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Alkoxyoxirane, a Unique Cyclic Monomer: Controlled Cationic Homopolymerization Mediated by Long-Lived Species and Copolymerization with Vinyl Ether via Alkoxy Group Transfer

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Abstract

1-Methoxy-2-methylpropylene oxide (MOMPO), an alkoxyoxirane that can generate a carbocation adjacent to an alkoxy group via ring opening, was demonstrated to polymerize in a controlled manner with the use of a metal chloride as a Lewis acid catalyst. The choice of the initiating system is critical for the successful controlled homopolymerization of this alkoxyoxirane; a $GaCl_3$/THF system was observed to be the best combination for the initiating system. Furthermore, the copolymerization of MOMPO with isopropyl vinyl ether (IPVE) generated long-lived species when CF_3SO_3H/*n*Bu_4NI was used as the initiating system. Surprisingly, the reaction proceeded via the transfer of the alkoxy group in the IPVE unit. More specifically, the isopropoxy group at the penultimate IPVE unit transferred to the MOMPO-derived propagating cation after the crossover reaction from the IPVE-derived carbocation to MOMPO. This type of reaction creates a side group that possesses the ring-opened MOMPO structure with the isopropoxy group. The generation of copolymers via the "alkoxy-group transfer" mechanism is unique to the copolymerization in this study and was confirmed by ^{1}H, ^{13}C, and 2D NMR analyses and by the acid hydrolysis and subsequent reacetalization reactions of the products.

Introduction

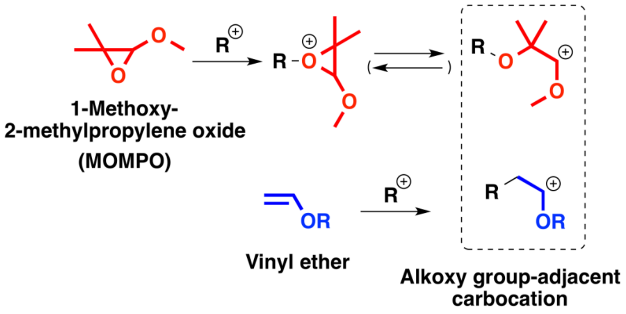
Certain cyclic ethers can be difficult to polymerize in a controlled manner via a cationic ring-opening mechanism because of inherent mechanistic problems even after the considerable advancements in cationic polymerization of cyclic ethers for a wide variety of applications including photoinitiated systems.[1,2] Of the two major mechanisms that have been proposed, i.e., the active-chain-end mechanism and the activated-monomer mechanism,[3−6] the active-end version, in which the reaction proceeds via the attack of a monomer molecule on the propagating oxonium ion, often involves side reactions such as back-biting and intermolecular chain exchange reactions. In addition, polymerization using a metal halide is terminated by the halide anion derived from a metal halide, which produces an irreversible covalent bond between the halogen and the carbon atom adjacent to the oxygen atom of the oxonium ion. During the polymerization of a monomer such as an alkylene oxide, the carbon–halogen bond is difficult to reactivate in the propagating cation because the carbon atom does not possess an electron-donating group to stabilize the carbocation.[3]

In contrast, the formation of a dormant growing end or a resting state of a propagating chain can be an important strategy for achieving living polymerization during addition polymerizations of vinyl monomers, especially for controlled/living cationic[7] or radical[8] mechanisms. A dormant species is generated through the formation of a covalent bond between an active center, e.g., a carbocationic or carbon radical center, and an atom or an atomic group. The covalent bond is reversibly activated to generate active species that can react with monomers, even in propagation reactions. In addition, side reactions such as two-molecule termination reactions in radical polymerization are suppressed because the concentration of the active species is maintained at a level much lower than that of the dormant species.

In the case of concurrent vinyl-addition and ring-opening copolymerization of vinyl and cyclic monomers, the keys to the efficient crossover reaction are the use of an oxirane that generates a relatively stable carbocation, i.e., a tertiary or resonance-stabilized carbocation, via ring opening during the propagation reaction through the active-chain-end mechanism and the use of a Lewis acid that produces a non-coordinating counteranion, such as $B(C_6F_5)_3$. However, studies that have successfully yielded copolymers via not only the cationic mechanisms[9,10] but also anionic/zwitterionic mechanisms[11−15] are scarce because of the difficulty in generating crossover reactions, although concurrent vinyl-addition and ring-opening copolymerization is highly expected to produce various functional polymers. On the basis of the aforementioned hypothesis, we have achieved the concurrent cationic copolymerization of alkyl vinyl ethers (VEs) and oxiranes.[16,17]

Despite the success of the concurrent copolymerization, the incompatibility of the strategies is a significant obstacle for realizing the controlled concurrent cationic copolymerization of VEs and oxiranes; this controlled copolymerization will allow the elaborate design of polymer structures using various types of monomers. The noncoordinating counteranion derived from $B(C_6F_5)_3$ is indispensable for concurrent copolymerization reactions. For example, the polymerization of isobutylene oxide (IBO) with isopropyl VE (IPVE) using $GaCl_3$ proceeded with few crossover reactions, yielding a small amount of a copolymer.[16] The ineffectiveness of $GaCl_3$ results from the generation of a carbon–chlorine bond at the IBO-derived propagating chain end. The bond was negligibly activated for the aforementioned reason, leading to the complete deactivation of the propagating species.

To circumvent this difficulty, the structural design of an oxirane is essential. The carbon–halogen bond at the oxirane-derived propagating chain end may be reactivated if the substituent on the oxirane has a strong electron-donating nature. Therefore, in this study, we focused on 1-methoxy-2-methylpropylene oxide (MOMPO), which is an oxirane that possesses an alkoxy group. The alkoxyoxirane would produce a carbocation that is stabilized by the adjacent oxygen atom and whose structure is similar to that of the VE-derived carbocation (Scheme 1); hence, the formed carbon–halogen bond may be sufficiently labile to be easily reactivated. The polymerization of MOMPO, however, has never been thoroughly investigated, although its polymerization via light-induced initiation has been reported.[18] In this study, we first examined the cationic homopolymerization of MOMPO using metal chlorides as Lewis acid catalysts. Copolymerizations with alkyl VEs were then examined on the basis of the results from the homopolymerization. The concurrent copolymerization was accompanied by the generation of long-lived species; however, microstructural analysis of the products revealed that the copolymerization occurred through a peculiar mechanism: alkoxy-group transfer.



Scheme 1. Possible carbocations that generate from MOMPO and a vinyl ether.

