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ABC Pseudo-Periodic Sequence Control by Cationic Orthogonal Terpolymerization of Vinyl Ether, Oxirane, and Ketone

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Abstract

For the purpose of achieving ABC-type periodic terpolymers, various vinyl ethers (VEs), oxiranes, and ketones were examined in the cationic vinyl-addition, ring-opening, and carbonyl-addition terpolymerization and suitable reaction conditions were identified. When the appropriate monomers are employed, the terpolymerization proceeds via a one-way cycle of crossover reactions, similar to "rock-paper-scissors". Homopropagation reactions of VE and oxirane need to be completely suppressed while attaining highly selective crossover reactions to achieve ABC-type periodic sequence control. By screening various monomers, VEs and oxiranes with moderate but sufficiently high reactivities were found to be appropriate for both the frequent crossover reactions and the polymerization itself. Appropriate ketones were also important for achieving efficient terpolymerization. In addition, more frequent crossover reactions occurred in the terpolymerizations conducted in less polar solvents at lower temperatures. Under the optimized conditions, the cationic terpolymerization of ethyl VE, 4-vinyl-1,2-cyclohexene oxide, and methyl ethyl ketone proceeded via frequent crossover reactions, and this process yielded an ABC pseudo-periodic terpolymer with averages of 1.2, 1.4 and 1.0 monomer units per block, respectively.

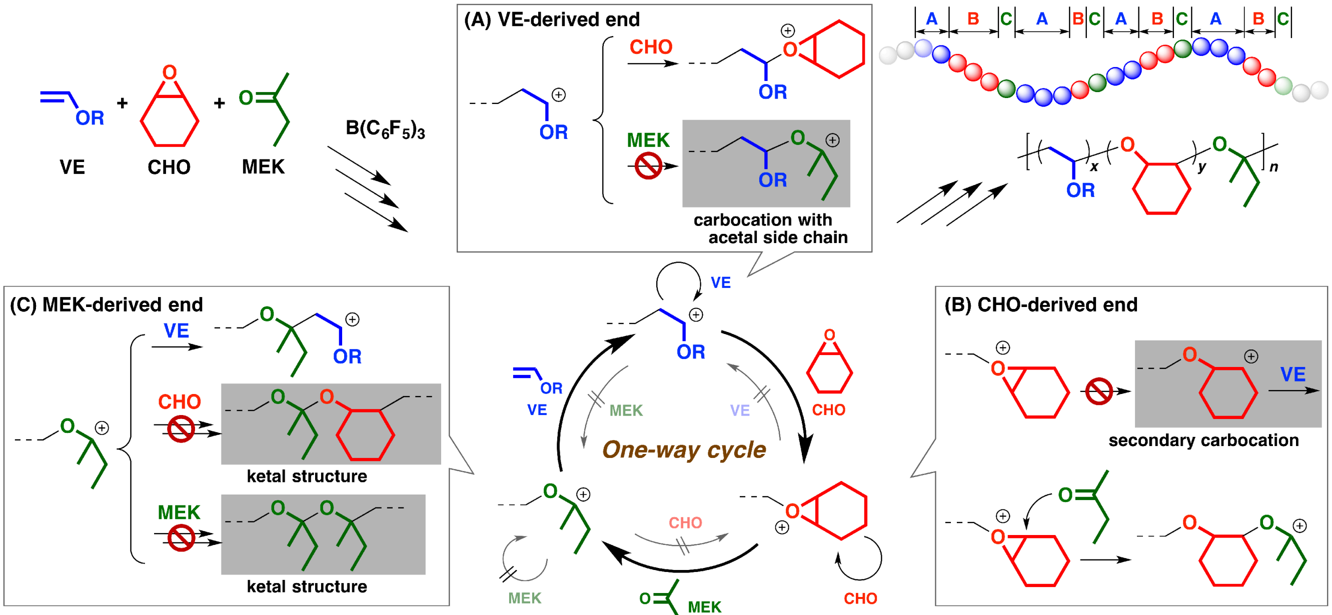
Introduction

The careful design of polymer structures, including their molecular weight (MW), chain ends, tacticity, and monomer sequences, is of great importance for tuning their functions and/or physical properties. Recently, methods for the precise control of monomer sequences in polymer chains have been attracting increasing interest due to the potential for accessing unique functions that are not possible from polymers with uncontrolled sequences.[1–4] Indeed, natural polymers such as proteins and DNA exert functions based on the precisely defined sequences of their monomers. To control the monomer sequences of synthetic polymers, various methods have been developed in the last several decades. Iterative methods, such as peptide synthesis on Merrifield resin,[5] allow the synthesis of polymers with the desired sequences through step-by-step reactions of monomers.[6–8] The polymerization of sequence-incorporated monomers is effective for the synthesis of polymers with periodic controlled sequences such as ABCABCABC.[9–18] Multicomponent reactions such as Passerini and Ugi reactions also allow the synthesis of polymers with periodic sequences.[19]

Direct chain-growth polymerizations of monomers can be used for the synthesis of polymers with controlled sequences, given that an extremely high selectivity is achieved in the propagation reactions. In the polymerization of two monomers, alternating copolymers are obtained when the homopropagation reactions of the monomers are completely suppressed.[20–22] Copolymers with specific sequences, such as AAB-type periodic sequences, are also produced via the appropriate monomer combinations under elaborately designed conditions.[23,24] However, more strict control is required in polymerizations of more than two monomers. Specifically, each propagating species must undergo a highly selective crossover reaction to a specific monomer. For example, in the terpolymerizations of monomers A, B, and C, the A-derived propagating species must react only with B but not with C, and a similar selectivity is required for the B- and C-derived species. Due to the difficulty of achieving this selectivity, to the best of our knowledge, only two examples of ABC-type periodic terpolymerizations by a chain-growth mechanism have been reported.[25,26]

Recently, our group developed a cationic terpolymerization that proceeds via a one-way cycle of crossover reactions.[27] Based on the relationship of the three monomers, we term this terpolymerization "rock-paper-scissors" polymerization. Specifically, the crossover reactions in the terpolymerization of an alkyl vinyl ether (VE), cyclohexene oxide (CHO), and methyl ethyl ketone

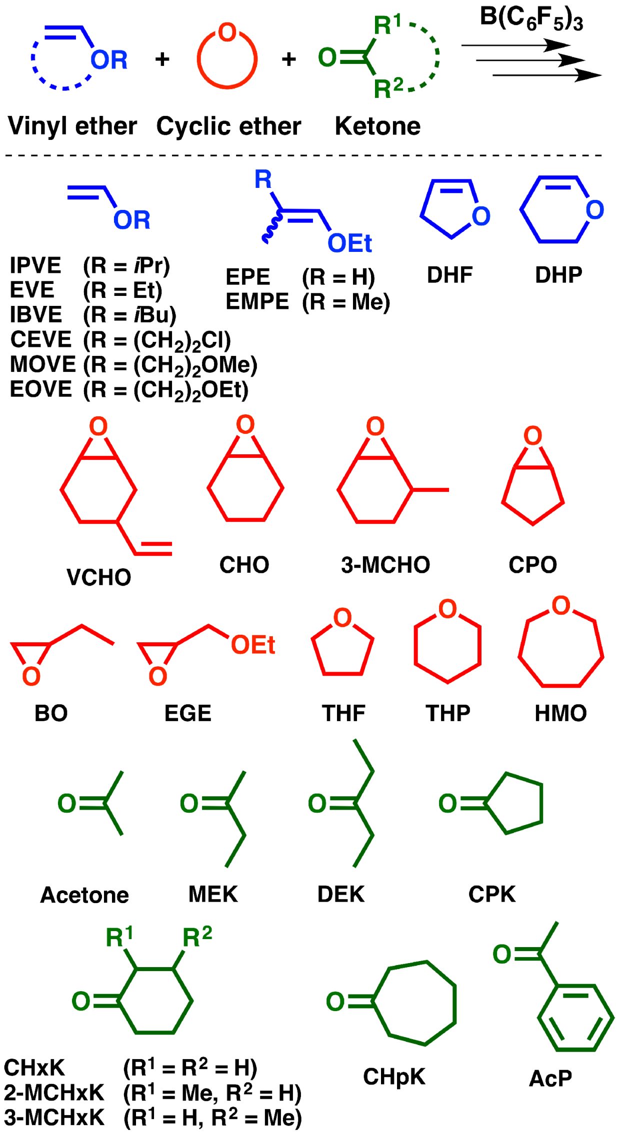
(MEK) occurred in the direction of VE→CHO, CHO→MEK, and MEK→VE (Scheme 1). The nature of both the propagating species and the resulting structures is most likely responsible for the high selectivity. The VE-derived carbocation does not react with MEK, probably due to the inefficient generation and instability of the acetal-adjacent carbocation (Scheme 1A). The VE-derived propagating species reacts with VE or CHO. The CHO-derived propagating species does not react with VE because the unstable secondary carbocation is not generated via the ring-opening of the oxonium ion (Scheme 1B). A carbocation must be generated for the crossover to VE, as demonstrated by our study on the copolymerization of VEs and oxiranes.[28] The CHO-derived oxonium ion, however, reacts with MEK via attack at the oxygen-adjacent carbon atom to generate an oxygen-adjacent carbocation, which is structurally similar to a VE-derived carbocation. This carbocation reacts with VE but does not react with CHO or MEK due to the instability of the resulting ketal structures (Scheme 1C). As a result of these selective crossover reactions and the homopropagation of VE and CHO, a multiblock-type terpolymer with a $[(VE)_x\text{-}(CHO)_y\text{-}MEK]_n$ sequence is produced by the cationic terpolymerization.



