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# Rational Design of Oxirane Monomers for Efficient Crossover Reactions in Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization with Vinyl Ethers

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**Abstract** Rational structural design of oxirane monomers is demonstrated here to be highly conducive to crossover reactions in the concurrent cationic vinyl-addition and ring-opening copolymerization of alkyl vinyl ethers and oxiranes. The key to the efficient crossover reactions was the smooth transformation of the once-formed oxirane-derived oxonium ion into the ring-opened carbocation, which then reacted with a vinyl monomer. For example, oxiranes that form resonance-stabilized, allyl-type carbocations (i.e., isoprene monoxide and butadiene monoxide) were polymerized through efficient crossover reactions in copolymerization with isopropyl vinyl ether, yielding copolymers composed of relatively short monomer sequences. In particular, the copolymerization of isoprene monoxide and isopropyl vinyl ether generated random or alternating-rich copolymers. The reaction using an oxirane that forms tertiary carbocations (isobutylene oxide) also proceeded via crossover

reactions; however, the crossover frequency was lower, which resulted in a multiblock-like copolymer. In contrast to the three oxiranes that yielded copolymers, oxiranes that resulted in secondary carbocations from their ring opening (3,3-dimethyl-1,2-butylene oxide and 1,2-butylene oxide) hardly induced crossover reactions. In addition to the ease of carbocation generation via ring opening, the nucleophilicity of the monomer and the reactivity of the oxirane-derived carbocations were shown to substantially affect the copolymerization behavior. These factors are discussed on the basis of the monomer reactivity ratios that were determined for the copolymerization systems using vinyl ethers with different reactivities, i.e., isopropyl vinyl ether or ethyl vinyl ether, toward oxiranes.

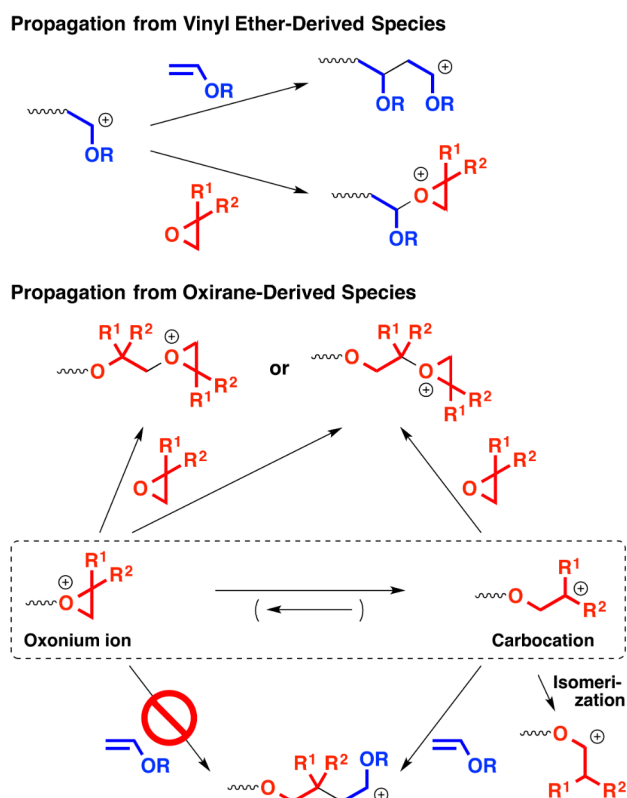
## Introduction

Vinyl and cyclic monomers constitute two major classes of compounds that produce polymers through chain polymerization by cationic, anionic, radical, and coordination mechanisms. However, the literature contains few examples of the successful synthesis of a polymer chain with both vinyl and cyclic monomer units in a random, gradient, or alternating sequence, which would provide novel features for polymers. Such a synthesis has remained a challenge, even after the development of novel polymerization techniques, including controlled/living polymerizations, that allow for the precise synthesis of various functional polymers. Thus, a very small number of studies have achieved concurrent copolymerization: anionic or zwitterionic copolymerizations of maleimides and oxazolines,<sup>1,2</sup> maleimides and propylene oxide,<sup>3,4</sup> and methacrylate and  $\epsilon$ -caprolactone<sup>5</sup> as well as cationic copolymerizations using cyclic formal.<sup>6-8</sup>

The difficulty in copolymerizing vinyl and cyclic monomers arises from the significant difference in the nature of the propagating species. More specifically, a vinyl

monomer-derived propagating species, such as a carbocationic or a carbanionic species, or a cyclic monomer-derived propagating species, such as an oxonium ion or an oxyanionic species, is difficult to react with a heteroatom or a heteroatom-adjacent carbon atom on a cyclic monomer or with a vinyl group on a vinyl monomer, respectively. In cationic polymerization, the characteristic reactivity of the cyclic monomer-derived propagating species, including oxonium ions, is a formidable barrier to copolymerization with a vinyl monomer.

Various cyclic ethers are cationically polymerized via oxonium-ion propagating species;<sup>9-11</sup> however, the oxonium ions cannot react with vinyl monomers because of the insufficient nucleophilicity of vinyl groups toward the oxonium ions and/or insufficient reactivity of the oxonium ions. To achieve efficient crossover reactions with vinyl monomers, ring-opened carbocations must be generated from the propagating oxonium ions. Few good examples of the formation of ring-opened carbocations in copolymerization have been reported. In the cationic copolymerizations of cyclic formals with vinyl monomers, crossover reactions were demonstrated to occur through microstructural analysis of the products.<sup>6,7</sup> The ring-opening reaction of an oxonium-type cation would be promoted by the stabilization of the generated carbocations by the electron donation from the adjacent oxygen atom.



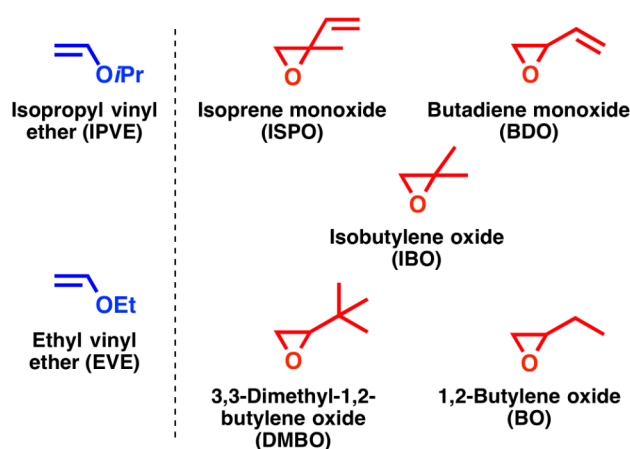
**Scheme 1.** Possible mechanisms for copolymerization of VE and oxirane.

