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ARTICLE

Influence of the Substituents of Oxiranes on Copolymerization with Vinyl Ethers via Concurrent Cationic Vinyl-Addition and Ring-Opening Mechanisms

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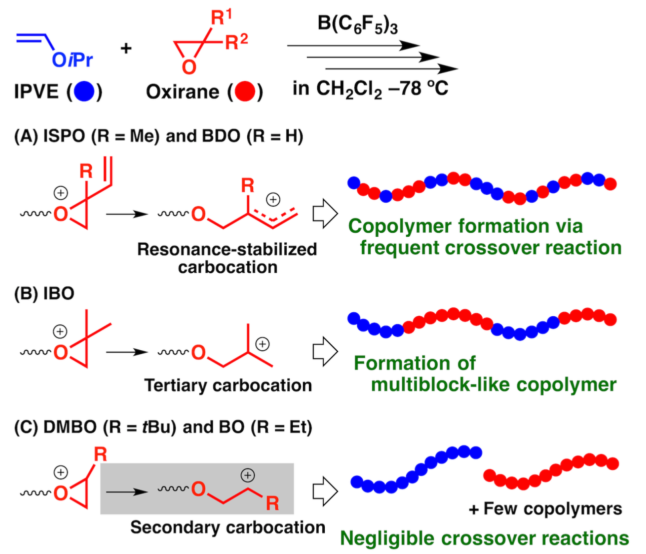
2,2-Disubstituted oxiranes with electron-withdrawing substituents were copolymerized with vinyl ethers (VEs) via concurrent cationic vinyl-addition and ring-opening mechanisms, leading to a design strategy for copolymerization via crossover reactions with high efficiency. β-Methylglycidyl ether (βMGE) and β-methylepichlorohydrin, which contain an alkoxy group and a chlorine atom, respectively, as electron-withdrawing groups, exhibited lower reactivity in copolymerization with VEs than isobutylene oxide, a dialkyl-substituted counterpart. Thus, VEs with appropriate reactivities depending on the reactivity of the oxirane were required. For example, 2-ethylhexyl βMGE (EHMGE) and phenyl βMGE ether were not efficiently consumed in the reaction with isopropyl VE but underwent copolymerization via crossover reactions with less reactive ethyl VE (EVE) or 2-chloroethyl VE. Specifically, the copolymerization of EVE and EHMGE yielded a copolymer with an M_n value of 7.5×10^3 via 8.3 times of crossover reactions from VE to βMGE per chain. The effects of oxirane substituents on the copolymerization behavior are discussed in terms of the reactivities of monomers and propagating species. In addition, a βMGE with an oxyethylenic chain was demonstrated to be effective for the generation of thermoresponsive copolymers.

Introduction

The synthesis of polymeric materials by copolymerization reactions is highly attractive because products with valuable functions that cannot be attained using homopolymers are potentially produced from conventional, general-purpose monomers. Copolymers such as statistical, random, and gradient copolymers[1] are generally obtained from comonomers that undergo crossover reactions via a single mechanism. A variety of block, graft, and star-shaped polymers are synthesized from not only mechanistically compatible monomers but also incompatible monomers, such as anionically and cationically polymerizable monomers or vinyl and cyclic monomers, by conducting polymerization reactions under completely different conditions in a stepwise manner.[2] By contrast, the copolymerization of different types of monomers via different mechanisms that simultaneously proceed under the same conditions[3,4] has recently attracted attention because of its potential to generate copolymers with novel characteristics.

The concurrent vinyl-addition and ring-opening copolymerization of vinyl and cyclic monomers is one of the promising strategies for the copolymerization of different types of monomers.[5–11] In the previous studies, we achieved the concurrent cationic copolymerization of vinyl ethers (VEs) and oxiranes by designing reactions based on the following three factors: (i) the use of oxiranes that generate carbocations via the ring opening of the propagating oxonium ions, (ii) the use of a Lewis acid catalyst that generates non- or



Scheme 1. Concurrent cationic vinyl-addition and ring-opening copolymerization of IPVE with (A) ISPO and BDO, (B) IBO, or (C) DMBO and BO.

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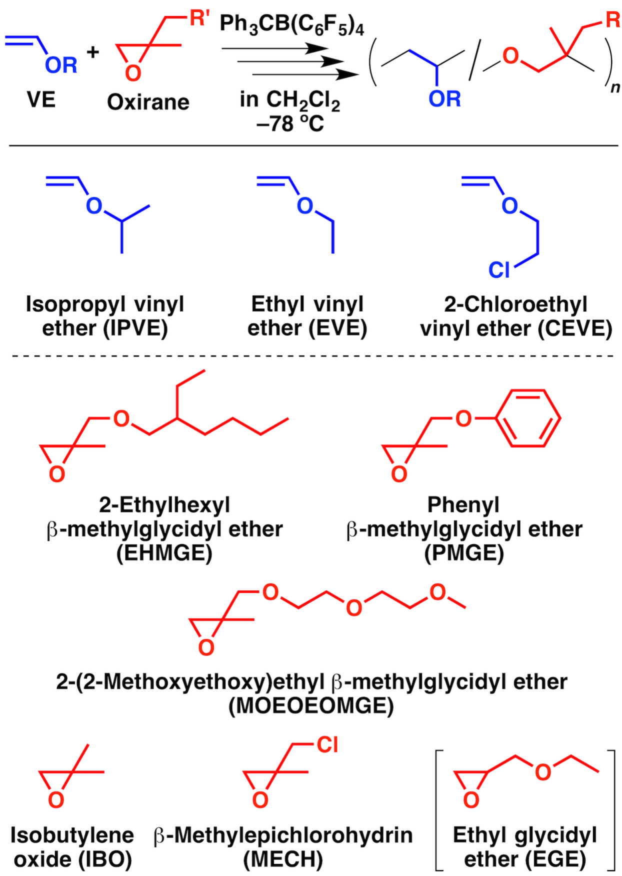
weakly coordinating counteranions, and (iii) the appropriate balance of reactivities (nucleophilicities) of both monomers.[12] In particular, the generation of the carbocation (factor i) from oxiranes is indispensable for the crossover reaction from the oxirane to VE (Scheme 1). For example, oxiranes, such as isoprene monoxide (ISPO), butadiene monoxide (BDO), and isobutylene oxide (IBO), that generate allyl-type (Scheme 1A) or tertiary carbocations (Scheme 1B) via ring-opening reactions were copolymerized with isopropyl VE (IPVE) using $B(C_6F_5)_3$ as a Lewis acid catalyst, which yielded alternating-rich (ISPO), random-like (BDO), or multiblock-like (IBO) copolymers depending on the frequency of the crossover reactions. By contrast, oxiranes such as 3,3-dimethyl-1,2-butylene oxide (DMBO) and 1,2-butylene oxide (BO) were completely inefficient at copolymerization because the oxonium ion generated from the monoalkyl-substituted oxirane did not generate a carbocationic species via a ring-opening reaction because of the instability of the secondary carbocation (Scheme 1C).

