Title	Concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl ethers and oxiranes
Author(s)	Kanazawa, Arihiro; Aoshima, Sadahito
Citation	Polymer Journal. 2016, 48(6), p. 679-687
Version Type	AM
URL	https://hdl.handle.net/11094/100940
rights	
Note	

[Focus Review]

Concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl ethers and oxiranes

Arihiro Kanazawa* and Sadahito Aoshima*

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan
E-mail: kanazawaa11@chem.sci.osaka-u.ac.jp, aoshima@chem.sci.osaka-u.ac.jp

Running Head: Vinyl-Addition and Ring-Opening Copolymerization
Key Words: vinyl polymerization, ring-opening polymerization, copolymerization, vinyl ether, oxirane, Lewis acid

Abstract

In this review, our recent results on the concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl ethers (VEs) and oxiranes are summarized, with particular emphasis on the strategies required to generate crossover reactions between different types of monomers. Most importantly, carbocation generation via the ring-opening reaction of the oxirane-derived oxonium ion is indispensable for the crossover reaction from oxirane to VE. Specifically, oxiranes with substituents that contribute to stabilizing these carbocations are suitable for concurrent copolymerization. Moreover, weak Lewis bases have been found to affect the frequency of crossover reactions through the promotion of the ring-opening reaction. This article also summarizes concurrent cationic vinyl-addition, ring-opening, and carbonyl-addition terpolymerization via the one-way cycle of crossover reactions, the copolymerization of an alkoxyoxirane with VEs through the alkoxy group transfer mechanism, and the long-lived species-mediated cationic polymerization of vinyl monomers and cyclic formals.

Introduction

Copolymerization reactions of different types of monomers, such as copolymerization of vinyl and cyclic monomers via concurrent vinyl-addition and ring-opening mechanisms, are expected to produce copolymers with unique properties; however, these reactions have been a challenging goal. The primary obstacle to copolymerization is the successful crossover reactions between monomers

that generate different types of propagating species. An elaborate design of monomers and/or initiating systems is required for both crossover reactions and the suppression of undesired reactions, including homopolymer generation, termination reactions, and chain transfer reactions such as cyclic oligomer formation. Only a few reported approaches have attained concurrent vinyl-addition and ring-opening copolymerization, such as the copolymerization of maleimides with oxazolines[1,2] or propylene oxide[3,4] via the zwitterionic mechanism, methyl methacrylate with ε-caprolactone[5] via the anionic mechanism, and styrene or vinyl ethers (VEs) with cyclic formals[6,7] via the cationic mechanism.

Oxiranes are prospective candidates as comonomers that copolymerize with vinyl monomers via the concurrent vinyl-addition and ring-opening mechanisms. The three-membered ring with an oxygen atom exhibits ring strain; hence, oxiranes homopolymerize via the anionic, coordination, or cationic ring-opening mechanisms.[8–14] During cationic ring-opening polymerization, the propagation reaction generally proceeds via the attack of oxirane monomers on the carbon atom adjacent to the cationic oxygen atom of the oxonium ions. The oxonium ions, however, do not react with vinyl monomers, thus preventing the copolymerization of vinyl monomers and oxiranes via the cationic mechanism. Several previous studies have demonstrated the copolymerization of styrene derivatives and oxiranes; however, it is unclear whether crossover reactions between monomers actually occurred, owing to the absence of analysis through spectroscopic methods such as NMR spectroscopy.[15,16] Moreover, copolymerization of VEs and oxiranes have been reported to produce only homopolymer mixtures.[17]

Our strategy for successful concurrent cationic vinyl-addition and ring-opening copolymerization is to use oxiranes that efficiently generate carbocations via the ring-opening reaction of the oxonium ions and to design suitable initiating systems. Depending on the substituents on the oxiranes, a carbocation may be generated through the ring-opening reaction of the oxonium ion (strategy I in Figure 1). Electron-donating groups contribute to the generation of carbocations. Indeed, cyclic formals generate carbocations that are stabilized through electron donation from the adjacent alkoxy group,[18] providing a restricted example of copolymerization with vinyl monomers.[6,7] A Lewis acid catalyst generating an appropriate counteranion that does not prevent propagating cations from reacting with different types of monomers is also required to induce efficient copolymerization (strategy II). Moreover, an appropriate balance of monomer reactivities is required for even incorporations of vinyl and cyclic monomers into polymer chains (strategy III). In addition, recent remarkable developments concerning living cationic polymerization of vinyl monomers[19–25] are expected to allow for concurrent cationic vinyl-addition and ring-opening copolymerization that proceeds in a highly controlled manner via the generation of the long-lived propagating species.

In this article, we review our recent studies on concurrent cationic vinyl-addition and ring-opening copolymerization (Figure 1). Most importantly, copolymerization of vinyl ethers and

2

oxiranes was found to proceed with the use of oxiranes with suitable substituents that contribute to the stabilization of the carbocation generated via the ring-opening reaction of the propagating oxonium ion.[26,27] This article also summarizes the following topics: strategies to control the frequency of the crossover reactions,[28] concurrent cationic terpolymerization via one-way cycle crossover reactions,[29] copolymerization using an alkoxyoxirane via the alkoxy group transfer mechanism,[30] and long-lived species-mediated copolymerization of cyclic formals with VEs or styrene.[31,32]
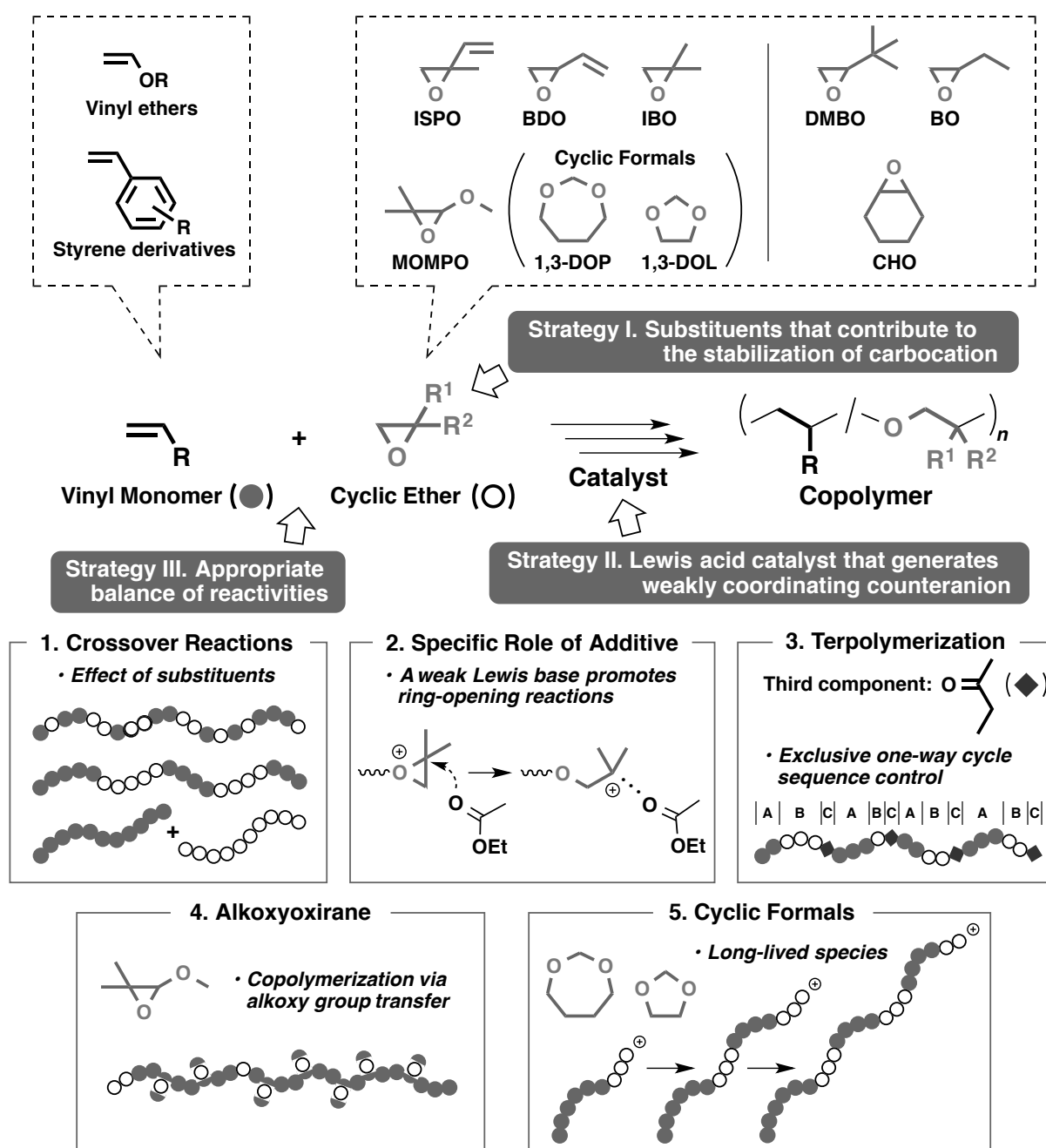
Figure 1. Strategies for and outcomes of concurrent cationic vinyl-addition and ring-opening polymerization.

Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization of Vinyl Ethers and Various Oxiranes

Substituents attached to an oxirane ring have been found to be responsible for the successful copolymerization of alkyl vinyl ethers and oxiranes through the concurrent cationic vinyl-addition and ring-opening mechanisms.[26,27] This is because a VE monomer does not add to the oxonium ion derived from an oxirane. The crossover reaction from an oxirane-derived propagating end to a VE monomer requires the transformation of the oxonium ion into the carbocation via a ring-opening reaction. Thus, substituents that contribute to the stabilization of the carbocations[33,34] generated via the ring-opening reaction of the oxonium ion are indispensable for efficient copolymerization reactions. For example, an oxirane with dimethyl groups at the α-position, isobutylene oxide (IBO), generates a tertiary carbocation through the ring-opening reaction of the oxonium ion (Figure 2). The copolymerization of IBO with isopropyl VE (IPVE) successfully proceeded with the use of $B(C_6F_5)_3$ as a Lewis acid catalyst through several rounds of crossover reactions per chain, yielding a multiblock-like copolymer. Moreover, the use of isoprene monoxide (ISPO), which is an oxirane that generates a more stable, resonance-stabilized carbocation, resulted in more frequent crossover reactions, yielding an alternating rich copolymer through copolymerization with IPVE. In contrast, oxiranes that may generate secondary carbocations, such as 3,3-dimethyl-1,2-butylene oxide (DMBO) and 1,2-butylene oxide (BO), did not copolymerize with VEs and resulted in products composed mainly of homopolymer mixtures (or a mixture of a VE homopolymer and cyclic oligomers of an oxirane). This result indicates that the carbocations were not generated from the DMBO- or BO-derived oxonium ions via ring-opening reactions due to the instability of the secondary carbocationic species. In the reactions using the oxirane monomers, the quantity of crossover reactions per 100 monomer units (or "run number"[35]) was clearly dependent on the carbocations generated via the ring-opening reaction of the oxirane-derived oxonium ions, as shown in Figure 3.

Another prerequisite for the concurrent vinyl-addition and ring-opening copolymerization of VEs and oxiranes is the use of a suitable Lewis acid catalyst that generates a weakly coordinating counteranion. $B(C_6F_5)_3$[36–38] effectively initiated copolymerization through the interaction with adventitious water, producing a proton and $B(C_6F_5)_3(OH)^-$, and/or through the interaction with an oxirane. In contrast, metal chlorides such as $GaCl_3$ were not suited for copolymerization of IPVE and IBO because the oxirane-derived propagating species were deactivated as a result of the generation of a carbon–chloride bond. The structure of this bond is similar to the propagating chain end produced in the cationic polymerization of isobutylene and is difficult to cleave under the conditions used (i.e.,

reactions in the presence of a large amount of weak Lewis bases),[39–42] resulting in negligible crossover reactions from IBO to IPVE. In addition, BF_3OEt_2 was ineffective for copolymerization although the reason is unclear.

The frequency of crossover reactions in copolymerization is highly dependent on the nucleophilicity of the monomers and the frequency of the ring-opening reactions of oxonium ions. The crossover reaction from VE to oxirane proceeds through the coordination of an oxirane monomer to the VE-derived carbocation and the subsequent ring-opening reaction of the generated oxonium ion via attack by an oxirane monomer or via generation of the carbocation. Because the former process is a reversible reaction, both the nucleophilicity of the oxirane and the ease of the ring-opening reaction of the oxonium ion,[43] which are evaluated by the hydrogen-bonding basicity[44–48] of oxiranes and the stability of the generated carbocations[33,34] via the ring-opening reaction, respectively, affect the frequency of the crossover reaction from VE to oxirane. The frequency of the crossover reaction from oxirane to VE primarily depends on the frequency of the ring-opening reaction of the oxirane-derived oxonium ion because a VE monomer does not add to the oxonium ion. Because the homopropagation reactions of oxiranes continue to proceed until the ring-opening reaction occurs, the number of oxirane units in each block of copolymers depends on the frequency of the carbocation generation via ring-opening reactions and the nucleophilicity of the oxirane monomers.

Another factor that affects the frequency of crossover reactions is the special reactivity of the oxirane-derived carbocations. The carbocations generated via the ring-opening reaction of the oxirane-derived oxonium ion most likely have a preference for a VE monomer or have an aversion to the oxirane monomer because the frequency of the crossover reactions from oxirane to VE does not depend on the reactivity of VE monomers. The copolymerization of ethyl vinyl ether (EVE), a less reactive VE than IPVE, with IBO, butadiene monoxide (BDO), or ISPO yielded copolymers with fewer numbers of VE units but with comparable numbers of oxirane units in each block compared with the copolymers obtained using IPVE. These trends were also supported by the monomer reactivity ratios[49,50] for the copolymerization of oxiranes with IPVE (entries 1, 8, and 12 in Table 1) or EVE (entries 6, 11 and 15). More specifically, the r_1 values in copolymerization using EVE were less than 0.1, but the r_2 values were comparable to those for copolymerization using IPVE. Given that an oxirane monomer reacts with both VE and oxirane monomers, the homopropagation reaction from the ring-opened, oxirane-derived carbocation to an oxirane monomer should occur more frequently in the copolymerization using EVE to result in a much larger r_2 value compared to the reaction using IPVE. Moreover, the monomer reactivity ratios in the copolymerization of IPVE and ISPO were less than one (entry 12 in Table 1), which cannot be explained simply by the nucleophilicity of the monomers. The hypothesis that the carbocation generated via the ring-opening reaction of the oxonium ion reacts preferentially with a VE monomer suitably explains such behavior although the reason for the aversion

