Title	tert-Butyl Esters as Potential Reversible Chain Transfer Agents for Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization of Vinyl Ethers and Oxiranes
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tert-Butyl Esters as Potential Reversible Chain Transfer Agents for Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization of Vinyl Ethers and Oxiranes

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Abstract

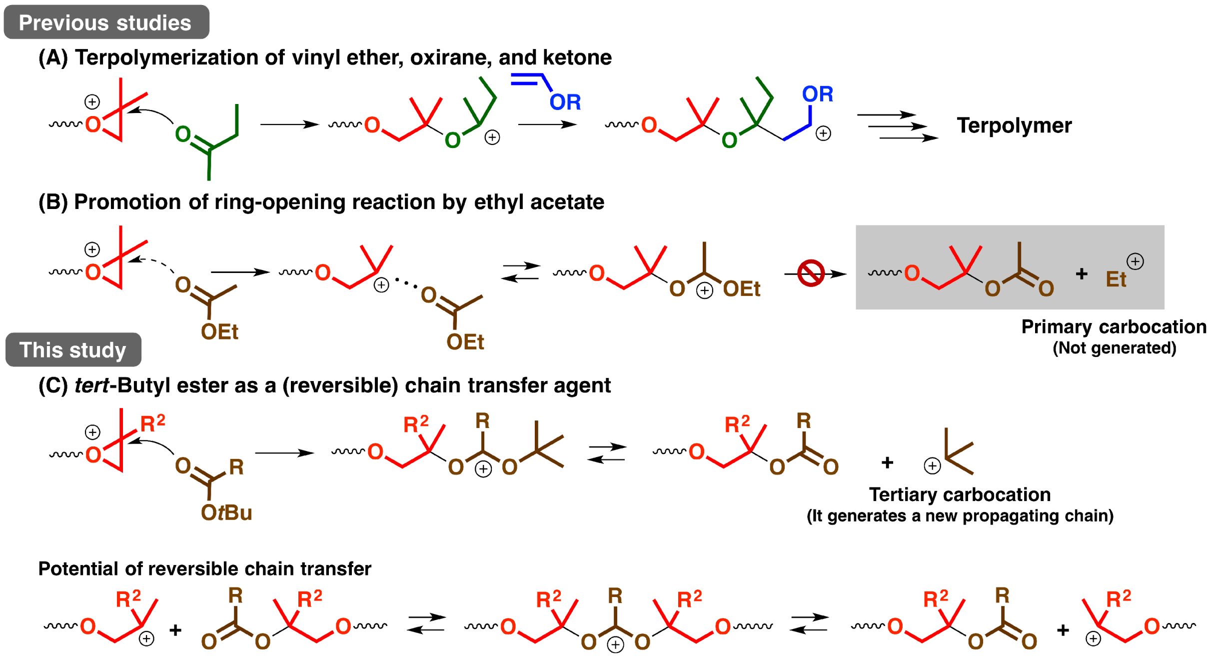
tert-Butyl esters are demonstrated to function as chain transfer agents (CTAs) in the cationic copolymerization of vinyl ether (VE) and oxirane via concurrent vinyl-addition and ring-opening mechanisms. In the copolymerization of isopropyl VE and isobutylene oxide (IBO), the IBO-derived propagating species reacts with *tert*-butyl acetate to generate a copolymer chain with an acetoxy group at the ω-end. This reaction liberates a *tert*-butyl cation; hence, a polymer chain with a *tert*-butyl group at the α-end is subsequently generated. Other *tert*-butyl esters also function as CTAs, and the substituent attached to the carbonyl group affects the chain transfer efficiency. In addition, ethyl acetate does not function as a CTA, which suggests the importance of the liberation of a *tert*-butyl cation for the chain transfer process. Chain transfer reactions by *tert*-butyl esters potentially occur reversibly through the reaction of the propagating cation with the ester group at the ω-end of another chain.

