Electronic Supplementary Information for:

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

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Figure S1. MWD curves of (A) a poly(EVE), (B) a product obtained by the polymerization of EHMGE in the presence of the poly(EVE) [dotted line: the same curve to (A)], (C) a poly(EHMGE) (black: the original product, blue: a low-MW portion including residual monomer was removed by preparative GPC), and (D) a product obtained by the polymerization of EVE in the presence of the poly(EHMGE) (in the presence of the portion separated by preparative GPC [the blue curve in (C)]) [dotted line: the same curve to the blue curve in (C)] {polymerization conditions: (A) $[EVE]_0 = 0.78$ M, $[Ph_3CB(C_6F_5)_4]_0 = 1.0$ mM; (B) $[EHMGE]_0 = 0.22$ M, $[Ph_3CB(C_6F_5)_4]_0 = 6.0$ mM, poly(EVE): 0.055 g/2.0 mL ([EVE unit] = 0.38 M); (C) $[EHMGE]_0 = 0.22$ M, $[Ph_3CB(C_6F_5)_4]_0 = 12$ mM; (D) $[EVE]_0 = 0.78$ M, $[Ph_3CB(C_6F_5)_4]_0 = 1.0$ mM, poly(EHMGE): 0.034 g/2.0 mL ([EHMGE unit] = 0.08 M); in dichloromethane (hexane: 5 vol%) at -78 °C}.



Figure S2. ¹H NMR spectra (in CDCl₃ at 30 °C) of (A) a poly(EVE), (B) a product obtained by the polymerization of EHMGE in the presence of the poly(EVE), (C) a poly(EHMGE) (a low-MW portion including residual monomer was removed by preparative GPC; the blue curve in Figure S1C), and (D) a product obtained by the polymerization of EVE in the presence of the poly(EHMGE) (see Figure S1 for the MWD curves and polymerization conditions). The spectrum of poly(EVE-*co*-EHMGE) is shown in (E) for comparison (* residual monomer, water, grease, or solvent).

Note for Figures S1 and S2: The MWD curves and the peaks in the ¹H NMR spectra of poly(EVE) or poly(EHMGE) remained intact after the polymerization of EHMGE or EVE, respectively. Moreover, EHMGE or EVE homopolymers appeared to be generated in the presence of poly(EVE) or poly(EHMGE), respectively, which was also suggested by the MWD curves and the ¹H NMR spectra. These results indicate that poly(EVE-*co*-EHMGE)s were generated not by scrambling reactions of homopolymer chains and propagating species but by the crossover reactions.



Figure S3. ¹³C and DEPT NMR spectra (in CDCl₃ at 30 °C) of (A) poly(EVE-*co*-EHMGE) (entry 5 in Table 1), (B) EHMGE homopolymer (the portion separated by preparative GPC [the purple curve in Figure S1C]), (C) EVE homopolymer (obtained using $ZrCl_4$ as a catalyst), and (D) expanded regions of (A). * CDCl₃.

(D) Expanded regions of (A)



Figure S3. (continued)



Figure S4. ¹H–¹H COSY NMR spectrum (in CDCl₃ at 30 °C) of poly(EVE-*co*-EHMGE) (entry 5 in Table 1).





Figure S5. ${}^{1}H{-}^{13}C$ HSQC NMR spectrum (in CDCl₃ at 30 °C) of poly(EVE-*co*-EHMGE) (entry 5 in Table 1).





Figure S6. ${}^{1}\text{H}-{}^{13}\text{C}$ HMBC NMR spectrum (in CDCl₃ at 30 °C) of poly(EVE-*co*-EHMGE) [entry 5 in Table 1; (A) wide and (B) narrow regions].





Figure S6. (continued)

* A correlation with a \dagger symbol [0.9ppm (¹H) and 19ppm (¹³C)] has not been assigned. Another possible structure other than those listed above would be responsible for these peaks.



Figure S7. MALDI-TOF-MS spectrum of poly(EVE-co-EHMGE) (entry 5 in Table 1).

Note for Figure S7. Most of the peaks were assigned to copolymer chains having the α -end derived from a proton and the ω -end derived from β -proton elimination reaction. Peaks assigned to the chains with the α -end derived from a trityl cation were negligibly detected, although the ¹H NMR spectrum had peaks assigned to a trityl group. Possible reasons are that ionization efficiency of chains with a trityl group was low and/or that a trityl group was eliminated during the ionization process.



Figure S8. M_n values of the poly(EVE-*co*-EHMGE)s obtained at different concentrations of the initiator at different reaction times {[EVE]₀ = 0.78 M, [EHMGE]₀ = 0.22 M, [Ph₃CB(C₆F₅)₄]₀ = 3.0 (red) or 6.0 (blue) mM, in dichloromethane (hexane: 5 vol%) at -78 °C. The data obtained at the Ph₃CB(C₆F₅)₄ concentration of 3.0 mM correspond to those shown in Table S1; The M_n (calcd) values are calculated from the [monomer]₀/[initiator]₀ ratio and the initiator and monomer conversion values, which is based on the assumption that one initiator molecule generates one polymer chain}.

