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Note	

Generation of "Living" Species Using Perfluoroalkylsulfonic Acids in Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization via Crossover Reactions

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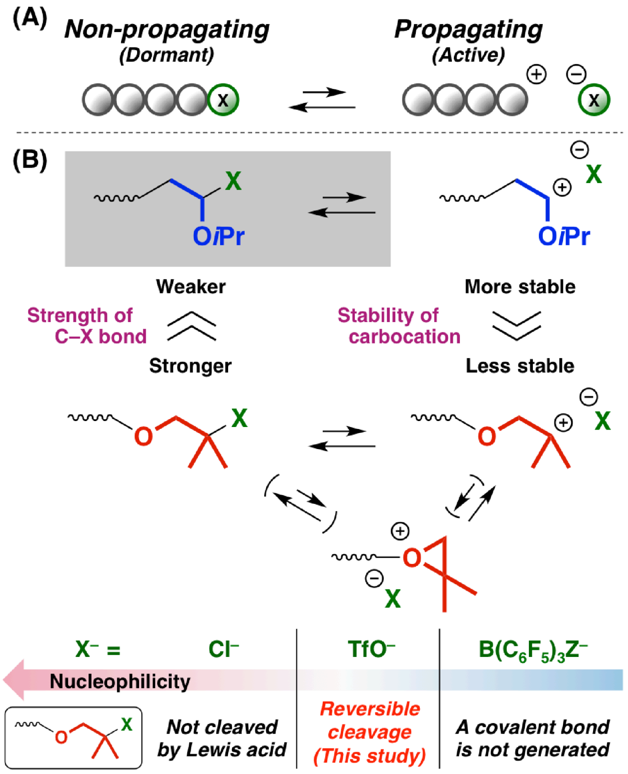
Abstract

"Living" species-mediated propagation reactions were demonstrated to occur in the cationic vinyl-addition and ring-opening copolymerization of isopropyl vinyl ether and isobutylene oxide (IBO) with CF_3SO_3H (TfOH) as an initiator. The polymerization proceeded by the carbocations as propagating species formed by the dissociation of a terminal covalent carbon–OTf bond. Importantly, the covalent species were generated exclusively at the IBO-derived propagating end, which was indicated by both the incorporation of a quencher fragment into the ω-end of the product copolymer and ^{19}F NMR analysis of the copolymerization reaction. The generation of reversibly dissociable covalent species, or "dormant" species, from one of the two monomers was crucial for allowing the even propagation of the propagating chains. Moreover, the reaction conditions were optimized to suppress side reactions such as chain transfer via β-proton elimination. Copolymers with molecular weights that agree relatively well with the theoretical values were produced using $C_4F_9SO_3H$ as an initiator in less polar solvents at lower temperature.

Introduction

The properties of polymers depend on their shapes, molecular weights (MWs), monomer compositions, and monomer sequences; hence, synthetic methods that allow the control of polymer structures are of great interest from both academic and industrial standpoints. Diversification of applicable monomers that are incorporated into a single polymer chain is one of the attractive ways of yielding polymers with unprecedented structures. In particular, copolymerization of monomers that inherently polymerize by different mechanisms through the generation of different types of propagating species is a promising strategy for fulfilling this objective. Examples of these copolymerization reactions include the zwitterionic copolymerization of monomers with electron-donating and electron-withdrawing groups,[1,2] vinyl-addition and ring-opening copolymerization of vinyl and cyclic monomers,[3–9] and interconvertible radical and cationic copolymerization.[10] However, copolymerization via different mechanisms is challenging in most cases because of the difficulty in realizing crossover reactions between different types of monomers. To overcome this difficulty, monomer structures and/or initiating systems were elaborately designed in previous successful studies. For example, the generation of a carbocation via the ring opening of an oxirane-derived oxonium ion was vital for the crossover reaction from an oxirane to a vinyl ether (VE) in a concurrent cationic vinyl-addition and ring-opening copolymerization.[8,9] Reaction conditions were also need to be elaborately designed for realizing crossover reactions in some cases of copolymerization of vinyl monomers with different structures such as VEs and styrene derivatives.[11,12]

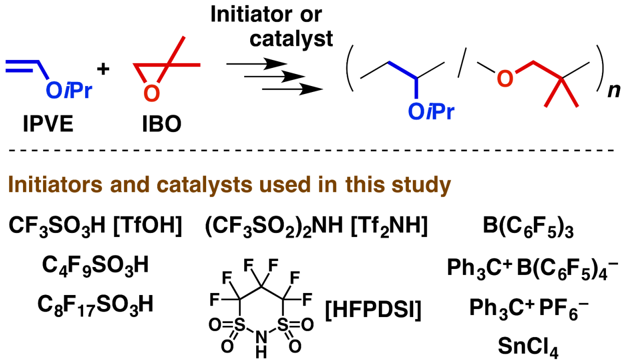
Living polymerization is a powerful tool for the precise synthesis of tailor-made polymeric architectures. Extensive studies by many researchers have contributed to the realization of living polymerization via various mechanisms, such as anionic, cationic, radical, coordination, and metathesis reactions. One of the key factors in the living cationic polymerization of vinyl monomers[13–23] is constructing an appropriate equilibrium between the non-propagating and the propagating species, or "dormant–active" equilibrium[24–26] (Scheme 1A). The generation of a carbocation through the dissociation of "dormant" species by a Lewis acid catalyst or through catalyst-free dissociation allows the even propagation of all the propagating chains. Therefore, in copolymerization, "dormant" species with comparable reactivities need to be generated from different monomers. The living cationic polymerization of cyclic ethers via the ring-opening mechanism proceeds when monomers such as tetrahydrofuran (THF) were used in conjunction with a suitable initiator.[27–29] The polymerization is mediated by the nucleophilic attack of a monomer to the propagating oxonium ion. However, living polymerization of oxiranes is difficult in many cases due to side reactions such as intramolecular chain transfer to polymer (back-biting).



Scheme 1. (A) Equilibrium between the Non-Propagating and the Propagating Species (the "Dormant–Active" Equilibrium) in Cationic Polymerization and (B) The Strategy to the Generation of "Living" Species in Cationic Copolymerization of IPVE and IBO (The Species with Gray Shadow Is Expected to Be Absent When TfOH Is Used As an Initiator; Z = OH, C_6F_5, etc.).

In this study, we aimed to develop a concurrent cationic vinyl-addition and ring-opening copolymerization mediated by living species.[30] In our previous study, crossover reactions between VEs and oxiranes were achieved via a copolymerization that proceeds without generating "dormant" species.[8] The use of $B(C_6F_5)_3$, a strong Lewis acid that generates a weakly coordinating anion,[31,32] was effective for copolymerization via crossover reactions, although the MWs of the products were not controlled due to the nonliving nature of the polymerization. In contrast, the coexistence of different "dormant" species was unsuitable for copolymerization because the covalent species generated from a more stable, VE-derived carbocation is much weaker than the covalent species generated from a less stable, oxirane-derived carbocation (Scheme 1B). Indeed, the polymerization of isopropyl VE (IPVE) and isobutylene oxide (IBO) using $GaCl_3$ as a catalyst did not proceed because of the generation of an inert carbon–chlorine bond at the IBO-derived propagating end.