Experimental Section

Materials. MOMPO (TCI; >95.0%, or Nard; >98%), isobutylene oxide (IBO; TCI; >97.0%), ethyl acetate (Wako; >99.5%) and heptane (Wako; 99.0+%) were distilled twice over calcium hydride. Ethyl glycidyl ether (EGE; TCI; >98.0%) and 2,6-di-*tert*-butylpyridine (DTBP; Aldrich, >97%) were distilled twice over calcium hydride under reduced pressure. Isopropyl vinyl ether (IPVE; Wako; 97.0+%) and isobutyl vinyl ether (IBVE; TCI; >99.0%) were sequentially washed with a 10% aqueous sodium hydroxide solution and water and were then distilled twice over calcium hydride. Tetrahydrofuran (THF) and 1,4-dioxane were distilled over calcium hydride and lithium aluminum hydride. The adduct of IBVE with HCl (IBVE—HCl) was prepared from the addition reaction of IBVE with HCl.[19] Toluene (Wako; 99.5%), dichloromethane (Wako; 99.0%), and hexane (Wako; 96.0%) were dried using solvent purification columns (Glass Contour). Commercially available $ZnCl_2$ (Aldrich; 1.0 M solution in diethyl ether) and $TiCl_4$ (Aldrich; 1.0 M solution in toluene) were used without further purification. For $GaCl_3$ and $ZrCl_4$, stock solutions in hexane or ethyl acetate were prepared from commercially available anhydrous $GaCl_3$ (Aldrich; 99.999+%) or $ZrCl_4$ (Aldrich; 99.99%), respectively. CF_3SO_3H (Aldrich; ≥99.0%) and $n$$Bu_4NI$ (Fluka; ≥99.0%) were used without further purification, and stock solutions of these reagents were prepared in dichloromethane. All chemicals, except for toluene, dichloromethane, and hexane, were stored in brown ampules under dry nitrogen.

Polymerization Procedures. A typical polymerization procedure was as follows. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; blowing temperature of approximately 450°C) under dry nitrogen. Toluene, THF, MOMPO, and IBVE–HCl were successively added to the tube using dry syringes. The polymerization was initiated by the addition of a prechilled 50 mM $GaCl_3$ solution in toluene/hexane (3/1 v/v) at –78°C. After a predetermined time, the reaction was terminated via the addition of methanol that contained a small amount of an aqueous ammonia solution. The quenched mixture was washed with water. The volatiles were then removed under reduced pressure at 50 °C to yield a polymer.

The monomer conversion for the homopolymerization of MOMPO was determined gravimetrically. The monomer conversion of IBVE or IPVE during the copolymerization was determined by gas chromatography (column packing material: PEG-20M-Uniport HP; GL Sciences, Inc.) using heptane (for IBVE; added before polymerization) or hexane (for IPVE; added after quenching) as a standard. The monomer conversion of MOMPO during the copolymerization with IBVE was determined gravimetrically on the basis of the result that the monomer conversion of IBVE determined by gas chromatography was approximately 0%. The monomer conversion of MOMPO during the copolymerization with IPVE was determined from the amount of residual monomer estimated by ^{1}H NMR using dichloromethane (polymerization solvent) as a standard.

Acid-Catalyzed Decomposition, Hydrolysis, and Acetalization. The acid-catalyzed decomposition of the MOMPO homopolymer was conducted with 0.5 M HCl(aq) in *n*-butanol at room temperature for two days (sample: approximately 1 wt%). The acid hydrolysis of the copolymers was conducted with 0.5 M HCl(aq) in 1,2-dimethoxyethane at room temperature for one day (sample: approximately 1 wt%). The acid-catalyzed acetalization of the hydrolysis product for the copolymer was conducted with 0.5 M HCl(aq) in ethanol at room temperature for one day (sample: approximately 1 wt%). The quenched mixtures were diluted with dichloromethane and then successively washed with an aqueous sodium hydroxide solution and water. The volatiles were removed under reduced pressure.

Characterization. The MWD of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40°C with three polystyrene gel columns [TSKgel $\mathrm{GMH_{HR}}$-M × 2 or 3 (exclusion limit molecular weight = 4×10^6; bead size = 5 μm; column size = 7.8 mm I.D. × 300 mm) or TSKgel $\mathrm{MultiporeH_{XL}}$-M × 3 (exclusion limit molecular weight = 2×10^6; bead size = 5 μm; column size = 7.8 mm I.D. × 300 mm); flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight ($M_\mathrm{w}/M_\mathrm{n}$)] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh; M_n = 577—1.09×10^6, $M_\mathrm{w}/M_\mathrm{n} \leq 1.1$). NMR spectra were recorded using a JEOL JNM-ECA 500 (500.16 MHz for ^{1}H and 125.77 MHz for ^{13}C) spectrometer. MALDI-TOF-MS spectra were recorded using a SHIMADZU/KRATOS AXIMA-CFR spectrometer (linear mode; voltage: 20 kV; pressure: $<1.9 \times 10^{-3}$ Pa) with dithranol as the matrix and sodium trifluoroacetate as the ion source. A solution (2-3 μL) containing a polymer, the matrix, and the ion source (polymer/matrix/ion source =1 mg/8 mg/1 mg in 1 mL of THF) was cast onto a stainless steel sample plate (Shimadzu Biotech, DE1580TA) and loaded into the spectrometer.

Results and Discussion

Controlled Cationic Homopolymerization of MOMPO

1. Polymerization and Product Analysis

The cationic homopolymerization of MOMPO was conducted using initiating systems that are efficient for the living cationic polymerization of alkyl vinyl ethers (Table 1).[7a,i] Various metal chlorides were used as Lewis acid catalysts in conjunction with the adduct of IBVE with HCl (IBVE–HCl) as a cationogen. Weak Lewis bases, including THF and ethyl acetate, were employed for possible control over the polymerization through the adjustment of the Lewis acidity of the catalysts and the stabilization of the propagating carbocation.[7h,i]

The polymerization behaviors of MOMPO in terms of the activity and the molecular weights of the products were dependent on the Lewis acid catalysts. The reactions using $GaCl_3$ in the presence of THF proceeded smoothly, yielding polymers with relatively large molecular weights and narrow MWDs (entries 1 and 2 in Table 1). $ZrCl_4$ induced a slow yet efficient polymerization in the presence of ethyl acetate, producing polymers with narrower MWDs but lower molecular weights compared to the case of $GaCl_3$ (entries 7 and 8). In contrast to these two catalysts, $ZnCl_2$ (entries 9 and 10) and $TiCl_4$ (entry 11) were hardly efficient for the polymerization of MOMPO. The reaction with $ZnCl_2$ proceeded very rapidly; however, the products had very small molecular weights. $TiCl_4$ was completely ineffective, yielding no polymers. An initiating system without any metal chloride was employed because a strong Lewis acid could break the acetal bonds in the main chain. The CF_3SO_3H/$n$$Bu_4NI$ system recently developed by our group,[20] however, only produced low-molecular-weight products (entry 12). The ^1H NMR analysis of the reaction mixture before purification (Figure

S1) indicated that most of the monomer molecules were transformed into cyclic products composed of a few monomer units in a manner similar to cyclization reactions of other oxiranes.[3,21−23]

Table 1. Cationic homopolymerization of MOMPO, IBO, and EGE [a]

entry	monomer	catalyst	additive	time	conv (%) [b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]
1	MOMPO	$GaCl_3$	THF	1 h	49	3.5	1.44
2				4 h	89	4.9	1.36
3			THF, DTBP [d]	4 h	86	4.4	1.38
4			1,4-Dioxane	4 h	38	2.8	1.68
5			None	4 h	40	2.6	1.74
6				24 h	88	5.1	1.74
7		$ZrCl_4$	Ethyl acetate	24 h	45	1.7	1.15
8				48 h	61	2.0	1.15
9		$ZnCl_2$	Ethyl acetate	7 sec	11	0.6	1.25
10				1 min	60	0.6	1.39
11		$TiCl_4$	Ethyl acetate	15 min	~0	–	–
12		$CF_3SO_3H/n\text{Bu}_4NI$	–	138 h	7 (94)[e]	0.6	1.15
13	IBO	$GaCl_3$	1,4-Dioxane	2 h	4 (25)[f]	0.3	1.10
14				8 h	4 (28)[f]	0.3	1.08
15			None	2 h	4 (13)[f]	0.3	1.07
16	EGE	$GaCl_3$	1,4-Dioxane	8 h	12 (20)[f]	0.5	1.19
17				28 h	17 (32)[f]	0.5	1.22