Controlling the frequency of crossover reactions is of great interest for designing the copolymer sequences in the concurrent cationic vinyl-addition and ring-opening copolymerization. A variety of factors, such as the monomer structures, polymerization conditions, and additives, potentially affect the copolymerization behavior. Indeed, weak Lewis bases such as esters and ethers, when used as additives, were demonstrated to affect the frequency of crossover reactions by promoting the ring opening of the propagating oxonium ion in a previous study.[13] Thus, we next focused on the electronic effect of substituents on the oxirane ring. Substituents that affect the electronic properties on an oxirane ring are considered to inherently affect the frequency of crossover reactions by influencing the nucleophilicity of the oxygen atom of an oxirane monomer and the electrophilicity and stability of the carbocation generated via the ring opening of the oxonium ion.

In this study, we aimed to examine the effect of electron-withdrawing substituents of 2,2-disubstituted oxirane monomers on copolymerization with VEs. *β*-Methylglycidyl ethers (βMGEs) and *β*-methylepichlorohydrin (MECH; 2-chloromethyl-2-methyloxirane), which contain an alkoxy group and a chlorine atom, respectively, as electron-withdrawing moieties, were used as oxirane monomers (Scheme 2).[14–18] The propagating oxonium ions derived from these 2,2-disubstituted oxiranes potentially generate tertiary carbocations via ring-opening reactions in a manner similar to IBO, although the stabilities of the carbocations are most likely affected by the electron-withdrawing substituents. As expected, βMGEs and MECH exhibited lower reactivities than IBO because of the electron-withdrawing effects. VEs with lower reactivities than what was efficient for the copolymerization with IBO were required to generate crossover reactions with βMGEs or MECH. The effects of the electron-withdrawing substituents were investigated in detail through the analysis of products in terms of the number of crossover reactions, block lengths, and molecular weights (MWs). In addition, a βMGE with an oxyethylenic chain was demonstrated to be effective for the generation of functional copolymers with thermoresponsivity.



Scheme 2. Cationic copolymerization of VEs and 2,2-disubstituted oxiranes and monomers used in this study.

Experimental Section

Materials

IPVE (Wako, 97.0+%) and ethyl VE (EVE; TCI, >98.0%) were washed with 10% aqueous sodium hydroxide solution, followed by water, and then distilled twice over calcium hydride. 2-Chloroehtyl VE (CEVE; TCI, >97.0%) was washed with 10% aqueous sodium hydroxide solution, followed by water, and then distilled twice under reduced pressure over calcium hydride. IBO (TCI, >97.0%) was distilled twice over calcium hydride. 2-Ethylhexyl βMGE [EHMGE; 2-(2-ethylhexyloxymethyl)-2-methyloxirane], phenyl βMGE [PMGE; 2-methyl-2-(phenoxymethyl)oxirane],[17] and 2-(2-methoxyethoxy)ethyl βMGE [MOEOEOMGE; 2-((2-(2-methoxyethoxy)ethoxy)methyl)-2-methyloxirane] were synthesized by the reaction of MECH [Chemexcel (Zhangjiakou) Fine Chemicals] with 2-ethylhexanol, phenol, and 2-(2-methoxyethoxy)ethanol, respectively, according to the method reported in the literature.[17] The crude EHMGE, PMGE, and MOEOEOMGE were distilled at least twice under reduced pressure before being used for polymerization [EHMGE: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.50 (d, 1H, CH_2O attached to the ring, J = 11 Hz), 3.40–3.30 (m, 3H, OCH_2CH and CH_2O attached to the ring), 2.72 (d, 1H, oxirane methylene, *J* = 5.0 Hz), 2.62 (d, 1H, oxirane methylene, *J* = 5.0 Hz), 1.48 (m, 1H, $CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 1.45–1.18 (m, 8H, $CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 1.37 (s, 3H, CH_3 attached to the ring), 0.88 (m, 6H, $CH(CH_2CH_3)CH_2CH_2CH_2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 74.4 and 74.3 (CH_2O attached to the ring and OCH_2CH), 56.0 (quaternary), 51.5 (oxirane methylene), 39.7 ($CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 30.5 ($CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 29.0 ($CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 23.8 ($CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 23.0 ($CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 18.3 ($CH_3$ attached to the ring), 14.0 ($CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 11.0 ($CH(CH_2CH_3)CH_2CH_2CH_2CH_3$). MOEOEOMGE: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.73–3.61 and 3.57–3.54 (m, 8H, $OCH_2CH_2OCH_2CH_2OCH_3$), 3.60 (d, 1H, CH_2O attached to the ring, *J* = 11 Hz), 3.45 (d, 1H, CH_2O attached to the ring, *J* = 11 Hz), 3.38 (s, 3H, $OCH_2CH_2OCH_2CH_2OCH_3$), 2.74 (d, 1H, oxirane methylene, *J* = 5.0 Hz), 2.61 (d, 1H, oxirane methylene, *J* = 5.0 Hz), 1.37 (s, 3H, CH_3 attached to the ring); ^{13}C NMR (125 MHz, $CDCl_3$): δ 74.5 (CH_2O attached to the ring), 71.9 ($OCH_2CH_2OCH_2CH_2OCH_3$), 70.7, 70.6, and 70.5 ($OCH_2CH_2OCH_2CH_2OCH_3$), 59.0 ($OCH_2CH_2OCH_2CH_2OCH_3$), 56.0 (quaternary), 51.4 (oxirane methylene), 18.3 (CH_3 attached to the ring)]. MECH and ethyl glycidyl ether (EGE; TCI, >98.0%) were distilled twice under reduced pressure over calcium hydride. Triphenylmethylium tetrakis(pentafluorophenyl)borate [$Ph_3CB(C_6F_5)_4$; TCI, >98.0%] was used as received. Dichloromethane (Wako, 99.0%) and hexane (Wako, 96.0%) were dried by passage through a solvent purification column (Glass Contour).

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; blow temperature, ~450 °C) under dry nitrogen. Dichloromethane, hexane, VE, and oxirane were added into the tube using dry syringes. The polymerization was started by the addition of a prechilled 30 mM $Ph_3CB(C_6F_5)_4$ solution in dichloromethane at –78 °C. After a predetermined period of time, the reaction was quenched with methanol containing a small amount of aqueous ammonia solution. The quenched mixture was diluted with dichloromethane and then washed with water. The volatiles were removed under reduced pressure at 50 °C to yield a polymer. The polymer was further dried under reduced pressure at 50 °C for at least 8 h to remove unreacted oxirane monomers. The monomer conversion was determined by gas chromatography (GC; column packing material: PEG-20M-Uniport-HP; GL Science Inc.) using hexane as an internal standard. The monomer conversion values determined by GC were revalidated by comparing with the values calculated using the weight of a polymer and the peak integral ratios from the ^{1}H NMR spectrum.