To enable the even propagation, i.e., the propagation without "left-behind" species, of all the propagating chains in the copolymerization of VEs and oxiranes, we devised a strategy in which the "dormant" species is generated exclusively at the oxirane-derived propagating end. Given that a reversibly cleavable covalent species is generated from IBO and not from IPVE, all the chains can propagate through the "dormant–active" equilibrium at the IBO-derived propagating ends. Examination of various initiators and catalysts (Scheme 2) led to the finding that perfluoroalkylsulfonic acids such as CF_3SO_3H (TfOH) are efficient in the generation of dissociable covalent species in the copolymerization of IPVE and IBO. Notably, the copolymerization proceeded via the formation and dissociation of a covalent carbon–OTf species at the IBO-derived propagating end (Scheme 1B), which was confirmed by the incorporation of a quencher fragment into a copolymer chain and ^{19}F NMR analysis of the copolymerization reaction. The generation of the carbon–OTf bond at the propagating ends is similar to the ring-opening polymerization of cyclic monomers such as THF,[33–37] oxetane derivatives,[38,39] oxepane,[40] and 1,3-dehydroadamantanes.[41] The optimization of the reaction conditions was also conducted to improve the control of the MWs of the product copolymers by suppressing side reactions such as β-proton elimination.



Scheme 2. Cationic Copolymerization of IPVE and IBO

Experimental Section

Materials. Isopropyl vinyl ether (IPVE; Wako; 97.0+%) was washed with 10% aqueous sodium hydroxide solution and then distilled twice from calcium hydride. Cyclohexyl vinyl ether (TCI; >98.0%) was washed with 10% aqueous sodium hydroxide solution and distilled from calcium hydride and then from sodium under reduced pressure. Isobutylene oxide (IBO; TCI; >97.0%) was distilled twice from calcium hydride. (+)-Limonene oxide (Aldrich; 97%, ee: 98%, mixture of *cis* and *trans*) and styrene oxide (Aldrich; 97%) were distilled twice from calcium hydride under reduced pressure. Dichloromethane (Wako; 99.0%) and hexane (Wako; 96.0%) were dried by passage through solvent purification columns (Glass Contour). Dichloromethane-d_2 was distilled from calcium hydride. Dichloropentafluoropropane {HCFC [Asahi Glass; ASAHIKLIN® AK-225, a mixture of $CF_3CF_2CHCl_2$ and CF_2ClCF_2CFHCl (45/55 w/w)]} was dried over 3 A and 4 A molecular sieves (Nacalai Tesque). Commercially available $B(C_6F_5)_3$ (Aldrich; 95%), TfOH (Aldrich; ≥99.0%), and Tf_2NH (Wako; 98.0+%) were used without further purification after preparing their stock solutions in dichloromethane. Nonafluoro-1-butanesulfonic acid ($C_4F_9SO_3H$; TCI; >98.0%) was used without further purification after preparing its stock solution in dichloromethane (the acid was partly insoluble). Perfluorooctanesulfonic acid ($C_8F_{17}SO_3H$; TCI; >98.0%) and 1,1,2,2,3,3-hexafluoropropane-1,3-disulfonimide (HFPDSI; TCI; >98.0%) were used without further purification after preparing their stock solutions in HCFC (AK-225) ($C_8F_{17}SO_3H$ was partly insoluble). $SnCl_4$ (Aldrich; 1.0 M solution in *n*-heptane), triphenylcarbenium hexafluorophosphate ($Ph_3C^+PF_6^-$; Aldrich), triphenylcarbenium tetrakis(pentafluorophenyl)borate ($Ph_3C^+B(C_6F_5)_4^-$; TCI, >98.0%), nBu$_4$NI (Aldrich; ≥99.0%), 3-buten-1-ol (TCI; >98.0%), and 3-methyl-3-buten-1-ol (TCI; >98.0%) were used as received. The IBVE–HCl adduct was prepared from the addition reaction of IBVE and HCl via a literature method.[42]

Polymerization Procedure. The following is a typical polymerization procedure with the TfOH initiating system. A glass tube equipped with a three-way stopcock was dried under dry nitrogen using a heat gun (Ishizaki; PJ-206A; blow temperature of ~450 ºC). Dichloromethane, hexane, IPVE, and IBO were added to the tube using dry syringes. After cooling the solution at –78 ºC, the polymerization was initiated by adding a solution of TfOH in dichloromethane. At predetermined intervals, the reaction was terminated by an alcohol (ethanol, 3-buten-1-ol, or 3-methyl-3-buten-1-ol) containing a small amount of aqueous ammonia solution. The quenched mixture was diluted with dichloromethane/hexane (2/8 v/v) and washed with water. The volatiles were then removed under reduced pressure at 50 ºC to yield a polymer. Monomer conversion was determined by gas chromatography (GC; column packing material: PEG-20M-Uniport-HP, GL Science Inc.) using hexane as an internal standard or by gravimetry and ^{1}H NMR integral ratios of both monomer units in the product polymers. The value obtained by GC corresponds to the amount of monomers consumed by both polymer generation and side reactions such as isomerization to an aldehyde, while the value obtained by gravimetry and ^{1}H NMR corresponds to the amount of monomers incorporated into the product polymers

Acid Hydrolysis. The acid hydrolysis of the copolymers was conducted using 0.5 M HCl(aq) in 1,2-dimethoxyethane at room temperature for 1 h (sample: ~1 wt%). The quenched mixture was diluted with dichloromethane and washed with an aqueous sodium hydroxide solution and then water. The volatiles were removed under atmospheric pressure at room temperature.

Characterization. The polymer molecular weight distributions (MWDs) were measured via gel permeation chromatography (GPC) in chloroform at 40 ºC on polystyrene gel columns (TSKgel GMH$_{\mathrm{HR}}$-M × 2 with an exclusion limit molecular weight = 4×10^6; bead size = 5 mm; column size = 7.8 mm i.d. × 300 mm; flow rate = 1.0 mL min^{-1}) 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 the polydispersity ratio (weight-average molecular weight/number-average molecular weight [M_w/M_n]) were calculated from the chromatographs based on 16 polystyrene standards (Tosoh; M_n = 577−1.09×10^6, $M_w/M_n \leq 1.1$). NMR spectra were recorded on a JEOL JNM-ECA 500 (500.16 MHz for ^{1}H, 125.77 MHz for ^{13}C, and 470.62 MHz for ^{19}F) or a JEOL JNM-ECS 400 (376.17 MHz for ^{19}F) spectrometer. Hexafluorobenzene (C_6F_6; −164.9 ppm) was used as an external standard for ^{19}F NMR. Electrospray ionization mass spectrometry (ESI-MS) data were recorded on an LTQ Orbitrap XL (Thermo Scientific) spectrometer. Polymer solutions in dichloromethane/methanol (1/1 v/v) were used for ESI-MS analysis.