[a] $[\text{monomer}]_0$ = 0.50 M, $[\text{IBVE–HCl}]_0$ = 0 (entry 12) or 5.0 (except for entry 12) mM, $[\text{Lewis acid}]_0$ = 5.0 mM, [additive] = 0, 1.0 (except for entries 7 and 8) or 1.1 (entries 7 and 8) M, in toluene at 0 °C. [b] By gravimetry. [c] Determined by GPC (polystyrene standards). [d] [DTBP] = 5.0 mM. [e] The value in the parentheses is the monomer conversion determined by ^{1}H NMR (Figure S1). [f] The values in the parentheses are the monomer conversions determined by gas chromatography.

The aforementioned results suggest that $GaCl_3$, which produced a product with the highest molecular weight, is the most promising catalyst to be examined in detail. The time–conversion curve, M_n and M_w/M_n plots, and the MWD curves of the products for the polymerization using $GaCl_3$ are shown in Figure 1. The figure shows that the smooth polymerization produced polymers in which the M_n linearly increased with the monomer conversion. The occurrence of even propagation reactions was also indicated by the symmetrical shapes of the narrowly distributed MWD curves of the products. The polymerization further proceeded without generating any side products, even after the addition of a fresh feed of the monomer at approximately 90% conversion. The M_n values for the polymers were almost in accordance with the straight line through the origin, and the MWD curves retained unimodal and symmetrical shapes. These results indicate that the polymerization of MOMPO using $GaCl_3$ proceeded in a highly controlled manner and was mediated by long-lived species.

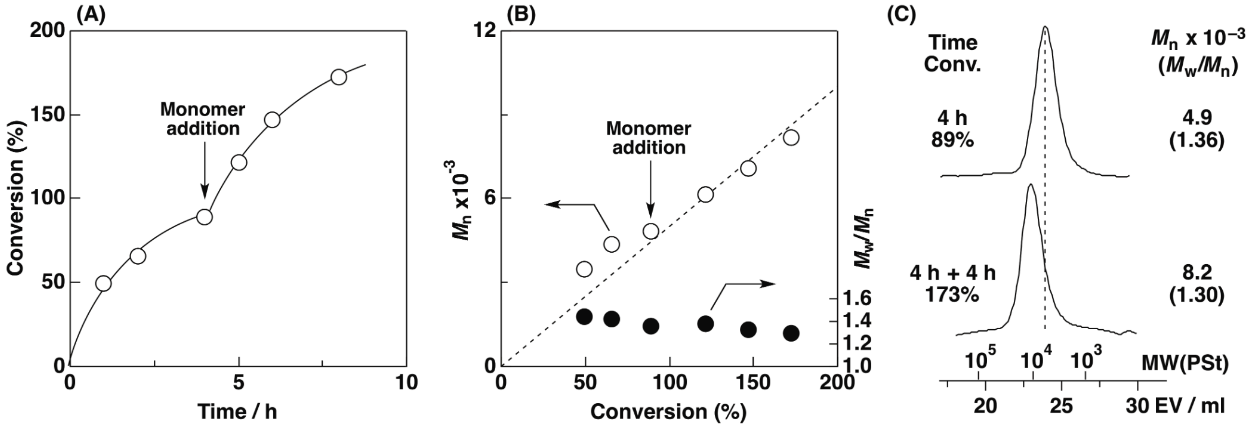


Figure 1. (A) Time–conversion curve, (B) M_n and M_w/M_n for the polymerization of MOMPO, and (C) MWD curves for the poly(MOMPO)s ($[MOMPO]_0$ = 0.50 M, $[MOMPO]_{added}$ = 0.50 M, $[IBVE–HCl]_0$ = 5.0 mM, $[GaCl_3]_0$ = 5.0 mM, [THF] = 1.0 M, in toluene at 0 °C; The dotted line in Figure 1B was forcibly drawn through the origin. See also note 24).

The ^{1}H NMR analysis revealed that the product polymer possessed a structure derived from clean ring opening (Figure 2). The spectrum shows the structure of the single main chain—the acetal main chains (peak *b*) with the dimethyl (peak *a*) and the methoxy (peak *c*) side chains—whereas the polymers possess different types of terminal structures. Although most of the ω-end structures were the expected acetal with dimethoxy groups (peak *j*) that was derived from the quenching with methanol, a tiny amount of an aldehyde structure at the chain end was also observed at 9.5 ppm (peak *k*). This structure results from the reaction of the propagating end with adventitious water[24] or the partial decomposition of the main chain. In contrast to the efficient incorporation of the quencher to the ω-end, a considerably smaller amount of initiator fragments were attached to the α-end (peaks *e*, *f*, *g*, and *h*). However, 80—90% of the polymer chains appeared to possess hydroxy groups at the α-end. The assignment of the peaks at 2.2—2.6 ppm to the hydroxy groups, labeled as peak *i*, was supported by the disappearance of these peaks in the presence of D_2O due to proton–deuteron exchange. The chain-end hydroxy groups were possibly generated from the initiation reactions by the adventitious water or by the coordination of $GaCl_3$ to MOMPO, as discussed later. The peaks of the α-end and the ω-end structures had similar integral ratios, suggesting that no branched structure is present in the polymer. The initiator efficiency of IBVE–HCl was estimated to be approximately 20—30% on the basis of the M_n(calcd) and the M_n(exp) obtained from GPC using polystyrene calibration. Incidentally, no THF molecules, which were used as an added base, were (co)polymerized during the MOMPO polymerization, as confirmed by the absence of peaks assignable to its polymeric structures in the spectrum.

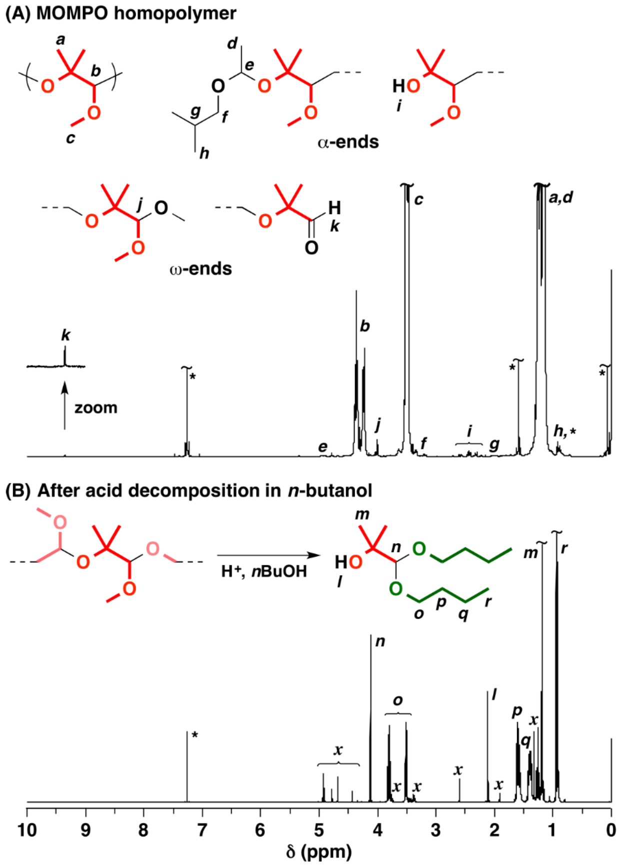


Figure 2. ^{1}H NMR spectra of (A) poly(MOMPO) (entry 2 in Table 1) and (B) its acetalized product (see Table 1 for the polymerization conditions; see Figures S2—S4 for the 2D NMR spectra; acetalization conditions: 6 mg/mL, 0.5 M HCl(aq) in *n*-butanol at room temperature for two days; the peaks labeled as *x* are probably assigned to cyclic products that generated during the acid decomposition reaction, see Figure S5 and Scheme S1 for the possible structures; * water, solvent, grease, and vaseline).