Scheme 1. Cationic Terpolymerization of VE, CHO, and MEK via a One-Way Cycle of Crossover Reactions.[a]

[a] Structures with gray shadow do not generate.

In this study, we investigated the cationic terpolymerization of various VEs, oxiranes, and ketones for the purpose of achieving a controlled, ABC-type periodic sequence via the complete suppression of the homopropagation of VE and oxirane (Scheme 2). In other words, we aimed to suppress the “draw” outcomes in the “rock-paper-scissors” terpolymerization. VEs and oxiranes with different reactivities and steric environments were employed to promote the crossover reactions. In addition, a series of acyclic, cyclic, and conjugated ketones were used as non-homopolymerizable monomers that only polymerize when combined with both VE and oxirane. Appropriate reaction conditions were also examined with a particular focus on monomer concentration, solvent polarity, and temperature. As a result of the optimization of several factors, ABC pseudo-periodic terpolymers with extremely short VE and oxirane blocks were successfully obtained via the favoring of crossover reactions over homopropagation reactions.



Scheme 2. Cationic Terpolymerization of Vinyl Ethers, Cyclic Ethers, and Ketones: Monomers Used in This Study.[a]

[a] Dashed lines indicate that several monomers have cyclic structures.

Experimental Section

Materials. Isopropyl VE (IPVE; Wako, 97.0+%), ethyl VE (EVE; TCI, >98.0%), and isobutyl VE (IBVE; TCI, >99.0%) were washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride. 2-Chloroethyl VE (CEVE; TCI, >97%) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight over sodium sulfate, and distilled twice under reduced pressure over calcium hydride. 2-Methoxyethyl VE (MOVE; kindly supplied by Maruzen Petrochemical) and 2-ethoxyethyl VE (EOVE; kindly supplied by Maruzen Petrochemical) were distilled over calcium hydride and then over metallic sodium. Ethyl 1-propenyl ether (EPE; Sigma-Aldrich, 98%; *cis*/*trans* mixture), 2,3-dihydrofuran (DHF; TCI, >98.0%), 3,4-dihydro-2*H*-pyran (DHP; Sigma-Aldrich, 97%), CHO (TCI, >98.0%), cyclopentene oxide (CPO; Sigma-Aldrich, 98%), 1,2-butylene oxide (BO; TCI, >99.0%), tetrahydrofuran (THF; Wako, 99.5+%), tetrahydropyran (THP; TCI, >98.0%), hexamethylene oxide (HMO; TCI, >98.0%), and diethyl ketone (3-pentanone, DEK; TCI, >98.0%) were distilled twice over calcium hydride. Ethyl 2-methyl-1-propenyl ether (EMPE) was prepared from isobutyraldehyde diethyl acetal (TCI, >96.0%) according to a literature method[29] and then distilled twice over calcium hydride. 4-Vinyl-1,2-cyclohexene oxide (1,2-epoxy-4-vinylcyclohexane, VCHO; TCI, >98.0%), ethyl glycidyl ether (EGE; TCI, >98.0%), cyclopentanone (CPK; TCI, >99.0%), cyclohexanone (CHxK; TCI, >99.0%), 2-methylcyclohexanone (2-MCHxK; TCI, >96.0%), 3-methylcyclohexanone (3-MCHxK; TCI, >97.0%), cycloheptanone (CHpK; Sigma-Aldrich, 99%), and acetophenone (AcP; Sigma-Aldrich, 99%) were distilled twice under reduced pressure over calcium hydride. 3-Methylcyclohexene oxide (3-MCHO)[30] was synthesized by the epoxidation of 3-methylcyclohexene (TCI, >93.0%) with monoperoxyphthalic acid magnesium salt hexahydrate (TCI, >65.0%)[31] and then distilled twice under reduced pressure over calcium hydride. MEK (Wako, 99.0+%, super dehydrated grade) was distilled twice over calcium hydride or used as received. Acetone (Wako, 99.5+%, super dehydrated grade) was used as received. $B(C_6F_5)_3$ (Sigma-Aldrich, 95%) was used without further purification after preparing its stock solution in dichloromethane. Dichloromethane (Wako, 99.0%), toluene (Wako, 99.5+%), and hexane (Wako, 96.0%) were dried by passage through solvent purification columns (Glass Contour).

Polymerization. The following is a typical polymerization procedure. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; the air temperature was approximately 450 °C) under dry nitrogen. Dichloromethane, hexane, IPVE, VCHO, and MEK were sequentially added into the tube using dry syringes. The polymerization was started by the addition of a prechilled solution of $B(C_6F_5)_3$ in dichloromethane to the monomer solution at –78 °C. After a predetermined time, the reaction was terminated by the addition of methanol containing a small amount of aqueous ammonia. The quenched mixture was diluted with hexane and then washed with water. The volatiles were then removed under reduced pressure at 50 °C to yield a polymer. The monomer conversion was determined by gas chromatography (column packing material: PEG-20M-Uniport HP or Gasukuropack; GL Sciences Inc.) using hexane as an internal standard or by combining the results from gas chromatography with the ratios of integrals in the ^{1}H NMR spectra of the products (the methods are shown in the footnotes of the tables).

Acid Hydrolysis. The acid hydrolysis of the polymers was conducted with 0.5 M HCl(aq) in 1,2-dimethoxyethane (polymer: approximately 1 wt%) at room temperature for 1 h. The quenched mixture was diluted with dichloromethane and washed with aqueous sodium hydroxide solution and then water. The volatiles were removed under atmospheric pressure at room temperature.

Characterization. The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [TSKgel GMH$_{HR}$-M × 2 (exclusion limit molecular weight = 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 ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatograms with respect to 16 polystyrene standards (Tosoh; MW = 5.0×10^2—1.09×10^6, $M_w/M_n < 1.2$). The NMR spectra were recorded using a JEOL JNM-ECA 500 (500.16 MHz for ^{1}H and 125.77 MHz for ^{13}C) spectrometer. Electrospray ionization mass spectrometry (ESI-MS) data were recorded on an LTQ Orbitrap XL (Thermo Scientific) spectrometer.

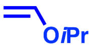
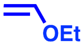
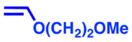
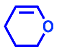
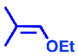
Results and Discussion

Cationic Terpolymerization of Various VEs, Oxiranes, and Ketones: Systematic Investigation of

Effective Monomers for Terpolymerization via A One-Way Cycle of Crossover Reactions

The cationic terpolymerization of IPVE, VCHO, and MEK, which is treated as the standard system in this study, was conducted using $B(C_6F_5)_3$ as a Lewis acid catalyst in dichloromethane at –78 °C. VCHO was generally used instead of CHO, which was the oxirane monomer used in our previous article,[27] because the olefinic moiety of VCHO simplifies the NMR analysis of the product polymers. The polymerization proceeded smoothly to yield a polymer with an M_n of 30.2×10^3 (entry 1 in Table 1; Figure 1A).[32] ^1H NMR analysis of the product indicated that all three monomers were incorporated into the polymer chains (Figure 2; see Figure S1 for ^{13}C NMR). The peak at 4.7 ppm was assigned to the acetal structure derived from the crossover from IPVE to VCHO. In addition, the peak of the methyl group of the MEK units appeared at 0.9 ppm. The number of MEK units per acetal unit was estimated to be one, which indirectly supports the occurrence of selective crossover reactions in a one-way cycle. The average numbers of IPVE/VCHO/MEK units per block, which corresponds to monomer units per acetal, were 8.2/2.0/0.98.