Oxiranes, or three-membered cyclic ethers, are widely used to produce a variety of functional polymers in industry; hence, their copolymerizations with vinyl monomers (Scheme 1) are of great interest and have been intensively studied by several groups in the past few decades.<sup>12,13</sup> However, whether the crossover reactions actually occurred between the vinyl and cyclic monomers is not clear because limited evidence based on microstructural analysis was provided. In addition, some reports on the copolymerization of a vinyl ether (VE) and oxiranes concluded that the reaction yielded homopolymer mixtures.<sup>14</sup>

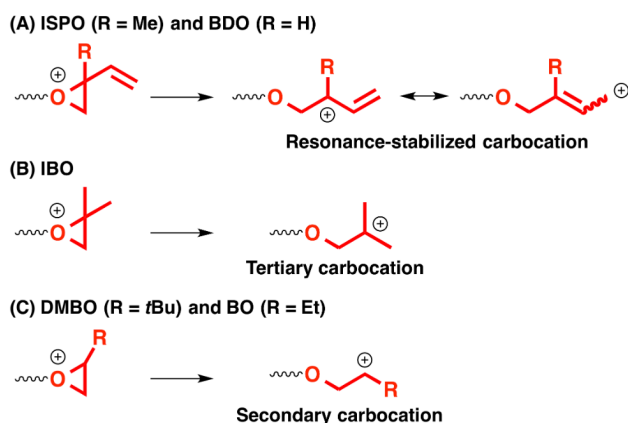
However, we have recently succeeded in copolymerizing an alkyl VE and isobutylene oxide (IBO) through efficient crossover reactions.<sup>15</sup> IBO was employed as an oxirane monomer because it can generate a tertiary carbocation via ring opening as a result of the stabilization by the dimethyl substituents. Another key to the efficient copolymerization was the use of a Lewis acid catalyst that generates a noncoordinating counteranion at the

propagating chain end. The copolymerization using  $B(C_6F_5)_3$  as a catalyst proceeded without forming dormant species, such as carbon–halogen bonds, which prevented uneven propagation reactions stemming from a large difference in reactivity between the covalent bonds derived from VE and IBO. The nucleophilicity balance of an alkyl VE and IBO was also important for the generation of copolymers.

Herein, we focused on oxirane substituents that directly contribute to the stabilization of the carbocations to promote their generation. Oxiranes with various substituents, as shown in Figure 1, were employed in this study. Because isoprene monoxide (ISPO) and butadiene monoxide (BDO) have a vinyl group, the carbocations possibly generated from these oxiranes are resonance-stabilized, allyl-type carbocations (Scheme 2A). These carbocations are expected to exhibit relatively comparable or slightly different stability compared to the tertiary carbocation generated from IBO (Scheme 2B). The stability difference among the carbocations with structures similar to these carbocations has been reported in previous studies.<sup>16,17</sup> The oxiranes 3,3-dimethyl-1,2-butylene oxide and 1,2-butylene oxide were used because the resultant carbocations would be secondary carbocations (Scheme 2C), which are less-stable species than resonance-stabilized or tertiary carbocations.



**Figure 1.** VEs and oxiranes used in this study.



**Scheme 2.** Carbocations that possibly generate from oxirane monomers via ring opening.

The copolymerization of these oxiranes with alkyl VEs was conducted using  $\text{B}(\text{C}_6\text{F}_5)_3$  as a Lewis acid catalyst. The occurrence and frequency of crossover reactions were examined by product analysis by NMR and acid hydrolysis. Acid hydrolysis is very efficient for confirming the occurrence of the crossover reaction from a VE-derived propagating end to an oxirane monomer<sup>15</sup> because this crossover produces an acetal structure, i.e., an acid-labile structure, in the main chain. In addition, we determined the monomer reactivity ratios for the systems that generated crossover reactions and discuss the copolymerization behaviors in detail.

## Experimental

**Materials.** Isopropyl vinyl ether (IPVE; Wako; 97.0+%) and ethyl vinyl ether (EVE; TCI; >98.0%) were washed with 10% aqueous sodium hydroxide solution and then water, and distilled twice over calcium hydride. Isoprene monoxide (ISPO; Alfa Aesar; 97%), butadiene monoxide (BDO; Alfa Aesar; 98%), isobutylene oxide (IBO; TCI; >97.0%), 3,3-dimethyl-1,2-butylene oxide (DMBO; Alfa Aesar; 95%), and 1,2-butylene oxide (BO; TCI;

>99.0%) were distilled twice over calcium hydride. Dichloromethane (Wako; 99.0%) and hexane (Wako; 96.0%) were dried by passage through solvent purification columns (Glass Contour). Commercially available  $\text{B}(\text{C}_6\text{F}_5)_3$  (Aldrich; 95%) was used without further purification after preparing its stock solution in dichloromethane. Dichloromethane- $d_2$  and carbon tetrachloride were distilled over calcium hydride. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was distilled over molecular sieves 4A. All chemicals except for dichloromethane were stored in brown ampules under dry nitrogen.

**Polymerization Procedures.** The following is a typical polymerization procedure. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; the blow temperature  $\sim 450\text{ }^\circ\text{C}$ ) under dry nitrogen. Dichloromethane, hexane, a VE, and an oxirane were added successively into the tube using dry syringes. The polymerization was started by the addition of a prechilled 10 mM  $\text{B}(\text{C}_6\text{F}_5)_3$  solution in dichloromethane at  $-78\text{ }^\circ\text{C}$ . After a predetermined time, the reaction was terminated with methanol containing a small amount of an aqueous ammonia solution. The quenched mixture was washed with water. The volatiles were then removed under reduced pressure at  $50\text{ }^\circ\text{C}$  to yield a polymer. The monomer conversion was determined by gas chromatography (column packing material: PEG-20M-Uniport HP for IPVE, EVE, IBO, and BO or Gasukuro-pack 54 for DMBO; GL Sciences Inc.) using hexane as an internal standard, except for the ISPO and BDO systems. The monomer conversions for the ISPO and BDO systems were determined by the gravimetry and  $^1\text{H}$  NMR integral ratios.

**Acid Hydrolysis.** The acid hydrolysis of the polymers was conducted with 0.5 M  $\text{HCl}$  in 1,2-dimethoxyethane at room temperature for 1 h (sample:  $\sim 1\text{ wt\%}$ ). The quenched mixture was diluted with dichloromethane and then washed with an aqueous sodium



hydroxide solution and water, successively. The volatiles were removed under atmospheric pressure at room temperature for several days.

**Characterization.** The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [TSKgel GMH<sub>HR</sub>-M × 2 or 3 (exclusion limit molecular weight =  $4 \times 10^6$ ; bead size = 5  $\mu$ m; column size = 7.8 mmI.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 ( $M_w/M_n$ )] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh;  $M_n = 577 - 1.09 \times 10^6$ ,  $M_w/M_n \leq 1.1$ ). The preparative polymer fractionation by GPC was conducted using similar equipment except that another polystyrene gel column [TSKgel G3000H<sub>HR</sub> (exclusion limit molecular weight =  $6 \times 10^4$ ; bead size = 5  $\mu$ m; column size = 21.5 mmI.D. × 300 mm); flow rate = 2.0 mL/min] was used. NMR spectra were recorded using JEOL JNM-ECA 500 (500.16 MHz for  $^1\text{H}$  and 125.77 MHz for  $^{13}\text{C}$ ) or JEOL JNM-ECS 400 (399.78 MHz for  $^1\text{H}$ ; used only for HSQC and HMBC spectra of BDO homopolymers) spectrometers.

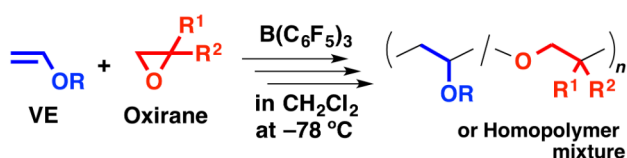
## Results and Discussion

### Cationic Vinyl-Addition and Ring-Opening Copolymerization of IPVE and Oxiranes with Various Substituents

Cationic copolymerizations of IPVE and oxiranes with different substituents were conducted using  $\text{B}(\text{C}_6\text{F}_5)_3$  as a Lewis acid catalyst in dichloromethane at 0 °C (Scheme 3). No

additional cationogen was used because the small amount of water remaining in the reaction mixture functioned as a cationogen. A proton generated by the reaction of adventitious water and the Lewis acid adds to a VE and/or an oxirane monomer to initiate the reaction. Another route to initiate polymerization would be the coordination of the catalyst to an oxirane molecule.<sup>9</sup> In addition, the propagation reaction for oxirane polymerization would proceed via the activated monomer mechanism, in which a monomer molecule coordinated to a proton or a Lewis acid catalyst is attacked by a hydroxyl group.<sup>18</sup> However, the amount of hydroxyl groups produced by the initiation of oxirane polymerization via the attack of protons may be very small compared to the amount of oxirane monomers; hence, the contribution of the activated monomer mechanism will be negligible.