The MALDI–TOF–MS analysis of the product (Figure 3) supported the structures deduced from the aforementioned analysis of the ^{1}H NMR spectrum. The mass spectrum contained two series of peaks. The differences between the peaks, 56, corresponded to the difference in the mass values between the dimethoxy acetal and the aldehyde group at the ω-ends. The α-end structures, however, were indistinguishable in the spectrum because the mass difference of polymers is only two between those with α-ends derived from the IBVE–HCl fragment and from a proton [102 (monomer unit) – 100 (difference between the IBVE–HCl fragment and a proton)].

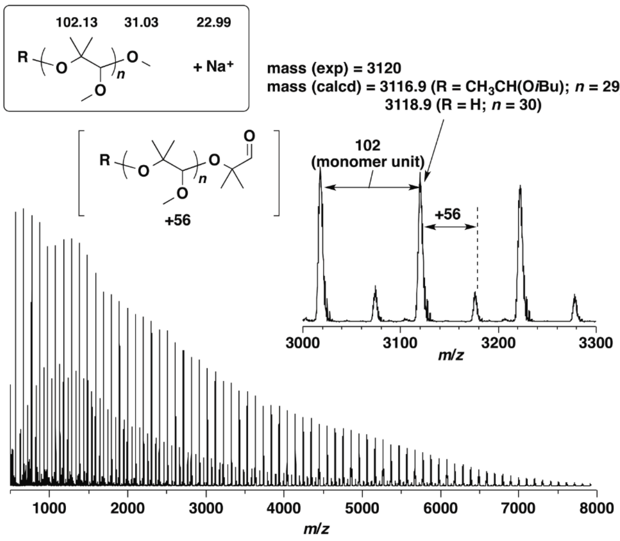


Figure 3. MALDI–TOF–MS spectrum of poly(MOMPO) obtained using the $GaCl_3$/THF initiating system (entry 2 in Table 1).

Because the MOMPO homopolymer contains acetal structures in its main chain, it was completely decomposed under acidic conditions. The decomposition reaction was conducted using 1.0 M HCl(aq) in *n*-butanol at room temperature for 2 h. The ^1H NMR spectrum of the decomposition product (Figure 2B) contained peaks assignable to the acetal structure with dibutoxy groups, indicating the occurrence of a clean reaction. In addition, GPC analysis indicated that the original polymer completely disappeared (Figure 4).

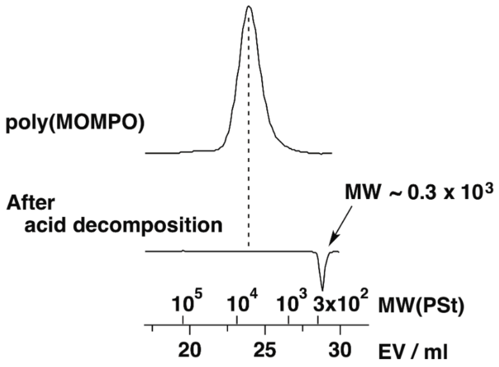
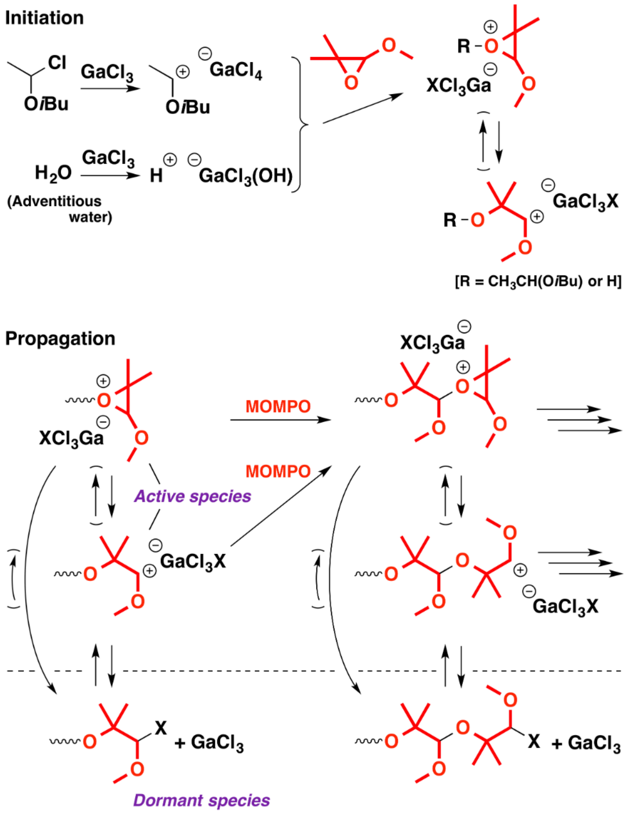


Figure 4. MWD curves of (A) poly(MOMPO) (entry 2 in Table 1) and (B) its acetalized product (see also Figure 2).

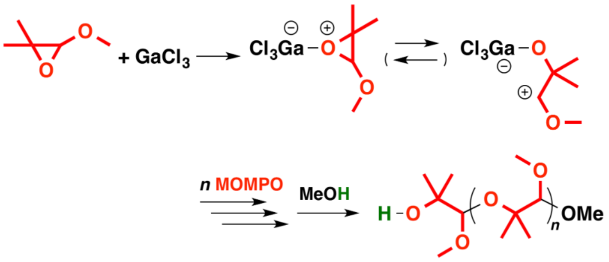
An excessively long polymerization time also caused scission of the acetal main chain, leading to significant decomposition of the previously produced polymer. When the polymerization using $GaCl_3$ remained unquenched for 24 h, long after quantitative monomer consumption, the resulting product had a very low MW ($M_n \sim 0.6 \times 10^3$) compared to that obtained after 4 h. This result is most likely due to the propagating species attacking the acetal structures in the main chain via the back-biting mechanism in the absence of monomer molecules. Another possible mechanism involves the scission of the acetal structures by Lewis acid catalysts.

