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Controlled Cationic Copolymerization of Vinyl Monomers and Cyclic Acetals via Concurrent Vinyl-Addition and Ring-Opening Mechanisms: The Systematic Study of Structural Effects on the Copolymerization Behavior

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The effects of the structure of cyclic acetals on their copolymerization with vinyl ethers (VEs) via concurrent vinyl-addition and ring-opening mechanisms were revealed through a systematic study using five-, six-, and seven-membered cyclic acetals with no substituents or one or two methyl substituents. The controlled cationic copolymerization of 2-chloroethyl vinyl ether (CEVE) and various cyclic acetals successfully proceeded in a living manner. Importantly, the copolymerization times (10 s—70 h) and the sequences of the copolymers (multiblock, random, or approximately alternating) significantly differed depending on the cyclic acetal used. An increase in the number of methyl substituents at the 2-position of the cyclic acetal improved the stability of the generated carbocation, which led to copolymerization with both frequent crossover reactions and at high polymerization rates. The ring member was responsible for the amount of ring strain and its Lewis basicity, which were also related to the frequency of the crossover reactions and the polymerization rates. The controlled copolymerization of cyclic acetals with isobutyl vinyl ether, which is a more reactive VE than CEVE, also proceeded, and the frequencies of the crossover reactions were lower. The key factors affecting the crossover reactions are discussed on the basis of the reactivities of the vinyl monomers and cyclic acetals.

Introduction

The structures of polymerizable monomers have a considerable influence on their polymerizability and the properties of the resulting polymers. The rational design of the propagating species based on the monomer structures is also of great importance for controlling the primary structure, including the molecular weight, chain end, and tacticity, of the resulting polymer. In addition, the polymerization of more than one monomer enables the precise synthesis of polymers with various structures, such as block, gradient, graft, and star-shaped polymers.[1-6] The copolymerization of different types of monomers, such as vinyl and cyclic monomers,[7-14] is an attractive method for synthesizing materials with novel functions that cannot be achieved in homopolymers or copolymers from similar types of monomers. However, the copolymerization of different types of monomers is inherently challenging because of the differences in the active species generated during the polymerization. Understanding the copolymerization mechanism based on systematic studies is expected to provide guidelines for designing propagating species derived from different types of monomers.

In the concurrent cationic vinyl-addition and ring-opening copolymerization, the generation of the carbocation through the ring-opening of the oxonium ion is critical because the oxonium ion species derived from the oxirane does not react with the vinyl monomer.[14] In our previous work, oxiranes, such as isobutylene oxide and isoprene monoxide, which generate tertiary and resonance-stabilized carbocations, respectively, by the ring-opening reactions of the oxonium ion, were demonstrated to efficiently copolymerize with isopropyl vinyl ether (VE) using $B(C_6F_5)_3$ as a Lewis acid catalyst. Moreover, the copolymerization of IPVE with alkoxyoxirane, which is a cyclic monomer that generates an alkoxy group-adjacent, VE-type carbocation via a ring-opening, proceeded efficiently despite the fact that the copolymerization involved an intramolecular alkoxy group transfer.[15] Long-lived propagating species were also generated in the latter case, which is partly due to the structural similarities between the active species derived from the alkoxyoxirane and VE.

Cyclic acetals also generate an alkoxy group-adjacent carbocation through ring-opening reactions. Indeed, conventional cationic copolymerizations of VEs or styrene with cyclic acetals were reported several decades ago.[7,8] Recently, we have achieved a controlled cationic copolymerization of 2-chloroethyl VE (CEVE) with 1,3-dioxepane (DOP) or 2-methyl-1,3-dioxolane (MDOL) using a carefully selected initiating system based on the living cationic polymerization of vinyl

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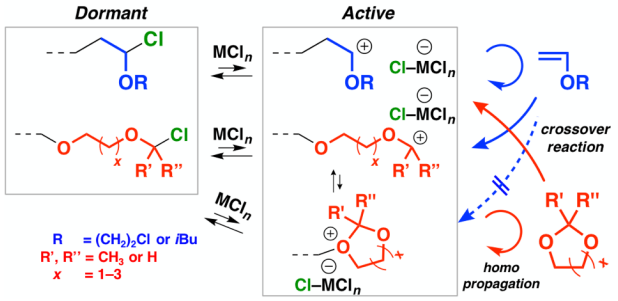
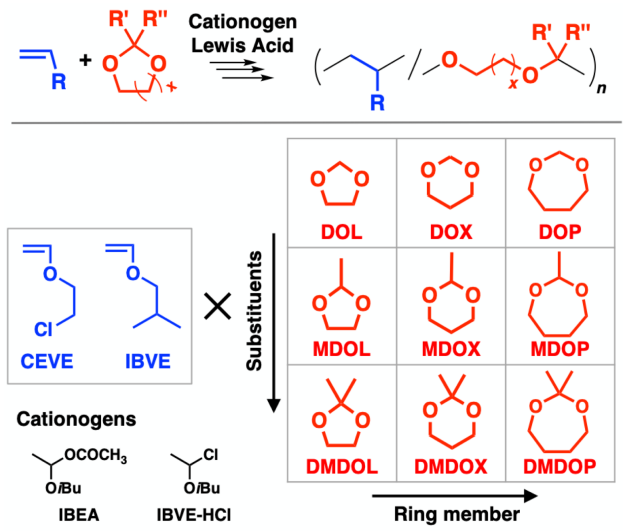
† Electronic Supplementary Information (ESI) available: Polymerization data and NMR spectra. See DOI: 10.1039/x0xx00000x

monomers.[16] The reversible activation–deactivation reaction of the carbon–chlorine bond at the propagating chain end was most likely required for achieving the appropriate dormant–active equilibrium (Scheme 1).