As summarized in Table 1, both vinyl and cyclic monomers were consumed and polymers were obtained in each copolymerization reaction. The analyses of the products by <sup>1</sup>H NMR and acid hydrolysis, however, revealed that the efficiency of the crossover reactions differed substantially among the oxiranes employed: the copolymerizations using ISPO, BDO, or IBO efficiently proceeded through crossover reactions between the vinyl and cyclic monomers, whereas the reactions using DMBO or BO involved few crossover reactions. Among these oxiranes, ISPO was copolymerized with IPVE through the most frequent crossover reactions. The detailed results of these polymerizations are described in the following sections.

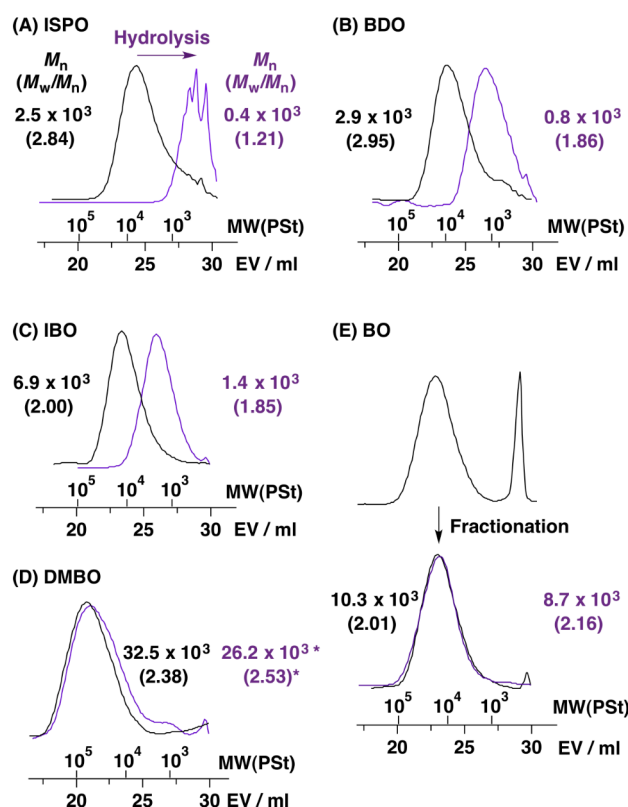


**Scheme 3.** Cationic copolymerization of VE and oxirane (structure derived from  $\beta$ -scission of oxirane is omitted).

**Table 1.** Cationic Homo- and Copolymerizations of Oxiranes and IPVE <sup>a</sup>

Entry	Oxirane	IPVE conc (M)	Oxirane conc (M)	Time	VE conv (%)	Oxirane conv (%)	$M_n \times 10^{-3}{}^b$	$M_w/M_n{}^b$	VE-oxirane crossover per chain <sup>c</sup>	Average number of VE units per one block <sup>d</sup>	Average number of oxirane units per one block <sup>d</sup>
1	ISPO	0.75	0.75	30 min	11	18	2.5	2.84	7.3	1.6	2.5
2	ISPO	2.2	0.44	20 min	6	15	3.8	2.89	10	2.9	1.4
3	ISPO	–	0.75	2 h	–	26	0.8	2.38	–	–	–
4	BDO	0.75	0.75	4 h	16	9	2.9	2.95	4.1	5.5	3.4
5	BDO	2.2	0.44	20 min	15	7	8.4	2.81	4.9	19	1.8
6	BDO	–	0.75	1 h	–	13	0.7	2.17	–	–	–
7	IBO	0.75	0.75	30 min	43	65	6.9	2.00	5.2	7.9	11
8	IBO	2.2	0.44	20 min	68	68	19.6	1.87	9.5	20	3.4
9	IBO	–	0.22	22 h	–	0	–	–	–	–	–
10	DMBO	0.75	0.74	15 min	44	28	32.5	2.38	n.d. <sup>e</sup>	–	–
11	DMBO	–	0.74	15 min	–	49	16.3	1.91	–	–	–
12	BO	0.75	0.76	30 min	28	13	10.0, 0.3 <sup>f</sup>	2.17, 1.04 <sup>f</sup>	~ 0	–	–
13	BO	–	0.76	23 h	–	13	0.3	1.03	–	–	–
14	–	0.75	–	3 min	93	–	37.4	3.18	–	–	–

<sup>a</sup>  $[B(C_6F_5)_3]_0 = 1.0$  (entries 1, 2, 4, 5, 7–9, and 14) or 5.0 (entries 3, 6, and 10–13) mM, in dichloromethane at  $-78$  °C. <sup>b</sup> By GPC (polystyrene calibration). <sup>c</sup> The number of the crossover reactions from IPVE to an oxirane per chain. Determined by  $^1H$  NMR for entries 7 and 8 or by  $^1H$  NMR and  $M_n$ (GPC) value for entries 1, 2, 4, 5, and 12. <sup>d</sup> Determined by  $^1H$  NMR for entries 7 and 8 or by  $^1H$  NMR and  $M_n$ (GPC) value for entries 1, 2, 4, and 5. <sup>e</sup> Not determined because the acetal peak overlapped with another peak in the  $^1H$  NMR spectrum (Figure S18). <sup>f</sup> The values for the higher and lower MW portions, respectively.