Table 1. Cationic Terpolymerization of Various VEs with VCHO and MEK[a]

entry	VE		time	conv. (%)			$M_n \times 10^{-3}$ [d] [$M_n \times 10^{-3}$ (hydrolysis)]	M_w/M_n [d]	units per acetal[e]		
				VE[b]	VCHO[b]	MEK[c]			VE	VCHO	MEK
1	IPVE		30 min	63	60	5	30.2 [0.8]	1.90	8.2	2.0	0.98
2	EVE		2 h	16	74	6	13.1 [0.4]	1.97	1.9	2.1	1.0
3	IBVE		2.5 h	14	73	6	9.1 [0.3]	2.02	1.8	2.0	0.97
4	CEVE		26 h	6	81	6	2.9 [0.3]	2.08	1.1	2.6	1.1
5	MOVE		48 h	3[c]	44	1	1.2 [0.5]	2.32	1.1	4.0	1.2
6	EOVE		68 h	18	67	4	2.3 [0.3]	2.56	1.3	2.9	1.1
7	DHF		3.5 h	6	50	3	5.1 [0.4]	2.78	1.8	2.9	1.2
8	DHP		22 h	8	36	2[b]	0.7	3.41	–	–	–
9	EPE		7 h	57	83	8	10.9 [0.9]	1.92	10	2.0	1.2
10	EMPE		2.5 h	0	83	8[b]	0.5	1.61	–	–	–

[a] $[VE]_0 = 0.80$ (except for entry 10) or 0.50 (entry 10) M, $[VCHO]_0 = 0.20$ M, $[MEK]_0 = 1.2$ M, $[B(C_6F_5)_3]_0 = 1.0$ (except for entry 10) or 5.0 (entry 10) mM, in dichloromethane at –78 ºC. See Figures S7 and S8 for MWD curves and ^1H NMR spectra of entries 4, 5, 7, and 9. [b] Determined by GC. [c] Determined from the VCHO

conversion value by GC and the integral ratio of NMR spectra of product polymers. [d] Determined by GPC (polystyrene standards). [e] Estimated by ^{1}H NMR analysis. The values correspond to the numbers of monomer units per block when terpolymerization proceeds via a one-way cycle of crossover reactions.

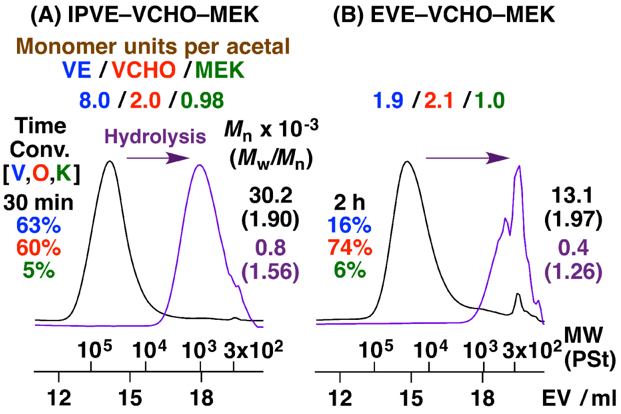


Figure 1. MWD curves of (A) IPVE–VCHO–MEK (entry 1 in Table 1) and (B) EVE–VCHO–MEK (entry 2) terpolymers (black), and the products obtained by acid hydrolysis of the terpolymers (purple) (see the footnote of Table 1 for the polymerization conditions).

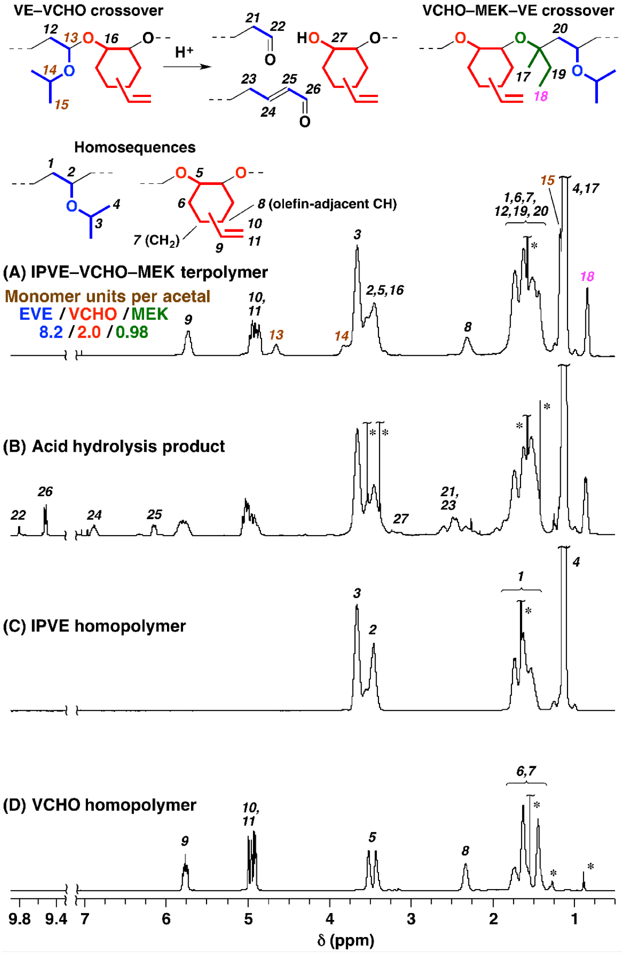
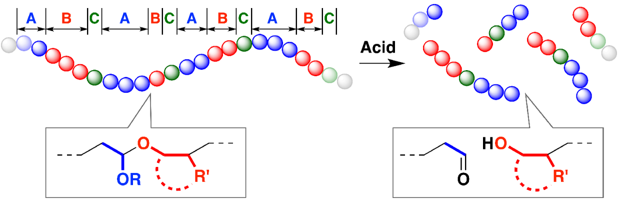


Figure 2. ^{1}H NMR spectra of (A) IPVE–VCHO–MEK terpolymer (entry 1 in Table 1), (B) the product obtained by acid hydrolysis of the terpolymer, (C) IPVE homopolymer (entry 1 in Table 2), and (D) VCHO homopolymer (entry 2 in Table 2) (see the footnotes of Tables 1 and 2 for the polymerization conditions; in $CDCl_3$ at 30 °C; * water, 1,2-dimethoxyethane, stabilizer, or hexane,).

The terpolymer was hydrolyzed into low-MW compounds under acidic conditions via the cleavage of the acetal moieties (Scheme 3). A peak for the original polymer was not observed in the GPC curve of the hydrolyzed product (purple curve in Figure 1A). In addition, the M_n value by GPC analysis was consistent with a value estimated from the average numbers of IPVE/VCHO/MEK units per block of the original terpolymer. In the ^{1}H NMR spectra (Figure 2), the peak of the acetal moieties (4.7 ppm) disappeared after acid hydrolysis, and peaks attributable to aldehyde moieties (9.5 and 9.8 ppm) were observed. These results suggest that the original polymer was not a mixture containing homopolymers but a terpolymer generated via crossover reactions of different monomers.



Scheme 3. Schematic Illustration of Acid Hydrolysis of the Terpolymer

The occurrence of highly selective crossover reactions in the direction of VE→VCHO, VCHO→MEK, and MEK→VE (Scheme 1) was strongly suggested by the results of the polymerizations of one or two of the three monomers (Table 2 and Figures S2–S5).[27] IPVE and VCHO undergo homopolymerization, while MEK alone did not undergo homopolymerization due to its very low ceiling temperature (entries 1–3 in Table 2). A diblock-like copolymer was obtained in the copolymerization of IPVE and VCHO according to ^{1}H NMR analysis and the result of acid hydrolysis (entry 4). In this copolymerization, crossover reactions occurred from IPVE to VCHO, while the crossover from VCHO to IPVE was negligible due to the inertness of the VCHO-derived oxonium ion to the addition of an IPVE monomer. Unlike in the terpolymerization, MEK was not consumed in the copolymerization with IPVE in the absence of VCHO (entry 5) and not incorporated into polymer chains in the copolymerization with VCHO in the absence of IPVE (entry 6; cyclic ketals were partly produced[33]), which is likely due to the inefficient generation of unstable carbocations and the corresponding sequences.