Scheme 1 Possible mechanisms of controlled cationic copolymerization of vinyl monomers and cyclic acetals



Scheme 2 Concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl monomers and cyclic acetals.

In this study, we aimed to synthesize various controlled copolymers and systematically investigate the effects of the structures of cyclic acetals on their polymerization behaviors. Cyclic acetals are prepared by the acetalization or the acetal exchange from the corresponding diols with carbonyl compounds or acetals, respectively;[17] hence, we first synthesized five-, six-, and seven-membered cyclic acetals with no substituents or one or two methyl substituents at the 2-position; the five- and unsubstituted six-membered cyclic acetals were obtained commercially (Scheme 2). The as-prepared cyclic acetals were used for the cationic copolymerization with CEVE. The copolymerizations of vinyl monomers and various cyclic acetals proceeded in a controlled manner using a suitably designed initiating system. Based on the results of the systematic copolymerizations, we discuss the effects of the number of substituents at the 2-position and the ring member, which are related to the stabilities of the generated carbocation and the ring strain, respectively, of the cyclic acetals on the polymerization rates and the frequencies of the crossover reactions.

Experimental

Materials

2-Chloroethyl VE (CEVE; TCI; >97.0%) and isobutyl VE (IBVE; TCI; >99.0%) were washed with sodium hydroxide solution and then water, and distilled twice over calcium hydride under reduced (CEVE) or at atmospheric (IBVE) pressure. 1,3-Dioxolane (DOL; TCI; >98.0%), 2,2-dimethyl-1,3-dioxolane (DMDOL; TCI; >98.0%), 1,3-dioxane (DOX; TCI; >98.0%), ethyl acetate (Wako; >99.5%), and heptane (Nacalai Tesque; >99.0%) were distilled twice over calcium hydride. 1,3-Dioxepane (DOP) was synthesized via the reaction of 1,4-butanediol (TCI; >99.0%) and paraformaldehyde (Sigma-Aldrich; 95%) according to a previously reported procedure.[18] 2-Methyl-1,3-dioxolane (MDOL; TCI; >98.0%) was distilled over calcium hydride and then lithium aluminum hydride. 2,6-Di-*tert*-butylpyridine (DTBP; Wako; 97%) was distilled twice over calcium hydride under reduced pressure. The adducts of IBVE with HCl (IBVE–HCl) or acetic acid (IBEA) were prepared from the addition reactions of IBVE and HCl or acetic acid, respectively.[19,20] $TiCl_4$ (Sigma-Aldrich; 1.0 M solution in toluene), $SnCl_4$ (Sigma-Aldrich; 1.0 M solution in heptane), and 3-buten-1-ol (TCI; >98.0%) were used without further purification. Toluene (Wako; 99.5%), dichloromethane (Wako; 99.0%), and hexane (Wako; >96.0%) were dried by passage through solvent purification columns (Glass Contour). All chemicals except for toluene, dichloromethane, hexane, and 3-buten-1-ol were stored in brown ampules under dry nitrogen.

Synthesis of 2-methyl-1,3-dioxane (MDOX), 2,2-dimethyl-1,3-dioxane (DMDOX), 2-methyl-1,3-dioxepane (MDOP), and 2,2-dimethyl-1,3-dioxepane (DMDOP)

The six- and seven-membered methyl and dimethyl cyclic acetals were synthesized by acetal exchange between the corresponding acetal and diol using indium (III) trifluoromethanesulfonate as a catalyst at room temperature.[17] After the acetal exchange, the reaction mixture was concentrated to remove ethanol or methanol, which was generated as a byproduct. The product was purified by distillation under reduced pressure (see Fig S1 and S2 for ^{1}H and ^{13}C NMR spectra).

2-Methyl-1,3-dioxane (MDOX)

Synthesized from diethylacetal (60 g) and 1,3-propanediol (40 g). Colorless liquid. Isolated yield: 28%. ^{1}H NMR ($CDCl_3$; 500MHz): δ 4.68 (1H, q), 4.11-4.07 (2H, m), 3.80-3.75 (2H, m), 2.12-2.02 (1H, m), 1.35-1.31 (1H, m), 1.30 (3H, d). ^{13}C NMR ($CDCl_3$; 125MHz): δ 99.4, 67.0, 25.7, 21.4. MS (ESI) *m/z* $[M+Na]^+$, calcd: 125.0537, found: 125.0537.