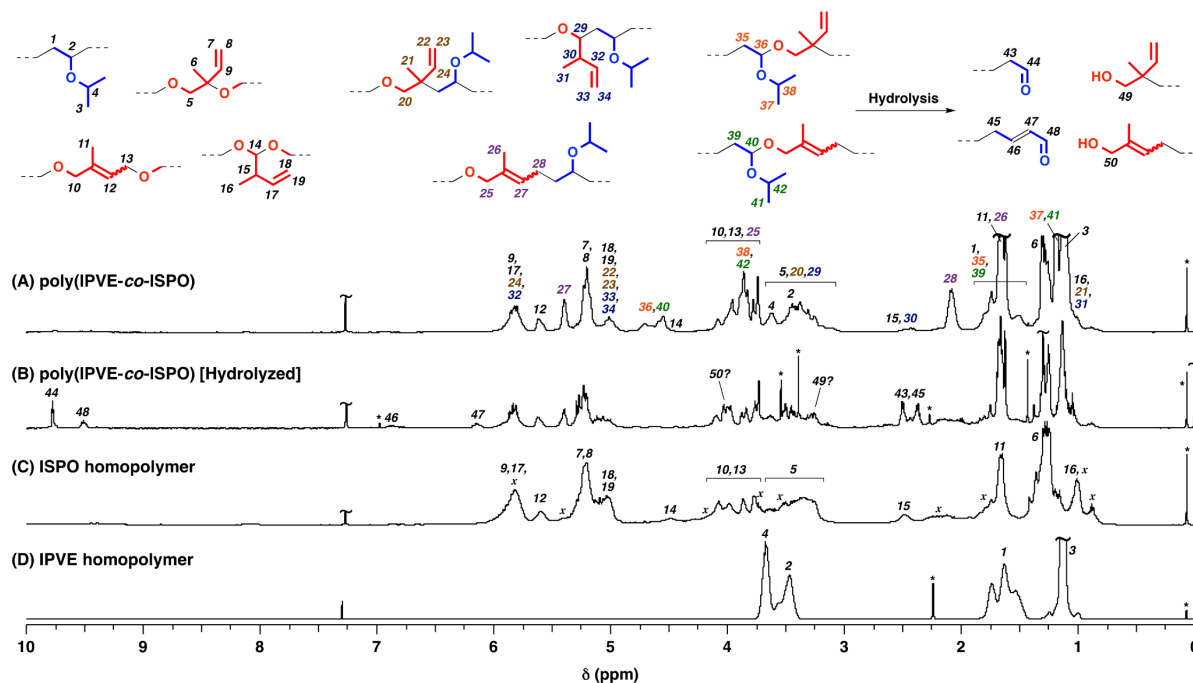


**Figure 2.** MWD curves for the copolymerization products before and after acid hydrolysis [black: polymerization products, purple: hydrolysis products; original samples: entries (A) 1, (B) 4, (C) 7, (D) 10, and (E) 12 in Table 1]. \* For a main peak.

### 1. Copolymerization Using ISPO, BDO, or IBO: Polymerization through Crossover Reactions

The copolymerization of ISPO with IPVE generated a product with a unimodal, though broad, MWD (entry 1 in Table 1 and Figure 2A). The  $^1\text{H}$  NMR spectrum of the product (Figure 3A) contained signals for the structures derived from both IPVE and ISPO, indicating that both monomers were polymerized simultaneously. Notably, ISPO was incorporated into the polymer via two different modes, i.e., 1,2- and 1,4-addition modes. The generation of the 1,4-addition mode may provide indirect proof for the generation of a carbocation via the ring opening of the propagating oxonium ion because such structures are

formed by the addition of an IPVE or ISPO monomer to the carbocation with an allyl-type resonance-stabilized structure.



**Figure 3.**  $^1\text{H}$  NMR spectra of (A) poly(IPVE-co-ISPO) (entry 1 in Table 1), (B) its hydrolysis product, (C) ISPO homopolymer (entry 3), and (D) IPVE homopolymer (entry 14) (in  $\text{CDCl}_3$  at 30  $^\circ\text{C}$ ; see Scheme S1 for peaks x; \* solvent, grease, vaseline, etc.).

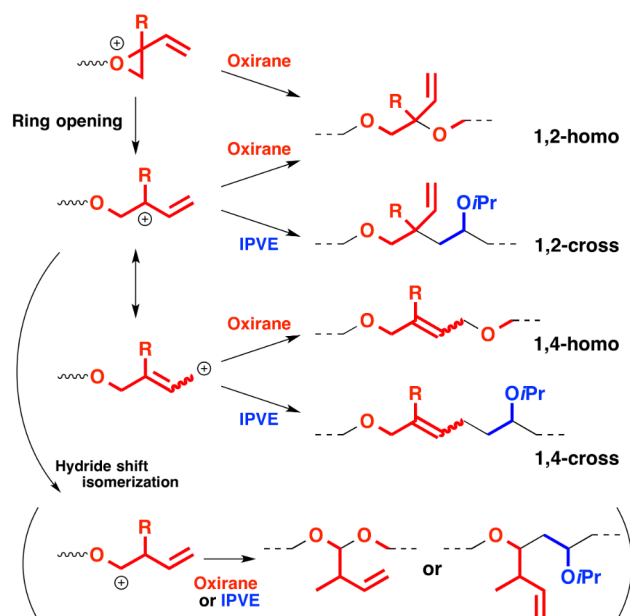
The  $^1\text{H}$  NMR spectrum also revealed the occurrence of crossover reactions between the two monomers. The crossover from IPVE to ISPO was confirmed by the generation of the peaks for acetal protons at 4.5–4.8 ppm (peaks 36 and 40). In addition, the peaks for the olefin protons at 5.0–5.2 ppm (peaks 22 and 23) indicated that the crossover reactions from ISPO to IPVE occurred via 1,2-addition, although the peaks for the structures that resulted from a hydride shift isomerization reaction of the ISPO propagating end carbocation (peaks 18, 19, 33, and 34; Scheme 1) overlapped with those peaks. The other mode for the crossover from IPVE to ISPO—the crossover via the 1,4-addition—generated the peak for the olefin

protons and the olefin-adjacent methylene protons at 5.3–5.4 and 2.1–2.2 ppm, respectively (*trans*- and *cis*-1,4-addition modes were not differentiated by NMR analysis). Analyses by  $^{13}\text{C}$  and 2D NMR also supported these peak assignments (Figures S2–S8).

The frequency of the crossover reactions was estimated from the  $^1\text{H}$  NMR integral ratios and from the molecular weight determined by GPC using polystyrene calibration. The composition ratio of IPVE and ISPO was calculated to be 1.0:1.6 on the basis of the integral ratios of the following three peak regions: the peaks for the olefin protons, the methyl protons of the ISPO unit derived from the 1,2-addition, and the methyl protons of the isopropyl group. The crossover reaction from IPVE to ISPO was estimated to occur  $\sim 7.3$  times per chain on the basis of the composition ratio, the  $M_n$  value by GPC, and the integral ratio of the acetal protons. The amount of acetal structure generated from the hydride-shift isomerization was very minor (peak 14) and was ignored. In addition, from these values (i.e., the frequency of the crossover reactions, the  $M_n$  value by GPC, and the composition ratio of IPVE and ISPO), the average numbers of IPVE and ISPO units in each segment were determined to be 1.6 and 2.5, respectively, indicating that the copolymerization proceeded via high-frequency crossover reactions.

Furthermore, the ratios of the structures derived from the different addition modes of ISPO (Scheme 4) were calculated from the integral ratios of the olefin protons at 5–6 ppm and the methine protons derived from the hydride shift isomerization at 2.5 ppm as follows: 1,2-homo:1,4-homo:1,2-crossover:1,4-crossover:isomerization = 0.40:0.16:0.07:0.29:0.08. Interestingly, homopropagation was more frequent than crossover in the case of the 1,2-addition mode, whereas crossover was more frequent than homopropagation in the case of the 1,4-addition mode. This trend is likely related to the frequency of carbocation generation and to the carbocation reactivity because only the 1,2-homopropagation is likely to proceed

without the ring opening of the oxonium ion. The ratio between the homopropagation and crossover reactions is discussed in a subsequent section.