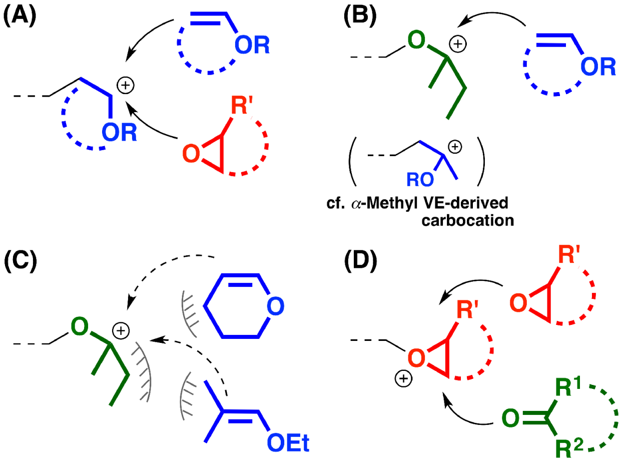
Table 2. Cationic Homo- and Copolymerization of IPVE, VCHO, and MEK[a]

	conc. (M)				GC conv (%)[b]				
entry	IPVE	VCHO	MEK	time	VE	VCHO	MEK	M_n ×10^{-3} [M_n ×10^{-3} (hydrolysis)][c]	M_w/M_n[c]
1	0.80	–	–	3 min	92	–	–	39.9	3.11
2	–	0.20	–	10 s	–	100	–	75.8	2.10
3	–	–	1.2	78 h	–	–	0	–	–
4	0.80	0.20	–	5 s	89	96	–	48.5 [14.1]	2.87
5	0.41	–	1.2	22 h	97	–	0	38.2 [38.2]	6.50
6	–	0.20	1.2	4 h	–	42	2	0.5	1.66

[a] $[B(C_6F_5)_3]_0$ = 1.0 (except for entry 3) or 3.0 (entry 3) mM, in dichloromethane at –78 ºC. Entries 3 and 5 are the same as the data reported in reference 27. See Figure S2 for MWD curves of entries 4–6. [b] Determined by GC. [c] Determined by GPC (polystyrene standards).

(a) The effects of VEs.

To suppress the homopropagation of VEs, various acyclic and cyclic VE derivatives (enol ethers) with different reactivities were tested in the terpolymerization with VCHO and MEK (Table 1). Terpolymers with shorter VE blocks were produced when EVE and IBVE, which are less reactive VEs than IPVE,[34] were used (entries 2 and 3 in Table 1; Figure 1B; Figure S6 for the ^{1}H NMR spectrum of the EVE–VCHO–MEK terpolymer). The average numbers of VE/VCHO/MEK units were about 2/2/1. Whether the VE-derived carbocation reacts with VE or oxirane depends on the relative reactivities of the two monomers (Scheme 4A); hence, the less reactive VE favors the crossover from VE to oxirane. However, the use of CEVE, which is a less reactive VE than EVE and IPVE, resulted in a product with a low MW even though further suppression of the VE homopropagation was achieved (entry 4). The reaction of a less reactive VE with the ketone-derived tertiary carbocation, which is comparable to a relatively stable tertiary carbocation derived from α-methyl VE[35,36] (unlike isobutene-derived tertiary carbocation, which does not have an adjacent oxygen atom and is less stable and more reactive than the α-methyl VE-type carbocation),[37,38] may occur in an inefficient manner (Scheme 4B). MOVE and EOVE, which are VEs with an oxyethylenic side chain, also resulted in frequent crossover reactions (entries 5 and 6), although the products had low MWs. DHF, a five-membered cyclic enol ether, was effective for achieving frequent crossover reactions, while DHP, its six-membered counterpart, was ineffective in the terpolymerization (entries 7 and 8). The terpolymerization proceeded with EPE, which has a methyl group at the β-position, although the VE units were not as short (entry 9). EMPE, a β,β-dimethyl VE, was completely inert in the terpolymerization, probably due to steric hindrance (entry 10). Notably, the inefficiency of DHP and EMPE, which are small and non-homopolymerizable, respectively,[35,39,40] is in sharp contrast to the alternating copolymerizations of these monomers with *o*-phthalaldehyde.[41] Steric hindrance between these vinyl monomers and the MEK-derived carbocation is likely responsible for their inertness (Scheme 4C). From these results, VEs with appropriate reactivities were demonstrated to be important to both suppress VE homopropagation and generate polymers with sufficiently high MWs.



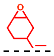
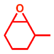
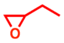
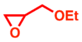
Scheme 4. Propagation Reactions at (A) VE-, (B), (C) Ketone-, and (D) Oxirane-Derived Propagating Ends.

(b) The effects of oxiranes.

Oxiranes with sufficient reactivities were indispensable for the terpolymerization via frequent crossover reactions (Table 3 and Figures S9 and S10). CHO and 3-MCHO, which are analogues of VCHO, functioned as effective monomers, although the MWs and the average numbers of monomer units per block somewhat differed from those achieved with VCHO (entries 2 and 3 in Table 3). CPO was also effective for the terpolymerization; however, the VE block was significantly longer than that of the VCHO counterpart due to the lower reactivity of CPO (entries 4 and 5). A less reactive oxirane is effective for the crossover from the oxirane to the ketone (Scheme 4D), while disfavoring the crossover from the VE to the oxirane (Scheme 4A). A terpolymer with shorter VE blocks was obtained when using EVE, although the MW also became lower (entry 6). CEVE, a far less reactive VE, was ineffective and resulted in oligomer formation (entry 7). Unlike the above oxiranes, negligible amounts of BO and EGE were consumed in the terpolymerizations with IPVE and MEK, which resulted in the generation of IPVE homopolymers (entries 8 and 10). When EVE was used instead of IPVE, BO was incorporated into the polymer chains (entry 9). However, EGE was inefficient even in the reaction using EVE (entry 11). The behavior of oxirane monomers in this terpolymerization is most likely related to their cationic homopolymerizability (Table S1). VCHO, CHO, and 3-MCHO exhibited high polymerizability and yielded homopolymers with high MWs (entries 1–3 in Table S1). Moreover, VCHO gave a homopolymer with a higher MW than those of CHO and 3-MCHO, which is consistent with the MWs of their corresponding terpolymers. The difference in MWs is strange because VCHO, CHO, and 3-MCHO have very similar structures. The reason is unclear presently. CPO underwent homopolymerization, although the conversion was low (entry 4). BO yielded only oligomers (entry 5), and EGE was completely inert (entry 6) under the examined conditions.

Cyclic ethers with five-, six-, and seven-membered rings were ineffective for the terpolymerization with VE and MEK (entries 12–17 in Table 3). Negligible amounts of THF, THP, and HMO were consumed in the polymerization. The lower ring strains in these cyclic ethers compared to oxiranes is likely responsible for their inertness toward the VE-derived carbocations (Scheme 4A). Oxetane, a four-membered cyclic ether, is effective for the terpolymerization via a one-way cycle of crossover reactions, as reported in our previous study.[42] Multiblock terpolymers with relatively long VE and oxetane blocks were generated under conditions other than those employed in the present study.