Table 1 Cationic Copolymerization of CEVE and Various Cyclic Acetals[a]

				conv[b] (%)				crossover per chain[d]		units per block[d]	
entry	vinyl	cyclic	time	vinyl	cyclic	$M_n \times 10^{-3}$ [c]	M_w/M_n[c]	V to A[e]	A to V[e]	vinyl	cyclic
1	CEVE	DOL	27 h	100	18(0[f])	11.5	1.10	—	—	—	—
2	—	DOL	48 h	—	22	1.5	3.68	—	—	—	—
3	CEVE	MDOL	70 h	60	31	5.2	1.37	30	25	2.7	0.98
4	—	MDOL	24 h	—	7	—	—	—	—	—	—
5	CEVE	DMDOL	30 s	36	11	3.2	1.33	11	11	2.1	0.96
6			13 min	75	34	9.9	1.19	59	59	2.5	0.96
7	—	DMDOL	10 min	—	0	—	—	—	—	—	—
8	CEVE	DOX	2 h	32	18(0[f])	3.1	1.10	—	—	—	—
9	—	DOX	96 h	—	15	—	—	—	—	—	—
10	CEVE	MDOX	2 h	68	24	7.2	1.19	21	21	5.1	1.0
11	—	MDOX	5 h	—	19	—	—	—	—	—	—
12	CEVE	DMDOX	30 s	84[f]	65[f]	16.5	1.85	74	74	1.3	1.0
13	—	DMDOX	49 h	—	37	—	—	—	—	—	—
14	CEVE	DOP	44 h	71	92	11.2	1.84	9.0	13	8.3	12
15	—	DOP	24 h	—	23	4.2	1.69	—	—	—	—
16	CEVE	MDOP	4 h	61	62	6.8	1.65	33	37	1.5	1.7
17	—	MDOP	4 h	—	29	0.3	1.58	—	—	—	—
18	CEVE	DMDOP	30 s	91[f]	72	15.6	1.41	66	66	1.7	0.92
19	—	DMDOP	24 h	—	22	—	—	—	—	—	—
20	CEVE	—	30 s	94	—	11.5	1.15	—	—	—	—

[a] $[CEVE]_0$ = 0 or 0.40 M, $[cyclic\ acetal]_0$ = 0 or 0.40 M, $[IBEA]_0$ = 4.0 mM, $[TiCl_4]_0$ = 5.0 mM, $[SnCl_4]_0$ = 20 mM, $[DTBP]_0$ = 10 mM, [ethyl acetate] = 20 mM in toluene/dichloromethane (9/1 v/v) at –78 °C. [b] Determined by gas chromatography. [c] Determined by GPC (polystyrene standards). [d] Estimated by ^{1}H NMR analysis. [e] V: vinyl monomer; A: cyclic acetal. [f] Determined by gravimetry and ^{1}H NMR analysis of products.

2,2-Dimethyl-1,3-dioxane (DMDOX)

Synthesized from 2,2-dimethoxypropane (54 g) and 1,3-propanediol (42 g). Colorless liquid. Isolated yield: 29%. ^{1}H NMR ($CDCl_3$; 500MHz): δ 3.91 (4H, dd), 1.70 (2H, m), 1.43 (6H, s). ^{13}C NMR ($CDCl_3$; 125MHz): δ 98.2, 60.3, 25.9, 24.6. MS (ESI) *m/z* $[M+Na]^+$, calcd: 139.0730, found: 139.0729.

2-Methyl-1,3-dioxepane (MDOP)

Synthesized from diethylacetal (126 g) and 1,4-butanediol (99 g). Colorless liquid. Isolated yield: 48%. ^{1}H NMR ($CDCl_3$; 500MHz): δ 4.90 (1H, q), 3.90-3.60 (4H, m), 1.76-1.65 (4H, m), 1.28 (3H, d). ^{13}C NMR ($CDCl_3$; 125MHz): δ 99.5, 65.4, 29.3, 20.8. MS (ESI) *m/z* $[M+Na]^+$, calcd: 139.0730, found: 139.0729.

2,2-Dimethyl-1,3-dioxepane (DMDOP)

Synthesized from 2,2-dimethoxypropane (107 g) and 1,4-butanediol (102 g). Colorless liquid. Isolated yield: 49%. ^{1}H NMR ($CDCl_3$; 500MHz): δ 3.68 (4H, m), 1.60 (4H, m), 1.33 (6H, s). ^{13}C NMR ($CDCl_3$; 125MHz): δ 101, 62.3, 29.8, 25.2. MS (ESI) *m/z* $[M+Na]^+$, calcd: 153.0886, found: 153.0885.

Polymerization procedure

The following is a typical polymerization procedure with the IBEA/$TiCl_4$/$SnCl_4$ initiating system. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; at 450 °C) under dry nitrogen. Dichloromethane, toluene, heptane or hexane (as an internal standard for gas chromatography), ethyl acetate, a solution of DTBP in dichloromethane, and a solution of IBEA in hexane were added into the tube using dry medical syringes. After cooling the solution to 0 °C for 10 min, a solution of $TiCl_4$ in toluene was added to the tube. After 15 min, the solution was cooled to −78 °C. The polymerization was started by sequentially adding a solution of $SnCl_4$ in toluene and a mixture of CEVE and cyclic acetals to the tube. After a predetermined interval, the reaction was terminated with methanol or 3-buten-1-ol containing a small amount of aqueous ammonia or triethylamine, respectively. The quenched mixture was diluted with dichloromethane and washed with water. The volatiles were then removed under reduced pressure at 50 °C to yield the polymer. The monomer conversion was determined by gas chromatography (or by gravimetry and ^{1}H NMR spectroscopy for some reactions).