Chain transfer agents (CTAs) are used in polymerization to control several elements of polymer structures, such as molecular weights (MWs) and chain end structures.[1–3] A propagating species reacts with a CTA, thereby generating a polymer chain with a fragment derived from the CTA at the chain end and a new propagating species. Moreover, CTAs that mediate reversible chain transfer reactions have been applied for living polymerization[4] by degenerative chain transfer processes,[5] such as reversible addition-fragmentation chain transfer (RAFT) polymerization,[6–8] in which propagating radical species are reversibly generated through the reactions of radical species with CTAs such as dithioesters. The RAFT process was also applied to the living cationic polymerization of vinyl ethers (VEs) and styrene derivatives.[9–17]

The copolymerization of different types of monomers, such as vinyl monomers and cyclic monomers,[18–24] has attracted increasing interest because of both interest in polymerization mechanisms and the potential of creating polymers with novel functions. Our group has also developed the concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl monomers and cyclic ethers.[22–24] For example, copolymerization of VEs and oxiranes was demonstrated to proceed via crossover reactions when appropriate oxiranes, such as isobutylene oxide (IBO), that generate a tertiary or resonance-stabilized carbocation via ring opening of the oxonium ion were used. Moreover, the obtained copolymers possess acid degradability due to the acetal linkages resulting from the crossover from VE to oxirane. However, the control of MWs and chain end structures is generally difficult because copolymerization with $B(C_6F_5)_3$, which is a catalyst that forms a weakly coordinating counteranion, proceeds in a nonliving manner via propagation and spontaneous chain transfer by β-proton elimination at the oxirane-derived ends. The great difference in reactivity between the VE- and oxirane-derived propagating species is responsible for the difficulty in controlling copolymerization. Recently, superstrong protic acids, such as trifluoromethanesulfonic acid (TfOH), were found to allow living species-mediated polymerization.[25] The polymerization proceeds via the reversible generation of propagating species by the spontaneous cleavage of covalent bonds, such as the C–OTf bond, exclusively at the oxirane-derived ends.

In this study, we aim to develop a new method to control the structures of copolymers of VEs and oxiranes by employing CTAs. In our previous study, ketones, such as methyl ethyl ketone, were used as monomers that reacted with the oxirane-derived oxonium ion and subsequently generated an alkoxy group-adjacent, VE-type carbocation in terpolymerization with VEs and oxiranes (Scheme 1A).[26] In addition, ethyl acetate (EtOAc) was shown to promote the ring opening of the oxonium ion (Scheme 1B).[27] These studies indicate that carbonyl compounds nucleophilically attack the carbon atom adjacent to the cationically charged oxygen atom of the oxirane-derived oxonium ion. Therefore, we thought that some esters might function as reversible CTAs through the generation of a relatively stable carbocation, such as a *tert*-alkyl cation, after the formation of an intermediate cation (Scheme 1C). MWs and chain end structures can be controlled when chain transfer reactions occur efficiently. Moreover, living copolymerization, such as RAFT polymerization, will be achieved if the reversible chain transfer reactions occur very frequently and side reactions such as β-proton elimination are suppressed completely. To the best of our knowledge, there has been no report on the study of the oxirane polymerization using esters as CTAs.

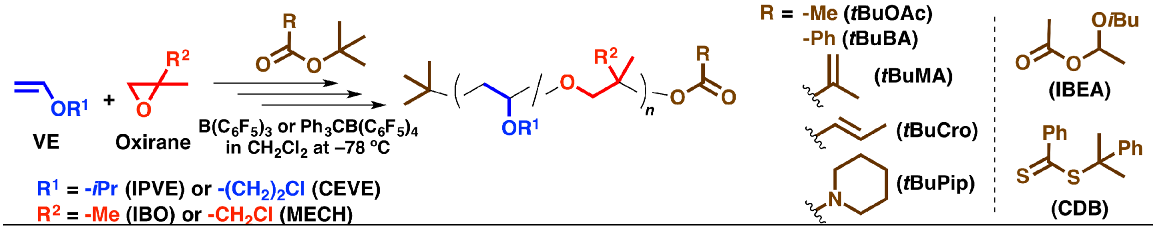
Isopropyl VE (IPVE) and IBO, which were demonstrated to copolymerize via crossover reactions to yield multiblock copolymers,[22] were adopted as monomers to evaluate the ability of transfer agents (the scheme in Table 1). A tertiary carbocation is generated via the ring opening of the IBO-derived oxonium ion; hence, *tert*-butyl acetate (*t*BuOAc), which potentially generates a *tert*-butyl cation (Scheme 1C, upper), was first employed as a CTA. A cationogen was not used because the polymerization is likely initiated from a proton derived from adventitious water.