Result and Discussion

Copolymerization of IPVE and IBO using various initiating systems

To evaluate effective initiating systems for both the generation of living species and crossover reactions, the cationic copolymerization of IPVE (0.75 M) and IBO (0.22 M) was conducted with various initiators or catalysts at –78 ºC. The polymerization results are summarized in Table 1. A metal chloride, which functions as an efficient Lewis acid catalyst for the living cationic polymerization of VEs,[13,15,20] was not suitable for the copolymerization.[8] When $SnCl_4$ was used (entries 14 and 15), the peak of the MWD curve shifted to the higher-MW region as the reaction proceeded (Figure 1D), which indicates that the living species were likely partly generated through the "dormant–active" equilibrium at the IPVE-derived propagating ends. However, the crossover reactions did not occur efficiently (approximately once from VE to IBO per chain). This inefficient copolymerization resulted from the generation of the IBO-derived carbon–chlorine bond (see Figure S1 for ^{1}H NMR) via the reaction between the IBO-derived propagating species and the metal chloride-derived counteranion. This carbon–chlorine bond was not activated again once formed under the conditions employed, which is similar to the inertness of isobutylene polymerization in the presence of a weak Lewis base.[43] Indeed, the polymerization became slower over the course of the polymerization due to an increase in the number of inactive carbon–chlorine bonds. This result is in sharp contrast to the formation and dissociation of the VE-derived carbon–chlorine bond in the "dormant–active" equilibrium in the living homopolymerization of VEs.

Table 1. Cationic Copolymerization of IPVE and IBO[a]

	conc (M)					conv by GC (%)[b]				crossover per chain[d]		average unit numbers per one block[d,e]	
entry	IPVE	IBO	initiator or catalyst	solvent	time	VE	IBO	$M_n \times 10^{-3}$ [c]	M_w/M_n	VE to IBO	IBO to VE	VE	IBO
1	0.75	0.22	TfOH	CH_2Cl_2	3 h	28	39	2.9	1.53	2.0	1.1	14	1.7
2	0.75	0.22			12 h	80	86	4.2	1.71	2.1	1.4	19	1.8
3	–	0.22			40 min	–	85	0.3	1.45	–	–	–	–
4	0.75	–			3 min	100	–	43.2	5.29	–	–	–	–
5	0.75	0.22		CH_2Cl_2/hexane (1/9 v/v)	24 h	13	12	2.5	1.57	2.3	1.2	8	2.1
6	0.75	0.22			93 h	37	35	4.3	1.55	3.2	2.1	11	2.3
7	0.75	0.22			261 h	74	61	5.7	1.57	3.6	2.6	13	2.3
8	0.75	0.22	Tf_2NH	CH_2Cl_2	1 s	92	70	5.5	2.39	0.8	0.3	42	2.0
9[f]	0.75	0.22	HFPDSI		10 s	65	26	14.6	1.99	2.1	1.7	85	3.0
10	0.75	0.22	$B(C_6F_5)_3$		10 min	45	33	9.1	1.91	4.7	3.9	22	5.5
11	0.75	0.22			2 h	84	69	10.0	1.80	4.7	3.3	21	4.4
12	0.75	0.22	$Ph_3C^+B(C_6F_5)_4^-$		1 min	95	55	10.4	2.04	3.7	2.8	28	4.6
13	0.75	0.22	$Ph_3C^+PF_6^-$		10 s	82	19	13.9	2.64	2.5	1.6	56	3.0
14[g]	0.75	0.22	IBVE–HCl/ $SnCl_4$		1 h	26	17	3.1	4.49	1.2	n.d.[h]	11	3.7
15[g]	0.75	0.22			24 h	52	48	4.7	4.05	1.3	n.d.[h]	12	4.0
16[i]	0.75	0.22	TfOH/nBu$_4$NI		48 h	4	0	–	–	–	–	–	–

[a] $[IPVE]_0$ = 0 or 0.75 M, $[IBO]_0$ = 0 or 0.22 M, [initiator or catalyst]$_0$ = 1.0 (for entries 9—13) or 5.0 (for entries 1–8 and 16), 10 mM (for entries 14 and 15), in dichloromethane (with 5 vol% of hexane as an internal standard for GC) at –78 ºC. [b] Determined by GC. [c] Determined by GPC (polystyrene standards). [d] Estimated by ^{1}H NMR analysis. [e] The values correspond to the unit numbers per acetal. [f] Containing 1 vol % of HCFC (AK-225) as a dilution solvent for HFPDSI. [g] IBVE–HCl (4.0 mM) was used as a cationogen. [h] Not determined because the peak of the initiator (IBVE–HCl) fragment overlapped with the peaks derived from the crossover reaction. [i] nBu$_4$NI (5.2 mM) was used as an additive.

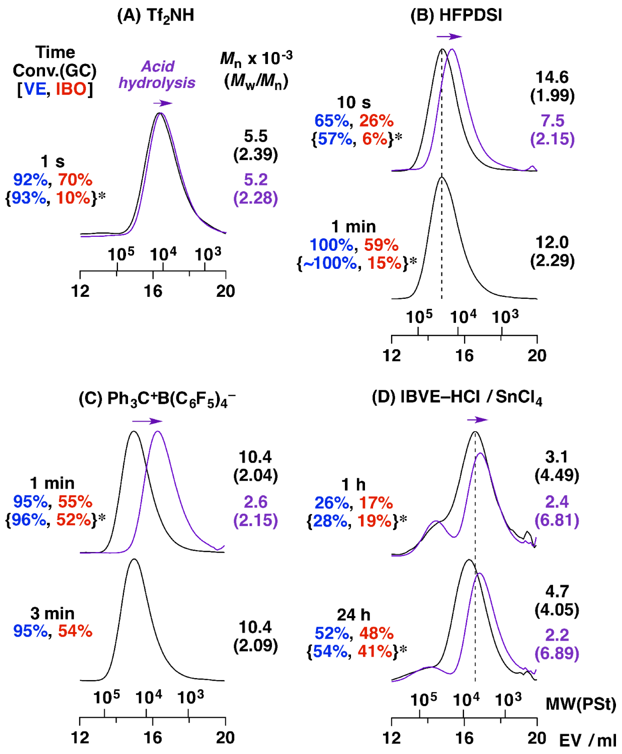


Figure 1. MWD curves of the products obtained in the copolymerization of IPVE and IBO by (A) Tf$_2$NH (entry 8 in Table 1), (B) HFPDSI (entry 9), (C) Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ (entry 12), and (D) SnCl$_4$ (entries 14 and 15) (see the footnote of Table 1 for the polymerization conditions; black: original polymers, purple: products obtained by acid hydrolysis); * monomer conversion values calculated from ^{1}H NMR and gravimetry.

Initiators that generate weakly coordinating counteranions were subsequently employed for the copolymerization at –78 °C. Copolymerization proceeded via the crossover reactions with the use of Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ (entry 12 in Table 1; Figure 1C); however, living species were not generated, as suggested by the observation that the quencher fragment was not incorporated into the products (vide infra). The polymerization likely proceeded without generating “dormant” species having a covalent bond. This behavior is similar to the copolymerization using B(C$_6$F$_5$)$_3$ (entries 10 and 11; Figure S2A). [8] The use of Ph$_3$C$^+$PF$_6^-$ (entry 13; Figure S2B) resulted in less frequent crossover reactions than the use of Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$, most likely because of the generation of an inert carbon–fluorine bond via the reaction between the IBO-derived propagating species and PF$_6^-$ (^{1}H and ^{19}F NMR in Figure S3). Perfluoroalkyl sulfonimides that generate weakly coordinating anions were also ineffective for polymerization mediated by living species. The polymerization initiated by Tf$_2$NH (entry 8) proceeded at a very high rate and yielded a product consisting mainly of IPVE homopolymer (Figure 1A). IBO was not incorporated into the polymer, whereas the oxirane was consumed, most likely via side reactions such as isomerization (vide infra). In the copolymerization using HFPDSI (entry 9), the MWD curves of the products did not shift to the higher-MW region as the monomer conversion values increased (Figure 1B), indicating that living species were not generated.