Acid hydrolysis

The acid hydrolysis of the copolymers was conducted using 1.0 M HCl(aq) in 1,2-dimethoxyethane at room temperature over 3 h (sample: 0.5 wt%). The quenched mixture was diluted with dichloromethane and washed with aqueous sodium hydroxide and then water. The volatiles were removed at ordinary temperature and normal pressure.

Characterization

The molecular weight distributions (MWDs) of the obtained polymers were measured via gel permeation chromatography (GPC) in chloroform at 40 °C on polystyrene gel columns (TSKgel GMH_{HR}-M × 2 with an 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^{-1}) 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 the polydispersity ratio (weight-average molecular weight/number-average molecular weight [M_w/M_n]) were calculated from the chromatographs based on 16 polystyrenes standards (Tosoh; M_n = 577—1.09 × 10^6, M_w/M_n ≤ 1.1). NMR spectra were recorded using a JEOL JNM-ECA 500 (500.16 MHz for ^1H and 125.77 MHz for ^{13}C) spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analyses were performed on a Shimadzu/Kratos AXIMA-Performance spectrometer (linear mode) using dithranol as a matrix and sodium trifluoroacetate as an ion source. Electrospray ionization mass spectra (ESI-MS) were recorded using a LTQ Orbitrap XL (Thermo Scientific) spectrometer.

Results and discussion

Controlled cationic copolymerization of CEVE and various cyclic acetals

Initially, the cationic copolymerization of DMDOL, which has two methyl substituents at the 2-position, with CEVE was conducted using an IBEA/$TiCl_4$/$SnCl_4$ initiating system in the presence of ethyl acetate and DTBP at –78 °C. Ethyl acetate was used as a Lewis basic additive to both suppress side reactions by stabilizing the growing carbocation and adjust the dormant–active equilibrium through the interaction with Lewis acid catalysts.[21] DTBP was employed as a proton trap reagent to suppress chain transfer reactions caused by adventitious water.[22,23] This initiating system was designed based on the living cationic polymerization of CEVE (entry 20 in Table 1).[24] In our previous study, DOL, which is unsubstituted at the 2-position, did not copolymerize with CEVE, while the copolymerization of CEVE and MDOL, which has one methyl substituent, proceeded in a highly controlled manner.[16] DMDOL also copolymerized with CEVE very efficiently to yield copolymers with unimodal MWDs (Fig. 1C). Interestingly, the copolymerization of DMDOL proceeded approximately 10^3-times faster than the reaction of MDOL, suggesting that the substituents at the 2-position significantly affected the polymerization behavior. The sharp MWD peaks (M_w/M_n = 1.2—1.3) of the obtained copolymers shifted to the high-molecular-weight region as the polymerization proceeded, indicating the generation of the long-lived propagating species. Moreover, the M_n values measured by GPC analysis were consistent with the values calculated from the conversions of the two monomers (Fig. 1B). These results suggest that the cationic copolymerization of CEVE and DMDOL proceeded in a highly controlled manner.

^1H NMR analysis of the copolymer of CEVE and DMDOL revealed the occurrence of frequent crossover reactions (Fig. 2, see Fig. S3–S6 for ^{13}C NMR and 2D NMR spectra). The peak at 4.9 ppm (peak 6) was assigned to the acetal proton derived from the crossover reaction from CEVE to DMDOL. However, the peaks assigned to the structure derived from the crossover from DMDOL to CEVE (peaks 9, 10) overlapped with peaks of the CEVE units at 3.4 ppm. The integral of the methyl peak at 1.2 ppm (peak 11) derived from DMDOL was almost six times that of the acetal peak (peak 6), indicating the