2. Possible Mechanisms for the Polymerization

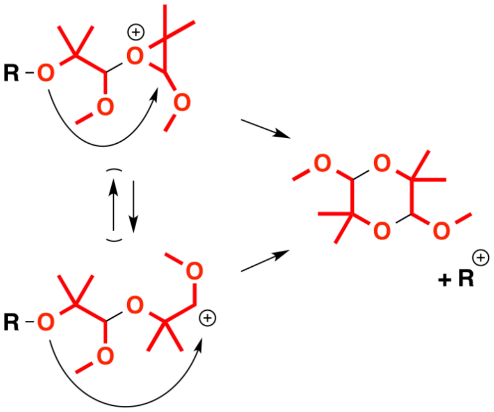
Possible mechanisms for the controlled cationic polymerization of MOMPO are summarized in Scheme 2. The reaction begins with the activation of IBVE–HCl with $GaCl_3$ or with the reaction of water and $GaCl_3$. The generated carbocation or a proton adds to a MOMPO molecule to form an oxonium ion. The initiation from the proton, however, might be very minor because the use of a proton-trapping reagent, DTBP, had a negligible effect on the MW of the product polymer (entry 3 in Table 1). Another possible initiation reaction is the coordination of a MOMPO molecule to $GaCl_3$, generating a zwitterionic species (Scheme 3).[3] In all of these cases, the oxonium ion may undergo ring opening to generate carbocationic species. Subsequently, the propagation reactions occur and continuously proceed via the attack of a MOMPO molecule on either of the active (cationic) species. A side reaction that frequently occurred with the CF_3SO_3H/$n$$Bu_4NI$ system (vide supra) is likely to be the generation of cyclic oligomers via back-biting reaction (Scheme 4).[3,21−23]



Scheme 2. Plausible reaction mechanism for the MOMPO homopolymerization using a Lewis acid catalyst (see Scheme 3 for another possible initiation reaction).



Scheme 3. Initiation reaction via zwitterionic mechanism that would occur by the reaction of MOMPO and $GaCl_3$.



Scheme 4. The generation of a cyclic oligomer via back-biting reaction (the formation of a dimer is shown; R = H or polymer chain; counteranions are omitted).

The ring opening of the oxonium ion can proceed via two possible pathways, i.e., via α- or β-scissions. Previous studies on the acid-catalyzed hydrolysis or alcoholysis of various oxiranes have indicated that the modes for the scissions are likely dependent on the stability of the generated carbocation or the carbocation-like intermediate, as well as on the nucleophilicity of the attacking species (water, alcohol, a chloride anion, etc.) and steric hindrance.[25−28] According to its structure, the MOMPO-derived oxonium ion should preferably undergo α-scission, i.e., the scission of the bond between the oxygen atom and the carbon atom that is adjacent to the methoxy group, due to both the carbocation stability (the alkoxy-adjacent carbocation is considerably more stable than the tertiary carbocation that contains three alkyl groups) and steric hindrance. Thus, the propagation reaction during the polymerization of MOMPO is most likely to proceed exclusively via α-scissions. However, the preference of the mode is difficult to empirically estimate because both modes produce polymers with acetal main chains that exhibit very similar spectroscopic features and are equally degradable via acid hydrolysis.

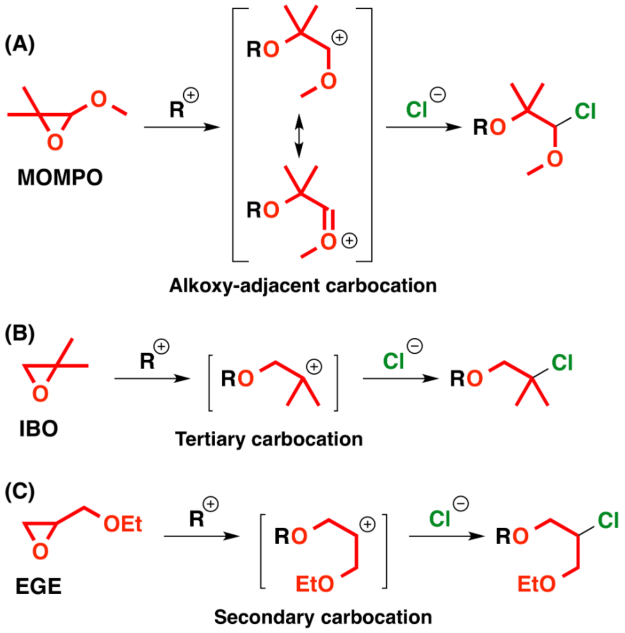
The propagation reactions may involve the formation of dormant species that possess a covalent carbon–heteroatom bond, similar to the living cationic polymerization of vinyl monomers. The propagating chain generated from the IBVE–HCl initiator will possess a carbon–chlorine bond at the chain end (X = Cl in Scheme 2). In contrast, the propagating chain generated from adventitious water will contain an unstable hemiacetal structure at the propagating end (X = OH in Scheme 2) because the counteranion that is generated via the reaction of $GaCl_3$ and water, $GaCl_3(OH)^-$, will not provide its chloride anion but will rather provide its hydroxy anion for the propagating species to generate the dormant species; this process is similar to the polymerization of VEs using an alcohol as a cationogen.[29] Because of the instability, the issue of whether such a structure with a hydroxy group is generated and functions as a dormant species is unclear.

A notable feature of the MOMPO polymerization is the effect of weak Lewis bases on the rate and controllability of the polymerization. The polymerization using $GaCl_3$ was also examined in the presence of another weak Lewis base, 1,4-dioxane (entry 4 in Table 1), and in the absence of any Lewis base (entries 5 and 6). The polymerizations were controlled in both cases to generate long-lived species, although the polymers had slightly broader MWDs. More interestingly, the polymerization rates were smaller than that in the presence of THF. The monomer conversion for the polymerization in the presence of THF reached 89% in 4 h (entry 2), whereas the conversions in the presence of 1,4-dioxane and in the absence of Lewis bases were 38% (entry 4) and 40% (entry 5) in 4 h, respectively. These trends in the rate and the controllability are completely different from those in the polymerizations of alkyl vinyl ethers. The cationic polymerization of alkyl vinyl ethers using $GaCl_3$ in the absence of any Lewis base completes in a second, yielding poorly defined polymers. In addition, the reaction in the presence of 1,4-dioxane proceeds much faster than that in the presence of THF (for example, monomer conversion = 97% in 6 s for 1,4-dioxane and 93% in 35 min for THF[30]). The decrease in the rate of VE polymerizations resulting from weak Lewis bases is due to the moderation of the Lewis acidity of the catalyst through acid–base interactions, and the greater effect of THF relative to 1,4-dioxane results from the stronger Lewis basicity.

One possible role of THF in the polymerization of MOMPO is to promote the ring opening of the oxonium ion. Because THF has a relatively large Lewis basicity, it may nucleophilically attack the carbon atom adjacent to the cationic oxygen atom on the oxonium ion. If the carbocation that is generated via ring opening possesses higher reactivity than the oxonium ion, then the promotion of the ring opening of MOMPO by THF would result in an increase in the polymerization rate.

3. Comparison with Cationic Polymerizations of Other Oxiranes

The control over polymerization is better with more stable ring-opened cationic species because the stability facilitates the ring opening of an oxonium ion and the reactivation of the resulting ring-opened dormant species of an oxirane unit. To confirm the effect of the carbocation stability on the polymerization behavior, particularly on the generation of long-lived species, we polymerized other oxiranes that may produce carbocations with different stabilities under similar conditions. MOMPO produces a VE-like propagating carbocation, which is one of the most stable species in cationic polymerization. Thus, we employed oxiranes that may create less stable carbocations by possible ring openings. The oxiranes examined are isobutylene oxide (IBO) and ethyl glycidyl ether (EGE), which may generate tertiary and secondary carbocations adjacent to alkyl groups, respectively (Scheme 5).