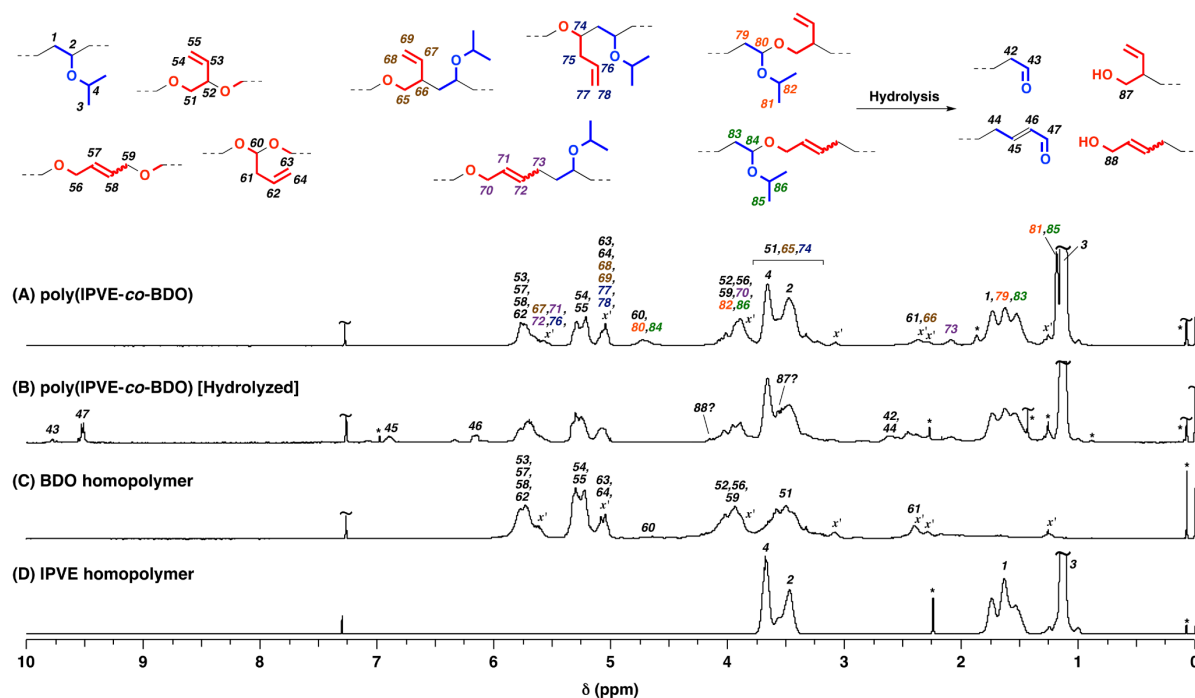
**Scheme 4.** Addition modes for the ISPO- or BDO-derived propagating species with a VE or an oxirane.

Acid hydrolysis of the product also suggested that the successful copolymerization proceeded through highly frequent crossover reactions. Because the crossover reaction from IPVE to ISPO generated acid-labile acetal structures in the main chain, the copolymer product was readily degraded under acidic conditions (Figure 2A). After hydrolysis, the MWD curve clearly shifted toward the lower-MW region, and an oligomeric product with a unimodal MWD was obtained. The very low MW value ( $M_n \sim 0.4 \times 10^3$ ) of the hydrolysis product corresponds to the above-estimated average numbers of IPVE and ISPO units per one block, which are 1.6 and 2.5, respectively. The  $^1\text{H}$  NMR analysis of the hydrolysis product (Figure 3B) also showed the disappearance of the acetal structures and the appearance of

aldehyde and hydroxyl structures (peaks 43–50) compared to the spectrum of the original copolymer, which is indicative of a clean degradation.

Another oxirane that has a vinyl substituent, BDO, generated copolymers with IPVE in a manner similar to the copolymerization using ISPO, although the crossover reaction occurred less frequently. The copolymerization produced a product with a unimodal MWD with a slight shoulder at the low-MW region (entry 4 in Table 1 and Figure 2B). The  $^1\text{H}$  NMR spectrum of the product (Figure 4A) indicated that the copolymer of IPVE and BDO was produced through the 1,2- and 1,4-addition reactions of BDO (Scheme 4, see Figures S9–S16 for the  $^{13}\text{C}$  and 2D spectra). The structures derived from the hydride shift isomerization of the BDO propagating end carbocation was also confirmed. An analysis similar to that of the case involving the ISPO copolymerization gave estimates that the crossover from IPVE to BDO occurred  $\sim 4.1$  times per chain and that the average number of IPVE and BDO units in each block were 5.5 and 3.4, respectively. The longer blocks compared to those of the ISPO copolymer indicates that the crossover frequency was lower for the BDO copolymerization. Furthermore, the acid hydrolysis of the BDO copolymer yielded a product with an MW greater than that of the hydrolysis product of the ISPO copolymer.





**Figure 4.**  $^1\text{H}$  NMR spectra of (A) poly(IPVE-*co*-BDO) (entry 4 in Table 1), (B) its hydrolysis product, (C) BDO homopolymer (entry 6), and (D) IPVE homopolymer (entry 14) (in  $\text{CDCl}_3$  at 30  $^\circ\text{C}$ ; see Scheme S1 for peaks  $x'$ ; \* solvent, water, grease, vaseline, etc.).

Both ISPO and BDO generated copolymers with IPVE through crossover reactions; however, the MWs of the products were not very high. Some side reactions originating from the oxirane monomers are most likely responsible for the low MW values because the IPVE homopolymerization under the same conditions yielded a polymer with a very high MW (entry 14). In fact, homopolymerizations of ISPO (entry 3) and BDO (entry 6) produced products with low MWs. In addition, a product with a higher MW was obtained by the copolymerization when a smaller amount of ISPO (entry 2) or BDO (entry 5) was used.  $^1\text{H}$  NMR analysis of the ISPO homopolymer showed peaks that can be assigned to chain end structures, although the peaks were very small.<sup>19</sup> In addition, the BDO homopolymer exhibited only negligible peaks that can be assigned to chain-end structures, such as diene structures (the chain-end diene structures were confirmed to be generated in the

polymerization at 0 °C, Figure S17). These results indicate that macrocyclic products with low MWs, which have no chain end, were partly generated in the ISPO and BDO polymerizations through the reaction of the  $\alpha$ -ends, such as the hydroxyl groups or the catalyst-coordinated boron–oxygen bonds, with the propagating ends.

Most of the olefinic groups in the main and side chains of the ISPO or BDO copolymers were intact during the copolymerization reactions because they have much lower nucleophilicity compared to the vinyl group of IPVE and the oxygen atoms on the oxiranes. However, a small part of the vinyl groups at the side chains appeared to undergo intramolecular cyclization reactions (peaks  $x$  and  $x'$  in Figures 3 and 4, respectively) in a particular situation. The details on the possible cyclization reactions are given in the Supporting Information (Scheme S1).

IBO was copolymerized with IPVE (entry 7) through crossover reactions that were less frequent than those occurring in the reactions using ISPO and BDO. In this copolymerization, the relatively preferential homopropagation reactions of each monomer led to the generation of a multiblock-like copolymer with average numbers of IPVE and IBO units of 7.9 and 11, respectively. The  $M_n$  value of  $1.4 \times 10^3$  for the acid hydrolysis product agreed relatively well with the value estimated from the average numbers of both units. The details of the copolymerization using IBO have already been summarized in our previous paper.<sup>15</sup>

The oxirane propagation reactions via the oxonium-ion species can involve two types of scission modes, i.e.,  $\alpha$ -scission, the scission of the bonds between the oxygen atom and the substituted carbon atom, and  $\beta$ -scission, the scission between the oxygen atom and the non-substituted carbon atom. The scission modes involved in the polymerizations are not yet clear; however, the results of previous studies on the acid-catalyzed reactions of oxirane will help extrapolate them. Acid-catalyzed hydrolysis of IBO using  $\text{HClO}_4$ <sup>20</sup> and alcoholysis using

BF<sub>3</sub>OEt<sub>2</sub>/primary or secondary alcohols<sup>21</sup> have been reported to proceed exclusively via the  $\alpha$ -scission, whereas hydrolysis using HCl<sup>22</sup> or alcoholysis using a tertiary alcohol<sup>23</sup> have been shown to yield products via both scission modes. These studies indicate that the IBO-derived oxonium ion tends to form a carbocation-like intermediate because of the electron donation from the dimethyl substituents to induce the  $\alpha$ -scission; however, strong or sterically hindered nucleophiles can attack the methylene carbon to lead to the  $\beta$ -scission. Therefore, the propagation reactions mediated by the ISPO-, BDO-, and IBO-derived oxonium ions without forming carbocations most likely proceed mainly via the  $\alpha$ -scission, given that the nucleophilicity and the steric hindrance of the oxirane are not too large. Alternatively, the propagation reactions after forming carbocations via ring opening undoubtedly proceed via  $\alpha$ -scission because the carbocations produced are far more stable than the primary carbocations that can be formed via  $\beta$ -scission.