Scheme 1. (A) Cationic terpolymerization of VE, IBO, and ketone (ref 26), (B) the promotion of ring opening of the IBO-derived oxonium ion via the attack of ethyl acetate (ref 27), and (C) a potential function of a *tert*-butyl ester as a (reversible) CTA. Counteranions are omitted.

Cationic copolymerization of IPVE and IBO was examined using $B(C_6F_5)_3$ as a catalyst in the presence of 100 mM *t*BuOAc (entry 2 in Table 1). The polymerization proceeded via the consumption of both monomers to yield a polymer (Figure 1A). The M_n value (4.9×10^3) was lower than that of a polymer obtained in the absence of *t*BuOAc (10.4×10^3; entry 1), which suggests that *t*BuOAc functioned as a CTA in the expected manner. However, a product obtained at lower monomer conversion also had a similar M_n value (Figure 1A, upper), suggesting the frequency of the chain transfer reactions was relatively low, in contrast to RAFT polymerization using efficient CTAs.

Table 1. Cationic copolymerization of IPVE and IBO in the presence of esters[a]



entry	monomers	ester	conc (mM)	time	VE conv (%)[b]	oxirane conv (%)[b]	$M_\mathrm{n} \times 10^{-3}$ [c]	$M_\mathrm{w}/M_\mathrm{n}$ [c]	ester-derived ω-ends (%)[d]
1[e]	IPVE/IBO	None	–	0.5 h	65	57	10.4	1.84	–
2		*t*BuOAc	100	5 h	72	50	4.9	1.72	77
3		*t*BuOAc	500	24 h	58	42	2.5	1.50	94
4		*t*BuBA	100	1 h	76	61	8.8	1.87	21
5		*t*BuMA	100	1 h	76	59	9.0	1.82	23
6		*t*BuCro	100	3 h	59	45	5.4	1.89	59
7		*t*BuPip	100	72 h	0	0	–	–	–
8		*t*BuPip	30	22 h	83	63	6.0	1.81	31[f]
9		IBEA	100	1 h	71	58	4.7	1.69	87
10		CDB	100	72 h	10	1[g]	<1[h]	–[h]	–
11		CDB	10	72 h	38	24	6.2	1.78	22
12[i]		EtOAc	1000	5 h	44	19	7.6	1.90	2[j]
13[k]	CEVE/MECH	None	–	1 h	79	47	11.2	2.15	–
14		*t*BuOAc	30	2 h	92	60	5.6	2.57	90
15	IPVE alone	None	–	3 min	>99	–	32.7	4.32	–
16		*t*BuOAc	100	22 h	74	–	11.6	4.13	0
17[e,l]	IBO alone	None	–	22 h	–	0	–	–	–
18[l]		*t*BuOAc	100	22 h	–	0	–	–	–

[a] In dichloromethane at –78 ºC. Entries 1–12: $[\mathrm{IPVE}]_0$ = 0.75 M, $[\mathrm{IBO}]_0$ = 0.22 M, $[\mathrm{B(C_6F_5)_3}]_0$ = 1.0 mM. Entries 13 and 14: $[\mathrm{CEVE}]_0$ = 0.78 M, $[\mathrm{MECH}]_0$ = 0.22 M, $[\mathrm{Ph_3CB(C_6F_5)_4}]_0$ = 1.0 mM. Entries 15 and 16: $[\mathrm{IPVE}]_0$ = 0.75 M, $[\mathrm{B(C_6F_5)_3}]_0$ = 3.0 mM. Entries 17 and 18: $[\mathrm{IBO}]_0$ = 0.22 M, $[\mathrm{B(C_6F_5)_3}]_0$ = 1.0 mM. [b] By gas chromatography. [c] By GPC (polystyrene calibration). [d] By ^{1}H NMR. [e] From ref 22. [f] The value contains nonnegligible error because of the overlap of peaks. [g] From VE conversion by gas chromatography and ^{1}H NMR analysis of the product. [h] A polymer peak partly overlapped with the peak of residual CDB. [i] From ref 27. [j] A very small peak that might be assigned to an ester-derived structure was observed (Figure S2). [k] From ref 24. [l] The homopolymerization of IBO did not proceed irrespective of the presence of *t*BuOAc. As reported in ref 22, the initiation of the IBO polymerization from adventitious water or by the coordination of $\mathrm{B(C_6F_5)_3}$ does not likely occur at –78 ºC under the examined conditions.