Scheme 5. Possible carbocations and dormant species with a carbon–chlorine bond generating from (A) MOMPO, (B) IBO, and (C) EGE. The carbon–chlorine bonds generating at the IBO and EGE propagating ends are hard to be cleaved under the reaction conditions employed in this study.

The structure of the possible ring-opened carbocation indeed significantly affected the polymerization behavior. The polymerizations of IBO and EGE using $GaCl_3$ ceased at low monomer conversions, yielding oligomeric products (entries 13—17, Table 1). The product polymer from IBO contained an ω-chain end structure that consisted of a carbon–chlorine bond with two methyl groups on the carbon as well as olefin structures, as evidenced by ^{1}H NMR (Figure S6). The formation of this tertiary chloride-type carbon–chlorine bond, which is similar to that of the isobutylene-derived dormant species, is indicative of the existence of the propagating tertiary carbocation that was transformed from the oxonium cation by the α-scission ring opening. The tertiary carbocation reacted with the chloride anion derived from IBVE–HCl or $GaCl_3$ to form a stable covalent bond. This type of carbon-chlorine bond is difficult to reactivate using a metal halide in the presence of a large amount of ester and ether or using stable metal halide–ether complexes, as previously reported in the polymerization of isobutylene.[31−34] The relatively greater stability of the carbon-chlorine bond (dormant) compared to that from MOMPO is responsible for the low reactivity of the IBO polymerization in which the IBO monomers and/or polymers function as Lewis bases to greatly moderate the activity of $GaCl_3$. In addition, the frequent occurrence of β-proton elimination reactions resulted in products with very low MWs. The amount of olefin structures derived from the side reaction were comparable to the amount of carbon–chlorine bonds. The difference in the monomer conversion values determined gravimetrically and using gas chromatography is due to the undesirable production of volatile, oligomeric products, which were removed during the purification process.

A similar explanation also holds for the polymerization of EGE; however, the carbon–chlorine bonds were not differentiated from the other peaks, and the peaks associated with olefin structures were very minor in the ^{1}H NMR spectrum (Figure S7). The β-elimination reaction occurred much less frequently because the resulting olefin structure, i.e., a VE-type structure with the adjacent alkoxy group, is relatively difficult to generate compared to the alkyl-substituted olefin structure derived from IBO.

Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization of MOMPO with Alkyl Vinyl Ethers

The results of the homopolymerization indicated the possibility of controlling the cationic copolymerization of MOMPO and VEs using the initiating systems that are suited for the living polymerization of VEs. Thus, the copolymerization with IBVE was first examined using the IBVE–HCl/$GaCl_3$ initiating system in toluene in the presence of THF at 0°C. This initiating system induces the controlled cationic homopolymerization of IBVE[30] and the controlled polymerization of MOMPO. The time–conversion plots for the copolymerization are shown in Figure 5. MOMPO was consumed at a rate similar to that of its homopolymerization under the same conditions, whereas IBVE never reacted.[35] The products were MOMPO homopolymers that had MWs and MWDs similar to those of the products obtained in the controlled homopolymerization of MOMPO.

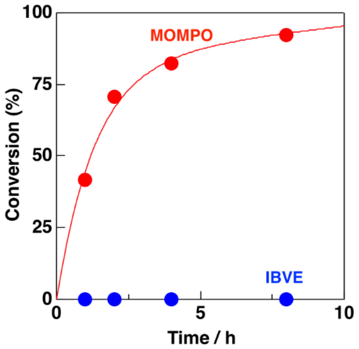


Figure 5. Time–conversion curves for the copolymerization of IBVE with MOMPO using $GaCl_3$ ($[IBVE]_0$ = 0.50 M, $[MOMPO]_0$ = 0.50 M, $[IBVE–HCl]_0$ = 5.0 mM, $[GaCl_3]_0$ = 5.0 mM, [THF] = 1.0 M, in toluene at 0 °C).

The difference in reactivity may be reduced through the use of a more reactive alkyl vinyl ether[36] and reaction conditions for slower ring-opening polymerizations of oxiranes. Thus, the reaction was conducted with a more reactive VE, IPVE, in a more polar solvent, dichloromethane, at a lower temperature, –78°C, with a high IPVE-to-MOMPO ratio (0.80 and 0.20 M, respectively). Both of the monomers were consumed under these conditions, although MOMPO still reacted considerably faster than IPVE, as shown in Figure 6A. The products had bimodal MWDs, as shown in the GPC profiles (Figure 6B). The acid hydrolysis of the product polymers resulted in a slight shift of the MWD curve of the higher-molecular-weight fraction to the lower-MW region and in the disappearance of the lower-molecular-weight fraction (purple curves). These results suggest that copolymers and MOMPO homopolymers were generated because an IPVE–IPVE sequence is not acid degradable, whereas a MOMPO homopolymer is completely degraded to a low-MW compound under acidic conditions.

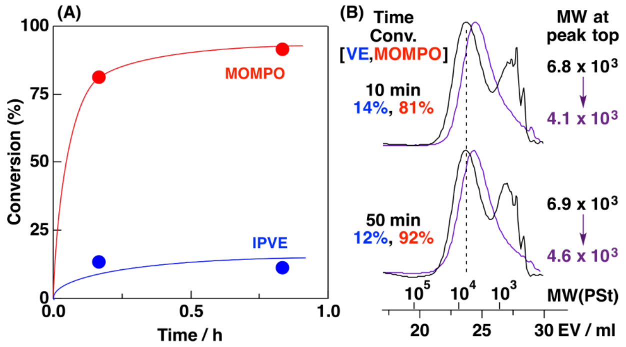


Figure 6. (A) Time–conversion curves for the copolymerization of IPVE with MOMPO using $GaCl_3$ and (B) MWD curves for the products (black) and their hydrolysis products (purple) (polymerization: $[IPVE]_0$ = 0.80 M, $[MOMPO]_0$ = 0.20 M, $[IBVE–HCl]_0$ = 5.0 mM,

$[GaCl_3]_0$ = 2.0 mM, [THF] = 0.50 M, in dichloromethane at –78 °C; hydrolysis: 6 mg/mL, 0.5 M HCl(aq) in 1,2-dimethoxyethane at r.t. for 28 h).

To suppress the homopolymerization of MOMPO during its copolymerization with IPVE, an initiating system suitable only for the polymerization of IPVE was employed. Our previous study showed that the CF_3SO_3H/*n*Bu_4NI system induces the living cationic polymerization of IPVE at –40°C.[20] However, this system is inefficient for the polymerization of MOMPO: a high conversion was achieved after a long reaction time (94% after 138 h), but the yield of nonvolatile product was very low (7%), as shown in the previous section (entry 12, Table 1). The oligomeric products most likely possess cyclic structures composed of a few monomer units; however, these products were removed during the purification process. The low activity for these reactions is expected to be advantageous for the copolymerization because the attack of the IPVE-derived carbocation on MOMPO will be the exclusive pathway for the consumption of MOMPO in the reaction using the CF_3SO_3H/*n*Bu_4NI system.