## 2. Copolymerization Using DMBO or BO: Polymerization with Few Crossover Reactions

In the copolymerization of DMBO and IPVE, both monomers were consumed and a product with a relatively high MW was obtained (entry 10). <sup>1</sup>H NMR analysis confirmed that both monomer units were incorporated into the product. However, the spectrum consisted of only very small peaks that are assignable to acetal protons, indicating that the crossover from IPVE to DMBO occurred less efficiently compared to the copolymerization using ISPO, BDO, and IBO. In addition, acid hydrolysis yielded a product with an MW slightly lower than that of the original polymer (Figure 2D), which also indicates that the copolymerization product contained a very small amount of the acetal structures originating from the crossover.

Homopolymerization of DMBO also proceeded under similar conditions and yielded a polymer with a relatively high MW. The polymer had a unimodal MWD with few low-MW

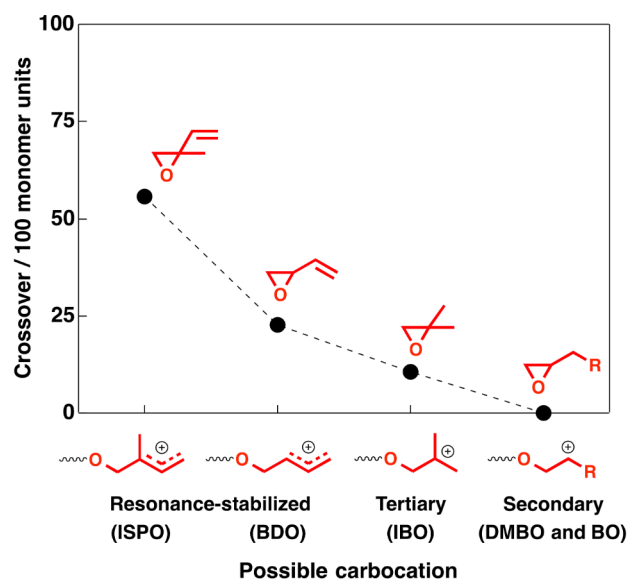
portions, indicating that side reactions, such as chain transfer reactions and cyclization reactions, occurred much less frequently compared to the propagation reactions.

Another oxirane that may form a secondary carbocation, BO, also did not generate crossover reactions efficiently; however, its behavior in the polymerization was different from that in the DMBO case. The copolymerization of BO with IPVE yielded a product with a bimodal MWD (Figure 2E). Fractionation of the two portions by preparative GPC and subsequent analysis by  $^1\text{H}$  NMR revealed that the higher-MW portion was composed mostly of IPVE units, whereas the lower-MW portion was composed mostly of BO units (Figure S19). The lower-MW products appear to contain primarily cyclic oligomers of BO because chain end structures, such as olefin structures generated via the  $\beta$ -proton elimination reaction, were observed in very small amounts in the  $^1\text{H}$  NMR spectrum. Similar low-MW products were also obtained in the BO homopolymerization (entry 13). Cyclic oligomers of BO have been reported to be obtained using Lewis acid catalysts in previous studies.<sup>24–26</sup>

### 3. Frequency of Crossover Reactions in Copolymerizations Using Various Oxiranes

The results of the copolymerizations using various oxiranes suggest that the ease of carbocation generation from oxirane monomers is most likely responsible for the frequency of crossover reactions. Figure 5 shows the relationship between the frequency of crossover reactions in the copolymerization with IPVE (the number of crossover reactions per 100 monomer units, similar to “run number” suggested by Harwood et al.<sup>27</sup>) and the structures of carbocations that are possibly generated from oxirane monomers. The oxiranes that generate resonance-stabilized, allyl-type carbocations, ISPO and BDO, were copolymerized with IPVE through very efficient crossover reactions, most likely because of the frequent generation of carbocations. In contrast, the carbocation generation via ring opening was much less frequent in the reactions involving DMBO and BO because the carbocations that could

be generated are less stable secondary carbocations. In the reaction involving DMBO and IPVE, the propagation reaction of DMBO appeared to proceed mostly via the oxonium-ion species, which cannot react with vinyl monomers without forming carbocations.



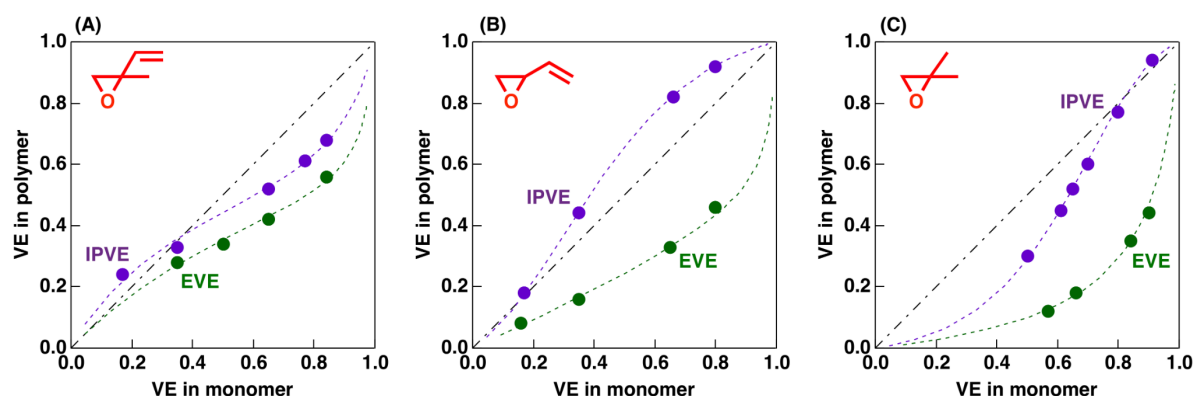
**Figure 5.** Relationship between the frequency of the crossover reactions in the copolymerizations with IPVE and the structure of carbocations that possibly generates from oxiranes ( $R = t\text{Bu}$  or  $\text{Me}$ ). The values of entries 1, 4, 7, and 12 in Table 1 were used for calculation.

The carbocation generation is related only to the oxirane-to-VE crossover reactions; hence, the VE-to-oxirane crossover reactions must also occur efficiently for copolymerization. In addition, for the crossover reactions, each monomer needs to react efficiently with the propagating carbocation generated from a different type of monomer. The nucleophilicity of both VE and the oxirane monomers is most likely related to these reactions. The details related to the frequency of the crossover reactions are discussed in terms of monomer reactivity ratios in the next section.

## Factors that Affect Crossover Efficiency: Discussion Based on Monomer Reactivity

### Ratios

To gain deeper insight into the factors that affect crossover efficiency, the monomer reactivity ratios were determined for the copolymerizations of ISPO, BDO, and IBO with IPVE. Figure 6 (purple symbols) shows the compositions of the products obtained in the copolymerizations at different initial monomer ratios (Table S2). The data were analyzed by the Kelen–Tüdös method (Figure S20);<sup>28,29</sup> the obtained monomer reactivity ratios are tabulated in Table 2.<sup>30</sup> The broken curves in Figure 6 were drawn using these  $r_1$  and  $r_2$  values.