Acid Hydrolysis

The acid hydrolysis of copolymers was conducted with 0.5 M HCl(aq) in 1,2-dimethoxyethane at room temperature (sample concentration: 0.5 wt%). The reaction was conducted for 3 (the CEVE–MECH copolymer) or 1 (the other copolymers) h (these reaction times were sufficient for the degradation of the acetal moieties in the copolymers, which was confirmed by ^{1}H NMR analysis). The quenched mixture was diluted with dichloromethane and washed with aqueous sodium hydroxide solution, followed by water. The volatiles were removed under reduced pressure.

Characterization

The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C on polystyrene gel columns [TSKgel GMH_{HR}-M × 2 (exclusion limit MW = 4×10^6; bead size = 5 μm; column size = 7.8 mm i.d. × 300 mm); flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and polydispersity index [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatograms with respect to 16 polystyrene standards (Tosoh; M_n = 577–1.09×10^6, $M_w/M_n \leq 1.1$). The preparative polymer fractionation by GPC was conducted using similar equipment except that another polystyrene gel column [TSKgel G3000H_{HR} × 1 (exclusion limit MW = 6×10^4; bead size = 5 μm; column size = 21.5 mm i.d. × 300 mm); flow rate = 2.0 mL/min] was used.

NMR spectra were recorded using a JEOL JNM-ECA 500 (500.16 MHz for ^{1}H and 125.77 MHz for ^{13}C, flip angle: 45 ° for ^{1}H and 30 ° for ^{13}C, the number of scans: 16 for ^{1}H and more than 10^3 for ^{13}C; in $CDCl_3$ at 30 °C) spectrometer. The average number of monomer units per chain, the number of the crossover reactions from a VE to an oxirane per chain, the average number of VE and oxirane units per block, and the M_n values by NMR were calculated from the integral ratio of the peaks of main chains and ω-ends in the ^{1}H NMR spectra. For example, the ^{1}H NMR spectrum of poly(EVE-*co*-EHMGE) was divided into the following eight regions: peaks at 0.9ppm, 1.0—2.0ppm, 3.0—3.8ppm, 4.3ppm, 4.6ppm, 5.1ppm, 6.1ppm, and 9.5ppm. Subsequently, simultaneous equations consisting of the integral ratios of these peaks were solved. In the cases of PMGE and MECH, the ratios of the ω-ends were estimated from the M_n value determined by GPC and the integral ratios of the peaks assigned to main chains in the ^{1}H NMR spectra.

Matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI–TOF–MS) was conducted using a Shimadzu/Kratos AXIMA-CFR spectrometer (linear mode) using dithranol as a matrix and sodium trifluoroacetate as an ion source.

Turbidity of a copolymer solution was recorded using a JASCO V-550 UV/vis spectrometer (by the transmittance at 500 nm) equipped with a Peltier-type thermostatic cell holder ETC-505. A glass cell with a light path length of 1 cm was used for the turbidity measurement. The heating and cooling rates were 1.0 ºC/min.

Table 1. Cationic Copolymerizations of VEs and Oxiranes [a]

entry	VE (M)	oxirane (M)	time	conv (%)		$M_n \times 10^{-3}$ [b]	M_w/M_n [b]	average no. of VE units per chain [c]	average no. of oxirane units per chain [c]	VE–oxirane crossover per chain [c,d]	average no. of VE units per block [c]	average no. of oxirane units per block [c]
				VE	oxirane							
1	IPVE (0.75)	IBO (0.22)	10 s	87	50	9.5	2.20	151	8.8	4.2	36	2.1
2	EVE (0.78)	(0.22)	10 min	13	79	1.9	2.04	11	16	2.5	4.6	6.6
3	CEVE (0.78)	(0.22)	6 h	0	40	0.7	2.15	–	–	–	–	–
4	IPVE (0.78)	EHMGE (0.22)	30 s	94[e]	12	16.2	1.97	200	7.4	2.1	95	3.5
5	EVE (0.78)	(0.22)	5 min	24	43	7.5	1.94	61	26	8.3	7.4	3.2
6	EVE (0.46)	(0.50)	3 min	6[e]	29	1.4	2.17	3.6	17	1.8	2.0	9.4
7	CEVE (0.78)	(0.22)	24 h	4	24	0.8	1.56	–	–	~0	–	–
8	IPVE (0.78)	PMGE (0.24)	3 min	58	1[e]	10.1	2.96	–	–	~0	–	–
9	EVE (0.78)	(0.22)	5 min	14	2[e]	4.9	1.95	65	1.4	1.6	41	0.9
10	EVE (0.50)	(0.50)	2 min	13	3[e]	2.0	1.99	17	5.3	1.9	8.9	2.8
11	CEVE (0.78)	(0.22)	141 h	16	79	2.1	1.76	5.8	9.2	2.0	2.9	4.5
12	IPVE (0.75)	MECH (0.22)	20 s	84	1	38.5	2.19	–	–	–	–	–
13	EVE (0.78)	(0.22)	5 min	52	0	8.2	1.72	–	–	–	–	–
14	CEVE (0.78)	(0.22)	1 h	79	47	11.2	2.15	87	18	2.6	34	7.0
15	CEVE (0.78)	EGE (0.22)	144 h	5	12	0.4[f]	1.35[f]	–	–	–	–	–

[a] $[Ph_3CB(C_6F_5)_4]_0$ = 1.0 (entries 4, 8–12, and 14), 3.0 (entries 1–3, 5–7, and 13), or 5.0 (entry 15) mM in dichloromethane (hexane: 5 vol%) at –78 ºC. See Figure 1 for the MWD curves. [b] By GPC (polystyrene calibration). [c] Determined by ^1H NMR for entries 1, 2, 4, 5 and 6 or by ^1H NMR and M_n(GPC) value for entries 9, 10, 11 and 13. See the Experimental section for the detail. [d] The number of the crossover reactions from a VE to an oxirane per chain. [e] These conversion values are determined from the ^1H NMR integral ratios and gravimetry because the values obtained by GC most likely contain non-negligible experimental errors. [f] For a main peak. A small and broad peak was present at the higher-MW region.

Results and Discussion

Cationic copolymerization of VEs and oxiranes with electron-withdrawing substituents

The cationic copolymerization of various VEs and oxiranes was examined under conditions similar to those for the previously reported system of IPVE and IBO (Scheme 2).[12] However, the use of $B(C_6F_5)_3$ as a catalyst was inefficient for several monomer combinations, particularly for monomers with low reactivities; hence, $Ph_3CB(C_6F_5)_4$, a highly reactive initiator with a non-coordinating counteranion,[19] was used in this study. In addition, excess amounts of VEs (approximately 0.75 M) compared to oxiranes (approximately 0.25 M) were employed to obtain products with high MWs (vide infra). After polymerization, the number of crossover reactions per chain and the monomer unit number per block were determined by NMR and GPC analyses. Acid hydrolysis of the products was also conducted to confirm the generation of copolymers because acetal moieties, which are acid labile, are generated in the main chain by the crossover reaction from VE to oxirane (Scheme 3).