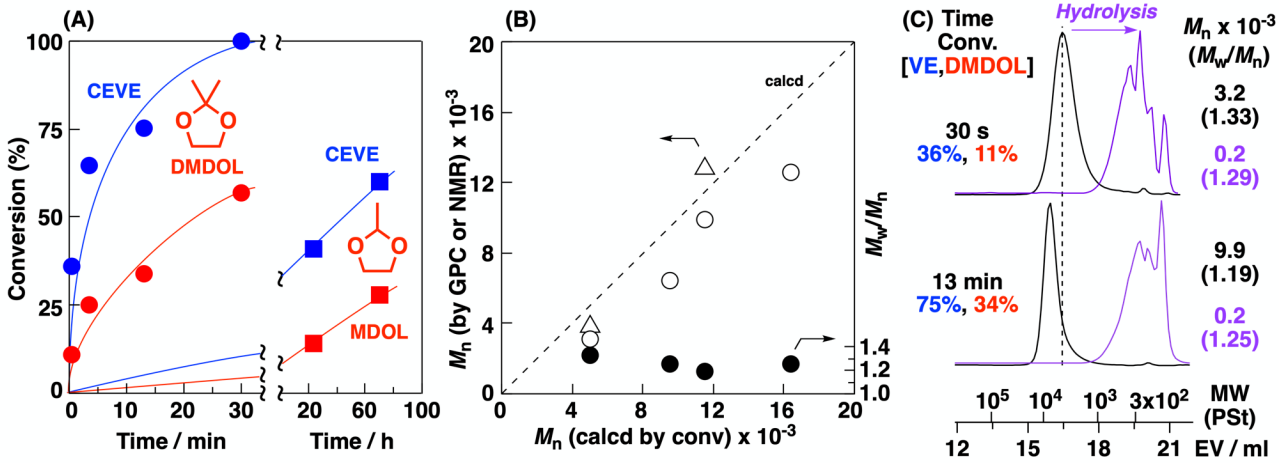


Fig. 1 (A) Time–conversion curves for the copolymerization of CEVE and DMDOL (circle) or MDOL (square), (B) the M_n determined by GPC (circle) or NMR (triangle; calculated from the integral ratios of the peaks of the main chain and the ω-ends) and M_w/M_n (filled) values of poly(CEVE-*co*-DMDOL)s, and (C) MWD curves of poly(CEVE-*co*-DMDOL)s (black) and acid hydrolysis products (purple). Polymerization conditions: $[CEVE]_0$ = 0.40 M, $[DMDOL]_0$ = 0.40 M, $[IBEA]_0$ = 4.0 mM, $[TiCl_4]_0$ = 5.0 mM, $[SnCl_4]_0$ = 20 mM, [ethyl acetate] = 20 mM,

$[DTBP]_0$ = 10 mM, in toluene/dichloromethane (9/1 v/v) at –78 °C. Hydrolysis conditions: 1.0 M HCl in 1,2-dimethoxyethane (0.5 wt% polymer) at room temperature for 3 h. The data correspond to entries 3, 5 and 6 in Table 1 and entry 3 in Table S1. The time–conversion curves were drawn by connecting the data points (not based on calculation).

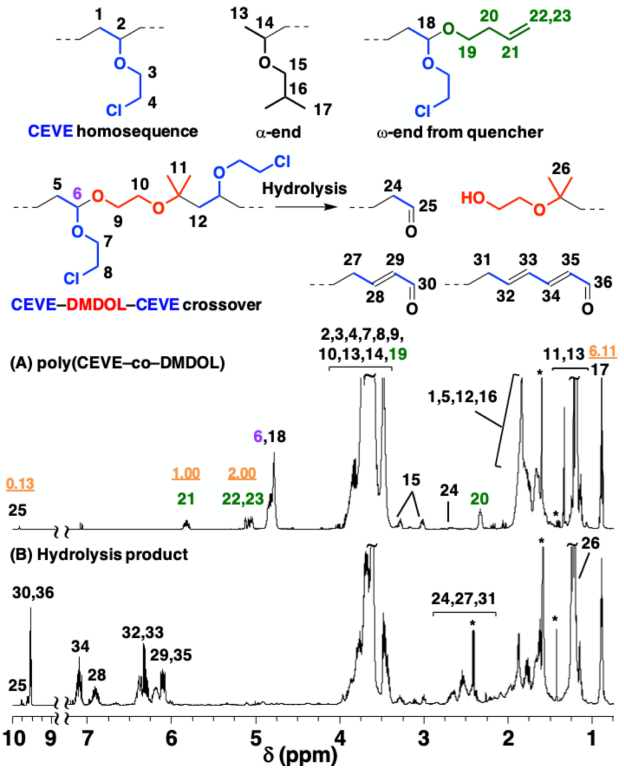


Fig. 2 ^{1}H NMR spectra of (A) poly(CEVE-*co*-DMDOL) (entry 5 in Table 1) and (B) the hydrolysis product (in $CDCl_3$ at 30 °C; * water, grease, etc; number written in orange: integral ratio).

generation of long-lived species in the copolymerization. 3-Buten-1-ol was used as a quencher because the olefin moiety is easily distinguishable from the other peaks by ^{1}H NMR

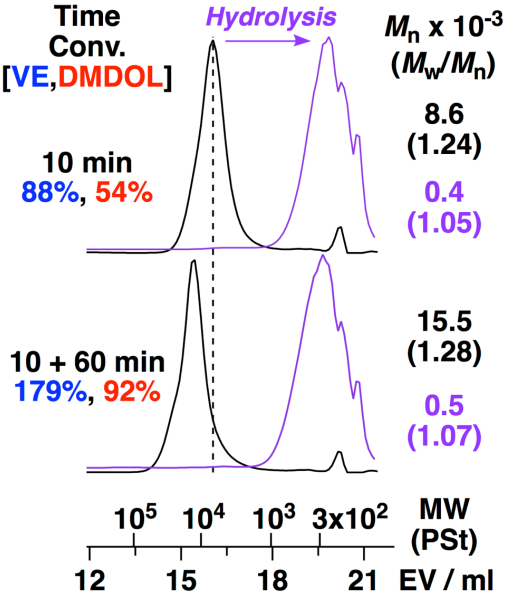


Fig. 3 MWD curves of poly(CEVE-*co*-DMDOL)s (black) and acid hydrolysis products (purple) obtained in the monomer-addition experiment. Polymerization conditions: $[CEVE]_0$ = $[CEVE]_{add}$ = 0.40 M, $[DMDOL]_0$ = 0.40 M, $[IBEA]_0$ = 4.0 mM, $[TiCl_4]_0$ = 5.0 mM, $[SnCl_4]_0$ = 20 mM, [ethyl acetate] = 20 mM, $[DTBP]_0$ = 10 mM, in toluene/dichloromethane (9/1 v/v) at –78 °C. Hydrolysis conditions: 1.0 M HCl in 1,2-dimethoxyethane (0.5 wt% polymer) at room temperature for 3 h.

homopropagation of DMDOL was negligible. This fact was also supported by the inefficient homopolymerization of DMDOL (entry 7 in Table 1). The numbers of crossover reactions from CEVE to DMDOL per chain were calculated to be 11 and 59 for the copolymers obtained after 30 s and 13 min, respectively (entries 5 and 6 in Table 1). The average numbers of CEVE/DMDOL monomer units per block were calculated to be 2.1/0.96 (30 s) and 2.5/0.96 (13 min) (the numbers of DMDOL units per block were less than one due to acceptable error), which suggests that the crossover reactions occurred at similar frequency regardless of monomer conversion.

