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Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization Using $B(C_6F_5)_3$ as a Catalyst: Copolymerization of Vinyl Ethers and Isobutylene Oxide via Crossover Propagation Reactions

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Supporting Information

ABSTRACT: Alkyl vinyl ethers and isobutylene oxide were concurrently copolymerized through cationic vinyl addition and ring opening using $B(C_6F_5)_3$ as a catalyst. NMR analyses and acid hydrolysis of the products demonstrated that the copolymerization successfully proceeded through crossover reactions between vinyl and cyclic monomers to yield multiblock-like copolymers. Appropriate catalyst and monomer combinations with suitable reactivities were key for copolymerization.

Combining polymerization techniques with different mechanisms should effectively produce copolymers with novel properties from conventionally incompatible monomers. In particular, concurrent vinyl-addition and ring-opening copolymerization is of great interest from both an academic and industrial perspective because large quantities of vinyl monomers and oxiranes (three-membered cyclic ethers) are used worldwide to synthesize general-purpose polymers. Despite its potential, only a few studies have reported such copolymerization reactions for vinyl and cyclic monomers, including maleimides and oxazolines,[1] maleimides and propylene oxide,[2] and methacrylate and ε-caprolactone,[3] which have proceeded via zwitterionic or anionic mechanisms.

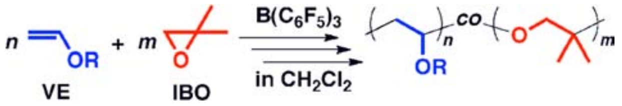
The dearth of successful examples is also true for cationic polymerization. Copolymerization of five- and seven-membered cyclic formals with vinyl monomers using BF_3OEt_2 as a catalyst has been used in a few studies, which have provided solid evidence for crossover reactions as confirmed by NMR analyses.[4] Although oxirane cationic copolymerization with vinyl monomers [e.g., epichlorohydrin, propylene oxide, or isobutylene oxide (IBO) with styrene] have also been reported, the product structures were deduced from the results using solvent fractionation.[5] Because of the lack of information on the microstructures through NMR analysis, the authors were unable to demonstrate whether the two monomers underwent crossover reactions. Furthermore, only homopolymer mixtures were generated from oxirane and vinyl ether (VE) copolymerization.[6]

The difficulty of cationic copolymerization of vinyl monomers and oxiranes is likely due to the fact that a vinyl group cannot nucleophilically attack a stable oxonium ion as well as reactivity differences between the monomers. It is also unfavorable for an oxonium ion to be transformed into a ring-opened carbocation for addition to a vinyl monomer. Successful copolymerization of five- and seven-membered cyclic formals may have proceeded through this ring-opening transformation because the propagating VE-type carbocation that results should be stabilized by an alkoxy group adjacent to the cation.[4]

Another essential prerequisite for copolymerization is the absence of covalent-type dormant growing ends, such as carbon−halogen bonds, which are often formed during living cationic polymerization of vinyl monomers.[7] Because of potentially significant differences in reactivity, activation of both ends from a vinyl monomer and an oxirane by a catalyst can be extremely uneven; hence, the presence of the covalent growing ends could produce no cross-propagation. A strong Lewis acid that forms a weakly coordinating counteranion, such as $B(C_6F_5)_3$,[8,9] may be required for copolymerization. Therefore, an appropriate catalyst and monomer combination is necessary for efficient crossover reactions.

Here we report cationic copolymerization of VEs and IBO (Scheme 1). IBO[10] was used as an oxirane monomer because it may form a relatively stable tertiary carbocation.[11] When $B(C_6F_5)_3$, which is a strong Lewis acid and forms a weakly coordinating counteranion,[8,9] was used as a catalyst, the crossover reactions between VEs and IBO were efficient and yielded copolymers with multiblock-like sequences.

Scheme 1. Cationic Copolymerization of Alkyl VE and IBO (R = *i*Pr, Et, *i*Bu)[a]



[a]The IBO segment obtained through 1,3-scission has been omitted.

Vinyl monomers and oxiranes should have similar nucleophilicities toward propagating carbocations for uniform propagation. Thus, cationic copolymerizations of alkyl VEs with different reactivities and IBO were first performed using $B(C_6F_5)_3$ as a catalyst in dichloromethane at −78 °C. When isopropyl VE (IPVE) was used, the two monomers were consumed at similar rates to produce polymers (M_n = 10.4 kg/mol) with ~60% conversion in 30 min (Table 1, entry 1). Interestingly, the product had a unimodal molecular weight distribution (MWD) with a symmetrical shape (M_w/M_n = 1.84), which suggested successful copolymerization.