Unlike the initiators and catalysts examined above, TfOH, which is a superstrong protic acid that is effective in the generation of covalent carbon-OTf species in the polymerization of cyclic ethers such as THF and oxetane,[33–40] was found to allow both the generation of living species and the crossover reactions (entries 1, 2, and 5—7 in Table 1). Thus, the copolymerization using TfOH was examined in detail, as demonstrated in the next section.

Investigation of the copolymerization using TfOH as an initiator

The copolymerization conducted using TfOH at –78 ºC proceeded through the consumption of both monomers at comparable rates (Figure 2A and S4A) and generated polymers with unimodal MWDs. The reaction in less polar solvents (entries 5—7 in Table 1) was superior to the reaction in dichloromethane (entries 1 and 2) in terms of the control of the MWs of the products; hence, the copolymerization in dichloromethane/hexane (1/9 v/v) is highlighted below, while the result in dichloromethane is shown in the Supporting Information (Figures S4 and S5). Importantly, the MWD curves obviously shifted to the higher-MW region as the reaction proceeded while maintaining M_w/M_n values of 1.5–1.6 (Figure 2B). These results indicate that the copolymerization using TfOH proceeded through propagation reactions mediated by living species. This superstrong protic acid was reported to enable the cationic ring-opening polymerization of cyclic ethers via the generation of both covalent bonding species and an oxonium ion/TfO^- pair.[33–40] Thus, similar covalent bonding and ion-pair species were potentially generated at the IBO-derived propagating ends during the copolymerization. In addition, no polymerization proceeded when $n\mathrm{Bu_4NI}$ was used in conjunction with TfOH (entry 16 in Table 1), indicating that the carbon-iodine bond derived from IBO was not cleaved at all. This result is in sharp contrast to the cationic polymerization of highly reactive monomers such as *N*-vinylcarbazole and alkyl VEs via the dissociation of the carbon-iodine bond.[44,45]

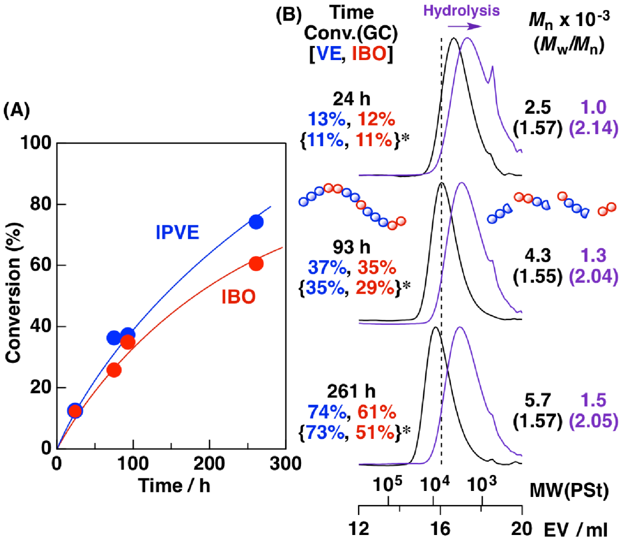


Figure 2. (A) Time–conversion plots for the copolymerization of IPVE (blue) and IBO (red), and (B) MWD curves of the obtained polymers (black: original polymers; purple: products obtained by acid hydrolysis); polymerization conditions: $[\text{IPVE}]_0$ = 0.75 M, $[\text{IBO}]_0$ = 0.22 M, $[\text{TfOH}]_0$ = 5.0 mM, in dichloromethane/hexane (1/9 v/v) at –78 ºC; * monomer conversion values calculated from ^{1}H NMR and gravimetry.

^{1}H NMR analysis (Figure 3) suggested that copolymers were produced through several rounds of crossover reactions per chain. The peaks at 4.7 ppm (peak 14) and 0.9ppm (peaks 8 and 12) were assigned to acetal moieties and methyl groups derived from the crossover reactions from IPVE to IBO and from IBO to IPVE, respectively, as reported in our previous study[8] (see Figure S6 for ^{13}C NMR analysis). From the integral ratios of these peaks and the peaks assigned to the ω-ends, the crossover reactions were determined to occur 2.3, 3.2, and 3.6 times from IPVE to IBO and 1.2, 2.1, and 2.6 times from IBO to IPVE per chain through analysis of the polymers obtained at 24, 93, and 261 h, respectively. The increase in the number of crossover reactions per chain along with the monomer consumption also indicates that the copolymerization was mediated by living species. The average unit numbers of IPVE and IBO per block were determined to be 8–13 and 2.1–2.3, respectively. In addition, the copolymers were hydrolyzed under acidic conditions via the degradation of the acetal moieties in the main chain. The MWD peaks of the hydrolysis products (purple curves in Figure 2B) clearly shifted to the lower-MW region, which indicates that homopolymers of IPVE and IBO were negligibly generated in the copolymerization.

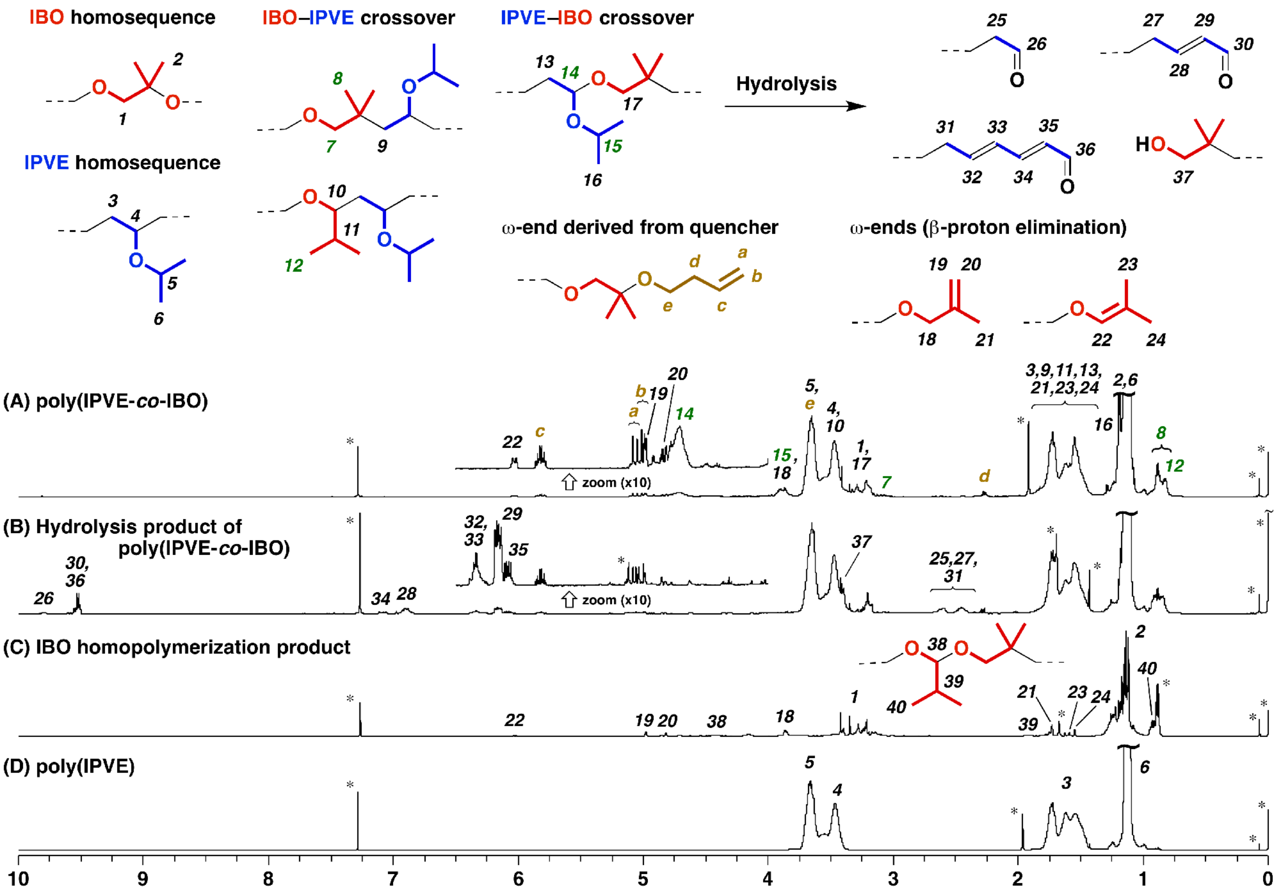
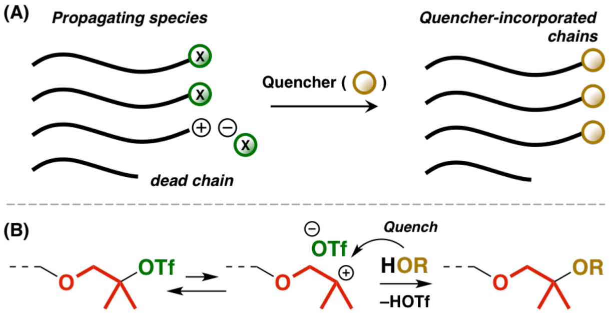


