; Thang, S. H. Toward living radical polymerization. *Acc. Chem. Res.* **2008**, *41*, 1133–1142.
- 16 Hill, M. R.; Carmean, R. N.; Sumerlin, B. S. Expanding the scope of RAFT polymerization: Recent advances and new horizons. *Macromolecules* **2015**, *48*, 5459–5469.
- 17 Perrier, S. RAFT polymerization - A user guide. *Macromolecules* **2017**, *50*, 7433–7447.
- 18 David, G.; Boyer, C.; Tonnar, J.; Améduri, B.; Lacroix-Desmazes, P.; Boutevin, B. Use of iodo compounds in radical polymerization. *Chem. Rev.* **2006**, *106*, 3936–3962.
- 19 Yamago, S. Precision polymer synthesis by degenerative transfer controlled/living radical polymerization using organotellurium, organostibine, and organobismuthine chain-transfer agents. *Chem. Rev.* **2009**, *109*, 5051–5068.
- 20 Debuigne, A.; Poli, R.; Jérôme, R.; Jérôme, R.; Detrembleur, C. Overview of cobalt-mediated radical polymerization: Roots, state of the art and future prospects. *Prog. Polym. Sci.* **2009**, *34*, 211–239.
- 21 Poli, R.; Allan, L. E. N.; Shaver, M. P. Iron-mediated reversible deactivation controlled radical polymerization. *Prog. Polym. Sci.* **2014**, *39*, 1827–1845.
- 22 Asandei, A. D. Photomediated controlled radical polymerization and block copolymerization of vinylidene fluoride. *Chem. Rev.* **2016**, *116*, 2244–2274.
- 23 Uchiyama, M.; Satoh, K.; Kamigaito, M. Diversifying cationic RAFT polymerization with various counteranions: Generation of cationic species from organic halides and various metal salts. *ACS Macro Lett.* **2017**, *6*, 393–398.
- 24 Uchiyama, M.; Satoh, K.; McKenzie, T. G.; Fu, Q.; Qiao, G. G.; Kamigaito, M. Diverse approaches to star polymers via cationic and radical RAFT cross-linking reactions using mechanistic transformation. *Polym. Chem.* **2017**, *8*, 5972–5981.
- 25 Guerre, M.; Uchiyama, M.; Folgado, E.; Semsarilar, M.; Améduri, B.; Satoh, K.; Kamigaito, M.; Ladmiral, V. Combination of cationic and radical RAFT polymerizations: A versatile route to well-defined poly(ethyl vinyl ether)-block-poly(vinylidene fluoride) block copolymers. *ACS Macro Lett.* **2017**, *6*, 393–398.
- 26 Guerre, M.; Uchiyama, M.; Lopez, G.; Améduri, B.; Satoh, K.; Kamigaito, M.; Ladmiral, V. Synthesis of PEVE-*b*-P(CTFE-*alt*-EVE) block copolymers by sequential cationic and radical RAFT polymerization. *Polym. Chem.* **2018**, *9*, 352–361.
- 27 Sugihara, S.; Konegawa, N.; Maeda, Y. HCl·Et₂O-catalyzed metal-free RAFT cationic polymerization: One-pot transformation from metal-free living cationic polymerization to RAFT radical polymerization. *Macromolecules* **2015**, *48*, 5120–5131.
- 28 Sugihara, S.; Okubo, S.; Maeda, Y. Metal-free RAFT cationic polymerization of *p*-methoxystyrene with HCl·Et₂O using a xanthate-type RAFT cationogen. *Polym. Chem.* **2016**, *7*, 6854–6863.
- 29 Perkowski, A. J.; You, W.; Nicewicz, D. A. Visible light photoinitiated metal-free living cationic polymerization of 4-methoxystyrene. *J. Am. Chem. Soc.* **2015**, *137*, 7580–7583.
- 30 Kottisch, V.; Michaudel, Q.; Fors, B. P. Cationic polymerization of vinyl ethers controlled by visible light. *J. Am. Chem. Soc.* **2016**, *138*, 15535–15538.
- 31 Kottisch, V.; Michaudel, Q.; Fors, B. P. Photocontrolled interconversion of cationic and radical polymerizations. *J. Am. Chem. Soc.* **2017**, *139*, 10665–10668.
- 32 Michaudel, Q.; Chauviré, T.; Kottisch, V.; Supej, M. J.; Stawiasz, K. J.; Shen, L.; Zipfel, W. R.; Abruña, H. D.; Freed, J. H.; Fors, B. P. Mechanistic insight into the photocontrolled cationic polymerization of vinyl ethers. *J. Am. Chem. Soc.* **2017**, *139*, 15530–15538.
- 33 Michaudel, Q.; Kottisch, V.; Fors, B. P. Cationic polymerization: From photoinitiation to photocontrol. *Angew. Chem. Int. Ed.* **2017**, *56*, 9670–9679.
- 34 Kottisch, V.; Supej, M. J.; Fors, B. P. Enhancing temporal control and enabling chain-end modification in photoregulated cationic polymerizations by using Ir-based catalysts. *Angew. Chem. Int. Ed.* **2018**, *57*, 8260–8264.
- 35 Peterson, B. M.; Lin, S.; Fors, B. P. Electrochemically controlled cationic polymerization of vinyl ethers. *J. Am. Chem. Soc.* **2018**, *140*, 2076–2079.
- 36 Sang, W.; Yan, Q. Electro-controlled living cationic polymerization. *Angew. Chem. Int. Ed.* **2018**, *57*, 4907–4911.
- 37 Peterson, B. M.; Kottisch, V.; Supej, M. J.; Fors, B. P. On demand switching of polymerization mechanism and monomer selectivity with orthogonal stimuli. *ACS Cent. Sci.* **2018**, *4*, 1228–1234.
- 38 Kishimoto, Y.; Aoshima, S.; Higashimura, T. Living cationic polymerization of vinyl monomers by organoaluminum halides. 4. Polymerization of isobutyl vinyl ether by ethylaluminum dichloride (EtAlCl₂) in the presence of ether additives. *Macromolecules* **1989**, *22*, 3877–3882.
- 39 Kamigaito, M.; Sawamoto, M.; Higashimura, T. Living cationic polymerization of isobutyl vinyl ether by protonic acid/zinc halide initiating systems: Evidence for the halogen exchange with zinc halide in the growing species. *Macromolecules* **1992**, *25*, 2587–2591.
- 40 Bordwell, F. G. Equilibrium acidities in dimethyl sulfoxide solution. *Acc. Chem. Res.* **1988**, *21*, 456–463.
- 41 Node, N.; Kumar, K.; Nishide, K.; Ohsugi, S.; Miyamoto, T. Odorless substituents for foul-smelling thiols: Synthesis and applications. *Tetrahedron Lett.* **2001**, *42*, 9207–9210.
- 42 Ciftci, M.; Yoshikawa, Y.; Yagci, Y. Living cationic polymerization of vinyl ethers through a photoinduced radical oxidation/addition/deactivation sequence. *Angew. Chem. Int. Ed.* **2017**, *56*, 519–1928.