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Table 1. Cationic Copolymerizations of Alkyl VEs and IBO[a]

		conc (M)					conv (%)[b]				crossovers per chain[d]	
entry	VE	VE	IBO	catalyst	T (°C)	time	VE	IBO	M_n (kg/mol)[c]	M_w/M_n[c]	VE−IBO[e]	IBO−VE
1	IPVE	0.75	0.22	$B(C_6F_5)_3$	−78	30 min	65	57	10.4	1.84	4.9 (4.8)	3.8
2	IPVE	0.75	0.44	$B(C_6F_5)_3$	−78	1 h	67	74	7.7	1.92	5.5 (5.3)	4.5
3	IPVE	1.5	0.44	$B(C_6F_5)_3$	−78	1 h	77	75	12.7	1.91	7.5 (6.7)	6.6
4	IPVE	2.2	0.44	$B(C_6F_5)_3$	−78	20 min	68	68	19.6	1.87	9.5 (8.1)	6.4
5	IPVE	0.75	0.22	$B(C_6F_5)_3$	−30	10 min	73	82	2.1	1.61	1.9 (1.6)	0.7
6	IPVE	0.75	0.22	BF_3OEt_2	−78	5 min	19	64	3.3	3.80	1.3 (0.4)	0.3
7	IPVE	0.75	0.22	$GaCl_3$	−78	40 min	15	25	9.1[f]	2.03[f]	1.7 (0.5)	0.6
8		–	0.22	$B(C_6F_5)_3$	−78	22 h	–	0	–	–	–	–
9		–	0.44	$B(C_6F_5)_3$	−30	20 min	–	63	0.6	1.39	–	–
10	IPVE	0.75	–	$B(C_6F_5)_3$	−78	3 min	93	–	37.4	3.18	–	–
11	EVE	1.5	0.22	$B(C_6F_5)_3$	−78	30 min	16	81	3.1	2.01	3.4 (3.0)	2.6
12	IBVE	1.5	0.22	$B(C_6F_5)_3$	−78	30 min	6	64	2.3	1.99	4.9 (3.6)	n.d.[g]

[a] $[VE]_0$ = 0−2.2 M, $[IBO]_0$ = 0−0.44 M, $[catalyst]_0$ = 1.0 mM for entries 1−5 and 8−10, 5.0 mM for entries 11 and 12, and 10 mM for entries 6 and 7, in dichloromethane at −30 or −78 °C. [b] Determined by gas chromatography. [c] Determined by GPC (polystyrene standards). [d] Determined by ^{1}H NMR analysis. [e] Values in parentheses are the number of VE−IBO units except for those existing at the α ends. [f] Value for the high-MW peak. [g] Not determined because the peaks of the methyl groups in the side chains disturbed.