Figure 3. ^{1}H NMR spectra of (A) poly(IPVE-*co*-IBO) (quencher: 3-buten-1-ol; the same sample to that shown in the middle of Figure 2B: entry 6 in Table 1), (B) its hydrolysis product, (C) a product obtained by the homopolymerization of IBO (entry 3), and (D) poly(IPVE) (entry 4) recorded in $CDCl_3$ at 30 ºC; * TMS, grease, stabilizer, water, vaseline, or $CHCl_3$.

The incorporation of a quencher fragment into the polymer chain is indicative of the living nature of the propagating species. A ^{1}H NMR spectrum of the copolymer obtained using 3-buten-1-ol as a quencher had peaks assigned to the structure derived from the alcohol (peaks a–e in Figure 3A). ^{13}C NMR analysis also supported the incorporation of the quencher fragment (Figure S6). The quencher fragment was incorporated mainly into the IBO-derived ends, as confirmed by the comparison with the ^{1}H NMR spectrum of an IPVE homopolymer obtained by quenching with 3-buten-1-ol (Figure S7).[46] The residual peaks of the quencher fragment in the ^{1}H NMR spectrum of the acid hydrolysis product also indicate the incorporation into the IBO-derived ends because an alkoxy group incorporated into the VE-derived acetal end is removed as an alcohol through the purification process after acid hydrolysis. These results suggest that "dormant" species exhibiting a propagating ability via dissociation were generated at the IBO-derived propagating chain ends. The quencher appeared to react with the "dormant" species via the mechanism shown in Scheme 3. Importantly, the quencher fragment was not incorporated into the products obtained using $Ph_3C^+B(C_6F_5)_4^-$ or $B(C_6F_5)_3$ (Figure S7), most likely because the copolymerization with these initiators or catalysts proceeded through the cycle of initiation, propagation, and β-proton elimination reactions without forming "dormant" species. Furthermore, the instantaneous concentration of the propagating species was very low in this cycle.



Scheme 3. (A) The Illustration for the Quenching of Cationic Polymerization by Alcohol (ROH) and (B) Possible Reaction of the IBO–OTf Covalent-Bonding Species with Alcohol (The Reaction of the IBO-Derived Oxonium Ion Is Not Shown: See Note 47)

ESI-MS analysis of the acid hydrolysis product of the copolymer also suggested the incorporation of the quencher fragment into the IBO-derived propagating ends. 3-Methyl-3-buten-1-ol was used as a quencher instead of 3-buten-1-ol because the alkoxy group derived from 3-buten-1-ol has the same mass value to that of the IBO unit derived from the β-proton elimination reaction. The ESI-MS spectrum (Figure 4) had peaks assigned to structures consisting of IPVE and/or IBO blocks with a hydrogen atom and an aldehyde moiety at chain ends, which is consistent with the degradation of the acetal moieties in the main chain by acid hydrolysis. More importantly, peaks whose *m*/*z* values agreed with those of structures consisting of a few IBO units and the quencher fragment were detected (peaks with brown circles in Figure 4), indicating that the "dormant" species was generated at the IBO-derived propagating ends in the copolymerization.

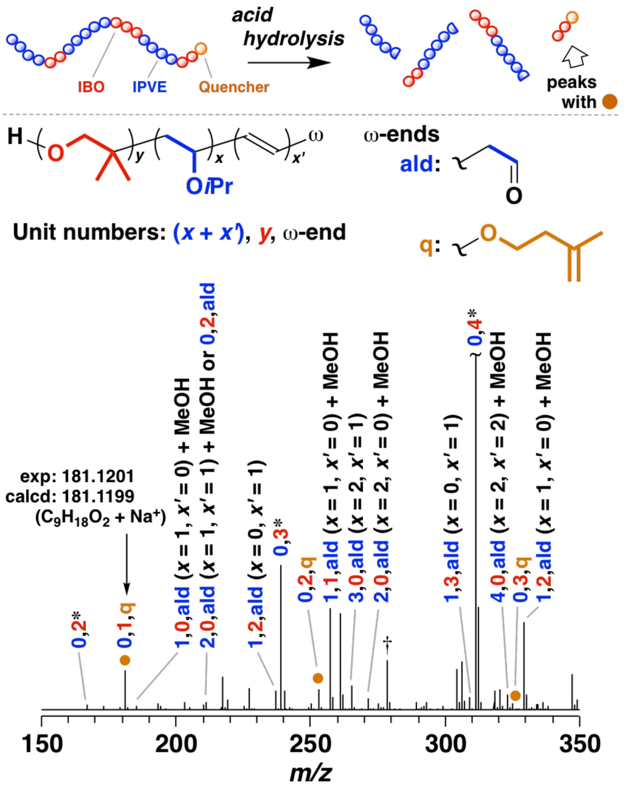


Figure 4. A high-resolution ESI-MS spectrum of an acid hydrolysis product of the IPVE–IBO copolymer obtained using 3-methyl-3-buten-1-ol as a quencher (polymerization conditions: $[\text{IPVE}]_0$ = 0.75 M, $[\text{IBO}]_0$ = 0.22 M, $[\text{TfOH}]_0$ = 5.0 mM, in dichloromethane at –78 ºC; before hydrolysis: M_n(GPC) = 4.7 × 10^3, M_w/M_n(GPC) = 1.59: after hydrolysis: M_n(GPC) = 1.8 × 10^3, M_w/M_n(GPC) = 2.67; Peaks with an asterisk are assigned to a cyclic structure or a linear chain with a hydrogen atom at the α-end and an olefinic structure at the ω-end); † contamination.