The copolymerization via crossover reactions was corroborated by acid hydrolysis (by HCl in 1,2-dimethoxyethane; see the experimental part) of the obtained copolymer. In the ^{1}H NMR spectrum of the acid hydrolysis product (Fig. 2B), the signals from the acid-labile acetal structures generated via the crossover reaction from CEVE to DMDOL (peak 6) had disappeared, and instead, aldehyde peaks at 9.5 and 9.8 ppm (peaks 25, 30, and 36) emerged.[16,25–29] Moreover, the hydrolysis products had much lower M_n values (0.2×10^3) than the original copolymers regardless of the monomer conversion, which supports the frequent occurrence of crossover reactions (Fig. 1C).

The introduction of the structures derived from the quencher was confirmed by chain-end analysis, indicating the analysis. The peaks at 2.3, 5.1 and 5.8 ppm (peaks 20, 22, 23 and 21) were assigned to the fragment derived from 3-buten-1-ol. A very small peak assigned to an aldehyde moiety (peak 25), which was generated from the reaction of the CEVE-derived propagating carbocation with adventitious water, was also detected (Scheme S1). Based on the ratios of the integrals of these peaks, approximately 90% of the ω-ends stemmed from the quencher, indicating the copolymerization was highly controlled via an appropriate dormant-active equilibrium of the propagating chain ends. In addition, the sum of the integrals from 3-buten-1-ol (peak 21) and aldehyde (peak 25) agreed with that of the α-end structures derived from IBEA (peak 17). Moreover, the M_n value calculated from the ratios of the integrals of the peaks from the detectable ω-ends and the main chain (3.6×10^3) was comparable to the value obtained by GPC analysis (3.2×10^3; Fig. 1B). These facts suggest that most of the dormant species were derived from CEVE instead of DMDOL because the DMDOL-derived ω-ends are difficult to detect due to the instability of the structure formed after the reaction with the quencher.[2828] In addition, most of the ω-ends stemmed from the quencher at higher monomer conversions, indicating that side reactions negligibly occurred even at the late stage of the copolymerization. MALDI-TOF-MS analysis also suggested the generation of

copolymers with the fragments derived from the cationogen and the quencher (Fig. S7).

The livingness of the copolymerization of CEVE and DMDOL was also confirmed by a monomer addition experiment (Fig. 3). The unimodal and sharp MWD curves shifted to the high-molecular-weight region after the addition of a second portion