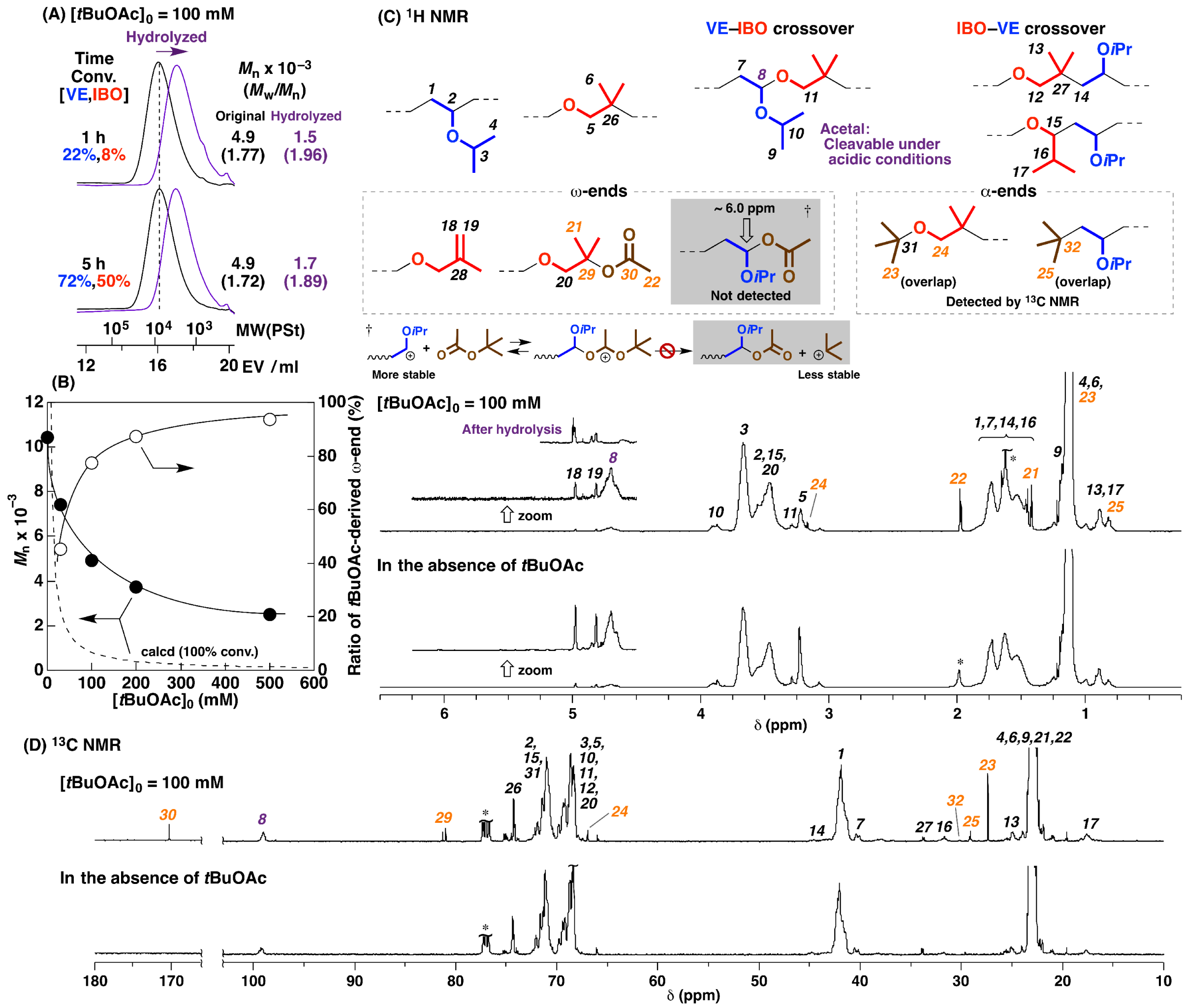


Figure 1. (A) MWD curves of the products obtained by the copolymerization of IPVE and IBO (black) and hydrolysis products (purple); (B) M_n (filled circles) and the incorporated ratio of *t*BuOAc (open circles) in the copolymerization at different amounts of *t*BuOAc (the broken line indicates the calculated M_n at 100% monomer conversion); and (C) ^{1}H and (D) ^{13}C NMR spectra of the products obtained in the presence (upper; entry 2 in Table 1) or the absence (lower; entry 1; ref 22) of *t*BuOAc (* water or chloroform). Polymerization conditions: [IPVE]$_0$ = 0.75 M, [IBO]$_0$ = 0.22 M, [B(C$_6$F$_5$)$_3$]$_0$ = 1.0 mM, [*t*BuOAc]$_0$ = 0–500 mM, in dichloromethane at –78 ºC.