^{19}F NMR analysis of the copolymerization reaction suggested that two types of the propagating species were generated in the copolymerization (Figure 5). The solution containing only TfOH exhibited a broad peak at –82.5 ppm (Figure 5C). However, this peak was not detected in the spectrum recorded during the copolymerization of IPVE and IBO using TfOH at –78 ºC (Figure 5A), which indicates that the initiator was consumed in the initiation reaction. Instead, the spectrum had sharp peaks at –77.2 and –81.5 ppm. The former and the latter peaks were assigned to the IBO-derived carbon-OTf bond and the TfO^- anion, respectively. The most likely counter cationic species of the observed TfO^- anion is the IBO-derived oxonium ion. These assignments are based on the ^{19}F NMR analysis of cationic polymerizations of THF or oxetane derivatives using TfOH as an initiator.[33,34,36,37,39] The spectrum of the IBO homopolymerization reaction solution (Figure 5B) had two peaks at the same chemical shifts, which also indicates that the two peaks were derived from the IBO-derived propagating ends. The generation of "dormant" species with a covalent carbon-OTf bond was reported in kinetic and mechanistic studies of the polymerization of cyclic ethers such as THF.[33–40] A similar covalent bond may have been generated at the IBO-derived end, although the IBO-derived carbon atom is a quaternary carbon, whereas the THF-derived carbon is secondary.

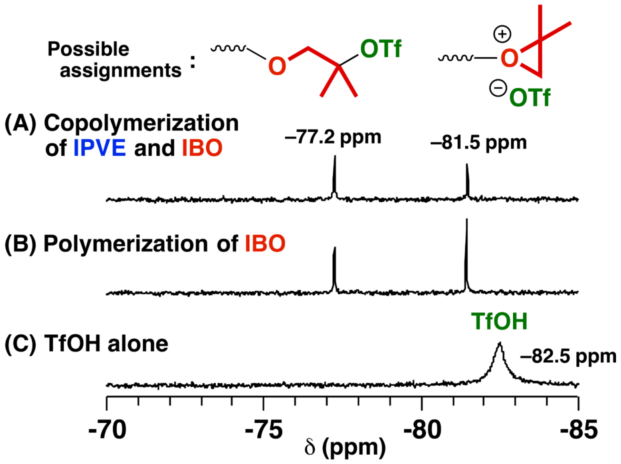
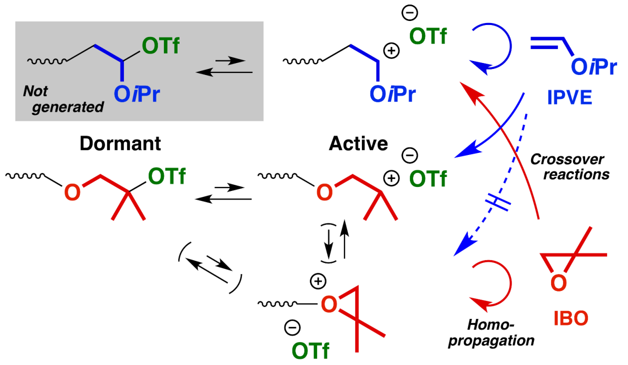


Figure 5. ^{19}F NMR spectra of (A) the reaction solution of the copolymerization of IPVE and IBO, (B) the reaction solution of the homopolymerization of IBO, and (C) the solution containing TfOH alone recorded in CD_2Cl_2 at –78 °C (376.17 MHz); polymerization conditions: $[IPVE]_0 = 0.79$ M, $[IBO]_0 = 0.22$ (for A) or 0.44 (for B) M, $[TfOH]_0 = 1.0$ (for A and B) or 5.0 (for C) mM.

Plausible copolymerization mechanisms

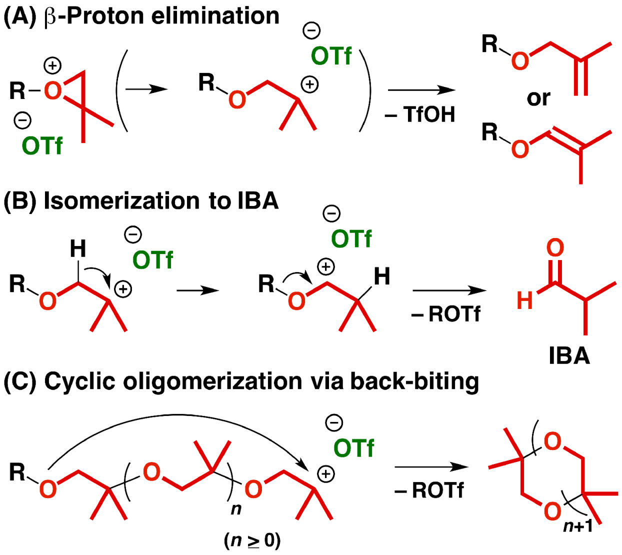
From the experimental results demonstrated above, the construction of a suitable "dormant–active" equilibrium is considered largely responsible for the copolymerization mediated by living species. "Dormant" and "active" species that are potentially generated during the copolymerization reaction are shown in Scheme 4. The copolymerization proceeds via the reactions of monomers with the VE-derived carbocation, the IBO-derived carbocation, and the IBO-derived oxonium ion. The IBO-derived covalent carbon–OTf species most likely functioned as a "dormant" species. In addition, the equilibrium between the covalent species and the propagating species is likely strongly shifted to the former side, which is responsible for the small polymerization rates. The covalent species dissociates to generate a tertiary carbocation that subsequently reacts with an IPVE or IBO monomer. The formation of the covalent carbon–OTf species is similar to the polymerization of THF,[33–37] oxetane derivatives,[38,39] and oxepane,[40] although the propagation reactions of these cyclic ethers proceed without generating an unstable primary carbocation via dissociation. Moreover, the formation of a covalent bond between the tertiary carbocation and a TfO^- anion was suggested in the ring-opening polymerization of 1,3-dihydroadamantanes.[41] The oxonium ion/OTf^- ion-pair also functioned as an active species that propagates via the attack by an IBO monomer. In contrast, the covalent carbon–OTf species was not generated at the VE-derived propagating ends due to the insufficient nucleophilicity of TfO^-. Indeed, the homopolymerization of IPVE using TfOH proceeded at a very high rate in an uncontrolled manner (entry 3 in Table 1). The exclusive generation of "dormant" species at the IBO-derived ends in the copolymerization was crucial for the even propagation of all the polymer chains.



Scheme 4. Possible Mechanisms for the Cationic Copolymerization of IPVE and IBO by TfOH; A Species with Gray Shadow Is Not Generated.