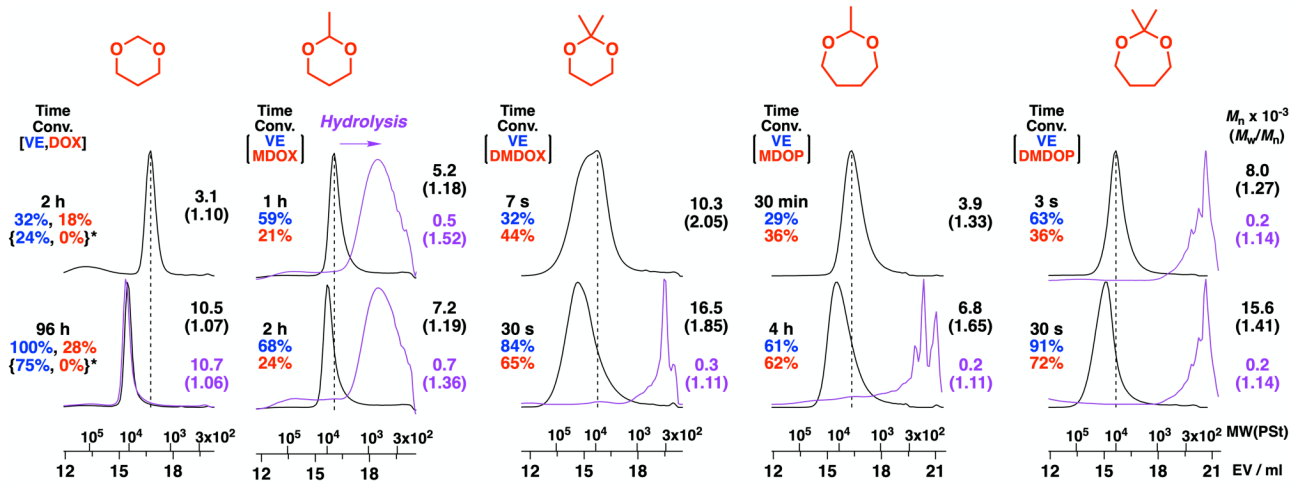


Fig. 4 MWD curves of poly(CEVE-*co*-cyclic acetal)s (black) and acid hydrolysis products (purple). Polymerization conditions: $[CEVE]_0$ = 0.40 M, [cyclic acetal]$_0$ = 0.40 M, $[IBEA]_0$ = 4.0 mM, $[TiCl_4]_0$ = 5.0 mM, $[SnCl_4]_0$ = 20 mM, [ethyl acetate] = 20 mM, $[DTBP]_0$ = 10 mM in toluene/dichloromethane (9/1 v/v) at –78 °C. Hydrolysis conditions: 1.0 M HCl in 1,2-dimethoxyethane (0.5 wt% polymer) at room temperature for 3 h; * monomer conversion values calculated from ^{1}H NMR and gravimetry. The data correspond to entries 8, 10, 12, 16, 18 in Table 1 and entries 6, 7, 9, 13, and 15 in Table S1

of CEVE late in the copolymerization reaction, indicating that the occurrence of side reactions such as chain transfer reactions was negligible.

Other cyclic acetals, except for DOL and DOX, were also successfully copolymerized with CEVE in a controlled manner (entries 10, 12, 14, 16 and 18 in Table 1 and entries 7, 9, 11, 13, and 15 Table S1; Fig. 4, see Fig. S8). MDOX, DMDOX, DOP, MDOP, and DMDOP were synthesized by acetalization or acetal exchange from 1,3-propandiol or 1,4-butandiol with paraformaldehyde, diethyl acetal, or 2,2-dimethoxypropane using an acid catalyst. In the copolymerizations of these cyclic acetals with CEVE, polymers with unimodal MWDs were produced under conditions similar to those used for MDOL and DMDOL. The peaks of the MWD curves shifted to higher molecular weights as the reactions progressed (Fig. 4). The molecular weights obtained by GPC analysis were consistent with the theoretical values. In addition, these M_n values increased linearly with increasing monomer conversion (Fig. S8B). The chain-end structures derived from the quencher were observed by ^{1}H NMR analysis (Table S2). The generation of low-MW compounds from the hydrolysis of the obtained copolymers indicated that acetal structures were introduced into the main chain by the crossover reaction from CEVE to the cyclic acetal (Fig. S8C).

The difference in the number of substituents at the 2-position and the ring member of the cyclic acetal had a remarkable influence on the polymerization rate and the frequencies of the crossover reactions in the copolymerization with CEVE (Fig. 5, left). Increasing the number of methyl groups at the 2-position resulted in an increase in the frequency of crossover reactions (e.g., CEVE/DOL: no copolymerization, CEVE/MDOL: 2.7/0.98 units per block, and CEVE/DMDOL: 2.1/0.96 units per block) and an acceleration of the copolymerization (e.g., MDOL: 40 h and DMDOL: 2 min, for 50% conversion of CEVE). The ring member also influenced the polymerization rate (e.g., MDOL: 40 h, MDOX: 1 h, and MDOP: 2 h, for 50% conversion of CEVE). The controlled copolymerization of six- (DMDOX) and seven-membered (DMDOP) analogues of DMDOL with CEVE also involved frequent crossover reactions (CEVE/DMDOX: 1.3/1.0 units per block and CEVE/DMDOP: 1.7/0.92 units per block) at very high rates (DMDOX: 7 s and DMDOP: 3 s, for 50% conversion of CEVE). Crossover reactions were also frequent in the copolymerizations of CEVE and cyclic acetals with one methyl group at the 2-position, although unlike MDOL and MDOX, homosequences were observed in the case of MDOP (CEVE/MDOL: 2.7/0.98 units per block, CEVE/MDOX = 5.1/1.0 units per block, CEVE/MDOP = 1.5/1.7 units per block).

The monomer reactivity ratios determined by the Kelen–Tüdõs method[29,30] (Table 2 and Fig. 6) were consistent with the frequencies of the crossover reactions. The decrease in the r_1 values was in agreement with the increase in the number of methyl substituents and indicates the crossover reaction is favored over homopropagation at the CEVE-derived propagating ends. The r_2 values of approximately zero in the cases of MDOL, DMDOL, MDOX, DMDOX and DMDOP are consistent with the nonhomopolymerizability of these cyclic acetals (Table 2).

Among the examined cyclic acetals, DOL, DOP and MDOP underwent homopolymerization under the conditions used in the copolymerizations (entries 2, 15, and 17 in Table 1). In the cases of DOL and DOP, long-lived species were generated, although the M_w/M_n values were relatively large (M_w/M_n =

1.7—3.7). The homopolymerization of MDOP gave oligomers (M_n = 0.3 × 10^3). The homopolymerizabilities of the other cyclic acetals were negligible (entries 4, 7, 9, 11, 13, and 19 in Table 1).