Table 3. Cationic Terpolymerization of Various Cyclic Ethers with VEs and Ketones[a]

	monomer						conv^b (%)					units per acetal^f		
entry	VE (M)	cyclic ether (M)		MEK (M)	temp (°C)	time	VE	cyclic ether	MEK	$M_n \times 10^{-3}$ ^{e} [$M_n \times 10^{-3}$ (hydrolysis)]	M_w/M_n^{e}	VE	cyclic ether	MEK
1	IPVE 0.80	VCHO 0.20		1.2	–78	30 min	63	60	5^c	30.2 [0.8]	1.90	8.2	2.0	0.98
2	IPVE 0.80	CHO 0.20		1.2	–78	30 min	19	69	10	8.6 [0.5]	2.03	4.1	3.7	1.0
3	IPVE 0.80	3-MCHO 0.20		1.2	–78	2 h	81	88	8	15.4 [0.8]	2.01	8.9	3.8	1^g
4	IPVE 0.80	CPO 0.21		1.2	–78	23 h	93	28	2^c	33.8 [7.8]	5.59	78	2.3	1.0
5	IPVE 0.80	CPO 0.21		5.0	–78	24 h	95	21	1^c	32.1 [2.1]	4.03	25	1.2	0.99
6	EVE 1.8	CPO 0.21		5.0	–78	52 h	16	38	1^c	1.6 [0.3]	1.84	4.3	1.4	0.84
7	CEVE 0.80	CPO 0.46		1.2	–78	96 h	5	47	1	0.5	1.87	–	–	–
8	IPVE 0.41	BO 0.81		1.2	–78	26 h	95	1	0	5.6	2.98	–	–	–
9	EVE 0.80	BO 0.81		5.0	–78	47 h	67	50	4^c	2.1 [0.5]	2.20	6.0	2.1	1.0
10	IPVE 0.40	EGE 0.80		1.2	–78	5 h	59	4	0	15.8 [14.7]	2.41	–	–	–
11	EVE 0.80	EGE 0.40		1.2	–78	24 h	8	0	3	2.3	2.71	–	–	–
12	IPVE 0.80	THF 0.25		1.2	–78	20 h	100	0^d	0	72.4	2.50	–	–	–
13	CEVE 0.80	THF 0.75		1.2	–40	30 min	29	0^d	0	11.8	3.03	–	–	–
14	EVE 0.80	THP 0.82		1.2	–78	70 h	0	7	2	–	–	–	–	–
15	IPVE 0.40	THP 0.83		1.6	–20	67 h	17	3	0	4.1	3.27	–	–	–
16	IPVE 0.80	HMO 0.20		1.2	–78	45 h	87	0	0	75.5	3.44	–	–	–
17	EVE 0.80	HMO 0.20		1.2	–78	21 h	4	2	0	–	–	–	–	–

[a] $[B(C_6F_5)_3]_0$ = 1.0 (entries 1—5, 10, and 14—17), 2.0 (entry 13), or 3.0 (entries 6—9, 11, and 12) mM, in dichloromethane (except for entry 15) or hexane (entry 15) at –78 °C. Entry 1 corresponds to entry 1 in Table 1. Entry 2 is the same as the data reported in reference 27. See Figures S9 and S10 for MWD curves and ^{1}H NMR spectra of entries 3, 5, and 9. [b] Determined by GC. [c] Determined from the conversion value of oxiranes by GC and the integral ratio of NMR spectra of product polymers. [d] Determined by NMR spectra of products. [e] Determined by GPC (polystyrene standards). [f] Estimated by ^{1}H NMR analysis. The values correspond to the numbers of monomer units per block when terpolymerization proceeds via a one-way cycle of crossover reactions. [g] This value was assumed to be 1 because the value was not estimated from the ^{1}H NMR spectrum due to the overlap of peaks.

(c) The effects of ketones.

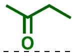
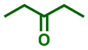
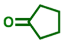
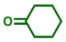
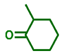
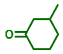
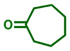
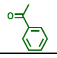
The structures of the ketones also influenced the frequency of the crossover reactions in the terpolymerization (Table 4 and Figures S11 and S12). The use of acetone resulted in the generation of a terpolymer with similar numbers of monomer units per acetal to those of the terpolymer synthesized with MEK (entry 2 in Table 4). In contrast, a terpolymer with longer VCHO blocks was obtained when

DEK was used (entry 3). The slight difference between the alkyl groups between MEK and DEK (methyl vs ethyl) likely affected the steric environment in the attack of the oxirane-derived oxonium ion by the ketone monomer (Scheme 4D) and/or the subsequent reaction of the DEK-derived carbocation and the VE monomer (Scheme 4B), although the latter case is based on the assumption that the generation of the ketone-derived carbocation is a reversible process. Notably, the IPVE blocks were also longer in the DEK case than in the MEK and acetone cases, which may be due to the interaction between the ketone monomers with the VE-derived carbocation, as discussed below (in the section concerning the effect of the ketone concentration).

The frequency of the crossover reactions slightly increased when five- and six-membered cyclic ketones were used. Terpolymers with slightly shorter VE and VCHO blocks were obtained in the terpolymerizations using CPK or CHxK compared those with acyclic ketones (entries 4 and 5 in Table 4). In addition, methyl substituents at the 2- or 3-positions of CHxK had a negligible influence on the frequency of the crossover reactions (entries 6 and 7). The basicities, which are related to nucleophilicity, of acyclic and cyclic ketones are comparable;[43] hence, other factors, such as the nature of the cyclic carbocation generated from the oxirane-derived oxonium ion and a cyclic ketone, may be responsible for the higher frequency of crossover reactions in the case of cyclic ketones than acyclic ketones. A decrease of torsional strain after the addition of a ketone to the oxirane-derived oxonium ion may be larger in the case of cyclic ketones than acyclic ketones, which is another potential reason of the higher reactivity of cyclic ketones. Unlike CPK and CHxK, a seven-membered cyclic ketone (CHpK) was completely ineffective for the terpolymerization (entry 9). In the terpolymerization using the cyclic ketones, however, a crossover reaction from the ketone to the oxirane did occur infrequently, particularly when VEs with low reactivity were used (vide infra).

Acetophenone, which generates a resonance-stabilized carbocation via the reaction with an oxirane-derived oxonium ion, yielded a terpolymer with longer VCHO blocks relative to what were seen with the above ketones (entry 9 in Table 4). This is probably due to the weaker nucleophilicity of acetophenone relative to nonconjugated ketones and/or the lower reactivity of the oxygen atom- and phenyl group-adjacent carbocation derived from acetophenone (the latter is based on the assumption that this process is reversible; vide supra).

Table 4. Cationic Terpolymerization of Various Ketones with IPVE and VCHO[a]

entry	ketone		time	Conv. (%)			$M_n \times 10^{-3}$ [d] $[M_n \times 10^{-3}$ (hydrolysis)]	M_w/M_n [d]	units per acetal[e]		
				IPVE[b]	VCHO[b]	ketone[c]			VE	VCHO	ketone
1	MEK		30 min	63	60	5	30.2 [0.8]	1.90	8.2	2.0	0.98
2	Acetone		1 h	77	69	7	17.4 [0.7]	2.00	8.1	1.9	1.1
3	DEK		15 min	85	83	3	37.7 [1.9]	1.96	18	4.0	1.0
4	CPK		3.5 h	38	47	5	9.5 [0.5]	2.08	5.8	1.6	1.0
5	CHxK		2 h	45	56	5	33.2 [0.5]	1.88	5.0	1.7	0.94
6	2-MCHxK		3.5 h	68	72	8	24.0 [0.6]	1.81	6.8	1.7	1.1
7	3-MCHxK		4 h	78	77	9	27.6 [0.5]	1.87	5.6	1.5	1.0
8	CHpK		5 h	18[c]	54	8[b]	0.5	1.73	–	–	–
9	AcP		1.5 h	53	67	4	13.6 [0.6]	2.32	7.9	2.7	1.0

[a] $[\text{IPVE}]_0 = 0.80$ M, $[\text{VCHO}]_0 = 0.20$ M, $[\text{ketone}]_0 = 1.2$ M, $[B(C_6F_5)_3]_0 = 1.0$ mM, in dichloromethane at –78 ºC. Entry 1 corresponds to entry 1 in Table 1. See Figures S11 and S12 for MWD curves and ^{1}H NMR spectra of entries 2, 3, 5, and 9. [b] Determined by GC. [c] Determined from the VCHO conversion value by GC and the integral ratio of NMR spectra of product polymers. [d] Determined by GPC (polystyrene standards). [e] Estimated by ^{1}H NMR analysis. The values correspond to the numbers of monomer units per block when terpolymerization proceeds via a one-way cycle of crossover reactions.

[For Editing: Please insert a blank line here because the following two paragraphs are not a part of the last subsection (subsection (c) The effect of ketones)]

The effective and ineffective monomers in the terpolymerization, which were determined based on the results described above, are summarized in Chart 1. The average numbers of monomer units per acetal, which correspond to block lengths, of the terpolymers obtained in the terpolymerization of three VEs with different reactivities, VCHO, and three cyclic and acyclic ketones are listed in Chart 2. As demonstrated above, the VE block lengths decreased with decreasing reactivity of the VEs (IPVE > EVE > CEVE) and in the order of DEK > MEK > CHxK.