As expected, the copolymerization using the CF_3SO_3H/*n*Bu_4NI system proceeded smoothly with comparable consumptions of both IPVE and MOMPO, yielding products with unimodal MWDs (Figure 7). In addition, the MWD curve shifted toward the higher-MW region with increasing monomer conversion, indicative of long-lived species. Furthermore, the production of copolymers was strongly supported by the shift of the MWD curves to lower-MW regions after the acid hydrolysis.

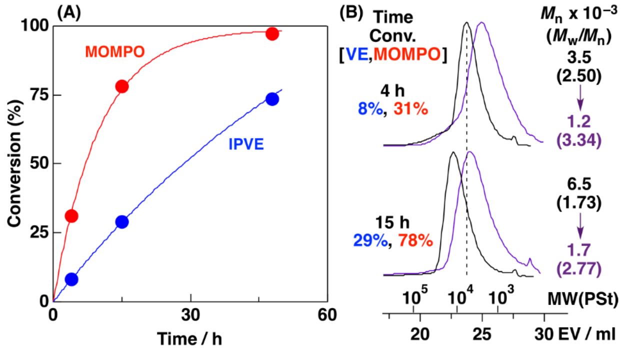


Figure 7. (A) Time–conversion curves for the copolymerization of IPVE with MOMPO using the CF_3SO_3H/$n$$Bu_4NI$ initiating system and (B) MWD curves for the products (black) and their hydrolysis products (purple) (polymerization: [IPVE] = 0.80 M, $[MOMPO]_0$ = 0.20 M, $[CF_3SO_3H]_0$ = 4.0 mM, $[nBu_4NI]_0$ = 4.2 mM, in dichloromethane at –40 °C; hydrolysis: 6 mg/mL, 0.5 M HCl(aq) in 1,2-dimethoxyethane at 60 °C for 6 h).

Despite the concurrent consumption of both monomers, the copolymer structure was completely unexpected, as confirmed by the ^1H NMR analyses of the obtained copolymer and its hydrolysis product (Figure 8). The absorption due to the acetal structure resulting from the crossover reaction of the IPVE-derived carbocation to MOMPO, shown as peak *12* in Figure 8A, was very small; instead, large peaks were present at 3.8—4.2 ppm (peaks *16* and *18*). These unexpected peaks were assigned to a structure with a side chain that possesses MOMPO and an isopropoxy group on the basis of ^{13}C and 2D NMR analyses (Figures S8—S11). The integral ratios of all the peaks in the ^1H NMR spectrum were consistent with these assignments. In addition, this characteristic structure was supported by the disappearance of these peaks and by the emergence of the aldehyde peak (peak *23* in Figure 8B) after acid hydrolysis and of acetal protons (peak *27*) of the product obtained from acetalization of the aldehyde groups with ethanol. The peak at 3.3 ppm (peaks *9* and *10*) was assigned to the structure derived from the crossover reaction from the MOMPO-derived carbocation to IPVE via a simple mechanism (Scheme 6A).

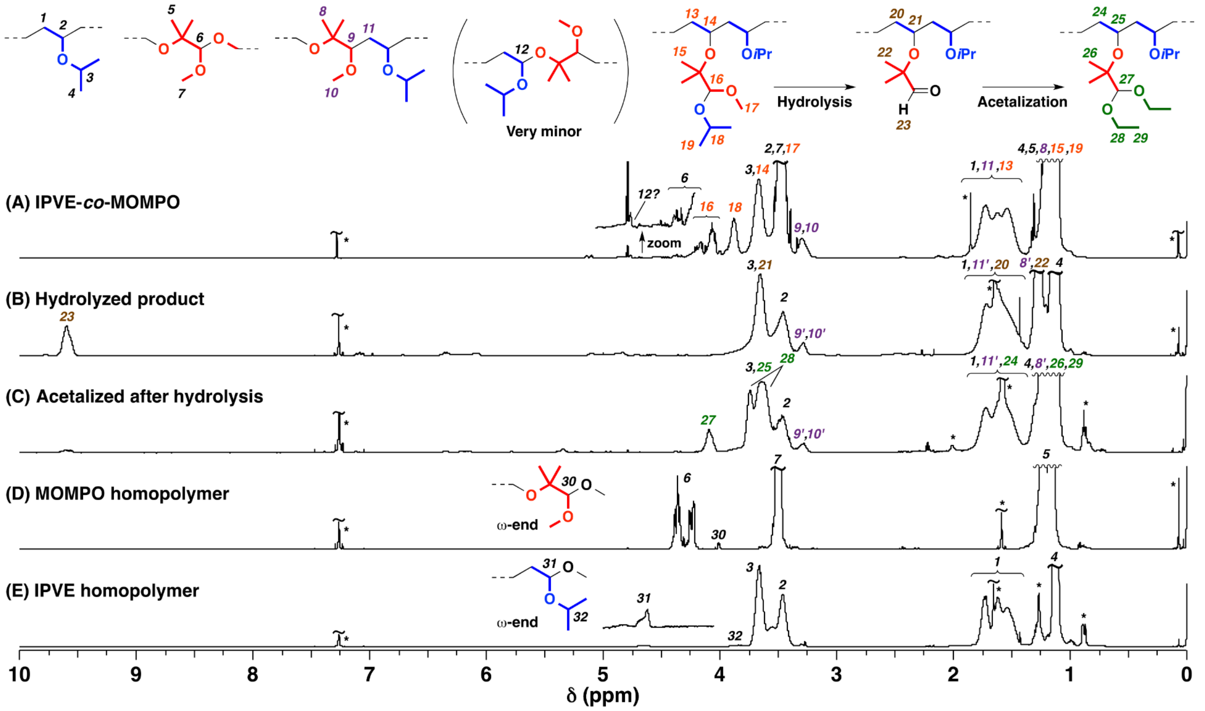
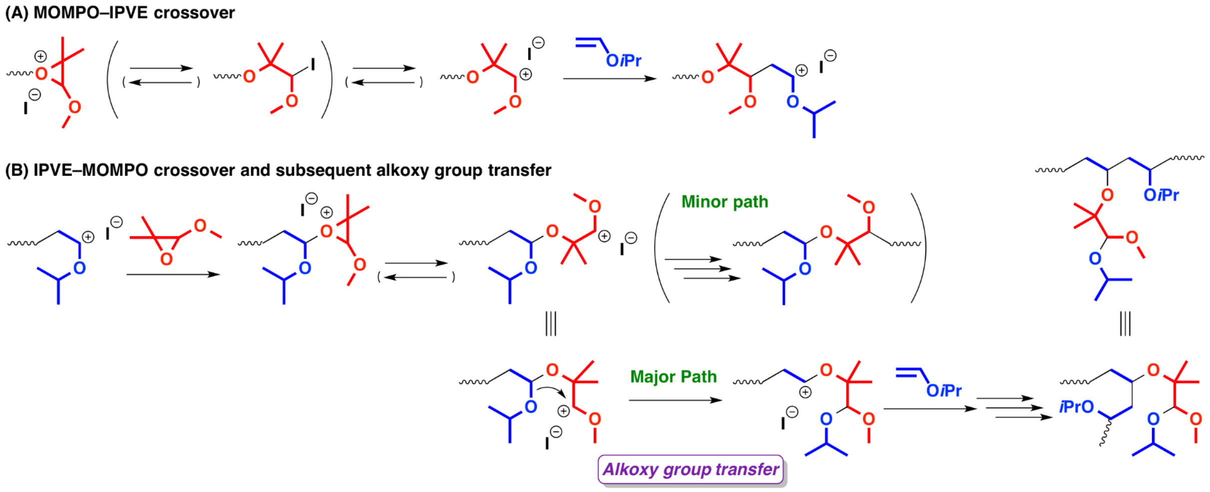


Figure 8. ^{1}H NMR spectra of (A) poly(IPVE–*co*–MOMPO) (the lower product in Figure 7B), (B) its hydrolysis product, (C) a polymer obtained by acetalizing the hydrolysis product with ethanol, (D) poly(MOMPO) (entry 2 in Table 1), and (E) poly(IPVE) (obtained using the CF_3SO_3H/nBu$_4$NI initiating system) for comparison (in $CDCl_3$ at 30 °C; see Figures S8—S17 for the ^{13}C and 2D NMR spectra; * solvent, grease, vaseline, water, etc.).