	VE	Oxirane	Time (min)	Conv (%)				Average	Average	VF_	Average	Average
Entry				VE	oxirane	$M_{\rm n}$ × 10 ^{-3 b}	$M_{ m w}/M_{ m n}{}^b$	no. of VE units	no. of	of oxirane ane crossover	no. of VE units	no. of
								v E units per	units per		per	units per
								chain ^c	chain ^c	per chain °	block ^c	block ^c
1	EVE	EHMGE	5	24	43	7.5	1.94	61	26	8.3	7.4	3.2
2			30	68	76	7.5	2.00	68	21	7.0	9.7	3.0
3			60	78	83	9.1	1.94	80	24	8.3	9.6	3.0
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Table S1. Cationic copolymerization of EVE and EHMGE^a

^{*a*} [EVE]₀ = 0.78 M, [EHMGE]₀ = 0.22 M, [Ph₃CB(C₆F₅)₄]₀ = 3.0 mM, in dichloromethane (hexane: 5 vol%) at -78 °C; entry 1: entry 5 in Table 1. ^{*b*} By GPC (polystyrene calibration). ^{*c*} Determined by ¹H NMR.



Figure S9. MWD curves of poly(EVE-*co*-EHMGE)s obtained at different reaction times (black) and their acid hydrolysis products (purple). See Table S1 for the reaction conditions.



Figure S10. ¹H NMR spectra of (A) the copolymer of EVE and PMGE (entry 9 in Table 1), (B) its hydrolysis product, (C) PMGE homopolymer (entry 17 in Table 2), and (D) EVE homopolymer (in CDCl₃ at 30 °C; * solvents, grease, water, stabilizer, or residual monomer).



Figure S11. ¹H NMR spectra of (A) the copolymer of CEVE and MECH (entry 14 in Table 1; the low-MW portion including residual monomer was removed by preparative GPC), (B) its hydrolysis product, (C) MECH homopolymer (synthesized using Ph_3CPF_6 as an initiator), and (D) CEVE homopolymer (in CDCl₃ at 30 °C; * solvents, grease, water, or stabilizer).



Figure S12. MWD curves of the products obtained in the homopolymerization of (A) EHMGE (entry 16 in Table 2; blue curve: high-MW portion separated by preparative GPC, purple curve: after hydrolysis of the high-MW portion) and (B) PMGE (entry 17).



Scheme S1. Isomerization of the propagating carbocation via hydride transfer.

Entry	VE	Oxirane	VE conc (M)	Oxirane conc (M)	Time	Total conv $(\%)^b$	$M_{\rm n} \times 10^{-3 c}$	$M_{ m w}/M_{ m n}{}^c$	VE in copolymer ^d
1	EVE	EHMGE	0.760	0.200	30 s	3	1.0	2.07	0.60
2			0.746	0.201	1 min	5	1.5	2.62	0.65
3			0.677	0.305	1 min	11	1.8	2.81	0.44
4			0.550	0.599	30 s	6	1.4	2.49	0.22
5			0.461	0.501	3 min	23	1.4	2.17	0.17
6			0.321	0.691	10 s	7	1.1	2.13	0.10
7	EVE	PMGE	0.685	0.305	2 min	7	2.3	2.21	0.89
8			0.485	0.500	3 min	9	2.4	2.13	0.73
9			0.465	0.520	2 min	4	2.1	1.99	0.76
10			0.288	0.658	3 min	14	1.8	1.89	0.52
11			0.171	0.819	3 min	6	1.2	1.82	0.28

Table S2. Cationic Copolymerizations of EVE with EHMGE or PMGE for the Determination of Monomer Reactivity Ratios ^{*a*}

^{*a*} $[Ph_{3}CB(C_{6}F_{5})_{4}]_{0} = 3.0$ (entries 1–6) or 1.0 (entries 7–11) mM, in dichloromethane (hexane: 5 vol%) at – 78 °C. ^{*b*} By gravimetry. ^{*c*} By GPC (polystyrene calibration). ^{*d*} By ¹H NMR.

Note for Table S2: Monomer conversion needs to be very low for the determination of the monomer reactivity ratios by the Kelen–Tüdõs method. Therefore, the polymerization reactions were quenched in a very short time, although the reaction time was changed depending on the reactivities of monomers. Specifically, the copolymerization of EHMGE required a shorter time compared to the copolymerization of PMGE.



Figure S13. MWD curves of (A) poly(EVE-*co*-MOEOEOMGE)s before (black; the values with an asterisk are M_n and M_w/M_n of the main peak) and after (blue) separation by preparative GPC and (B) a homopolymerization product of MOEOEOMGE {(A) the same sample to that shown in Figure 6B; (B) [MOEOEOMGE]_0 = 0.22 M, [Ph₃CB(C₆F₅)₄]_0 = 3.0 mM, in dichloromethane (hexane: 5 vol%) at -78 °C}.



Figure S14. ¹H NMR spectra of (A) the copolymer of EVE and MOEOEOMGE (Figure 6B), (B) the high-MW portion separated by preparative GPC (the blue curve in Figure S13A), (C) the hydrolysis product, (D) homopolymerization product of MOEOEOMGE (Figure S13B), and (E) EVE homopolymer (in CDCl₃ at 30 °C; * residual monomer, degradation product of MOEOEOMGE, solvents, grease, water, or stabilizer).