First, EHMGE, PMGE, or MECH were copolymerized using IPVE, an efficient comonomer for IBO (entry 1 in Table 1 and Figure 1), in dichloromethane at –78 °C, which resulted in an inefficient incorporation of oxiranes into the products (entries 4, 8, and 12). A copolymer that is extremely rich in IPVE units was obtained when EHMGE was used (entry 4). Oxirane monomers were negligibly consumed when using PMGE or MECH, resulting in the generation of an IPVE homopolymer (entries 8 and 12). The electron-withdrawing substituents of these oxiranes are most likely responsible for the much lower reactivities than IBO. Therefore, VE monomers with lower reactivities than IPVE were used for the copolymerization of EHMGE, PMGE, or MECH. The results are explained in the following paragraphs.

The copolymerization of EHMGE with EVE, a VE that is less reactive than IPVE,[20] efficiently proceeded (Figure 2A) to yield copolymers via frequent crossover reactions per chain (entry 5 in Table 1 and Figure 1). Both monomers were smoothly consumed at similar rates to reach relatively high levels of monomer conversion. The products had unimodal MWDs, which indicates that side reactions, such as cyclic oligomerization, negligibly occurred during the copolymerization.[21] In the ^1H NMR spectrum of the product (Figure 3A; see Figures S3–S6 for the ^{13}C and 2D NMR spectra), a peak assigned to acetal structures (peak *16* in Figure 3A) was observed at 4.6–4.7ppm, suggesting the occurrence of the crossover reaction from VE to oxirane. The MALDI–TOF–MS spectrum (Figure S7) also indicated the generation of copolymers. In addition, the ^1H NMR spectrum contained peaks assigned to *exo*- and *endo*-olefin structures (*27, 28, 30,* and *35* in Figure 3A) resulting from a β-proton elimination reaction at the oxirane-derived propagating chain end. The M_n value calculated from the area ratio of these olefin peaks and other peaks (9.7×10^3) was consistent with the M_n value determined by GPC using polystyrene calibration (7.5×10^3), which indicates that most of the ω-ends of the copolymer chains were generated by the β-proton elimination reaction of EHMGE. From the area ratio of the olefin peaks, the number of VE-oxirane crossover reactions per chain was calculated to be 8.3 from EVE to EHMGE. The average unit numbers of EVE and EHMGE in each block were 7.4 and 3.2, respectively. The M_n

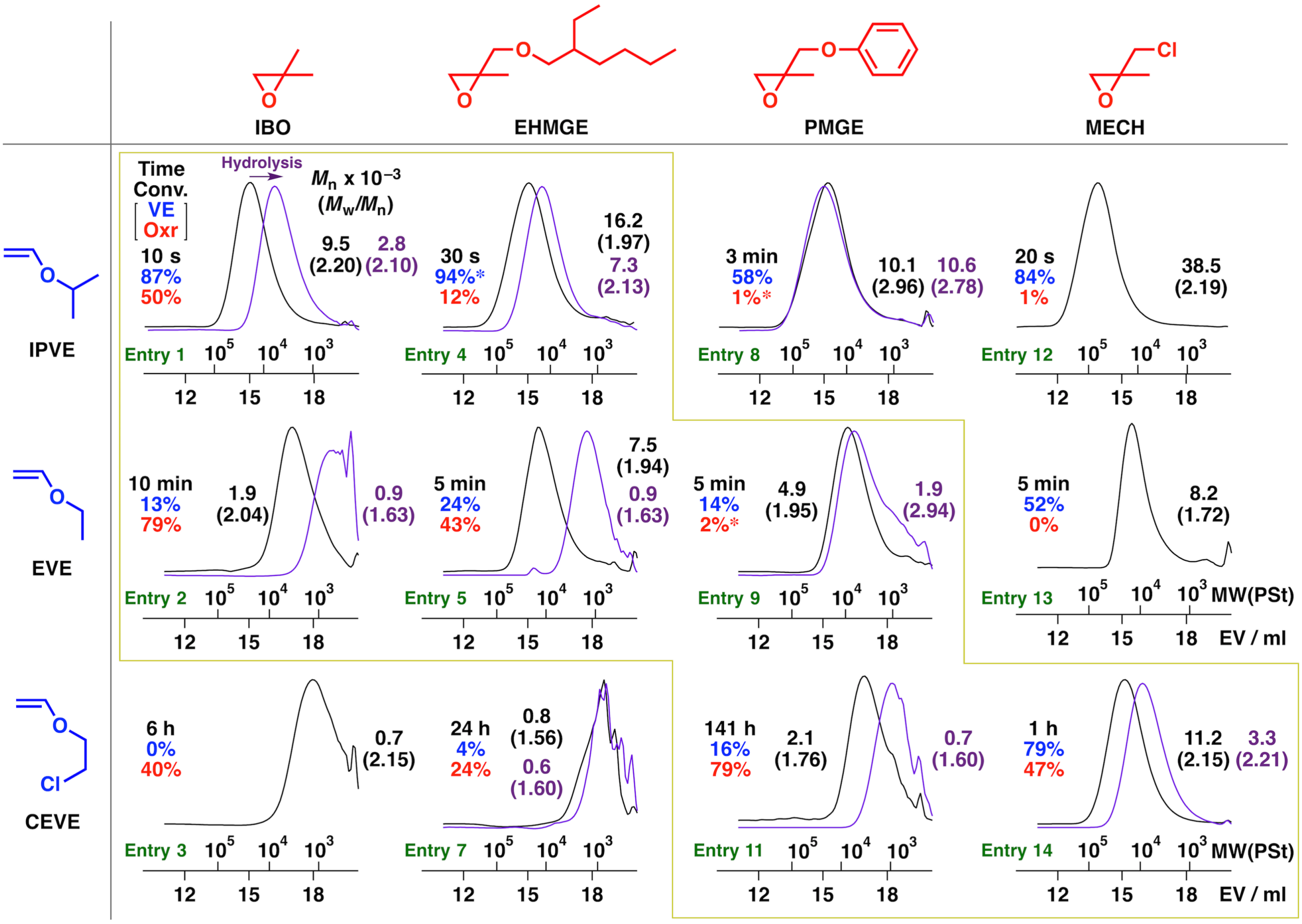
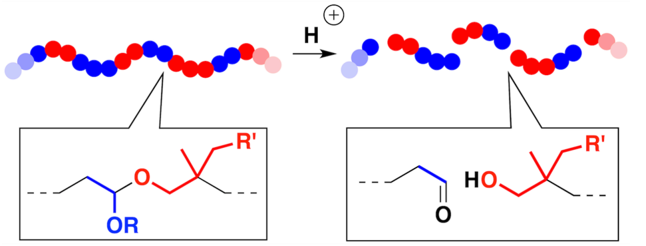


Figure 1. MWD curves of the products obtained in the copolymerization of VEs and oxiranes (black) and their hydrolysis product (purple). The data corresponds to those of the same entries listed in Table 1 (see the footnote of Table 1 for the polymerization conditions and the conversion values with * symbols).



Scheme 3. Acid hydrolysis of the product copolymers (blue: VE units, red: oxirane units).

values of the obtained copolymers partly depended on the amount of the initiator (Figure S8). However, not all the chains were derived from the initiator because chain transfer reactions occurred as a result of the β-proton elimination. Indeed, copolymers with similar block lengths and MWs were obtained at different reaction times (Table S1 and Figure S9).