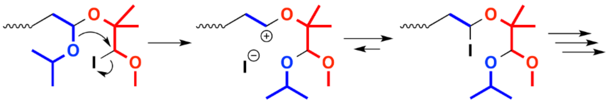
A possible mechanism for the generation of the unexpected structure is shown in Scheme 6B. The IPVE-derived carbocation reacts with MOMPO to generate an oxonium ion. After the subsequent ring opening of the oxonium ion, the generated carbocation abstracts the isopropoxy group at the penultimate unit derived from IPVE. This reaction, or “alkoxy-group transfer" through acetal formation and fragmentation, results in rearrangement of the carbocation and the incorporation of the MOMPO unit with the transferred isopropoxy group into the polymer side chain.



Scheme 6. Postulated mechanism for the copolymerization of IPVE with MOMPO.

The driving force for the alkoxy-group transfer is most likely the relative positions of the components that participate in the reaction. The atoms that are linked from the MOMPO-derived carbocationic center to the oxygen atom of the isopropoxy group at the penultimate unit can form a five-membered ring-like transition state, which facilitates the 1,5-transfer of the isopropoxy group. The dimethyl groups of the MOMPO unit would also contribute to the formation of this transition state, given that the copolymerizations using other oxiranes, including isobutylene oxide and isoprene monoxide, did not induce the alkoxy-group transfer.[17]

The almost exclusive occurrence of the alkoxy-group transfer, without generating the simple IPVE-to-MOMPO crossover reactions, may also be related to the activity of the dormant species. Both of the carbocations derived from IPVE and MOMPO can form dormant species that contain carbon–iodine bonds; however, the activity, or the frequency of the scission, of the IPVE-derived bond is most likely considerably higher than that of the MOMPO-derived bond. This higher activity stems from the alkoxy group at the side chain affecting the reactivity of VEs, i.e., a VE with a secondary alkoxy group is much more active than a VE with a primary alkoxy group.[36] Thus, after the reaction of the IPVE-derived carbocation with MOMPO, the MOMPO-derived propagating species forms the carbon–iodine bond; however, cleavage of this bond would be difficult under the investigated conditions. The penultimate isopropoxy group, however, may be able to attack the carbon atom of the carbon–iodine bond via an S_N2-like mechanism because of their appropriate positions, resulting in the generation of a carbocation containing a tertiary alkoxy group at the side chain (Scheme 7). The formation of the carbon–iodine dormant end derived from MOMPO was suggested by the ^1H and ^{13}C NMR peaks assigned to the MOMPO-derived acetal structures with dimethoxy groups, which was produced by the reaction of the carbon–iodine bond with a methanol molecule as a quencher (2D NMR spectra supported the assignments; see Figures S3, S4, S10 and S11).



Scheme 7. Alkoxy group transfer through the cleavage of the carbon–iodine bond.

Figure 9 shows schematic illustrations of the product copolymer and its hydrolysis product. These illustrations were drawn on the basis of the numbers of each unit that were calculated from the integral ratios in the ^{1}H NMR spectra and the GPC analysis. The main chain of the polymer is primarily composed of IPVE units and of structures derived from the alkoxy-group transfer. In addition, a small amount of MOMPO units was most likely partially incorporated into the middle region of the main chain because the acetalization of the hydrolysis product with ethanol afforded a product with a considerably lower MW than that of the original copolymer but only slightly larger than that of the hydrolysis product (Figure S18).

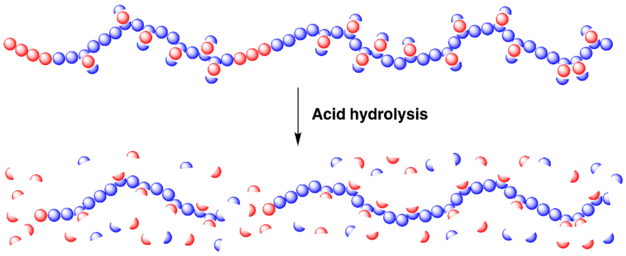


Figure 9. Schematic illustration for the copolymer and its hydrolysis product (blue: VE unit, red: MOMPO unit).

Conclusions

In conclusion, the cationic homopolymerization of MOMPO proceeded in a controlled manner with the use of $GaCl_3$ as a Lewis acid catalyst. The advantage of this oxirane over other oxiranes, such as IBO and EGE, is the alkoxy group that contributes to the stabilization of the carbocation obtained via ring opening. Thus, dormant–active equilibrium was possibly established in a manner similar to the living cationic polymerization of alkyl vinyl ethers, allowing the generation of long-lived species. In addition, the copolymerization of MOMPO with IPVE was demonstrated to proceed using the $CF_3SO_3H/n\text{Bu}_4\text{NI}$ system through a reaction mediated by long-lived species, yielding products with unimodal MWDs. The microstructure analysis of the product, however, revealed that the copolymerization occurred via a peculiar mechanism. The isopropoxy group at the penultimate unit transferred exclusively to the MOMPO-derived carbocation at the chain end after the crossover reaction from the IPVE-derived propagating end to MOMPO. This “alkoxy-group transfer” mechanism yielded a copolymer in which MOMPO units containing the transferred isopropoxy group were incorporated into the side chains. The results obtained in this study will lead to the synthesis of various functional copolymers from ever-incompatible monomers, i.e., vinyl and cyclic monomers, via controlled copolymerization reactions.

ASSOCIATED CONTENT

Supporting Information. ^{1}H, ^{13}C, and 2D NMR spectra, and GPC curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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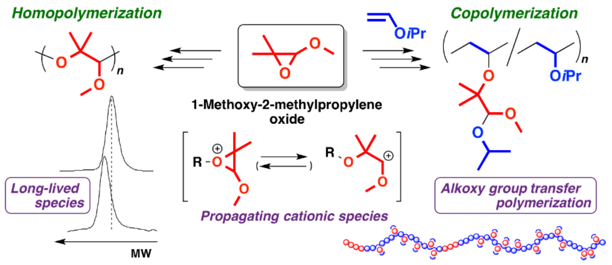

Title:

“Alkoxyoxirane, a Unique Cyclic Monomer: Controlled Cationic Homopolymerization Mediated by Long-Lived Species and Copolymerization with Vinyl Ether via Alkoxy Group Transfer”

Authors:

Arihiro Kanazawa, Shungo Kanda, Shokyoku Kanaoka, and Sadahito Aoshima