to an oxirane monomer is unclear.
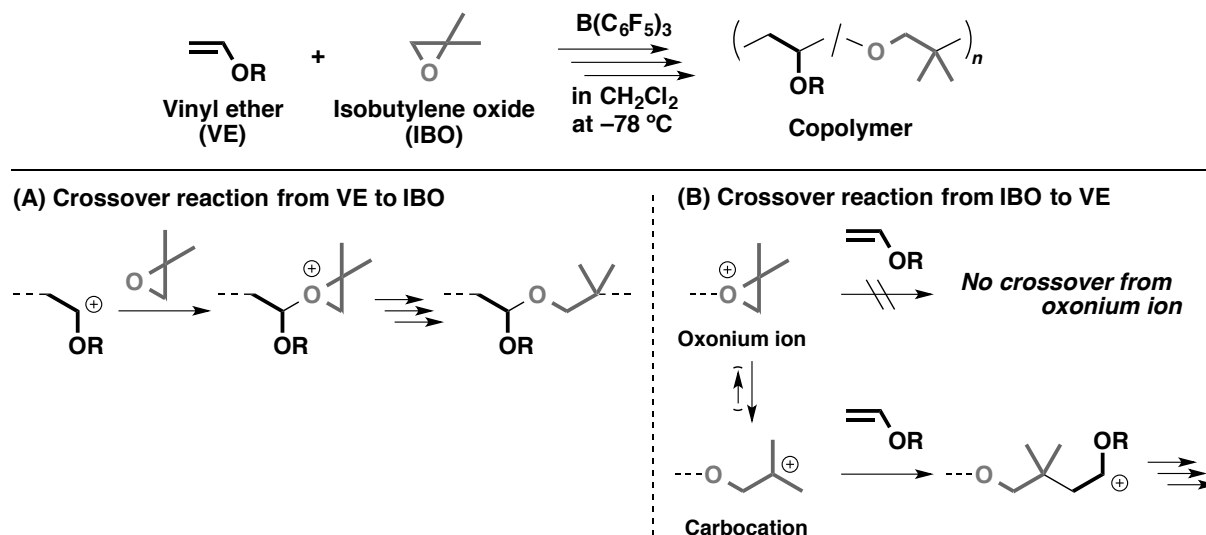
Figure 2. Crossover reactions that generate in the concurrent cationic vinyl-addition and ring-opening copolymerization of VE and IBO (counteranions are omitted).
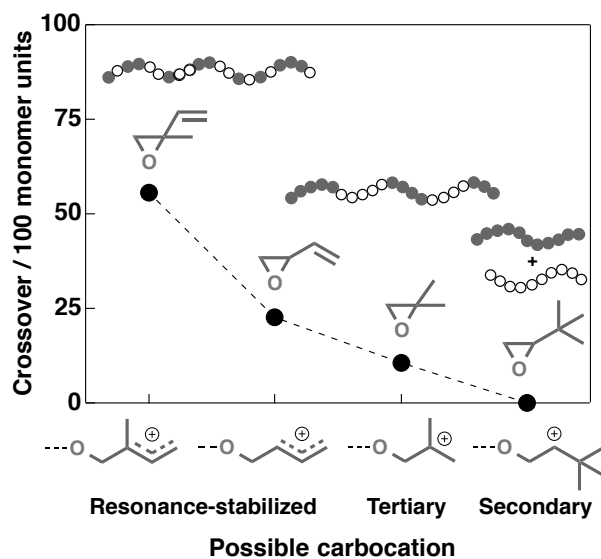
Figure 3. The numbers of crossover reactions per 100 monomer units in the concurrent cationic polymerization of IPVE and various oxiranes.

Table 1. Monomer reactivity ratios for cationic copolymerizations of VEs and oxiranes.[a]

entry	M_1	M_2	additive	solvent (v/v)	r_1	r_2
1	IPVE	IBO	None	CH_2Cl_2	2.4	7.3
2			EtOAc	CH_2Cl_2	1.9	0.35
3			None	Hex/CH_2Cl_2 (7/3)	0.98	7.0
4			1,4-Dioxane	CH_2Cl_2	1.2	0.41
5			Et_2O	CH_2Cl_2	2.3	6.4
6	EVE		None	CH_2Cl_2	0.08	8.7
7			EtOAc	CH_2Cl_2	0.23	0.80
8	IPVE	BDO	None	CH_2Cl_2	3.8	1.5
9			EtOAc	CH_2Cl_2	2.6	0.28
10			None	Hex/CH_2Cl_2 (7/3)	0.75	1.9
11	EVE		None	CH_2Cl_2	0.05	2.2
12	IPVE	ISPO	None	CH_2Cl_2	0.24	0.56
13			EtOAc	CH_2Cl_2	0.22	0.50
14			None	Hex/CH_2Cl_2 (7/3)	0.23	0.69
15	EVE		None	CH_2Cl_2	0.09	0.99

[a] By the Kelen-Tüdõs method. The values are cited from References 27 and 28.

Effects of Weak Lewis Bases and Solvent Polarity on the Frequency of Crossover Reactions
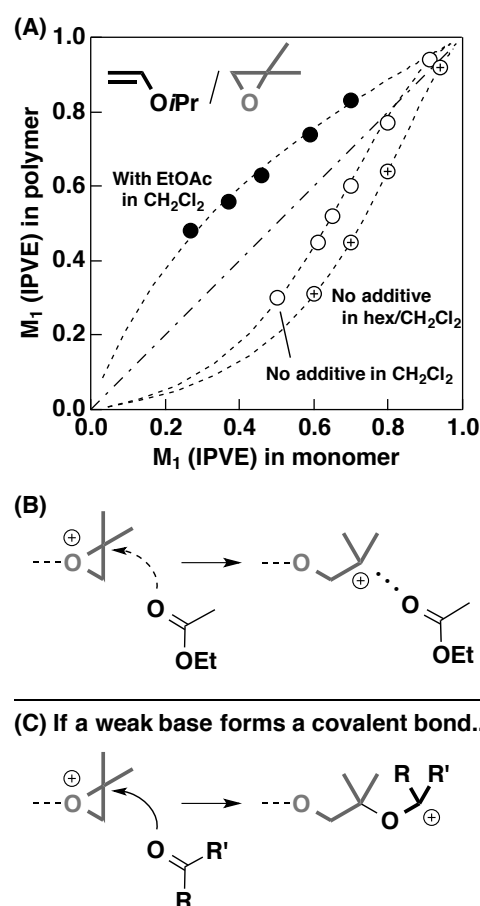
Weak Lewis bases significantly affected the frequency of the crossover reactions, which most likely resulted from the promotion of the ring-opening reaction of the oxonium ion through the nucleophilic attack by the Lewis basic group.[28] As shown in Figure 4A, the ratios of IPVE units in the IPVE–IBO copolymers obtained in the presence of ethyl acetate were considerably higher than those in the copolymers obtained in the absence of an additive. The monomer reactivity ratios[49,50] were r_{IPVE} = 1.9 and r_{IBO} = 0.35 in the presence of ethyl acetate and r_{IPVE} = 2.4 and r_{IBO} = 7.3 in the absence of an additive (entries 2 and 1 in Table 1, respectively). These values suggest that the homopropagation reactions of IBO were highly suppressed in the presence of ethyl acetate. The most probable explanation for this effect of the weak Lewis base is that the nucleophilic attack of the carbonyl oxygen of ethyl acetate on the carbon atom adjacent to the oxygen atom of the oxonium ion promoted the ring-opening reaction to generate the carbocation (Figure 4B). Because of the preference of the oxonium ions for VE or the aversion to oxirane as previously explained, the carbocations derived from the oxonium ions reacted selectively with a VE monomer, resulting in the highly frequent crossover reactions from oxirane to VE in the presence of ethyl acetate. Other weak Lewis bases, such as 1,4-dioxane, glyme, and diglyme, also exhibited similar effects in copolymerization reactions.