The relatively small numbers of IBO units per block of the obtained copolymers indirectly indicates that the covalent species were frequently generated at the IBO-derived propagating ends. This supposition is based on the fact that the IBO-derived carbocation shows a preference for VE monomers or an aversion to IBO monomers.[9] The IBO blocks of the copolymers obtained using TfOH consisted of approximately two IBO units, whereas those obtained using $B(C_6F_5)_3$ had approximately five units. The frequent generation of both the IBO-derived covalent carbon–OTf species and the carbocations via the dissociation of these covalent species led to short IBO blocks due to the preferential crossover reactions from the carbocation to IPVE. Indeed, the homopolymerization of IBO using TfOH resulted in oligomeric products (entry 4 in Table 1), probably because of the inefficient homopropagation of IBO arising from the aversion of the IBO-derived carbocation to an IBO monomer and the frequent β-proton elimination reactions.

Not all the propagating chains maintain the living nature during the copolymerization of IPVE and IBO because of the occurrence of three types of side reactions. The most troubling but inevitable side reaction is the β-proton elimination reaction from the IBO-derived propagating ends (Scheme 5A). The β-proton elimination reaction was confirmed by the peaks assigned to the exo- and endo-olefin structures in the ^{1}H NMR spectrum (Figure 3). This reaction generates a proton that induces a chain-transfer reaction, which is responsible for the MWs of the copolymers being lower than the calculated values, particularly in the later stage of the polymerization (vide infra). Figure 6 shows the ratio of the quencher-incorporated ω-ends. This ratio roughly corresponds to the ratio of the living species based on the assumption that the quencher fragment is incorporated into all the “dormant” species.[47,48] The gradual decrease in the quencher-incorporated ω-ends along with the increase in the monomer conversion value mainly stemmed from the β-proton elimination reaction. Another side reaction is the isomerization of IBO to isobutyraldehyde (IBA) under acid catalysis (Scheme 5B and Figure S8).[49,50] The generation of IBA was confirmed by ^{1}H NMR and GC analysis of the quenched polymerization solution. Aliphatic aldehydes potentially react with oxiranes during the polymerization and are incorporated into a product polymer;[51] however, IBA had slight effects on the polymerization behavior and the MWs and compositions of the obtained copolymers, which was suggested by the copolymerization in the presence of IBA (Figure S8C). The other side reaction that potentially occurs is the back-biting reaction (Scheme 5C). This reaction produces cyclic oligomers;[52] however, oligomeric portions with MWs less than 10^3 were negligible in most MWD peaks of the copolymerization products. Thus, back-biting reactions negligibly occurred, although cyclic oligomers with low MWs, such as cyclic trimers and dimers, might be removed during the purification process. The second and third side reactions are responsible for the difference in the monomer conversion values determined by GC and gravimetry, particularly in the polymerization in dichloromethane. This is because IBO monomers are consumed in these reactions but not incorporated into polymers. The side products, such as IBA, are removed during the purification process. In the following section, the theoretical M_n values were therefore calculated based on the monomer conversion determined by gravimetry.



Scheme 5. Possible Side Reactions: (A) β-Proton Elimination Reaction, (B) Isomerization to IBA, and (C) Cyclic Oligomerization (R = H or polymer chain).

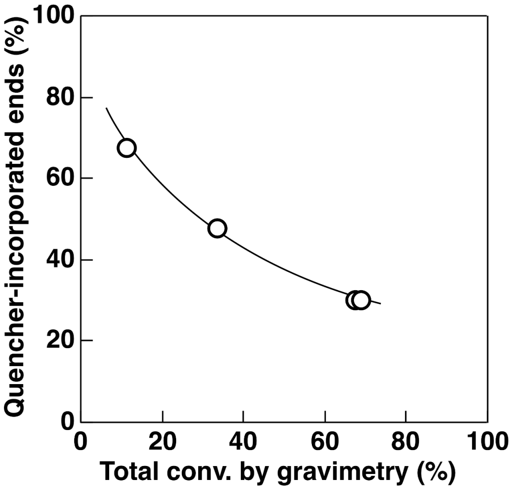


Figure 6. The ratio of the quencher-incorporated ω-ends calculated by the following equation: (quencher-incorporated ends) = X_q/(all ω-ends) × 100 = $X_q/(X_q + X_\beta + X_{ald}) \times 100$; X_q: quencher-incorporated ω-ends, X_β: ω-ends derived from β-proton elimination reaction, X_{ald}: VE-derived aldehyde ends possibly derived from a degradation of the acetal moieties (less than 5% of all ω-ends); these ratios were determined by ^{1}H NMR. See Figure 2 for the polymerization conditions.

The use of TfOH as an initiator was also effective for cationic vinyl-addition and ring-opening copolymerization of other monomers such as cyclohexyl VE, (+)-limonene oxide, and styrene oxide (Figure S9). However, the reaction conditions for the copolymerization of these monomers have not been optimized yet. We are currently examining the copolymerization of various monomers using TfOH and other initiators or catalysts such as $B(C_6F_5)_3$.

Investigation for the control of MWs of copolymers with the use of an appropriate perfluoroalkylsulfonic acid and the design of reaction conditions

On the basis of the results obtained above, we subsequently aimed to optimize the reaction conditions to improve the control of the MWs of the product copolymers. To examine the effects of the nucleophilicity of the counteranions, other perfluoroalkylsulfonic acids were employed as initiators for the copolymerization of IPVE and IBO. $C_4F_9SO_3H$ and $C_8F_{17}SO_3H$, which have longer perfluoroalkyl groups than TfOH, were demonstrated to also be effective in the generation of dissociable covalent species in the polymerization in dichloromethane at –78 ºC (entries 3, 4, 9, and 10 in Table 2). The polymerization rates were in the order of $C_8F_{17}SO_3H > C_4F_9SO_3H >$ TfOH (Figure S10). The difference likely indicates that the nucleophilicity of the counteranions depends on the length of the perfluoroalkyl chains. $C_4F_9SO_3H$ and TfOH were reported to exhibit slightly different pK_a values.[53] Figure 7 (open circles) shows the relationship between the M_n values of the obtained polymers and the theoretical M_n values calculated from the amount of the acid initiator and the monomer conversion based on gravimetry (the products obtained with $C_8F_{17}SO_3H$ are not included because this acid was partly insoluble). Notably, the polymers obtained with

$C_4F_9SO_3H$ had larger M_n values than those obtained with TfOH. This result possibly stemmed from the fact that chain transfer through β-proton elimination was less frequent in the polymerization using the former acid than that using the latter one.

Table 2. Cationic Copolymerization of IPVE and IBO Under Various Conditions[a]

entry	initiator	solvent	temp (ºC)	time	conv[b] (%) VE	conv[b] (%) IBO	$M_n \times 10^{-3}$ [c]	M_w/M_n	crossover per chain[d] VE to IBO	crossover per chain[d] IBO to VE	average unit numbers per one block[d,e] VE	average unit numbers per one block[d,e] IBO
1	TfOH	CH_2Cl_2	–95	42 h	14	21	2.7	1.44	1.9	1.6	13	2.5
2				116 h	41	59	4.9	1.41	2.2	1.9	19	2.6
3	$C_4F_9SO_3H$	CH_2Cl_2	–78	1 h	15	24	2.6	1.75	1.9	1.2	20	2.1
4				6 h	54	63	4.7	1.94	1.9	1.4	23	2.1
5		CH_2Cl_2/hexane (1/9 v/v)	–78	24 h	18	15	3.3	1.82	3.3	2.3	11	2.2
6				168 h	71	61	6.7	1.83	4.0	3.5	17	2.5
7		CH_2Cl_2	–95	42 h	16	17	5.0	1.41	2.7	2.3	16	2.9
8				116 h	39	51	8.0	1.50	2.9	3.2	21	3.1
9[f]	$C_8F_{17}SO_3H$	CH_2Cl_2	–78	45 min	25	39	2.2	1.63	<3.6[g]	<1.6[g]	11	1.4
10[f]				5 h	75	74	4.8	1.72	<3.0[g]	<1.5[g]	19	1.6