	Potentially effective for ABC periodic sequence	Effective for terpolymerization	Ineffective
VE	EVE, IBVE, CEVE, MOVE, EOVE, DHF	IPVE, EPE	EMPE, DHP
Cyclic ether	VCHO, CHO, 3-MCHO	CPO, BO	EGE, THF, THP, HMO
Ketone	MEK, Acetone	DEK, CPK, CHxK, 2-MCHxK, 3-MCHxK, ACP	CHpK

Chart 1. Effectiveness of monomers in terpolymerization via selective crossover reactions.[a]
[a] Monomers are categorized in terms of the efficiency, frequency, and selectivity of crossover reactions.

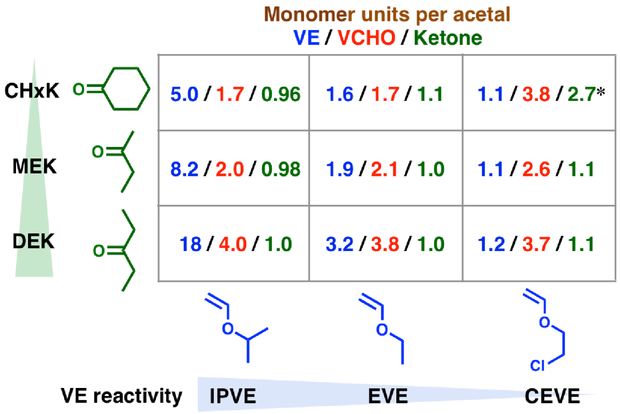
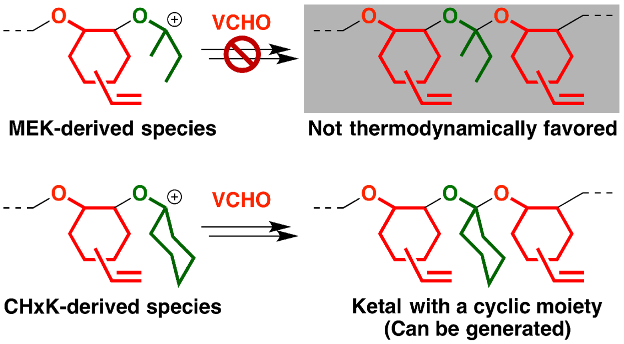


Chart 2. The numbers of monomer units per acetal of terpolymers obtained in the terpolymerizations of VEs, VCHO, and ketones ($[\mathrm{VE}]_0 = 0.80$ M, $[\mathrm{VCHO}]_0 = 0.20$ M, $[\mathrm{ketone}]_0 = 1.2$ M, $[\mathrm{B(C_6F_5)_3}]_0 = 1.0$ mM, in dichloromethane at –78 ºC). * The number of CHxK units per acetal is more than one, which indicates that the crossover from CHxK to VCHO occurred.

The numbers of ketone monomer units per acetal are approximately 1.0 in almost all cases (Chart 2), which means that the crossover reactions occurred in a one-way cycle. However, the units of ketone per acetal is 2.7 in the case of the terpolymer obtained from CEVE, VCHO, and CHxK, which is due to the generation of VCHO–CHxK–VCHO sequences. This sequence is derived from the crossover reactions occurring in the reverse direction (from CHxK to VCHO). The result is in sharp contrast to the case of VCHO and MEK, in which a copolymer was not generated due to the negligible crossover from MEK to VCHO (Scheme 5). A ketal with a cyclic moiety is considered to be more stable than its acyclic analogue,[44] which is likely responsible for the formation of the putative VCHO–CHxK–VCHO sequence. The occurrence of such an irregular crossover reaction was also confirmed by the copolymerization of VCHO and CHxK (Figures S13–S15).



Scheme 5. Reactions of a VCHO monomer with the MEK-derived (upper) and CHxK-derived (lower) propagating species.

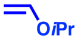
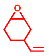
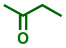
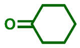
Investigation of the Reactions Conditions: Ketone Concentration, Solvents, and Temperature

To achieve an ABC-type periodic sequence in the terpolymerization, we examined the effects of the ketone concentration, solvents, and temperature on the block lengths of the resulting polymers. The block lengths could be shortened under the appropriate conditions. The results are explained below.

The number of VCHO units per block decreased when the terpolymerization was conducted at higher concentrations of ketones (Table 5). For example, the number of VCHO units per block was 2.7 at an MEK concentration of 0.52 M, while the number was 1.3 at 5.0 M (entries 1–3 in Table 5).[45] The MWs of the terpolymers were also lower at 5.0 M. The MW of the VE homopolymer obtained in the presence of MEK (entry 5 in Table 2) is not as low as that of the polymer obtained in the absence of MEK (entry 1 in Table 2); hence, side reactions may occur at the oxirane- or ketone-derived propagating ends in the presence of ketone. Interestingly, the VE block lengths also decreased at higher concentrations of ketones. A ketone monomer can potentially interact with not only the oxirane-derived propagating species but also the VE-derived carbocation, even though in the latter case, a covalent bond is not generated via the reaction with the next monomer. Thus, such an interaction between the VE-derived carbocation and a ketone monomer may favor the reactions of the VE-derived carbocation with an oxirane over that of VE (Scheme S1). In such cases, less frequent or less efficient interactions between the VE and ketone at lower concentrations of the ketone or with less efficient ketones such as

DEK (vide supra) result in longer VE blocks. The concentrations of ketones also affected the polymerization rates. The terpolymerization proceeded slower at higher concentrations of ketones (the polymerization time ranged from 30 min to 46 h in Table 5) because ketones moderated the catalytic activity of $B(C_6F_5)_3$ through the Lewis acid-base interaction.

Table 5. Cationic Terpolymerization of VE, VCHO, and Ketone: Effects of Concentrations of Ketones[a]

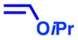
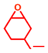
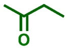
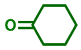
	monomer				conv (%)					units per acetal[e]		
entry	VE	oxirane	ketone	time	VE[b]	VCHO[b]	ketone[c]	$M_n \times 10^{-3}$ [d] [$M_n \times 10^{-3}$(hydrolysis)]	M_w/M_n[d]	VE	VCHO	ketone
1	IPVE	VCHO	MEK 0.52 M	30 min	93	78	10	30.9 [1.1]	2.05	12	2.7	1.0
2			 1.2 M	30 min	63	60	5	30.2 [0.8]	1.90	8.2	2.0	0.98
3			5.0 M	24 h	81	97	3	9.7 [0.5]	1.97	4.7	1.3	1.0
4			CHxK 0.52 M	1 h	57	51	10	30.9 [0.7]	1.96	8.1	2.0	0.92
5			 1.2 M	2 h	45	56	5	33.2 [0.5]	1.88	5.0	1.7	0.94
6	EVE	VCHO	MEK 1.2 M	2 h	16	74	6	13.1 [0.4]	1.97	1.9	2.1	1.0
7			5.0 M	46 h	22	73	2	2.1 [0.3]	1.76	1.7	1.5	1.1

[a] $[VE]_0 = 0.80$ M, $[VCHO]_0 = 0.20$ M, $[B(C_6F_5)_3]_0 = 1.0$ mM, in dichloromethane at –78 °C. Entries 2, 5, and 6 correspond to entry 1 in Table 1, entry 5 in Table 4, and entry 2 in Table 1, respectively. [b] Determined by GC. [c] Determined from the VCHO conversion value by GC and the integral ratio of NMR spectra of product polymers. [d] Determined by GPC (polystyrene standards). [e] Estimated by ^{1}H NMR analysis. The values correspond to the numbers of monomer units per block when terpolymerization proceeds via a one-way cycle of crossover reactions.

The VE block lengths decreased at lower temperatures, while the VCHO block lengths were negligibly affected. The IPVE/VCHO/MEK units per acetal were 8.2/2.0/0.98 and 5.9/2.1/1.0 at –78 and –100 °C, respectively (entries 1 and 2 in Table 6). Similar behaviors were observed in the terpolymerizations of different monomers (entries 5, 6, 9, and 10; ketal structures were likely generated in the case of CHxK). The differences in the activation energies of each homopropagation and crossover reaction are responsible for the effects of polymerization temperature on the monomer sequences of the resulting polymers.