Solvent polarity affected the frequency of the crossover reactions in a manner different from the effect of weak Lewis bases. The monomer reactivity ratios were r_{IPVE} = 0.98 and r_{IBO} = 7.0 in hexane/dichloromethane (7/3 v/v) (entry 3 in Table 1), indicating that the number of VE units in the

copolymers decreased in a less polar solvent whereas the number of IBO units was comparable to those obtained in dichloromethane (Figure 4A). The results suggest that solvent polarity affected the reactivity of the VE-derived carbocation more significantly than the reactivity of the oxirane-derived oxonium ion.

Weak Lewis bases and solvent polarity were found to show similar effects on copolymerization using BDO (entries 8–10 in Table 1) but showed only slight effects on copolymerization using ISPO (entries 12–14). Weak Lewis bases did not affect the frequency of the crossover reactions in the copolymerization using ISPO, possibly because the oxonium ions derived from ISPO very frequently underwent ring-opening reactions to generate carbocations, even in the absence of weak Lewis bases. The higher stability of the carbocation generated via the ring-opening reaction of the ISPO-derived oxonium ion compared with the carbocations derived from IBO and BDO was responsible for the frequent occurrence of the ring-opening reactions.

Figure 4. (A) Copolymer compositions for the cationic copolymerization of IPVE and IBO in the absence of an additive in dichloromethane (open circle), in the presence of ethyl acetate in dichloromethane (filled circle), or in the absence of an additive in hexane/dichloromethane (7/3 v/v; circle with cross) ($[IPVE]_0 + [IBO]_0 = 1.5$ M, $[B(C_6F_5)_3]_0 = 1.0$ mM, [ethyl acetate] = 0 or 1.0 M, at –

78 ºC; see entries 1–3 in Table 1 for the monomer reactivity ratios obtained from these data), (B) a nucleophilic attack of ethyl acetate onto the IBO-derived oxonium ion to promote the ring-opening reaction, and (C) a nucleophilic attack of MEK onto the IBO-derived oxonium ion to form a covalent bond.

Concurrent Cationic Vinyl-Addition, Ring-Opening, and Carbonyl-Addition Terpolymerization through Crossover Reactions in a One-Way Cycle

The precise control over monomer sequences of synthetic polymers has attracted considerable interest from many researchers; hence, various strategies, such as iterative methods and the polymerization of template monomers or sequence-incorporated monomers, have been developed over the past decades.[51–54] Sequence control via the direct polymerization of plural monomers is the simplest approach but is extremely difficult to achieve. Even in the polymerization of three monomers, or terpolymerization, only two studies have achieved precise sequence control to yield ABC-type alternating terpolymers: the terpolymerization of ethylene oxide, maleic anhydride, and tetrahydrofuran via the ring-opening mechanism[55] and the terpolymerization of ethylene phenylphosphonite, a vinyl monomer with an electron-withdrawing group, and carbon dioxide via the zwitterionic mechanism.[56] The primary step to accomplish sequence control in direct polymerization is for all of the propagating ends to exhibit very high selectivity to react with a specific monomer. Thus, concurrent cationic vinyl-addition and ring-opening copolymerization is a possible strategy for sequence control because different types of propagating species, which possess different reactivities, are generated from vinyl and cyclic monomers.

We focused on a ketone as the third component for terpolymerization with VE and oxirane because the ketone was expected to promote the ring-opening reaction of the oxirane-derived oxonium ion in a manner similar to ethyl acetate, subsequently forming a covalent bond and generating a carbocation similar in structure to the VE-derived carbocation (Figures 4C and 5). This strategy successfully led to the terpolymerization of IPVE, cyclohexene oxide (CHO), and methyl ethyl ketone (MEK) with the use of $B(C_6F_5)_3$ as a catalyst.[29] More interestingly, the crossover reactions among the three monomers proceeded selectively in a one-way cycle, yielding a terpolymer with constitutional repeating units of $(IPVE_x\text{-}CHO_y\text{-}MEK_1)_n$. Specifically, the crossover reactions occurred only in the directions of IPVE→CHO, CHO→MEK, and MEK→IPVE. Moreover, MEK was incorporated into the polymer chains only when both IPVE and CHO were used; MEK did not copolymerize with IPVE or CHO in the absence of either one of the two.

The stabilities of the propagating species and the resulting sequences are responsible for the selectivity in crossover reactions in concurrent cationic vinyl-addition, ring-opening, and

carbonyl-addition terpolymerization. At the IPVE-derived propagating end, the crossover reaction to MEK does not proceed because a carbocation with an acetal side chain is difficult to generate, possibly due to the instability. The crossover reaction selectively proceeds from IPVE to CHO. At the CHO-derived propagating end, the crossover reaction to IPVE does not proceed because the carbocation generation via the ring-opening reaction of the oxonium ion occurs to a negligible extent due to the instability of the secondary carbocation. In fact, IPVE and CHO did not copolymerize efficiently in the absence of MEK. The crossover reaction from the CHO-derived end selectively proceeds to MEK via the nucleophilic attack of the carbonyl oxygen atom on the oxonium ion. At the MEK-derived propagating end, the propagation reaction exclusively proceeds to an IPVE monomer. The instability of ketal structures resulting from the addition reaction of CHO or MEK to the MEK-derived carbocation is responsible for the selectivity.

The use of IBO or cyclohexanecarboxaldehyde (CHA) instead of CHO or MEK, respectively, also resulted in concurrent vinyl-addition, ring-opening, and carbonyl-addition terpolymerization; however, the selectivity was lost in the crossover reactions at the IBO- or CHA-derived propagating ends. The crossover reaction from IBO proceeds to both MEK and IPVE through the generation of the tertiary carbocation via the ring-opening reaction in a manner similar to the copolymerization of IPVE and IBO.[26] In the reaction using CHA as an aldehyde instead of a ketone, the structure generated via the addition reaction of the CHA-derived carbocation to CHO is an acetal structure. In contrast to the ketal structure, which is not generated in the reaction using MEK, the acetal structure is stably generated for incorporation into the main chain.