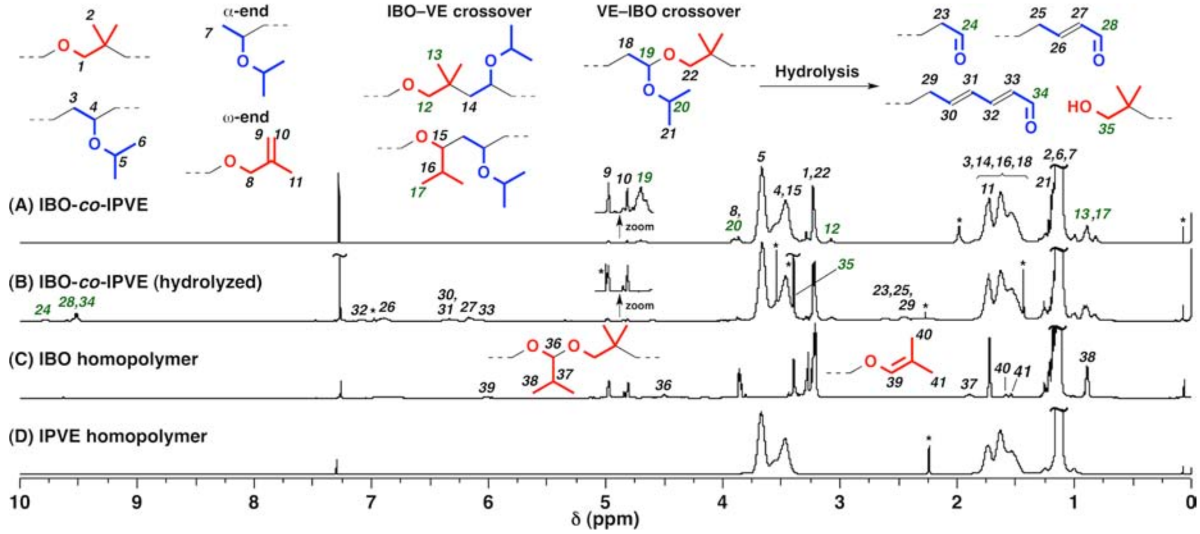


Figure 1. ^{1}H NMR spectra of (A) poly(IPVE-*co*-IBO) (Table 1, entry 1), (B) poly(IPVE-*co*-IBO) after acid hydrolysis, (C) IBO homopolymer (entry 9), and (D) IPVE homopolymer (entry 10) recorded in $CDCl_3$ at 30 °C. See Table 1 for the polymerization conditions. Peaks labeled with * are due to water, grease, DME, and stabilizer (BHT).

The product microstructure was elucidated through NMR analyses, which confirmed that crossover reactions between the two monomers occurred. The ^{1}H NMR spectrum of a copolymer (Figure 1A) exhibited a peak at 4.6−4.7 ppm (peak *19*), which was assigned to the acetal proton originating from the crossover reaction from IPVE to IBO. Moreover, the peaks at 0.8−1.0 ppm (peaks *13* and *17*) indicated structures formed through crossover from IBO to IPVE. Analyses using 2D NMR (^{1}H−^{13}C HMBC) further supported the assignments, as the overlapping peaks at 0.8−1.0 ppm in the ^{1}H NMR spectrum were clearly separated into two series (vide infra), such as H^{17}−C^{16} and H^{13}−C^{42} correlations [Figure 2; see Figures S1−S5 in the Supporting Information (SI) for more NMR spectra]. In addition, the peaks generated by crossover reactions did not appear in the ^{1}H NMR spectra of the homopolymers (Figure 1C,D). NMR analyses also revealed that the copolymer had almost uniform chain ends (i.e., an α end derived from the protic initiation by IPVE and an ω end derived from β-proton elimination from the IBO-propagating carbocation).

The crossover reaction frequencies were then estimated from the ^{1}H NMR spectrum. The integral ratios of peaks *19*, *13*, and *17* to the peaks at the ω end (peaks *9* and *10*) demonstrated that crossover reactions from IPVE to IBO and IBO to IPVE transpired ~4.9 and ~3.8 times per chain, respectively. The difference of ~1 was also evidence that the polymer contained an IPVE α end and an IBO ω end.

From the results described above, the copolymerization mechanisms illustrated in Scheme 2 are proposed. The reaction is initiated by an addition reaction involving a proton derived from adventitious water and $B(C_6F_5)_3$ to IPVE[9,12] (eqs 1 and 2); because the IBO homopolymerization did not occur at −78 °C (entry 8), neither adventitious water nor coordination of $B(C_6F_5)_3$ to IBO is likely to initiate the polymerization from IBO. IPVE homopropagation proceeds from the generated carbocation (eq 3) until a crossover reaction to IBO occurs (eq 5). The ensuing IBO homopropagation then creates a poly(IBO) segment (eq 4), in which the reaction may also proceed through direct IBO attack on the oxonium ion without

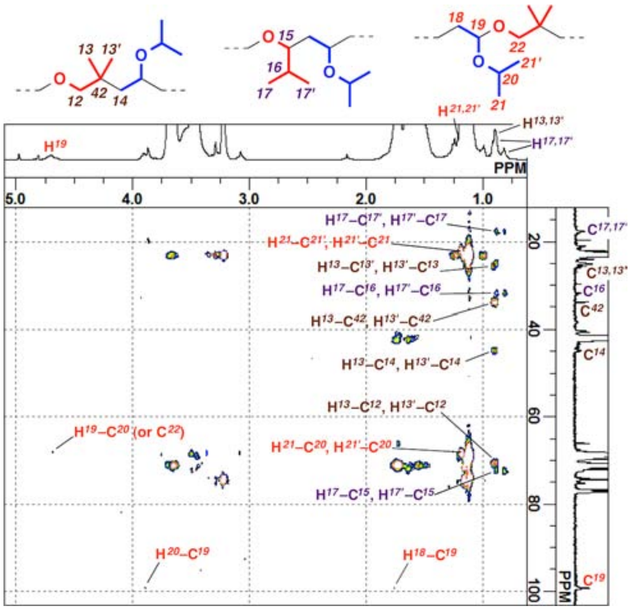
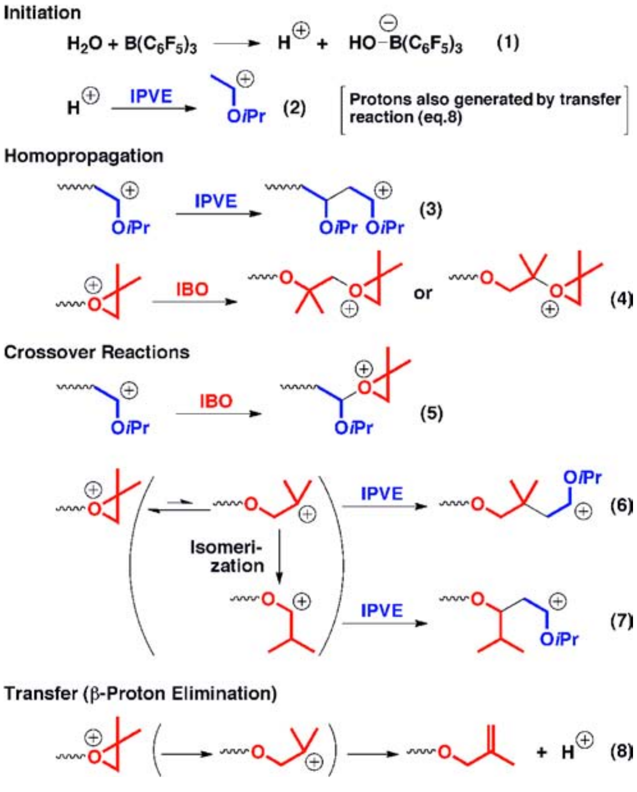