The copolymer was hydrolyzed under acidic conditions because of the degradation of the acetal moieties in the main chain (Figure 3B), which yielded a product with a much smaller MW than that of the original copolymer (the purple curve of entry 5 in Figure 1). The hydrolysis product most likely had a diblock structure consisting of EVE and EHMGE segments. Indeed, the MW determined by GPC (0.9×10^3) was consistent with the value calculated from the above average unit numbers before hydrolysis (1.1×10^3).

The copolymerization of EVE and PMGE also produced copolymers via crossover reactions (entry 9 in Table 1 and Figure 1). PMGE was consumed at a lower rate than EVE (Figure 2B), which is in contrast to the similar consumption rates of EVE and EHMGE. The ^{1}H NMR spectrum of the product (Figure S10) had a peak assigned to acetal structures, suggesting that the crossover reactions occurred from EVE to PMGE. In addition, the MWD curve shifted to the smaller-MW region after hydrolysis (the purple curve of entry 9 in Figure 1). However, the incorporation ratio of PMGE (41 and 0.9 units of EVE and PMGE per block, respectively) and the number of crossover reactions from EVE to PMGE per chain were smaller than those obtained when using EHMGE. The lower reactivity (the word “reactivity” is used for describing the degree of polymerizability that depends on several factors such as the nucleophilicity and the efficiency of ring-opening reaction) of PMGE compared to EHMGE is responsible for the less efficient copolymerization.

A VE monomer that is less reactive than EVE was found to be more efficient for the copolymerization of PMGE. The reaction using CEVE as a comonomer yielded a product with an

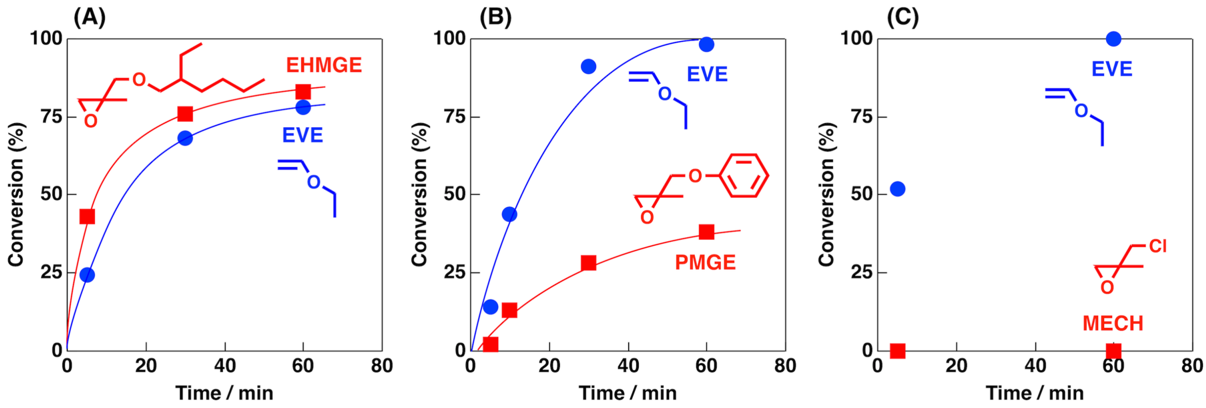


Figure 2. Time–conversion plots of the copolymerization of EVE (blue circles) with (A) EHMGE, (B) PMGE, or (C) MECH (oxiranes: red squares) {[EVE]$_0$ = 0.78 M, [oxirane]$_0$ = 0.22 M, [Ph$_3$CB(C$_6$F$_5$)$_4$]$_0$ = 3.0 (for A and C) or 1.0 (for B) mM, in dichloromethane (hexane: 5 vol%) at –78 ºC; the samples of the MWD curves corresponds to the data of (A) entry 5, (B) entry 9, and (C) entry 13 in Table 1}.

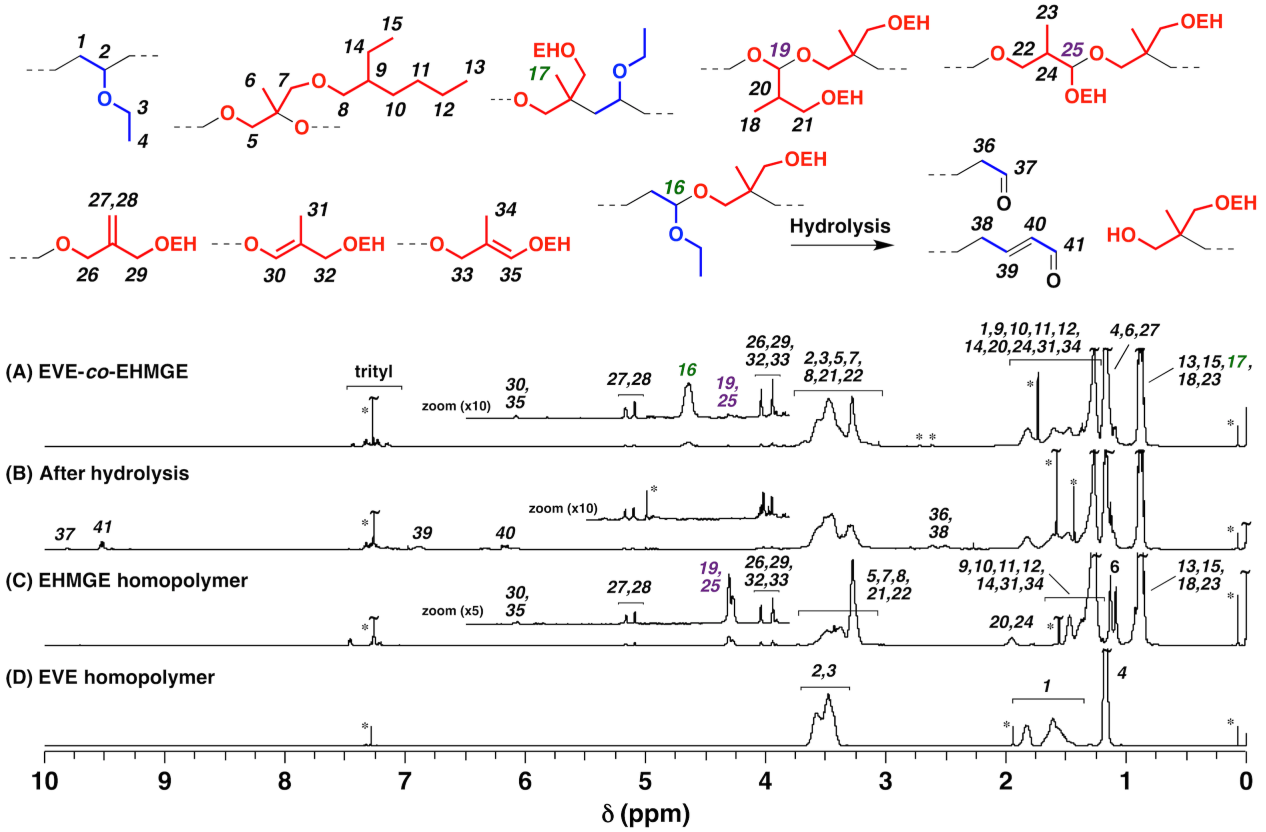


Figure 3. ^{1}H NMR spectra of (A) the copolymer of EVE and EHMGE (entry 5 in Table 1), (B) its hydrolysis product, (C) EHMGE homopolymer (entry 16 in Table 2; the low-MW portion including residual monomer was removed by preparative GPC), and (D) EVE homopolymer [obtained using Ph$_3$CB(C$_6$F$_5$)$_4$ as an initiator] (in CDCl$_3$ at 30 ºC; EH: 2-ethylhexyl group; * solvents, grease, water, stabilizer, or residual monomer). Structures resulting from the crossover to EVE after isomerization of the EHMGE-derived carbocation were also potentially generated (see Figures S3 and S6B for the assignments).