The total suppression of the homopropagation reactions of IPVE and CHO in IPVE–CHO–MEK terpolymerization leads to the synthesis of ABC-type alternating terpolymers. Currently, copolymers with average IPVE, CHO, and MEK units of ~2, ~2, and 1, respectively, were produced as a result of the tuning of reaction conditions such as monomer concentrations and solvent polarity. The generation of these copolymers was confirmed through NMR and ESI–MS analyses of the copolymers or acid hydrolysis products. Further investigation to achieve alternating terpolymerization is currently in progress.
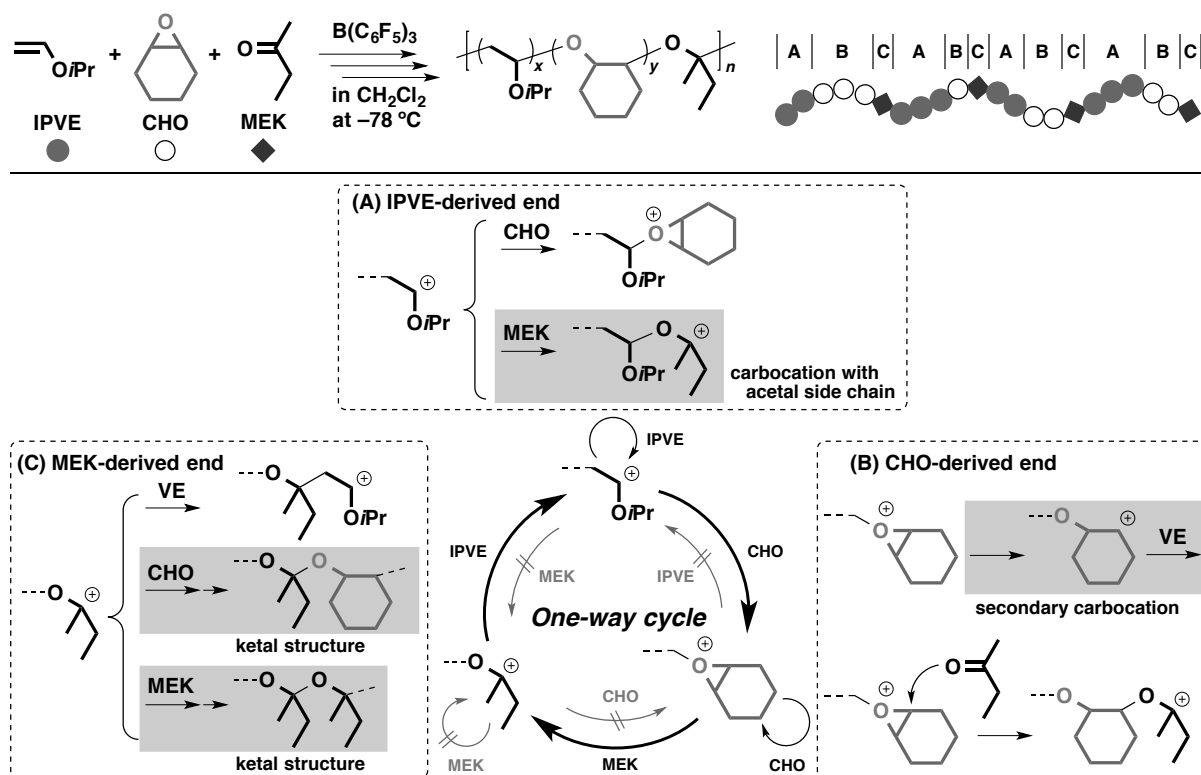
Figure 5. Concurrent cationic vinyl-addition, ring-opening, and carbonyl-addition terpolymerization of IPVE, CHO, and MEK via the one-way cycle crossover reactions: Reactions that occur at (A) the IPVE-, (B) CHO-, and (C) MEK-derived propagating ends (structures with gray shadow are negligibly generated due to instability).

Copolymerization Using Alkoxyoxirane: Alkoxy Group Transfer Mechanism

The generation of long-lived species in concurrent cationic vinyl-addition and ring-opening copolymerization allows for the synthesis of copolymers with well-defined primary structures from vinyl and cyclic monomers. To achieve living copolymerization, dormant species with similar reactivities must be generated from vinyl and cyclic monomers. Thus, we focused on an alkoxyoxirane as a monomer that generates a VE-type carbocation via the ring-opening reaction of the oxonium ion. In the cationic copolymerization with a VE, alkoxyoxirane and VE are thought to generate similar dormant species containing carbon–halogen bonds.

Cationic copolymerization using 1-methoxy-2-methylpropylene oxide (MOMPO) as an alkoxyoxirane with IPVE successfully produced copolymers with the use of an initiating system composed of trifluoromethanesulfonic acid (TfOH) and nBu$_4$NI in dichloromethane at –40 °C.[30] This initiating system[57] induces living cationic homopolymerization of IPVE through the generation of the dormant species with the carbon–iodine bond. The molecular weight distribution curves of the copolymerization products shifted to the higher molecular weight region with increasing monomer

conversion, indicating the generation of long-lived species. However, a detailed analysis of the copolymers obtained revealed that copolymerization proceeded via unique mechanisms involving alkoxy group transfer reactions. As shown in Figure 6, the isopropoxy group transfers to the MOMPO-derived carbocation after the addition reaction of a MOMPO monomer to the IPVE-derived carbocation. The carbocation that results from the alkoxy group transfer reaction reacts with the next monomer, which generates a structure that possesses a MOMPO unit and an isopropoxy group at the side chain. The generation of copolymers with these structures was also confirmed through acid hydrolysis and the subsequent acetalization reactions of the copolymers.

Cationic ring-opening homopolymerization of MOMPO also proceeded in a controlled manner with the use of the initiating system that is effective for the living polymerization of alkyl VEs.[25,58] The polymerization using $GaCl_3$ as a Lewis acid catalyst, in conjunction with an isobutyl VE–HCl adduct as a cationogen, produced polymers with molecular weights that increased linearly with increasing monomer conversion. The reaction most likely proceeded through the dormant–active equilibrium between the propagating ends with carbon–chlorine bonds and the carbocationic species. In addition, the product polymers were fully decomposed into low-molecular-weight compounds under acidic conditions because the polymers contained acetal structures in each monomer unit in the main chain. Unlike copolymerization with IPVE, the alkoxy group transfer reaction did not occur in the homopolymerization, which was supported by NMR analysis. The alkoxy groups and/or the main chain structures at the penultimate units would be responsible for the difference in polymerization mechanisms.
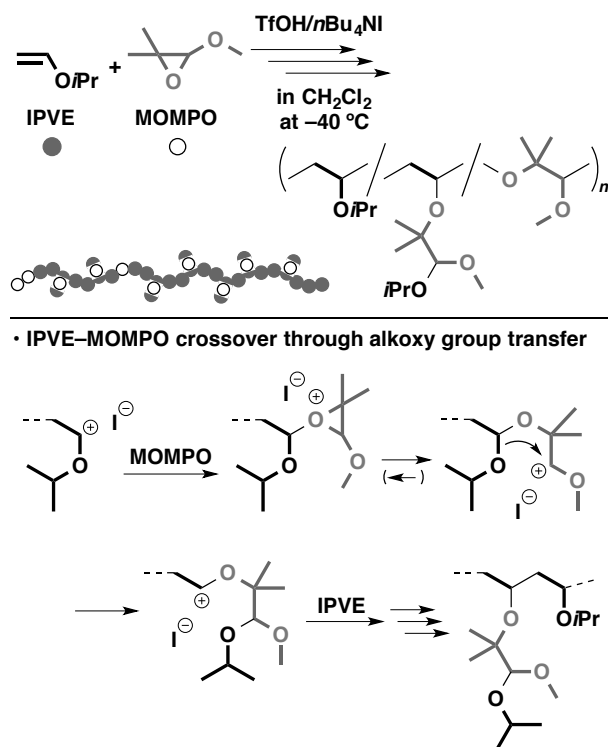
Figure 6. Cationic copolymerization of IPVE and MOMPO via the alkoxy group transfer mechanism.

Controlled Cationic Copolymerization of Vinyl Ethers and Cyclic Formals

Cyclic formals are also possible candidates as comonomers for living copolymerization with VEs because the carbocation generated via the ring-opening reaction of the oxonium ion derived from cyclic formals is an alkoxy group-adjacent carbocation. Although copolymerization of alkyl VEs and 1,3-dioxepane (1,3-DOP) or styrene and 1,3-dioxolane (1,3-DOL) have been reported to proceed in previous studies, the reactions were mainly conducted with classical initiating systems using Lewis acid catalysts such as BF_3OEt_2,[6,7] which resulted in nonliving polymerization to yield polymers with uncontrolled molecular weights. However, our group has recently developed a variety of new initiating systems for the living cationic polymerization of alkyl vinyl ethers with the use of various metal halides as catalysts.[25,58] Therefore, we sought to achieve living cationic copolymerization of vinyl monomers and cyclic formals using those initiating systems.