Figure 2. ^{1}H−^{13}C HMBC NMR spectrum of poly(IPVE-*co*-IBO) (Table 1, entry 1). Peaks relating to crossover reactions are labeled (see Figure S5 for the other assignments).

Scheme 2. Copolymerization Mechanisms (Minor or Negligible Paths Are Omitted)



forming a carbocation. Subsequently, the crossover reaction from IBO to IPVE can employ two modes, a direct addition reaction between IPVE and the IBO carbocation (eq 6) and an addition reaction after carbocation isomerization through a hydride shift (eq 7).[11] The fraction of crossover occurring through isomerization is 40−50%. The driving force for the isomerization reaction is the stabilization of the resulting carbocation by an adjacent alkoxy group. After several crossover reactions, the IBO-propagating end (eq 8) generates a new chain (eq 2) through a β-proton elimination reaction. Though not examined yet, the reactivity ratios of the two monomers (r_1 and r_2) should be >1, given the long VE and IBO segments.

To examine the factors that affect the molecular weights (MWs) and crossover reactions, the copolymerization reactions were performed under various conditions. With a larger amount of IBO (Table 1, entry 2), the crossover reaction frequency increased; however, the MW was lower, likely because of more frequent chain-transfer reactions. A further increase in the amount of IBO produced white turbidity and gelation during the reaction because the longer IBO segments were less soluble in dichloromethane. Polymers with larger MWs were produced when larger amounts of IPVE were used (entries 3 and 4), likely because the transfer reaction frequency comparatively decreased. The transfer reactions were more frequent at a higher temperature (−30 °C) and produced a polymer with a much lower MW (entry 5), as is typically observed for other cationic polymerization reactions. Copolymerization reactions were also examined using cationogens, but the reactions produced polymers similar to products obtained without cationogens (Table S1 in the SI).

One of the important factors for successful copolymerization was the use of a suitable Lewis acid catalyst. When the copolymerization was conducted using BF_3OEt_2 or $GaCl_3$ instead of $B(C_6F_5)_3$, the crossover reaction frequency decreased significantly [Table 1, entries 6 and 7; see Figure S6 for detailed analyses of the products by gel-permeation chromatography (GPC) fractionation and ^{1}H NMR spectroscopy]. While BF_3OEt_2 has been widely used in past copolymerization studies,[4−6] it is a poor catalyst for such copolymerizations, although the reason for this remains unclear. $GaCl_3$ was not suitable, perhaps because the chloride anion capped the IBO-propagating carbocation to form a dormant IBO−Cl end. This bond is relatively stable and difficult to activate under the conditions examined.

The VE reactivity was important for efficient VE and IBO consumption at similar rates. Ethyl VE (EVE) and isobutyl VE (IBVE) are less reactive VEs and were consumed at much lower rates than IPVE (Table 1, entries 11 and 12). The product MWs were small because the VE segments were shorter.

Although the acetal structures in the copolymer main chains generated by the crossover from VE to IBO were stable under neutral and basic conditions, the bonds were readily hydrolyzed using HCl in 1,2-dimethoxyethane (DME). Hydrolysis yielded diblock-type products with hydroxyl and aldehyde ends (Scheme 3). After reaction for 1 h, ^{1}H NMR analysis confirmed that the acetal protons entirely disappeared (peak *19*; Figure 1B). Instead, peaks assigned to aldehyde structures emerged (peaks *23*−*34*). For IBO, a peak for methylene protons adjacent to a hydroxyl group also appeared at 3.4 ppm (peak *35*).