Less polar solvents effectively suppressed the relative ratio of the homopropagation reactions of VEs and oxiranes over the crossover reactions. The terpolymerizations in toluene (entry 3 in Table 6) or hexane/dichloromethane (8/2 v/v; entry 4) smoothly proceeded at polymerization rates comparable to those in dichloromethane but resulted in shorter VE and VCHO block lengths. In less polar solvents, the solvation effect is weaker. Instead, the interactions between the propagating cation and the surrounding monomers are stronger in less polar solvents, which may favor reactions with more polar monomers. The dielectric constant, which is related to solvent polarity, increases in the order of EVE (3.0)[46] < CHO (9.1)[47] < MEK (18.5).[48] Thus, in less polar solvents, the crossover reactions to an oxirane monomer and a ketone monomer at the VE-derived carbocation and the oxirane-derived oxonium ion, respectively, are favored over the homopropagation reactions. The homopropagation of ketone does not occur; hence, the ketone-derived carbocation exclusively reacts with the VE monomer regardless of solvent polarity.

Table 6. Cationic Terpolymerization of VE, VCHO, and Ketone: Effects of Temperature and Solvents[a]

	monomer						conv (%)					units per acetal[e]		
entry	VE	oxirane	ketone	solvent	temp (°C)	time	VE[b]	VCHO[b]	ketone[c]	$M_n \times 10^{-3}$ [d] [$M_n \times 10^{-3}$ (hydrolysis)]	M_w/M_n[d]	VE	VCHO	ketone
1	IPVE	VCHO	MEK	CH_2Cl_2	–78	30 min	63	60	5	30.2 [0.8]	1.90	8.2	2.0	0.98
2				CH_2Cl_2	–100	3 h	45	78	6	19.8 [0.6]	1.94	5.9	2.1	1.0
3				toluene	–78	4 h	68	87	10	29.1 [0.5]	1.82	4.5	1.5	1.0
4				hex/CH_2Cl_2 (8/2 v/v)	–78	1 h	60	82	9	15.6 [0.6]	1.68	4.7	1.7	1.0_6
5	EVE	VCHO	MEK	CH_2Cl_2	–78	2 h	16	74	6	13.1 [0.4]	1.97	1.9	2.1	1.0
6				CH_2Cl_2	–100	3 h	15	77	6	10.3 [0.4]	2.18	1.4	2.2	1.0
7				toluene	–78	2.5 h	19	78	9	9.9 [0.3]	1.95	1.4	1.5	1.0_5
8				toluene	–100	2.5 h	20[c]	89	11	17.3 [0.3]	1.74	1.2	1.4	1.0
9	EVE	VCHO	CHxK	CH_2Cl_2	–78	2 h	19	78	8	19.9 [0.3]	1.84	1.6	1.7	1.1
10				CH_2Cl_2	–100	3 h	5	65	6	13.9 [0.3]	1.97	1.3	2.4	1.4
11	DHF	VCHO	MEK	CH_2Cl_2	–78	3.5 h	6	50	3	5.1 [0.4]	2.78	1.8	2.9	1.2
12				toluene	–78	8 h	31	79	9	11.9 [0.3]	2.19	1.7	1.6	1.1

[a] $[VE]_0 = 0.80$ M, $[VCHO]_0 = 0.20$ M, $[ketone]_0 = 1.2$ M, $[B(C_6F_5)_3]_0 = 1.0$ (entries 1, 3, 4, 5, 7, 9, 11, and 12) or 3.0 (entries 2, 6, 8, and 10) mM. Entries 1, 5, and 11 correspond to entries 1, 2, and 7 in Table 1, respectively. See Figures S16 for MWD curves of entries 6, 7, and 12. [b] Determined by GC. [c] Determined from the VCHO conversion value by GC and the integral ratio of NMR spectra of product polymers. [d] Determined by GPC (polystyrene standards). [e] Estimated by ^{1}H NMR analysis. The values correspond to the numbers of monomer units per block when terpolymerization proceeds via a one-way cycle of crossover reactions.

ABC Pseudo-Periodic Sequence Control Under the Optimized Conditions

Based on the results obtained above, the terpolymerization was conducted under the optimized conditions. EVE, VCHO, and MEK were selected as the appropriate monomers. The polymerization in toluene at –100 °C proceeded smoothly, yielding a polymer with an M_n of 17.3 × 10^{-3} (entry 8 in Table 6; Figure 3). The product obtained by hydrolysis of the terpolymer had a very sharp low-MW peak in the GPC trace (purple curve in Figure 3),[49] which suggests that the original polymer was generated via very frequent crossover reactions. Indeed, the EVE/VCHO/MEK units per acetal were estimated to be 1.2/1.4/1.0 from ^{1}H NMR analysis (Figure 4; see Figure S18 for ^{13}C NMR), indicating that the terpolymer has an ABC pseudo-periodic sequence.

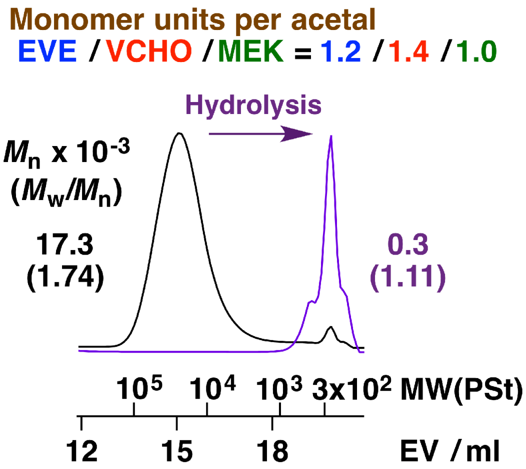


Figure 3. MWD curves of EVE–VCHO–MEK terpolymer produced in toluene at –100 ºC (black; entry 8 in Table 6) and the product obtained by acid hydrolysis of the terpolymer (purple) ($[EVE]_0$ = 0.80 M, $[VCHO]_0$ = 0.20 M, $[MEK]_0$ = 1.2 M, $[B(C_6F_5)_3]_0$ = 3.0 mM, in toluene at –100 ºC).

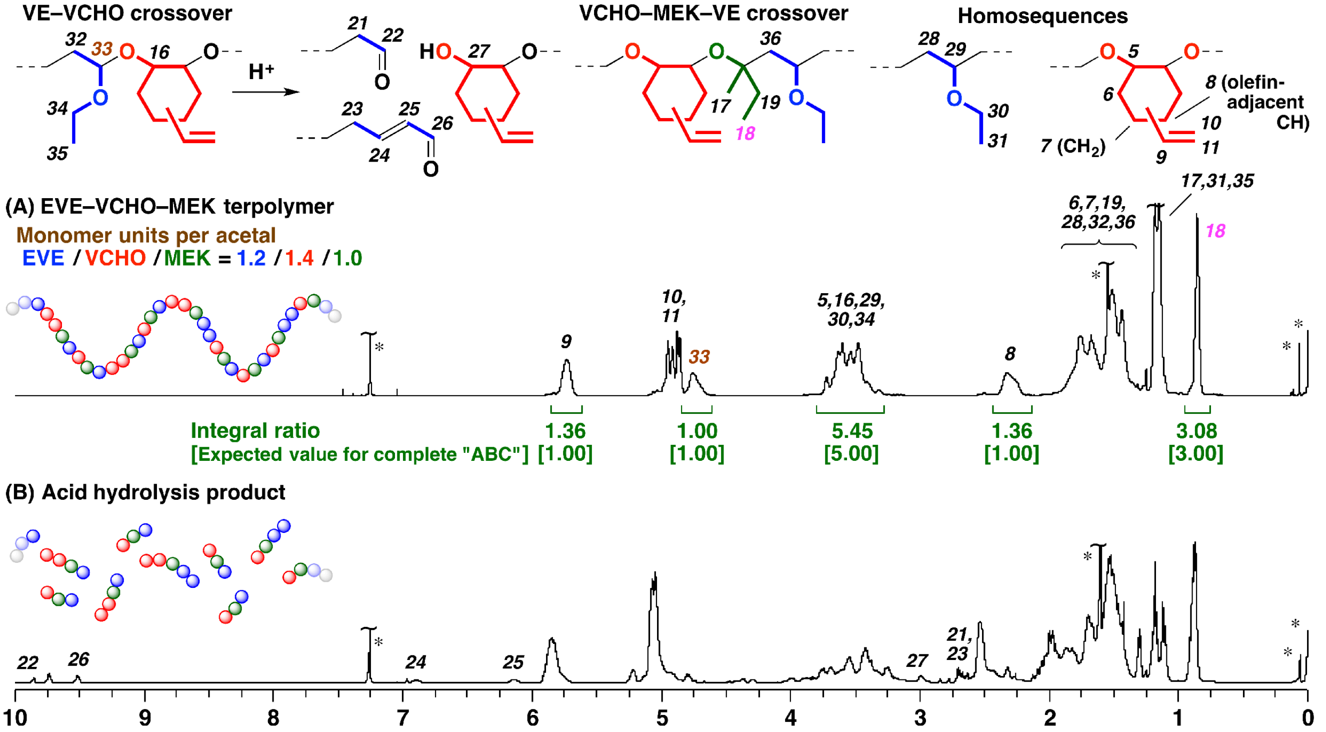
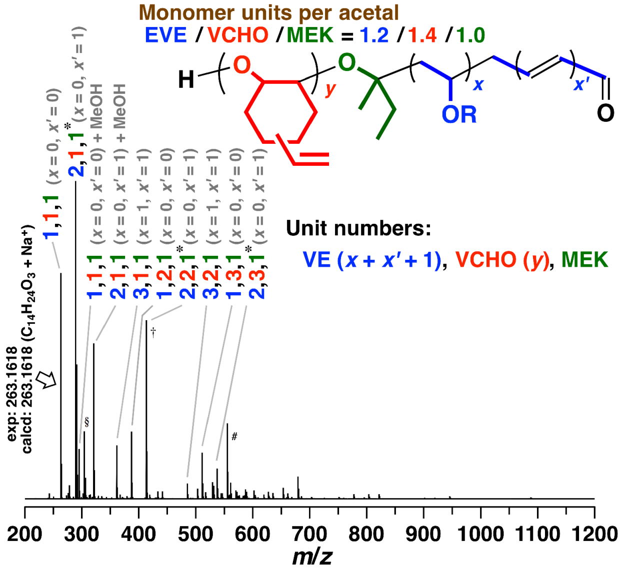