^{1}H NMR analysis of the product indicated that the AcO group of *t*BuOAc was incorporated into a chain end via the chain transfer reaction. A peak at 2.0 ppm (peak 22) is assignable to the AcO group. In addition, the peaks at 1.4–1.5 ppm (peak 21), which have integral ratios twice that of peak 22, are assignable to the methyl groups of the IBO unit attached to the AcO group. These structures were most likely generated via the reaction of *t*BuOAc with the IBO-derived propagating species and the subsequent liberation of a *tert*-butyl cation (Scheme 1C, upper). In addition, α-ends derived from the initiation of the *tert*-

butyl cation were confirmed by ^{13}C NMR analysis (Figures 1D; see also Figure S1 for the comparison of chemical shifts with those of model compounds and DEPT 135 NMR spectra). An additional possible process of the generation of a new propagating chain is the initiation from a proton derived from the β-proton elimination from the *tert*-butyl cation although it is difficult to detect this process because a proton is also generated via the β-proton elimination at the propagating chain end. Notably, the AcO fragment was negligibly incorporated into polymer chains when EtOAc was used (entry 12 in Table 1; Figure S2) instead of *t*BuOAc, which indicates that the liberation of a *tert*-butyl cation is important for the function of esters as CTAs (Scheme 1B and 1C). In addition, to examine whether *t*BuOAc functions not as a CTA but as a cationogen via the generation of a *tert*-butyl cation through the activation by $B(C_6F_5)_3$, the reaction of *t*BuOAc and $B(C_6F_5)_3$ was conducted in the presence of 1,3-dimethoxybenzene under conditions similar to those for the copolymerization ([*t*BuOAc]$_0$ = 0.10 M, $[B(C_6F_5)_3]_0$ = 1.0 mM, [1,3-dimethoxybenzene]$_0$ = 0.40 M, in dichloromethane at –78 ºC; reaction time: 5 h). If a *tert*-butyl cation is generated, Friedel–Crafts reaction will occur between the cation and 1,3-dimethoxybenzene.[28] However, the reaction did not occur, which suggests that *t*BuOAc is not cleaved by $B(C_6F_5)_3$ and does not likely function as a cationogen in the copolymerization.

The chain transfer reaction by *t*BuOAc likely occurred exclusively at the IBO-derived cation, as confirmed by the absence of the hemiacetal ester structure consisting of IPVE and an AcO group (no peak at 6.0 ppm, Figure 1C). The inertness of *t*BuOAc to the IPVE-derived carbocation was also confirmed by the homopolymerization of IPVE in the presence of *t*BuOAc (entry 16 in Table 1). The difference in stability between the *tert*-butyl cation and the alkoxy-adjacent carbocation is probably responsible for the inertness of *t*BuOAc as a CTA for the VE-derived propagating species (Figure 1C, †). A similarity in structures and reactivities between the *tert*-butyl cation and the IBO-derived tertiary alkyl cation is likely responsible for the chain transfer reactions using *t*BuOAc.[9–17] The ω-ends other than those derived from *t*BuOAc involve the *exo*-olefin structure resulting from the β-proton elimination at the IBO-derived propagating end (peaks 18 and 19). The ratio of the *t*BuOAc-derived end was 77%. The M_n value calculated from these ω-ends was 3.9×10^3, which is comparable to the value obtained by gel permeation chromatography (GPC) using polystyrene calibration.