The copolymers' MWDs before and after hydrolysis also supported successful degradation. The MWD curve for the copolymer with M_n = 10.4 kg/mol generated using $B(C_6F_5)_3$ (Table 1, entry 1) shifted to lower MW after degradation while maintaining its unimodal and symmetrical shape (Figure S7). The M_n of the degradation product was 2.4 kg/mol, which agreed relatively well with the value expected for the frequency of crossover from IPVE to IBO (~4.9 times per chain). In addition, the absence of homopolymers in the original products was indicated by the clean shift. A small overlapping MW region after degradation of the high-MW copolymer (entry 4) strongly suggested that the copolymerization products did not contain

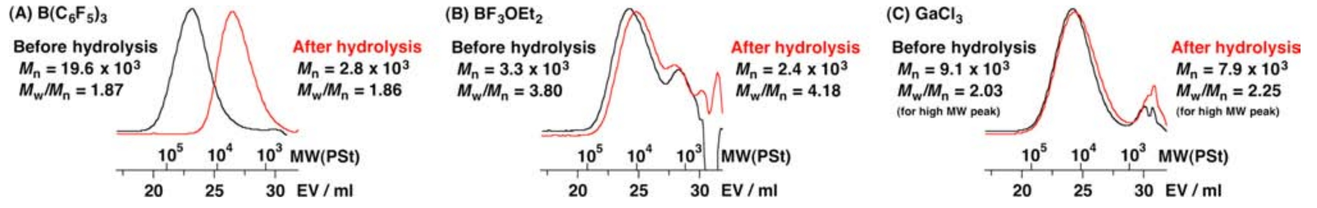
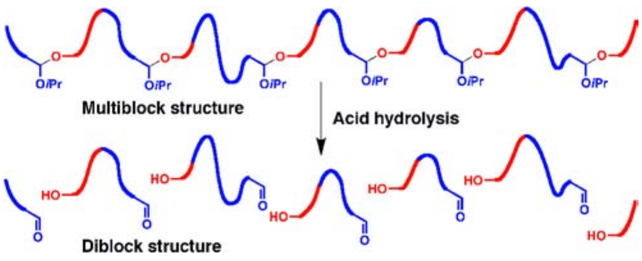


Figure 3. MWD curves for poly(IPVE-*co*-IBO)s before (black) and after (red) acid hydrolysis (Table 1, entries 4, 6, and 7).

Scheme 3. Acid Hydrolysis of Poly(IPVE-*co*-IBO)[a]



[a] Poly(IPVE) and poly(IBO) segments are shown in blue and red, respectively.

homopolymers (Figure 3A). In contrast to the copolymers generated using B(C_6F_5)$_3$, acid hydrolysis of the products obtained using BF_3OEt_2 and $GaCl_3$ produced poor degradation results. As expected from the few crossovers with these catalysts, the MWD curves for the copolymers shifted only slightly after hydrolysis (Figure 3B,C).

The copolymers generated in this study have various characteristics, such as acid degradability, multiblock-like structures, and uniform chain ends. A preliminary study of the copolymer thermal properties revealed a low glass transition temperature ($T_g \approx -33$ °C) and crystalline properties based on the IBO segment ($T_c \approx 10$ °C and broad T_m of 80−130 °C), which supports a multiblock-like sequence [see Figure S8 for differential scanning calorimetry (DSC) curves of the homo- and copolymers]. The copolymers exhibited an elastomeric texture differing from gummy poly(IPVE) and solid poly(IBO). The functional groups at the copolymer chain ends before and after degradation, such as *exo*-olefin, aldehyde, and hydroxyl structures, can facilitate various types of modification reactions.

In conclusion, concurrent vinyl-addition and ring-opening copolymerizations of VEs and IBO were performed for the first time using B(C_6F_5)$_3$ as a catalyst. Crossover reactions between the vinyl and cyclic monomers were successful several times per chain and yielded multiblock-like copolymers. Appropriate catalyst and monomer combinations with suitable reactivities were key for successful copolymerization. Copolymerizations using oxiranes with various substituents are presently being investigated to elucidate further the factors important for efficient crossover reactions. Because oxiranes are easily accessible through olefin oxidation and are widely used in both academic and industrial fields, the present results will expand the available synthetic strategies for producing novel functional copolymers from a range of common vinyl and oxirane monomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section and additional data. 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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