Figure 4. ^{1}H NMR spectra of (A) EVE–VCHO–MEK terpolymer produced in toluene at –100 ºC (entry 8 in Table 6; Figure 3) and (B) the product obtained by acid hydrolysis of the terpolymer (see the caption of Figure 3 for the polymerization conditions; in $CDCl_3$ at 30 ºC; * TMS, grease, water, or $CHCl_3$).

The monomer sequences in the terpolymer were analyzed by ESI-MS of the hydrolysis product. The hydrolysis products have structures corresponding to the constitutional repeating units of the original terpolymer as a result of the cleavage of the acetal moieties derived from the crossover reactions from VE to oxirane. Several major peaks were detected in the analysis, as shown in Figure 5A.[50] All these peaks were confidently assigned to structures consisting of EVE, VCHO, and MEK monomers. The numbers of EVE/VCHO/MEK, such as 1/1/1, 2/1/1, 1/2/1, and 1/3/1, correspond to the number of monomer units in the constitutional repeating units of the original terpolymer. In addition, the spectrum is dramatically different from the spectrum of the hydrolysis product of the terpolymer with IPVE/VCHO/MEK block lengths of 8.2/2.0/0.98 (Figure 5B). In the latter spectrum, the peaks were in a substantially higher *m*/*z* region than that from the optimized product. Thus, the crossover reactions appeared to occur more frequently in the terpolymerization under the optimized conditions. Only a single peak assigned to “1/1/1” will be observed in an ESI-MS spectrum when complete

ABC-type periodic terpolymerization is achieved.


(A) Hydrolysis product of EVE–VCHO–MEK terpolymer

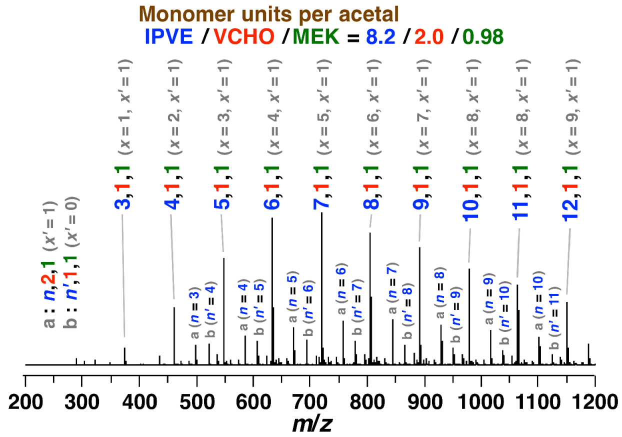

(B) Hydrolysis product of IPVE–VCHO–MEK terpolymer

Figure 5. ESI–MS spectra of the products obtained by hydrolysis of (A) EVE–VCHO–MEK terpolymer (entry 8 in Table 6; Figure 3) and (B) IPVE–VCHO–MEK terpolymer (entry 1 in Table 1; Figure 1A) (see the caption of Figure 3 and the footnote of Table 1 for the polymerization conditions). The numbers in blue, red, and green correspond to monomer units of VE, VCHO, and MEK, respectively, in a repeating constitutional unit of the original terpolymers. See note 50 for peaks with an asterisk. † A contaminated plasticizer (dioctyl phthalate [$C_{24}H_{38}O_3$]) has the same *m*/*z* value to this peak. # This peak ($C_{32}H_{52}O_6$) is not assigned suitably. § This peak is likely assigned to contamination. The same peak existed in the spectrum of the solvents.

Conclusion

The effective monomers and reaction conditions for suppressing the homopropagation reactions of VE and oxirane in the cationic terpolymerization of VE, oxirane, and ketone via a one-way cycle of crossover reactions were investigated. The use of VEs and oxiranes with moderate but sufficient reactivities was important both for suppressing the homopropagation reactions and achieving efficient crossover reactions. In addition, conducting the reaction in less polar solvents, such as toluene, at lower temperatures resulted in more frequent crossover reactions. Based on the screening of these factors, an ABC pseudo-periodic terpolymer was generated from the terpolymerization of EVE, VCHO, and MEK in toluene at –100 °C. More elaborate designs in terms of both monomers, such as non-homopolymerizable monomers with very high crossover reactivity, and reaction conditions is required for complete ABC-type periodic control, which will be investigated by our group. Furthermore, the strategy developed in this study, i.e., selective crossover reactions based on the nature of the propagating species and the resulting sequences, is expected to be applicable to sequence control via the chain-growth polymerization of various types of monomers.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxx

NMR spectra and polymerization data (PDF)

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Notes

The authors declare no competing financial interest.

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49. The MWD curve of the hydrolysis product had a trimodal shape. The main peak corresponds to an MW of 200–300 and the peak at the higher-MW region corresponds to an MW of approximately 500 (see Figure S17 for the comparison with the peaks of polystyrene standards). This shape and the MW values are consistent with the ESI-MS spectrum (Figure 5A). Thus, the GPC analysis likely gave a reasonable result without adsorption to columns.

50. The ether bond between VCHO and MEK units (an ether with secondary and tertiary alkyl groups) is potentially cleaved under acidic conditions. If this occurs, peaks with *m*/*z* values of H–VCHO$_n$–OH are detected in the ESI-MS analysis. However, peaks with an asterisk in Figure 5A have the same *m*/*z* values to those of H–VCHO$_n$–OH (n = 2, 3, and 4 for the peaks of 2/1/1 [$C_{16}H_{26}O_3$], 2/2/1 [$C_{24}H_{38}O_4$], and 2/3/1 [$C_{32}H_{50}O_5$] units of EVE/VCHO/MEK, respectively; the second one also overlaps with a peak of a contaminated plasticizer). Thus, it is difficult to judge whether such ether cleavages occurred or not.

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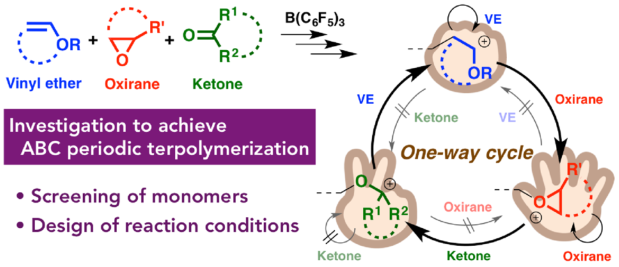

ABC Pseudo-Periodic Sequence Control by Cationic Orthogonal Terpolymerization of Vinyl Ether, Oxirane, and Ketone

Maki Mimura, Arihiro Kanazawa, and Sadahito Aoshima**