**Figure 6.** Copolymer compositions for the cationic copolymerizations of VEs and oxiranes (see Table 2 for the monomer reactivity ratios obtained; broken curves: curves that were drawn using the  $r$  values obtained by the Kelen–Tüdös method, dashed-dotted lines: azeotropic lines; the copolymerization data used for the plots are summarized in Table S2).

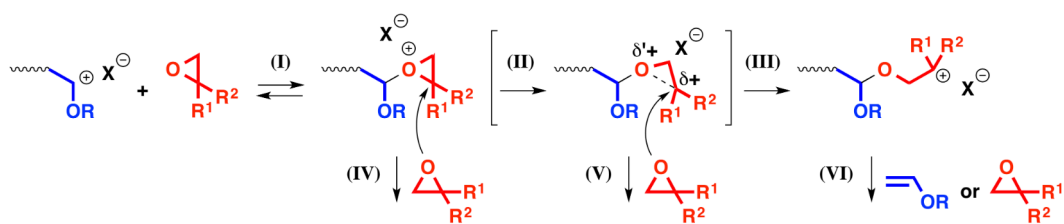
**Table 2.** Monomer Reactivity Ratios <sup>a</sup>

M <sub>1</sub> (VE)	M <sub>2</sub> (Oxirane)	$r_1$	$r_2$
IPVE	ISPO	0.24	0.56
	BDO	3.8	1.5
	IBO	2.4	7.3
EVE	ISPO	0.09	0.99

BDO	0.05	2.2
IBO	0.08	8.7

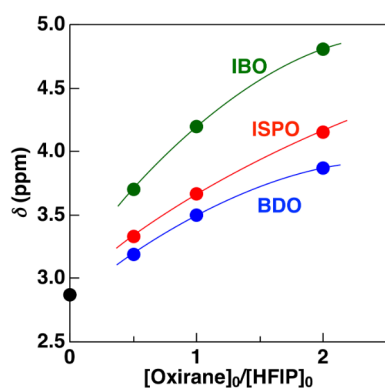
<sup>a</sup> Determined by the Kelen–Tüdös method (references 28 and 29). See Figure S20 for the  $\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$  plots. See Figure 6 for the copolymer composition curves.

The values for the reactivity of the IPVE-derived propagating cation,  $r_1$ , were as follows: ISPO system ( $r_1 = 0.24$ ) < IBO system (2.4) < BDO system (3.8). This order appears to be explained in part by the two factors suggested for the ring-opening copolymerization of cyclic monomers,<sup>31</sup> which explain that the reactivities of cyclic monomers are dependent on the nucleophilic coordination power of a cyclic monomer to the propagating cation (reaction **I** in Scheme 5) and the subsequent ring-opening of the coordinating monomer, or the oxonium ion (reaction **III**). The former process is in equilibrium between coordination and dissociation, and the coordination power is related to the nucleophilicity or basicity of the monomers. The latter process is assumed to be the irreversible reaction, where the bond dissociation energy for the carbon–oxygen bond of the oxonium ion is responsible for its occurrence. We believe that the latter process, the ring opening of the oxonium ion, does not necessarily generate carbocations as in the  $S_N1$  process (reactions **III** and **VI**), but includes the scission of the carbon–oxygen bond via the attack of an oxirane monomer to the oxonium ion as in the  $S_N2$  process (reaction **IV**). The scission, the formation of the carbocation-like species, and the attack of an oxirane monomer would occur via a concerted mechanism (reactions **II** and **V**). These two processes, the coordination and the ring opening, were discussed in terms of the oxirane nucleophilicity and the carbocation stability in the present study.



**Scheme 5.** Possible pathways for the crossover reaction from the VE-derived carbocation to an oxirane monomer.

Hydrogen-bonding basicity<sup>32–37</sup> has often been employed as a measure for nucleophilicity. In the present study, the hydrogen-bonding basicity was preliminarily estimated by the NMR measurements on the interaction between the oxiranes and HFIP. Figure 7 shows the change in the chemical shift of the hydroxyl group of HFIP in the presence of 0.5–2 equivalents of the oxiranes in CD<sub>2</sub>Cl<sub>2</sub>/CCl<sub>4</sub> (3/7 v/v). When the amount of oxiranes was increased, the hydroxyl peak shifted downfield. The degree of the downfield shift decreased in the following order: IBO > ISPO > BDO. The order did not agree with the order of the  $r_1$  values for the copolymerizations with IPVE.



**Figure 7.** <sup>1</sup>H NMR chemical shifts of the peak for the hydroxy proton of HFIP in the presence of ISPO (red), IBO (green), and BDO (blue) {[HFIP]<sub>0</sub> = 50 mM, [oxirane]<sub>0</sub> = 25, 50, or 100 mM, in CD<sub>2</sub>Cl<sub>2</sub>/CCl<sub>4</sub> (3/7 v/v) at 25 °C}.



Another factor, the ring opening of the oxonium ion, is most likely related to the stability of the generated carbocation. The stability of the carbocations with structures similar to those generated from the oxirane-derived oxonium ions were reported to be as follows:  $(\text{CH}_3)_2\text{C}^+-\text{CH}=\text{CH}_2$  [ $\leftrightarrow$   $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2^+$ ] (ISPO-type)  $>$   $(\text{CH}_3)_3\text{C}^+$  (IBO-type)  $>$   $\text{CH}_3\text{CH}^+-\text{CH}=\text{CH}_2$  [ $\leftrightarrow$   $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2^+$ ] (BDO-type).<sup>16,17</sup> In addition to the stability of the carbocations, the oxirane nucleophilicity is also hypothesized to be responsible for the ring opening through an  $\text{S}_{\text{N}}2$ -like or concerted process involving the attack of the oxirane monomer on the oxonium ion.

The balance of the two factors possibly affected the  $r_1$  values. For example, IBO coordinates to the VE-derived propagating carbocation more strongly than the other oxiranes, but the subsequent ring opening of the IBO-derived oxonium ion proceeds less easily compared to that of the ISPO-derived species. The agreement between the orders of the  $r_1$  values and the carbocation stability indicates that the ring opening of the oxonium ion, via both  $\text{S}_{\text{N}}1$ - and  $\text{S}_{\text{N}}2$ -like processes, contributed to the crossover reactions more heavily than the nucleophilicity of the monomers. On the other hand, the nucleophilicity of IPVE is primarily responsible for the  $r_1$  values because the values obviously reflect the relative reactivities of both the vinyl and oxirane monomers. In fact, the copolymerizations using a VE with a lower reactivity resulted in very small  $r_1$  values, as shown below.