M_n value of 2.0 × 10^3 and a unimodal MWD (entry 11 in Table 1 and Figure 1). Notably, PMGE was consumed faster than CEVE to result in a copolymer rich in PMGE units, unlike the case of EVE. The average unit numbers of CEVE and PMGE in each block were 2.9 and 4.5, respectively.

The copolymerization of MECH proceeded via crossover reactions when combined not with EVE but with CEVE, in a manner similar to the reactions of PMGE. MECH was not consumed in the reactions with EVE (Figure 2C), which resulted in the generation of an EVE homopolymer (entry 13 in Table 1 and Figure 1). However, both the VE and oxirane monomers were consumed when using CEVE, yielding a polymer with a unimodal MWD (entry 14). ^{1}H NMR analysis (Figure S11) and the result of the acid hydrolysis of the product indicated that a copolymer was generated via crossover reactions.

VEs with low reactivity were not suitable for the copolymerization with IBO, in contrast to the reactions using PMGE and MECH. In the reaction with IBO, CEVE was not consumed, resulting in the generation of an IBO oligomer (entry 3 in Table 3 and Figure 1). EVE was consumed to yield copolymers with IBO (entry 2), although the consumption rate of EVE was much lower than that of IBO. These results indicate that VE and oxirane monomers with an appropriate balance of reactivity are required for copolymerization, as discussed below.

The β-methyl group of βMGEs and MECH was highly responsible for the sufficient reactivity in the copolymerization and efficient crossover reactions, which was suggested by the reaction using EGE as a counterpart with no β-methyl group. The monomer conversion values were extremely low even at a long reaction time in the copolymerization of EGE with CEVE (entry 15 in Table 1). Moreover, the reaction yielded only oligomers with a MW of 0.4 × 10^3. The low efficiency of copolymerization most likely stemmed from both the low nucleophilicity of EGE and the inefficient generation of the secondary carbocation via the ring-opening reaction of the EGE-derived oxonium ion.

Homopolymerization of βMGEs

To investigate the propagation and side reactions in detail, homopolymerization of EHMGE and PMGE was conducted under conditions similar to those of copolymerization (Table 2; Figure S12 for the MWD curves).[22] Polymerization proceeded at lower rates compared to the copolymerization with VEs. The products had relatively low MWs, which most likely resulted from the occurrence of β-proton elimination reactions at the propagating chain ends. Moreover, *exo*- and *endo*-olefin peaks were observed in the ^{1}H NMR spectra (Figures 3C and S10C for the EHMGE and PMGE homopolymers, respectively), as was the case with the copolymerization product. Moreover, a peak assigned to acetal structures existed at 4.3 ppm (peaks 19 and 25 in Figure 3), a lower chemical shift than the acetal peak derived from the crossover reaction from VE to oxirane. The decrease in MW after acid hydrolysis of the homopolymers (Figure S12) also supported the generation of acetal structures in the main chain. The isomerization of the propagating carbocation via hydride transfer (Scheme S1)[12] is responsible for the acetal generation. Similar isomerization reactions also likely occurred during the copolymerization with VEs, as confirmed by ^{1}H NMR analysis (Figures 3A and S10A).

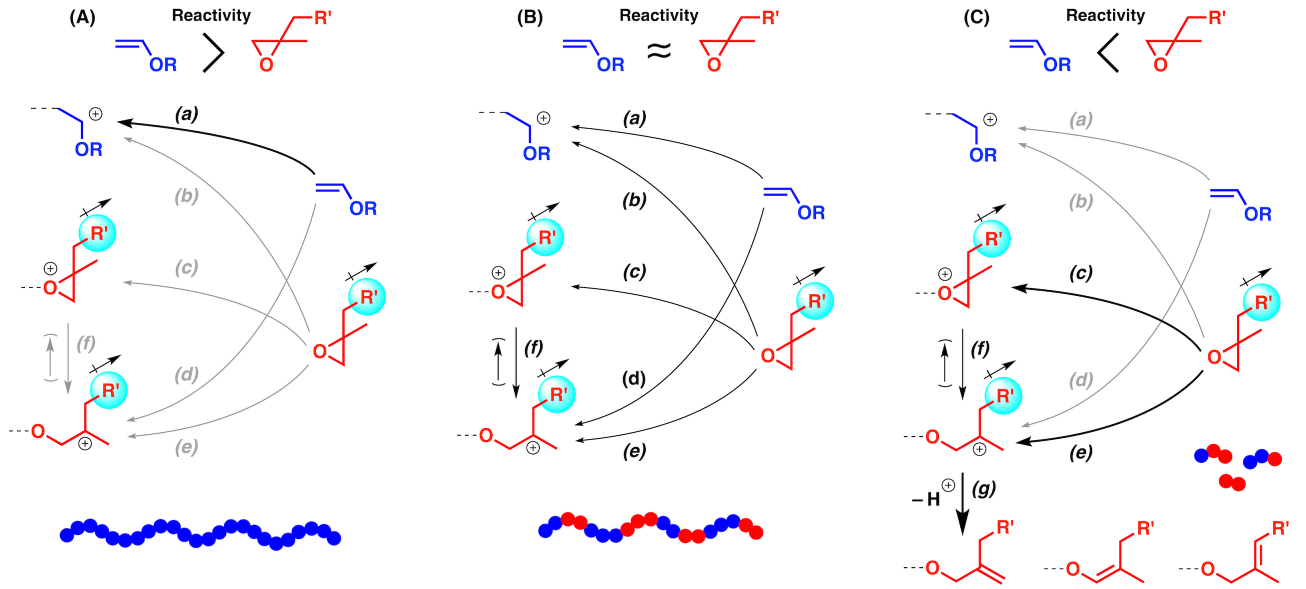
Table 2. Homopolymerization of Oxiranes[a]

entry	oxirane	time	conv. (%)	M_n [b]	M_w/M_n [b]
16	EHMGE	74 h	69	0.7	3.93
17	PMGE	24 h	62	2.2	1.94

[a] $[\text{oxirane}]_0$ = 0.22 M, $[Ph_3CB(C_6F_5)_4]_0$ = 12 (entry 16) or 3.0 (entry 17) mM, in dichloromethane (hexane: 5 vol%) (entry 16) or hexane/dichloromethane (1/1 v/v; entry 17) at –78 ºC. See Figure S12 for the MWD curves.