^{1}H NMR analysis also suggested that the copolymerization proceeded via the crossover reactions between IPVE and IBO even in the presence of *t*BuOAc. A peak at 4.7 ppm (peak 8 in Figure 1C) is assigned to an acetal moiety resulting from the crossover from IPVE to IBO, while peaks at 0.8–0.9 ppm (peaks 13 and 17) are assigned to the methyl groups of the IBO unit that reacted with an IPVE monomer.[22] The number of IPVE and IBO units per block, which is related to the frequency of the crossover reactions, was estimated to be 17 and 3.0, respectively, which were slightly lower than those of the product obtained in the absence of *t*BuOAc (IPVE/IBO = 22/4.8). Moreover, the number was lower when the amount of *t*BuOAc was increased (IPVE/IBO = 12/1.8; $[t\text{BuOAc}]_0$ = 500 mM, entry 3 in Table 1). The decrease in IBO units per block was most likely due to the promotion of the ring-opening reaction by *t*BuOAc as in the case of EtOAc (see ref 27 for the detail). The reason of the decrease in IPVE units per block is unclear presently. In addition, the copolymers were degraded via the cleavage of the acetal structures under acidic conditions to yield products with lower MWs (purple curves in Figure 1A), which also indicates successful copolymerization via crossover reactions.

An increase in the amount of *t*BuOAc resulted in a decrease in M_n and an increase in the incorporated ratio of the AcO group (Figure 1B; see Figure S3 for molecular weight distribution (MWD) curves) because of the increase in the frequency of the chain transfer reactions. For example, the M_n was less than one-fourth that in the absence of *t*BuOAc, and approximately 94% of the ω-ends were derived from *t*BuOAc in the reaction at 500 mM (entry 3 in Table 1). However, the chain transfer efficiency was obviously low, as demonstrated by the much larger M_n values than those calculated based on the amount of *t*BuOAc (broken line in Figure 1B; based on the assumption that all the *t*BuOAc molecules used undergo chain transfer reactions). The low efficiency also suggests that the propagating species negligibly reacted with the AcO-attached chain ends, in contrast to RAFT processes, although reversible chain transfer reactions potentially occur (Scheme 1C, lower).

To examine the effects of the substituent of the carbonyl group, copolymerization was examined using other *tert*-butyl esters. When *tert*-butyl benzoate (*t*BuBA), *tert*-butyl methacrylate (*t*BuMA), or *tert*-butyl crotonate (*t*BuCro) was used, the obtained polymers had smaller ratios of ester-derived ω-ends and higher MWs than *t*BuOAc (entries 4, 5, and 6 in Table 1; see Figure S4 for ^{1}H NMR spectra). The carbonyl groups of these unsaturated esters likely exhibit smaller basicities than alkyl esters[29] such as *t*BuOAc due to the effect of the phenyl, isopropenyl, or 1-propenyl group, which is responsible for less efficient chain transfer reactions in the polymerization.

As a candidate for an efficient CTA, we focused on a carbamate [1-(*tert*-butoxycarbonyl)piperidine (*t*BuPip)] because dithiocarbamates were reported to function very efficiently in the cationic RAFT polymerization of VEs due to the electron-donating ability of amino groups.[9] The reaction did not proceed in the presence of 100 mM *t*BuPip (entry 7 in Table 1), probably because the activity of $B(C_6F_5)_3$ was suppressed through Lewis acid–base interaction with *t*BuPip. At a lower concentration of *t*BuPip (30 mM; entry 8; see Figure S5 for ^{1}H NMR spectrum), the copolymerization smoothly proceeded to yield a copolymer; however, the chain transfer efficiency was not especially remarkable compared to that of *t*BuOAc.

A hemiacetal ester compound, which is an adduct of a VE with acetic acid,[30] also functioned as a CTA. A copolymer with an AcO-derived end of 87% was obtained by the copolymerization of IPVE and IBO in the presence of 100 mM 1-isobutoxyethyl acetate

(IBEA) (entry 9 in Table 1). However, unlike the cases of *tert*-butyl esters, IBEA reacted not only with the IBO-derived propagating species but also with the IPVE-derived carbocation,[9] as confirmed by a peak assignable to a hemiacetal ester structure in the ^{1}H NMR spectrum (6.0 ppm; Figure S6). The comparable stabilities of the IPVE-derived carbocation and the carbocation generated after the reaction with IBEA, in contrast to the case of *tert*-butyl ester (Figure 1C, †), are most likely responsible for the reactions of IBEA with both the IPVE- and IBO-derived propagating species.