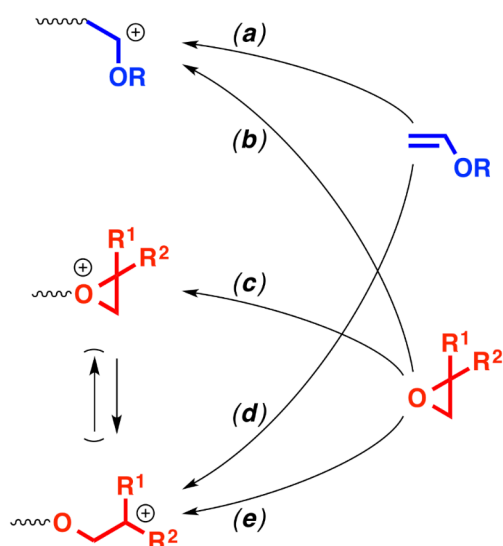
The  $r_2$  values were expected to exhibit an order opposite that of the  $r_1$  values, i.e., the highest and lowest  $r_2$  values for the ISPO and BDO systems, respectively, given that similar factors—the nucleophilicity of monomers and the ring opening of the oxonium ions—are responsible for the addition reactions at the oxirane-derived propagating ends. In contrast, the  $r_2$  values unexpectedly showed the following order: ISPO system ( $r_2 = 0.56$ )  $<$  BDO system (1.5)  $<$  IBO (7.3). For the ISPO system, the  $r_1$  and  $r_2$  values were both less than one, suggesting that the crossover reactions occur preferentially over the homopropagation

reactions. This estimation agreed very well with the copolymerization that produced copolymers with average IPVE and ISPO units of 1.6 and 2.5 per block, respectively, as shown in the previous section. In addition, the large  $r_1$  and  $r_2$  values for the IBO system, which indicates that the homopropagation reactions are preferred, properly explain the generation of the copolymer with a multiblock-like structure of average IPVE and IBO units of 7.9 and 11 per block, respectively.

The singular  $r_2$  values likely stemmed partly from the fact that the oxonium ions do not react with vinyl monomers. The  $r_2$  value for the IBO system was much greater than one, possibly because the reactions of IBO preferentially proceed via the oxonium ion propagating species rather than through the carbocation formation. The smaller  $r_2$  value for the BDO system is attributable to the smaller nucleophilicity of BDO compared to that of IBO because of the weaker attack of BDO on the oxonium ion, as discussed with respect to the  $r_1$  values. Meanwhile, the  $r_2$  value for the ISPO system, which was less than one, suggests that the carbocations generated from the oxirane exhibit selectivity of the monomers to be reacted.

The characteristic reactivity of the oxirane-derived carbocations was further supported by the copolymerization using a VE with a smaller reactivity, EVE (green symbols in Figure 6; Table 2). The  $r_1$  values are all less than 0.1 for the three systems, indicating that the EVE-derived propagating ends preferentially react with oxiranes. This behavior most likely resulted from the much smaller nucleophilicity of EVE compared to those of the oxiranes and IPVE. In contrast to these reasonable  $r_1$  values, the  $r_2$  values for all the systems using EVE were merely slightly larger than the values for the corresponding IPVE systems. Much higher  $r_2$  values were expected for the EVE systems, given that the oxiranes have nucleophilicities much greater than that of EVE. The  $r_2$  value of 0.99 for the ISPO system indicates that the ISPO-derived propagating ends react almost equally with both EVE and ISPO, in contrast to the very high reactivity of ISPO toward the EVE-derived propagating end.

These behaviors of the copolymerizations of VEs and oxiranes can be explained by the following three factors: the frequency of the carbocation generation via ring opening, the monomer nucleophilicity, and the special reactivity of the oxirane-derived carbocations. The propagation reactions for the copolymerization are composed of the following five elementary reactions shown in Scheme 6. The frequency of reactions **a** and **b**, i.e., the reactions of a VE-derived carbocation, appear to depend primarily on the nucleophilicity balance of VE and oxirane, as indicated by the large difference in the  $r_1$  values between the IPVE and EVE systems. The difference in the  $r_1$  values among the oxiranes is possibly explained by the nucleophilicity of oxiranes and the ring-opening behaviors of the oxonium ions that formed. Reaction **c** is the exclusive homopropagation reaction of oxirane mediated by the oxirane-derived oxonium ion. This reaction continuously occurs until the propagating oxonium ion undergoes ring opening to generate a carbocation; hence, the average number of oxirane units in each block is dependent on the frequency of the carbocation generation via ring opening and the nucleophilicity of the oxirane monomers. In contrast to the reasonable behaviors of these three reactions, the selectivity of the last two reactions, **d** and **e**, are not clear yet. The carbocation generated via the ring opening of the oxonium ion most likely shows a “preference” for VE monomers or a “aversion” of oxirane monomers, i.e., reaction **d** preferentially occurs rather than reaction **e**, which is different from the reactivity of the VE-derived carbocations. The elucidation of such unique behaviors is the subject of our next study, which is currently under way.



**Scheme 6.** The reactions of the VE- or oxirane-derived propagating species with a VE or an oxirane.

## Conclusion

In conclusion, the carbocation generation, the nucleophilicity of monomers, and the characteristic reactivity of the oxirane-derived carbocations were observed to affect the behaviors of the concurrent cationic vinyl-addition and ring-opening copolymerization of alkyl vinyl ethers and oxiranes. First, the carbocation generation via ring opening of the oxirane-derived oxonium ion was essential for the crossover reactions between the different types of monomers. Oxiranes that generate resonance-stabilized or tertiary carbocations via ring opening, ISPO, BDO, and IBO, can be copolymerized with IPVE through crossover reactions to yield copolymers, whereas oxiranes that hardly generate carbocations because of their unstable secondary structures, DMBO and BO, were not efficiently copolymerized with IPVE. Furthermore, the crossover frequency varied among the three oxiranes that yielded copolymers, which provided products with different sequences, including random or alternating-rich copolymers with short VE and ISPO blocks and multiblock-like copolymers

with long VE and IBO blocks. The monomer reactivity ratios indicated that the nucleophilicity balance of vinyl and cyclic monomers and the ring-opening behavior of the oxonium ions decisively influence the frequency of the crossover reactions from the VE-propagating end to an oxirane. In contrast, the characteristic reactivity of the oxirane-derived carbocations appeared to affect the crossover reactions from the oxirane-propagating end to a VE. The results obtained in this study will provide a new perspective for the synthesis of a variety of functional copolymers from different types of monomers, even those that were previously thought incompatible. Furthermore, the success of this type of concurrent copolymerization suggests high potential for a more precise sequence control of copolymers, which could not be attained without the characteristic and distinctive reactivities of propagating species.

## **ASSOCIATED CONTENT**

**Supporting Information.** Polymerization data and  $^1\text{H}$ ,  $^{13}\text{C}$ , and 2D NMR spectra of polymers. 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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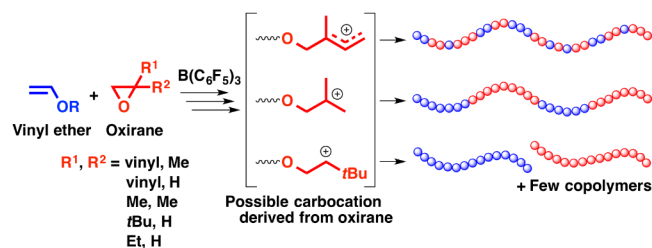


shift were reported in the studies using methanol<sup>36</sup> or *tert*-butanol<sup>37</sup> as hydrogen-bonding donors.

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*Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization*



Title:

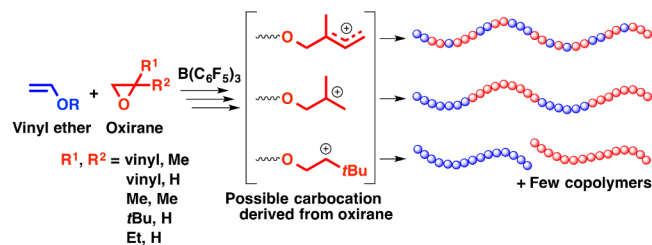
“Rational Design of Oxirane Monomers for Efficient Crossover Reactions in Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization with Vinyl Ethers”

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Because we are not sure whether the label, title, and authors should be included in the figure file, another version, which includes the information in the graphic, was prepared as follows:

*Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization*



For Table of Contents Use Only

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