[a] $[IPVE]_0$ = 0.75 M, $[IBO]_0$ = 0.22 M, $[initiator]_0$ = 5.0 mM, in dichloromethane (with 5 vol % of hexane as an internal standard for GC) or dichloromethane/hexane (1/9 v/v) at –78 or –95 ºC. [b] Determined by GC. [c] Determined by GPC (polystyrene standards). [d] Estimated by ^1H NMR analysis. [e] The values correspond to the unit numbers per acetal. [f] Containing 5 vol % of HCFC (AK-225) as a dilution solvent for $C_8F_{17}SO_3H$. [g] The numbers are likely overestimated because the quencher-derived ends, which may have been generated but were not assigned by ^1H NMR analysis, were not considered for the calculation.

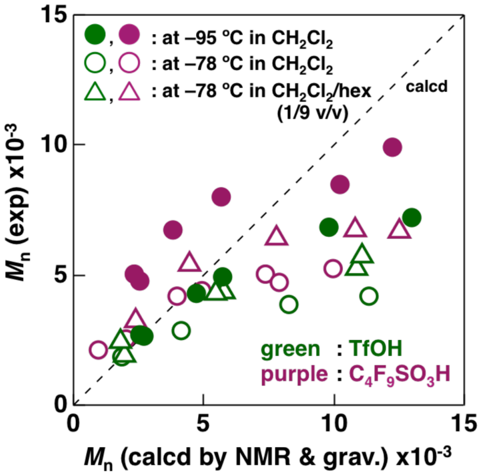


Figure 7. M_n values of the polymers produced under various conditions: $[IPVE]_0$ = 0.75 M, $[IBO]_0$ = 0.22 M, $[initiator]_0$ = 5.0 mM (green: TfOH; purple; $C_4F_9SO_3H$), in dichloromethane (circle) or

dichloromethane/hexane (1/9 v/v) (triangle) at –78 (open) or –95 ºC (filled). The M_n (calcd by NMR & grav.) values were calculated based on the amounts of the monomers incorporated into the product polymers (the monomer conversion values estimated by this method are lower than the values by GC due to side reactions such as isomerization to IBA, a volatile compound).

Less polar solvents and lower temperature were also effective in improving the control of the MWs of the copolymers. The M_n values of the polymers obtained in dichloromethane/hexane (1/9 v/v; entries 5–7 in Table 1, entries 5 and 6 in Table 2; triangles in Figure 7) were larger than those obtained in dichloromethane. This result suggests that, in the present copolymerization reaction, chain transfer through β-proton elimination was less frequent in less polar solvents. The isomerization of IBO to IBA was also less frequent in dichloromethane/hexane (1/9 v/v) than in dichloromethane (Figure S8). In addition, the polymerization at lower temperature, i.e., –95 ºC (entries 1, 2, 7, and 8 in Table 2; filled circles in Figure 7), produced polymers with larger M_n values than the polymerization at –78 ºC. This resulted from the frequency of chain-transfer reactions by β-proton elimination decreasing compared to that of propagation reactions due to thermodynamic factors, which is a typical phenomenon in cationic polymerization.

Improved control of the copolymerization was achieved when the reaction was conducted in dichloromethane/hexane (1/9 v/v) at –95 ºC (Figure 8). The M_n values of the products increased in approximate agreement with the theoretical values in the copolymerization of IPVE and IBO using 5.0 or 10 mM of $C_4F_9SO_3H$ or TfOH. The decreased frequency of side reactions is most likely responsible for the control of the MWs of the copolymers.

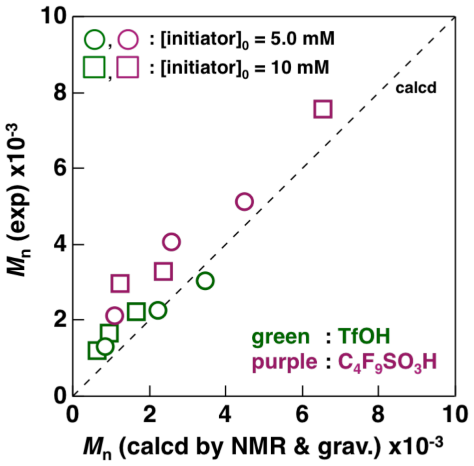


Figure 8. M_n values of the polymers produced in dichloromethane/hexane (1/9 v/v) at –95 ºC: $[IPVE]_0$ = 0.75 M, $[IBO]_0$ = 0.22 M, $[initiator]_0$ = 5.0 (circle) or 10 mM (square) (green: TfOH; purple; $C_4F_9SO_3H$). See Figure S11 for the MWD curves. See the caption of Figure 7 for the M_n (calcd by NMR & grav.) values.

Conclusion

The concurrent cationic vinyl-addition and ring-opening copolymerization of IPVE and IBO proceeded via the mediation of "living" species with TfOH as an initiator. A covalent carbon-OTf bond that formed exclusively at the IBO-derived propagating end most likely functioned as a "dormant" species. The covalent bond reversibly generates the propagating species through catalyst-free dissociation, which allowed the even propagation of all the polymer chains. The generation of this "dormant" species was confirmed by both the incorporation of the quencher fragment into the copolymer and ^{19}F NMR analysis. Moreover, the control of the MWs of the product copolymers was improved in less polar solvents at lower temperature when $C_4F_9SO_3H$ was used as a result of the decreased frequency of side reactions. The strategy devised in this study will contribute to the design of initiating systems for the copolymerization of different types of monomers.

Associated Content

Supporting Information: NMR spectra and polymerization data.

Acknowledgments

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46. Slight amounts of the quencher fragment were incorporated into the VE-derived ends. These ω-ends were likely generated by the reaction between the quencher and the propagating oxonium ion with a penultimate IPVE unit (Scheme S1; –IPVE–IBO$^+$ was converted to –IPVE–OR through the reaction with ROH). Relatively short IBO blocks (2.1-2.3 units per block) also support the frequent generation of this type of “dormant” species.

47. In the previous study on the terpolymerization of VE, oxetane, and ketone (reference 48), an alcohol quencher was inefficient for the reaction with the oxetane-derived oxonium ion. Thus, it is unclear whether the IBO-derived oxonium ion smoothly reacts with an alcohol quencher or not.

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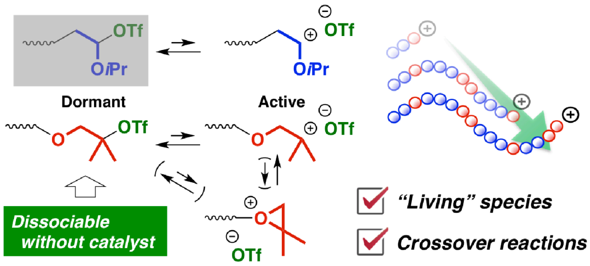
TOC Graphic



Generation of "Living" Species Using Perfluoroalkylsulfonic Acids in Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization via Crossover Reactions

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