Effects of electron-withdrawing substituents on the copolymerization behavior

Based on the copolymerization results discussed above, the effects of oxirane substituents on the copolymerization behavior are discussed, particularly focusing on the reactivities of the monomers and propagating species. The homopropagation (paths a, c, and e) and crossover (paths b and d) reactions shown in Scheme 4 occur during copolymerization. The oxygen atom on the oxirane ring of βMGE has lower nucleophilicity than IBO due to the electron-withdrawing effect of the alkoxy substituent; hence, the reactions of VE- or βMGE-derived propagating species with a βMGE monomer likely occur less efficiently than do the same reactions with IBO. In addition, the carbocation generated via the ring opening of the βMGE-derived oxonium ion is



Scheme 4. Homopropagation reactions (paths a, c, and e), crossover (paths b and d) reactions, ring-opening reaction of an oxonium ion (path f), and β-proton elimination reaction (path g) in the copolymerization of VEs and oxiranes. Reactions with shaded arrows infrequently or negligibly occur.

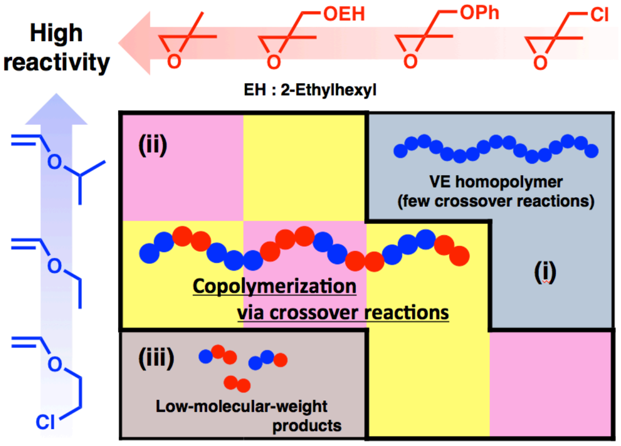


Figure 4. Schematic illustration of the products obtained in the copolymerization of VEs and oxiranes with different reactivities (see Figure 1 for the MWD curves of the copolymers and hydrolysis products).

destabilized by the electron-withdrawing substituent, which likely leads to an inefficient generation of the carbocation (path f in Scheme 4A) and a reduced frequency of the reaction with the VE or βMGE monomers (paths d and e). Thus, VEs with relatively high reactivities, such as IPVE, were not suited for the copolymerization of βMGE because of the preferential occurrence of homopropagation reactions of VE [(i) in Figure 4].

The efficient copolymerization of βMGE was achieved when combined with VEs that had lower reactivity than the VE suitable for copolymerization with IBO [(ii) in Figure 4]. The use of less reactive VEs reduced the frequency of VE homopropagation, which resulted in the occurrence of all the reactions (paths a–e in Scheme 4B) and generated copolymers consisting of both monomers. Most importantly, an appropriate balance of reactivities between the VE and oxirane monomers was indispensable for the copolymerization via efficient crossover reactions (pink regions in Figure 4). Specifically, EVE was suited for EHMGE, whereas CEVE, a less reactive VE, was suited for PMGE and MECH, which are less reactive oxiranes.

The balance between the efficient generation of carbocations via ring opening and the nucleophilicity is also of great importance for copolymerization reactions. The reactivity (or nucleophilicity) of the oxirane monomers used in this study likely decreases depending on the degree of the electron-withdrawing effect of the substituents in the following order: IBO > EHMGE > PMGE > MECH. This order also appears to be consistent with the order of the stability, or the generation efficiency, of the carbocation via the ring-opening reaction of the oxonium ion. The crossover reactions from oxirane to VE proceed when a carbocation is generated; however, the frequency of this crossover reaction does not simply agree with the order or the generation efficiency of carbocations. This is because the frequency of the homopropagation reactions of oxirane (paths c and d) also affects the frequency of the crossover reactions. The specific reactivity of the oxirane-derived carbocation, i.e., a "preference" for VE monomers or an "aversion" to oxirane monomers, also affects the crossover efficiency in the copolymerization, as demonstrated in our previous study.[12]

The homopropagation of oxirane preferentially proceeds when the reactivity of the VE is much lower than that of oxirane due to the reduced frequency of the reactions of VE [paths a and d in Scheme 4C; (iii) in Figure 4]. In this case, however, polymers with low MWs were generated because of the frequent occurrence of side reactions, such as β-proton elimination reactions (path g). Cyclic oligomerization[23,24] may have also occurred in some cases. Therefore, the number of crossover reactions per chain is small even when the crossover reactions with VEs occurred to some extent.

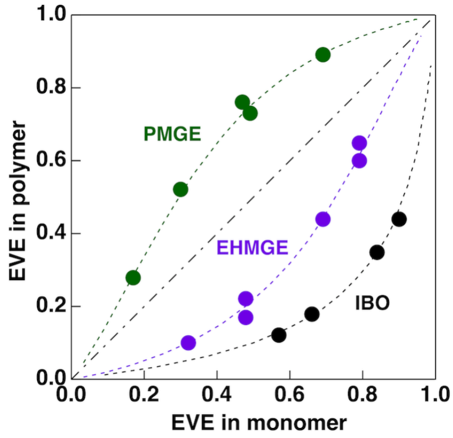


Figure 5. Copolymer compositions in the copolymerization of EVE with IBO (black), EHMGE (purple), or PMGE (green) {[EVE]$_0$ + [oxirane]$_0$ = 1.5 (for IBO) or 1.0 (for EHMGE and PMGE) M, [$Ph_3CB(C_6F_5)_4$]$_0$ = 3.0 (for EHMGE) or 1.0 (for PMGE) mM, [$B(C_6F_5)_3$]$_0$ = 1.0 mM (for IBO), in dichloromethane (hexane: 5 vol%) at –78 ºC. The data of IBO are cited from reference 12}.

Table 3. Monomer reactivity ratios.[a]

M_1 (VE)	M_2 (oxirane)	r_1	r_2
EVE	IBO	0.08[b]	8.7[b]
EVE	EHMGE	0.76	5.3
EVE	PMGE	4.6	0.79

[a] By the Kelen–Tüdős method (references 25,26). The values were determined using the data shown in Figure 5. See Table S2 for the polymerization data. The polymerization reactions were conducted at –78 ºC. [b] From reference 12.

The monomer reactivity ratios[25,26] determined for the copolymerization of EVE (M_1) with oxiranes (M_2) supported the above results and discussion (Figure 5 and Table 3). The r_1 and r_2 values were very low and high, respectively, in the copolymerization with IBO, which indicates that IBO monomers preferentially react with both EVE- and IBO-derived propagating species. In the case of EHMGE, the difference between the r_1 and r_2 values was smaller than in the case of IBO, although the reactions of the oxirane still occurred preferentially. By contrast, the r_1 value is very high, and the r_2 value is less than one in the case of PMGE, suggesting that EVE reacts more preferentially with both the EVE- and PMGE-derived propagating ends than PMGE does.