The initiating system consisting of dual catalysts, $TiCl_4$ and $SnCl_4$, was demonstrated as effective for the long-lived species-mediated cationic copolymerization of 2-chloroethyl VE (CEVE) and 1,3-DOP in the presence of ethyl acetate and 2,6-di-*tert*-butylpyridine (DTBP) at -78 ºC (Figure 7).[31] The molecular weights of the products increased as the monomer conversion increased. Moreover, copolymerization proceeded through several rounds of crossover reactions between the two monomers, yielding multiblock-like copolymers with unimodal molecular weight distributions. The generation of the long-lived species most likely resulted from the efficient initiation reaction by $TiCl_4$ and the

controlled propagation reaction by SnCl4. However, small amounts of cyclic oligomers composed of several monomer units were also produced during polymerization. Suppression of the cyclization reactions will allow for living copolymerization of the vinyl and cyclic monomers.

Long-lived species were also found to form through the copolymerization of styrene and 1,3-DOL with the use of the initiating systems that are suited for the controlled cationic homopolymerization of styrene.[59–61] Conditions that were more active than those for the copolymerization of CEVE and 1,3-DOP were required for the reactions of the less reactive monomers.
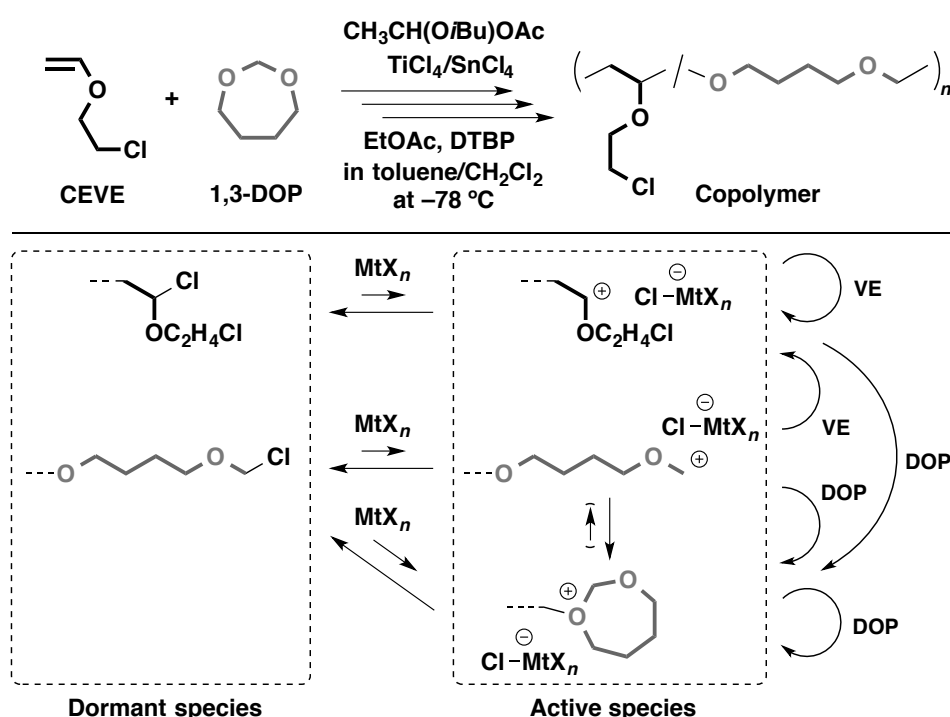
Figure 7. Long-lived species-mediated copolymerization of CEVE and 1,3-DOP.

Conclusion

Concurrent cationic vinyl-addition and ring-opening copolymerization of VEs and oxiranes was achieved through the generation of suitable propagating species that allowed for the crossover reactions to a different monomer. In particular, the generation of carbocations via the ring-opening reaction of the oxirane-derived oxonium ion was indispensable for the crossover reaction from oxirane to VE. The use of oxiranes with appropriate substituents and the design of suitable initiating systems were required for successful copolymerization. In addition, weak Lewis bases such as ethyl acetate were found to promote carbocation generation to induce frequent crossover reactions. However, in

contrast to ester and ether, a ketone group functioned as a weak Lewis base and as a monomer for incorporation into a polymer chain as a result of covalent bond formation via the nucleophilic attack onto the oxonium ion by the carbonyl bond. Moreover, terpolymerization of IPVE, CHO, and MEK proceeded via a one-way cycle of crossover reactions, leading to precise sequence control that enabled the synthesis of polymers with definite sequences, such as ABC-type alternating terpolymers. The stability of both the propagating species and the generating sequences is responsible for the high selectivity in the crossover reactions. However, long-lived species were generated in the copolymerization of an alkoxyoxirane or cyclic formals with vinyl monomers using initiating systems that are suited for the living polymerization of vinyl monomers. We are investigating the copolymerization reactions of incompatible monomers through the elaborate design of monomers and initiating systems.

References

1. Simionescu, C. I., Grigoras, M., Bicu, E. & Onofrei, G. Spontaneous copolymerization of 2-methyl-2-oxazoline and N-phenyl maleimide. *Polym. Bull.* **14**, 79–83 (1985).

2. Rivas, B. L., Pizarro, G. del C. & Canessa, G. S. Copolymerization via zwitterion 11. N-phenylmaleimide with 2-ethyl-2-oxazoline. *Polym. Bull.* **19**, 123–128 (1988).

3. Hagiwara, T., Takeda, M., Hamana, H. & Narita, T. Copolymerization of *N*-phenylmaleimide and propylene oxide initiated with organozinc compounds. *Macromolecules* **22**, 2026–2028 (1989).

4. Ikeda, Y., Yoshida, Y., Ishihara, K., Hamana, H., Narita, T. & Hagiwara, T. Copolymerization of 3,3,3-trifluoro-1,2-epoxypropane with *N*-phenylmaleimide using organozinc initiators. *Macromol. Rapid Commun.* **17**, 713–721 (1996).

5. Yang, H., Xu, J., Pispas, S. & Zhang, G. Hybrid copolymerization of ε-caprolactone and methyl methacrylate. *Macromolecules* **45**, 3312–3317 (2012).

6. Okada, M, Yamashita, Y. & Ishii, Y. Cationic copolymerization of 1,3-dioxolane and styrene. *Makromol. Chem.* **94**, 181–193 (1966).

7. Okada, M. & Yamashita, Y. Cationic copolymerization of cyclic formals and vinyl ethers.

Makromol. Chem. **126**, 266–275 (1969).

8. Furukawa, J. & Saegusa, T. *Polymerization of Aldehydes and Oxides* (Wiley Interscience Publishers, New York, USA, 1963).

9. Kubisa, P. & Penczek, S. Cationic activated monomer polymerization of heterocyclic monomers. *Prog. Polym. Sci.* **24**, 1409–1437 (1999).

10. Nuyken, O. & Pask, S. D. Ring-opening polymerization—an introductory review. *Polymers.* **5**, 361–403 (2013).

11. Brocas, A.-L., Mantzaridis, C., Tunc, D. & Carlotti, S. Polyether synthesis: from activated or metal-free anionic ring-opening polymerization of epoxides to functionalization. *Prog. Polym. Sci.* **38**, 845–873 (2013).