Cumyl dithiobenzoate (CDB), with the potential to generate a cumyl cation, was also examined as a CTA. The polymerization was very slow when 100 mM CDB was used (entry 10 in Table 1). The polymerization proceeded at a smaller concentration (10 mM; entry 11); however, the reaction gradually ceased (see Figures S7 and S8 for the time-conversion plots and ^{1}H NMR spectrum). CDB was ineffective for the copolymerization of IPVE and IBO, probably because the carbon–sulfur bond derived from IBO was not efficiently cleaved under the examined conditions, which is in contrast to the cationic RAFT polymerization of VEs using dithioesters.[9,10] Another possibility of the inefficiency is a difficult dissociation of the stable cationic intermediate into a propagating carbocation,[11,16] which might be also true for the polymerization using *t*BuPip.

Monomers with lower reactivities potentially undergo more efficient chain transfer reactions with *tert*-butyl esters because a more reactive carbocation derived from a lower-reactive monomer is expected to react efficiently with CTAs. Thus, 2-chloroethyl VE (CEVE) and β-methylepichlorohydrin (MECH),[24] which exhibit lower reactivities than IPVE and IBO, respectively, were copolymerized in the presence of *t*BuOAc using $Ph_3CB(C_6F_5)_4$ as an initiator (the scheme in Table 1). As expected, *t*BuOAc efficiently functioned as a CTA, resulting in 90% ester-derived ω-ends when 30 mM *t*BuOAc was used (entry 14; Figures 2B, 2C, and S9). The ratio (90%) is much higher than for IPVE and IBO under similar conditions

(45%). Based on this preliminary but promising result, we are currently investigating the possibility of reversible chain transfer reactions using monomers with low reactivities.