These values are consistent with the reactivities of oxiranes (IBO > EHMGE > PMGE) and with the average block lengths of the copolymers produced at equimolar feed ratios of EVE and oxiranes (entries 6 and 10 in Table 1).

Copolymerization of βMGE having an oxyethylenic chain and the thermoresponsive behavior of the obtained copolymer in water

To demonstrate the effect of a polar substituent on copolymer properties, we designed MOEOEOMGE, a βMGE with an oxyethylenic chain (Scheme 2), as a functional monomer. Oxyethylenic chains are effective for providing polymers with a variety of properties such as hydrophilicity, thermoresponsivity, and biocompatibility.[27,28] Cationic copolymerization of MOEOEOMGE was conducted using EVE as a comonomer because MOEOEOMGE was expected to have a similar reactivity to EHMGE, a βMGE that efficiently copolymerized with EVE. Indeed, copolymerization successfully proceeded via the consumption of both monomers to yield a copolymer (Figure 6A). The M_n value of the main peak of the MWD curve (Figure 6B) was 3.0 × 10^3. The average VE and βMGE units per block in the copolymer were calculated to be 14 and 2.0, respectively, from the ^{1}H NMR spectrum of the high-MW portion separated by preparative GPC (Figures S13 and S14). In addition, the crossover reaction from VE to βMGE occurred 4.2 times per chain. These results indicate that copolymerization of MOEOEOMGE proceeded in a manner similar to the other βMGEs. However, a distinct difference between MOEOEOMGE and the other disubstituted oxiranes was the much smaller polymerization rate of MOEOEOMGE. The copolymerization reaction was several hundred times slower than those of EHMGE or PMGE. The interaction between the oxyethylenic chain and the propagating cations was most likely responsible for the retardation of the copolymerization of MOEOEOMGE.

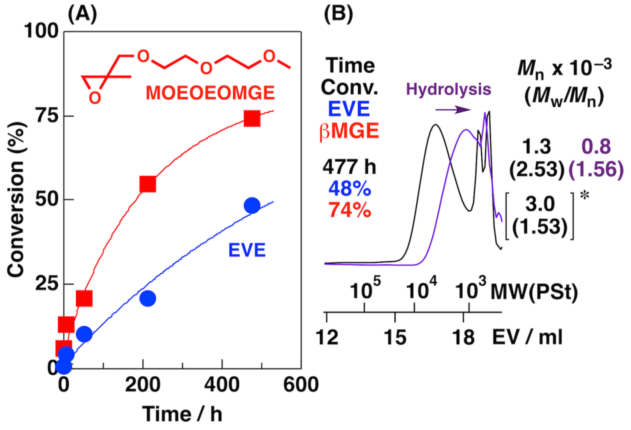


Figure 6. (A) Time–conversion plots of the copolymerization of EVE (blue circles) and EHMGE (red squares) and (B) the MWD curves of the copolymer (black; the values with an asterisk are M_n and M_w/M_n of the main peak) and the hydrolysis product (purple) {[EVE]$_0$ = 0.78 M, [MOEOEOMGE]$_0$ = 0.22 M, [$Ph_3CB(C_6F_5)_4$]$_0$ = 3.0 mM, in dichloromethane (hexane: 5 vol%) at –78 ºC}.

The obtained poly(EVE-*co*-MOEOEOMGE) was found to dissolve in water at low temperature[29] (the high-MW fraction separated by preparative GPC was used for the solubility test). Because poly(EVE) is insoluble in water, the oxyethylenic chains are responsible for the hydrophilicity of the copolymer.[30] Moreover, the copolymer exhibited lower critical solution temperature (LCST)-type thermoresponsive behavior. The copolymer was soluble in water at 0 ºC, whereas the solution became opaque as the temperature rose due to the phase separation (Figure 7). These preliminary results show that copolymer properties are potentially designed by introducing functional substituents into βMGE monomers. The effects of copolymer structures, such as block lengths, the ratio of VE and βMGE units, and MWs, on properties also need to be examined in future research.

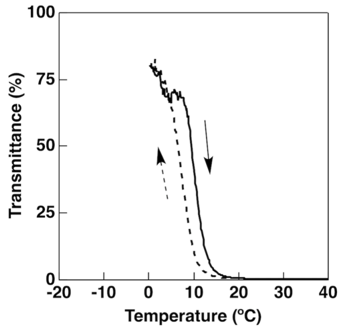


Figure 7. Turbidity measurement of poly(EVE-*co*-MOEOEOMGE) (the high-MW fraction separated by preparative GPC; see Figure S13A) in water (concentration: 0.5 wt%; solid line: heating scan, dotted line: cooling scan; scan rate: 1.0 ºC/min).

Conclusions

In conclusion, 2,2-disubstituted oxiranes with electron-withdrawing substituents were successfully copolymerized with VEs via concurrent cationic vinyl-addition and ring-opening mechanisms. An appropriate balance of reactivities between the VE and oxirane monomers was indispensable for efficient copolymerization via crossover reactions. Specifically, βMGEs were successfully copolymerized with VEs that were less reactive than the VEs suitable for the copolymerization of IBO, a counterpart with no electron-withdrawing groups. In addition, PMGE, a βMGE with a phenoxy groups, was less reactive than EHMGE, a βMGE with a 2-ethylhexyl group. The results obtained in this study contribute to the development of design strategies for the concurrent cationic vinyl-addition and ring-opening copolymerization of various vinyl and cyclic monomers. Furthermore, a variety of functional polymers can be synthesized by designing βMGEs using alkoxy moieties as functional groups and by introducing functional groups via substitution onto the chloroalkyl groups of copolymer side chains derived from MECH. Indeed, an oxyethylenic chain was introduced into a βMGE monomer, which led to the generation of a copolymer that exhibits LCST-type phase separation behavior in water. Sequences of copolymers, such as block-like, random, and alternating-like sequences, which can be partly controlled by the monomer combinations and reaction conditions, potentially affect their properties. The design of those functional copolymers, particularly focusing on the substituents of βMGE monomers and sequence control, is underway in our group.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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21 The products resulting from other side reactions such as macrocyclic polymer formation and inter- and intramacromolecular reactions are not detectable by GPC analysis even if these reactions occurred. However, those side reactions most likely negligibly occurred, which was deduced from the results of chain end analysis by ^{1}H NMR analysis (vide infra) and the homopolymerization of EVE or EHMGE in the presence of poly(EHMGE) or poly(EVE), respectively (Figures S1 and S2).

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29 A small amount of agglomeration remained insoluble even at low temperature. The insoluble portion consisted of copolymer chains with lower contents of MOEOEOMGE units, which was confirmed by ^{1}H NMR.

30 Solubility of an MOEOEOMGE homopolymer was not examined because high-MW products had not been obtained under the conditions examined. Oligomers consisting of chains with MWs lower than 10^3 were mainly obtained by the homopolymerization (Figure S13B).