12. Deffieux, A., Carlotti, S. & Barrère, A. In *Polymer Science: A Comprehensive Reference* (eds Matyjaszewski, K. & Möller, K.) Vol. 4.07 (Elsevier B. V., Amsterdam, Netherlands, 2012).

13. Kubisa, P. In *Polymer Science: A Comprehensive Reference* (eds Matyjaszewski, K. & Möller, K.) Vol. 4.08 (Elsevier B. V., Amsterdam, Netherlands, 2012).

14. Kanazawa, A. Polyethers. In: *Encyclopedia of Polymeric Nanomaterials* (eds Kobayashi, S. & Müllen) DOI: 10.1007/978-3-642-36199-9_251-1 (Springer-Verlag, Berlin Heidelberg, Germany, 2014).

15. Aoki, S., Fujisawa, K.; Otsu, T. & Imoto, M. The copolymerization of the vinyl monomer with a cyclic compound. III. The cationic copolymerization of styrene with substituted ethyl oxides. *Bull. Chem. Soc. Jpn.* **39**, 729–733 (1966).

16. Minoura, Y. & Mitoh, M. Copolymerization of cyclic ethers with vinyl compounds I. Copolymerization of epichlorohydrin with styrene. *Makromol. Chem.* **99**, 186–192 (1966).

17. Solaro, R., D'Antone, Orsini, M., Andruzzi, F. & Chiellini, E. Hybrid copolymerization of alkyl vinyl ethers with glycidyl ethers. *J. Appl. Polym. Sci.* **28**, 3651–3663 (1983).

18. Kubisa, P. & Vairon, J. P. In *Polymer Science: A Comprehensive Reference* (eds Matyjaszewski, K. & Möller, K.) Vol. 4.10 (Elsevier B. V., Amsterdam, Netherlands, 2012).

19. Sawamoto, M. Modern cationic vinyl polymerization. *Prog. Polym. Sci.* **16**, 111–172 (1991).

20. Kennedy, J. P. & Ivan, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice* (Hancer, New York, USA, 1992).

21. Matyjaszewski, K. & Sawamoto, M. in *Cationic Polymerizations* (ed. Matyjaszewski, K.) Ch. 4 (Marcel Dekker, New York, USA, 1996).

22. Puskas, J. E. & Kaszas, G. Living carbocationic polymerization of resonance-stabilized monomers. *Prog. Polym. Sci.* **25**, 403–452 (2000).

23. De, P. & Faust, R. In *Macromolecular Engineering. Precise Synthesis, Materials Properties, Application.* (eds Matyjaszewski, K., Gnanou, Y. & Leibler, L) Ch. 3 (Wiley-VCH GmbH & Co.

KGaA, Weinheim, Germany, 2007).

24. Goethals, E. J. & Du Prez, F. Carbocationic polymerizations. *Prog. Polym. Sci.* **32**, 220–246 (2007).

25. Aoshima, S. & Kanaoka, S. A renaissance in living cationic polymerization. *Chem. Rev.* **109**, 5245–5287 (2009).

26. Kanazawa, A., Kanaoka, S. & Aoshima, S. 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. *J. Am. Chem. Soc.* **135**, 9330–9333 (2013).

27. Kanazawa, A., Kanaoka, S. & Aoshima, S. Rational design of oxirane monomers for efficient crossover reactions in concurrent cationic vinyl-addition and ring-opening copolymerization with vinyl ethers. *Macromolecules* **47**, 6635–6644 (2014).

28. Kanazawa, A. & Aoshima, S. Frequency control of crossover reactions in concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl ethers and oxiranes: specific roles of weak Lewis bases and solvent polarity. *Polym. Chem.* **6**, 5675–5682 (2015).

29. Kanazawa, A. & Aoshima, S. Exclusive one-way cycle sequence control in cationic terpolymerization of general-purpose monomers via concurrent vinyl-addition, ring-opening, and carbonyl-addition mechanisms. *ACS Macro Lett.* **4**, 783–787 (2015).

30. Kanazawa, A., Kanda, S., Kanaoka, S. & Aoshima, S. Alkoxyoxirane, a unique cyclic monomer: controlled cationic homopolymerization mediated by long-lived species and copolymerization with vinyl ether via alkoxy group transfer. *Macromolecules* **47**, 8531–8540 (2014).

31. Shirouchi, T., Kanazawa, A., Kanaoka, S. & Aoshima, S. Cationic copolymerization of vinyl ether and 1,3-dioxepane through concurrent vinyl-addition and ring-opening mechanisms: toward controlled copolymerization mediated by long-lived species. *Polym. Prepr., Jpn.* **63**, 3958–3959 (2014).

32. Shirouchi, T., Kanazawa, A., Kanaoka, S. & Aoshima, S. Concurrent vinyl-addition and ring-opening cationic copolymerization of vinyl ethers or styrenes with cyclic acetals: toward controlled copolymerization mediated by long-lived species. *Polym. Prepr., Jpn.* **64**, 2Pd012 (2015).

33. Kim, J. D., Han, G., Jeong, L, S., Park, H.-J, Zee, O. P. & Jung, Y. H. Study of the stability of carbocations by chlorosulfonyl isocyanate reaction with ethers. *Tetrahedron* **58**, 4395–4402 (2002).

34. Lossing, F. P. & Holmes, J. L. Stabilization energy and ion size in carbocations in the gas phase. *J. Am. Chem. Soc.* **106**, 6917–6920 (1984).

35. Harwood, H. J. & Ritchey, W. M. The characterization of sequence distribution in copolymers. *J. Polym. Sci., Part B: Polym. Lett.* **2**, 601–607 (1964).

17

36. Piers, W. E. & Chivers, T. Pentafluorophenylboranes: from obscurity to applications. *Chem. Soc. Rev.* **26**, 345–354 (1997).

37. Ishihara, K. & Yamamoto, H. Arylboron compounds as acid catalysts in organic synthetic transformations. *Eur. J. Org. Chem.* 527–538 (1999).

38. Erker, G. Tris(pentafluorophenyl)borane: a special boron Lewis acid for special reactions. *Dalton Trans.* 1883–1890 (2005).

39. Faust, R., Iván, B., & Kennedy, J. P. Living carbocationic polymerization. XXXVIII. On the nature of the active species in isobutylene and vinyl ether polymerization. *J. Macromol. Sci., Part A: Chem.* **28**, 1–13 (1991).

40. Liu, Q., Wu, Y., Yan, P., Zhang, Y. & Xu, R. Polyisobutylene with high exo-olefin content via β-H elimination in the cationic polymerization of isobutylene with $H_2O/FeCl_3$/dialkyl ether initiating system. *Macromolecules* **44**, 1866–1875 (2011).

41. Dimitrov, P., Emert, J. & Faust, R. Polymerization of isobutylene by $AlCl_3$/ether complexes in nonpolar solvent. *Macromolecules* **45**, 3318–3325 (2012).

42. Kumar, R., Dimitrov, P., Bartelson, K. J., Emert, J. & Faust, R. Polymerization of isobutylene by $GaCl_3$ or $FeCl_3$/ether complexes in nonpolar solvents. *Macromolecules* **45**, 8598–8603 (2012).

43. Kagiya, T., Sumida, Y. & Inoue, T. Reactivities of cyclic monomers in cationic copolymerizations. Nucleophilic coordination and ionic ring-opening of the bond. *Polym. J.* **1**, 312–321 (1970).

44. Gordy, W. Spectroscopic comparison of the proton-attracting properties of liquids. *J. Chem. Phys.* **7**, 93–99 (1939).