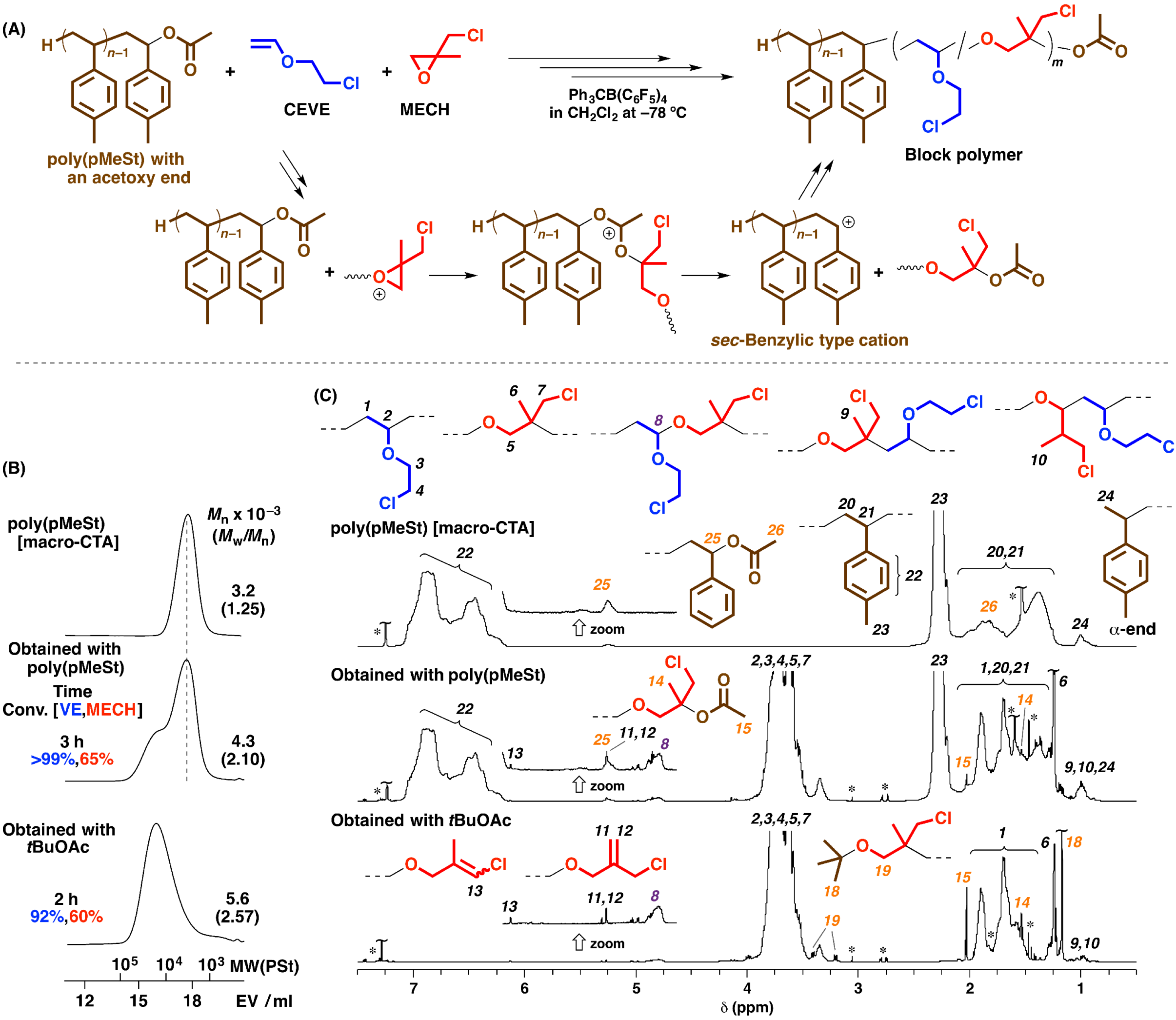


Figure 2. (A) Copolymerization of CEVE and MECH using poly(pMeSt) with an acetoxy end as a macro-CTA. (B) MWD curves and (C) ^{1}H NMR spectra (* residual MECH monomer, water, or chloroform) of the macro-CTA used (upper; the same ^{1}H NMR spectrum as that shown in Figure S10B) and the copolymerization products obtained in the presence of the macro-CTA (middle) or *t*BuOAc (lower; entry 14 in Table 1) ([CEVE]$_0$ = 0.78 M, [MECH]$_0$ = 0.22 M, [Ph$_3$CB(C$_6$F$_5$)$_4$]$_0$ = 1.0 mM, [CTA]$_0$ = 30 mM, in dichloromethane at –78 ºC).

To demonstrate both the reversibility of the chain transfer reactions and the wide applicability of esters as reversible CTAs, block copolymerization was tentatively examined using a macro-CTA. First, poly(IPVE-*co*-IBO) with an acetoxy end was used as a macro-CTA for the copolymerization of CEVE and MECH. However, polymerization negligibly proceeded (monomer conversion was very low) although the reason is unclear. Therefore, we used poly(*p*-methylstyrene) [poly(pMeSt)] with an acetoxy end (Figure S10), which potentially generates a *sec*-benzylic type cation (instead of a *tert*-butyl cation) via the reaction with the propagating carbocation (Figure 2A), as a macro-CTA for the copolymerization of CEVE and MECH. The polymerization proceeded under conditions similar to those for the polymerization using *t*BuOAc (vide supra), which resulted in a product with a bimodal MWD (Figure 2B). ^{1}H NMR analysis (Figure 2C) suggested that 30–40% of the acetoxy ends were consumed and MECH units with an acetoxy group were generated; hence, block polymer chains were probably partly generated via the copolymerization of CEVE and MECH from the *sec*-benzylic type cation derived from the poly(pMeSt). These results also suggest that the reversible chain transfer reactions potentially occur at the acetoxy group of a copolymer chain end in the copolymerization of VEs and oxiranes.

In conclusion, *tert*-butyl esters were demonstrated to function as CTAs in the cationic copolymerization of IPVE and IBO. The carbonyl group of *t*BuOAc reacted with the IBO-derived propagating species, which was followed by the incorporation of the acetoxy group into the polymer chain end and the liberation of a *tert*-butyl cation. Other *tert*-butyl esters also functioned as CTAs, while a dithioester was not effective, in contrast to the cationic RAFT polymerization of VEs. Importantly, chain transfer reactions have the potential to occur reversibly, like the RAFT process, given that the ester moiety incorporated into the chain end efficiently reacts with a propagating species. We will investigate appropriate ester structures for achieving the living copolymerization of VEs and oxiranes via a degenerative chain transfer process.

Conflict of Interest

The authors declare no financial/commercial conflict of interest.

Acknowledgments

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tert-Butyl esters are demonstrated to function as chain transfer agents in the cationic copolymerization of vinyl ether and oxirane via concurrent vinyl-addition and ring-opening mechanisms. The oxirane-derived propagating species reacts with *tert*-butyl acetate to generate a copolymer chain with an acetoxy group at the ω-end. This reaction liberates a *tert*-butyl cation; hence, a polymer chain with a *tert*-butyl group at the α-ends is subsequently generated.

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