45. Iwatsuki, S., Takigawa, N., Okada, M., Yamashita, Y. & Ishii, Y. Basicity as a factor in the cationic copolymerization of cyclic ethers. *J. Polym. Sci., Part B: Polym. Lett.* **2**, 549–552 (1964).

46. Laurence, C., Graton, J., Berthelot, M., Besseau, F., Le Questel, J.-Y., Luçon, M., Ouvrard, C., Planchat, A. & Renault, E. An enthalpic scale of hydrogen-bond basicity. 4. Carbon π bases, oxygen bases, and miscellaneous second-row, third-row, and fourth-row bases and a survey of the 4-fluorophenol affinity scale. *J. Org. Chem.* **75**, 4105–4123 (2010).

47. Symons, M. C. & Thomas, V. K. Solvation of anions by protic solvents. *J. Chem. Soc., Faraday Trans. 1* **77**, 1891–1897 (1981).

48. Symons, M. C. R. & Robinson, H. L. A near infrared and NMR spectroscopic study of the solvation of basic aprotic solvents and anions in *tert*-butanol. *Phys. Chem. Chem. Phys.* **3**, 535–541 (2001).

49. Kelen, T. & Tüdõs, F. A new improved linear graphical method for determining copolymerization reactivity ratios. *React. Kinet. Catal. Lett.* **1**, 487–492 (1974).

50. Kennedy, J. P., Kelen, T. & Tüdõs, F. Analysis of the linear methods for determining copolymerization reactivity ratios. II. A critical reexamination of cationic monomer reactivity

ratios. *J. Polym. Sci., Polym. Chem. Ed.* **13**, 2277–2289 (1975).

51. Lutz, J.-F. Sequence-controlled polymerizations: the next Holy Grail in polymer science? *Polym. Chem.* **1**, 55–62 (2010).

52. Lutz, J.-F., Ouchi, M., Liu, D. R. & Sawamoto, M. Sequence-controlled polymers. *Science* **341**, doi: 10.1126/science.1238149 (2013)

53. Yokota, K. Periodic copolymers. *Prog. Polym. Sci.* **24**, 517–563 (1999).

54. Cho, I. New ring-opening polymerizations for copolymers having controlled microstructures. *Prog. Polym. Sci.* **25**, 1043–1087 (2000).

55. Hsieh, H. L. Terpolymerization of cyclic ethers with cyclic anhydride. *J. Macromol. Sci., Chem.* **A7**, 1525–1535 (1973)

56. Saegusa, T., Kobayashi, S. & Kimura, Y. Polymerization via zwitterion. 12. Novel 1:1:1 alternating terpolymerization of 2-phenyl-1,3,2-dioxaphospholane, electron deficient vinyl monomers of acrylonitrile and acrylate, and carbon dioxide. *Macromolecules* **10**, 68–72 (1977).

57. Kanazawa, A., Hashizume, R., Kanaoka, S. & Aoshima, S. Design of benign initiator for living cationic polymerization of vinyl ethers: facile in situ generation of vinyl ether–hydrogen halide adducts and subsequent controlled polymerization without a Lewis acid catalyst. *Macromolecules* **47**, 1578–1585 (2014).

58. Kanazawa, A., Kanaoka, S. & Aoshima, S. Major progress in catalysts for living cationic polymerization of isobutyl vinyl ether: effectiveness of a variety of conventional metal halides. *Macromolecules* **42**, 3965–3972 (2009).

59. Ishihama, Y., Sawamoto, M. & Higashimura, T. Living cationic polymerization of styrene by the methanesulfonic acid/tin tetrachloride initiating system in the presence of tetra-n-butylammonium chloride. *Polym. Bull.* **23**, 361–366 (1990).

60. Ishihama, Y., Sawamoto, M. & Higashimura, T. Living cationic polymerization of styrene by the 1-phenylethyl chloride/tin tetrachloride initiating system in the presence of tetra-n-butylammonium chloride. *Polym. Bull.* **24**, 201–206 (1990).

61. Higashimura, T., Ishihama, Y. & Sawamoto, M. Living cationic polymerization of styrene: new initiating systems based on added halide salts and the nature of the growing species. *Macromolecules* **26**, 744–751 (1993).

Graphical Abstract
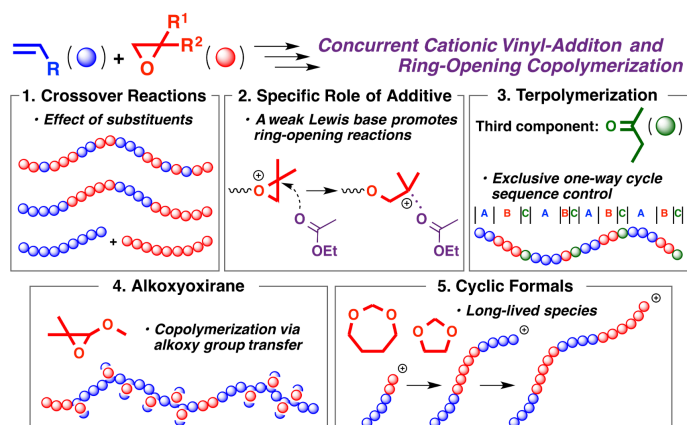
Our recent results in the concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl ethers and oxiranes are summarized with particular emphasis on the strategies required to generate crossover reactions between different types of monomers. Most importantly, carbocation generation via the ring-opening reaction of the oxonium ion is indispensable for the crossover reaction from oxirane to vinyl ether. This article also summarizes concurrent cationic vinyl-addition, ring-opening, and carbonyl-addition terpolymerization, the copolymerization using an alkoxyoxirane through the alkoxy group transfer mechanism, and the long-lived species-mediated polymerization using cyclic formals.

Figure Legends

Figure 1. Strategies for and outcomes of concurrent cationic vinyl-addition and ring-opening polymerization.

Figure 2. Crossover reactions that generate in the concurrent cationic vinyl-addition and ring-opening copolymerization of VE and IBO (counteranions are omitted).

Figure 3. The numbers of crossover reactions per 100 monomer units in the concurrent cationic polymerization of IPVE and various oxiranes.

Figure 4. (A) Copolymer compositions for the cationic copolymerization of IPVE and IBO in the absence of an additive in dichloromethane (open circle), in the presence of ethyl acetate in dichloromethane (filled circle), or in the absence of an additive in hexane/dichloromethane (7/3 v/v; circle with cross) ($[IPVE]_0 + [IBO]_0 = 1.5$ M, $[B(C_6F_5)_3]_0 = 1.0$ mM, [ethyl acetate] = 0 or 1.0 M, at -78 ºC; see entries 1–3 in Table 1 for the monomer reactivity ratios obtained from these data), (B) a nucleophilic attack of ethyl acetate onto the IBO-derived oxonium ion to promote the ring-opening reaction, and (C) a nucleophilic attack of MEK onto the IBO-derived oxonium ion to form a covalent bond.

Figure 5. Concurrent cationic vinyl-addition, ring-opening, and carbonyl-addition terpolymerization of IPVE, CHO, and MEK via the one-way cycle crossover reactions: Reactions that occur at (A) the IPVE-, (B) CHO-, and (C) MEK-derived propagating ends (structures with gray shadow are negligibly generated due to instability).

Figure 6. Cationic copolymerization of IPVE and MOMPO via the alkoxy group transfer mechanism.

Figure 7. Long-lived species-mediated copolymerization of CEVE and 1,3-DOP.