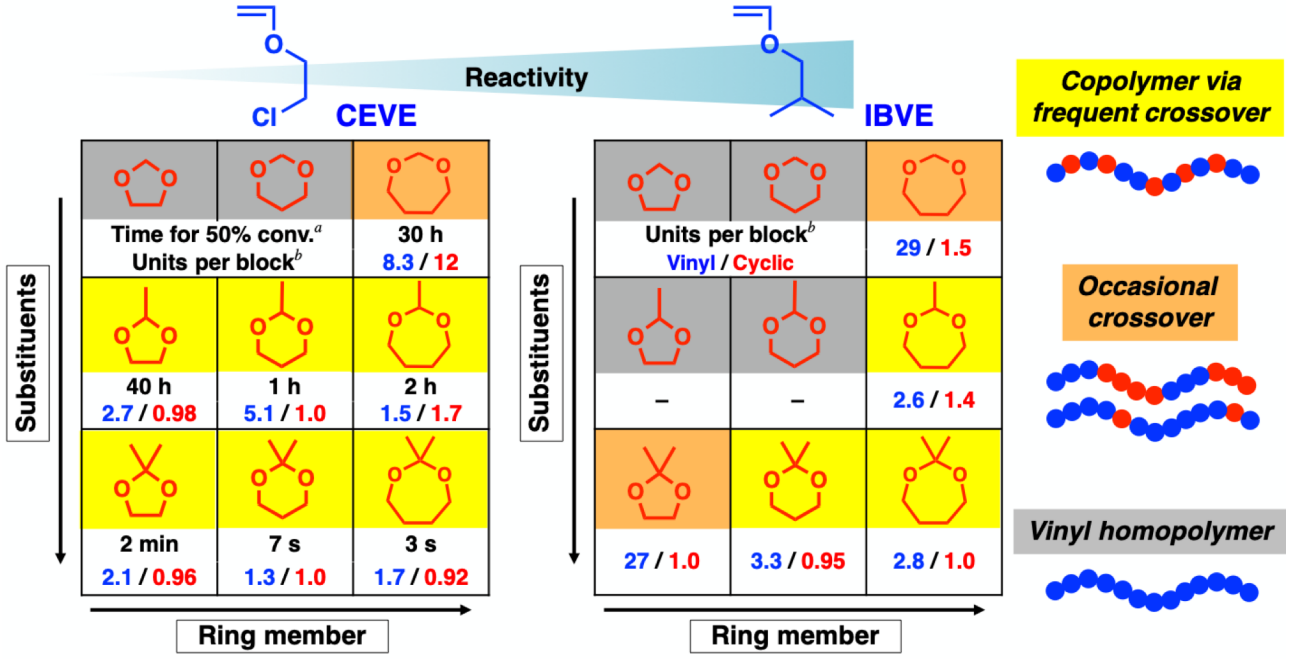


Fig. 5 Summary of the products obtained in the copolymerization of VEs and cyclic acetals ([a] Time for 50% conversion of CEVE. [b] Average numbers of VE (blue) and cyclic acetal (red) units per block).

Table 2 Monomer Reactivity Ratios[a]

M_1	M_2	r_1	r_2
CEVE	DOL	—	—
	MDOL	2.6[b]	0.06[b]
	DMDOL	1.4	0.01
	DOX	—	—
	MDOX	1.7	0.02
	DMDOX	0.32	0.09
	DOP	4.8[b]	18[b]
	MDOP	1.6	1.3
	DMDOP	0.58	0.01
IBVE	DMDOX	1.2	0.02
	MDOP	2.8	0.24
	DMDOP	2.0	0.07

[a] Determined by the Kelen–Tüdõs method. The values were calculated from the data shown in Fig. 6. The data used for the determination of the monomer reactivity ratios are shown in Fig. 6 (CEVE) and S13 (IBVE). [b] Values reported in reference 16.

Discussion of the effects of substituents at the 2-position and the ring member on the copolymerization behavior

The differences in the copolymerization behaviors, such as the polymerization rate and the frequency of the crossover reactions, most likely stemmed from several factors based on the structure of the cyclic acetals. The ring-opening reaction of cyclic acetals at the propagation step proceeds in the manner shown in Fig. 7. A cyclic acetal adds to the propagating species and subsequently forms an oxonium ion, which is then converted to a carbocation via a ring-opening reaction. In this reaction, the nucleophilicities of the cyclic acetals toward the propagating cationic species are primarily responsible for the addition of the cyclic acetal to the cation. Increasing the ring strain in the oxonium ion and the stability of the generated carbocation facilitate the ring-opening of the oxonium ion. Therefore, the number of substituents at the 2-position and the ring member of the cyclic acetal most likely affect the propagation reaction. The effects of these factors are discussed in the following sections.

(a) Effects of the number of methyl groups at the 2-position

The number of methyl groups at the 2-position of the cyclic acetal mainly influences the stability of the carbocation generated by the ring-opening reaction of the oxonium ion. Cyclic acetals with zero, one, or two substituents generate primary, secondary, or tertiary carbocations, respectively. The ring-opening of the oxonium ion occurs more efficiently when the generated carbocation is more stable (primary < secondary < tertiary), resulting in an acceleration of the copolymerization due to the facilitation of the crossover reaction to CEVE. This trend is consistent with the high reaction rates of the acid hydrolysis reactions of cyclic acetals with larger numbers of substituents at the 2-position.[31]

Crossover reactions were more frequent in the copolymerizations of cyclic acetals with larger numbers of methyl groups (Fig. 8) likely because the addition-ring elimination equilibrium of a cyclic acetal monomer forms at the propagating end derived from CEVE (Fig. 7). An inefficient ring-opening reaction, related to the instability of the

carbocation generated via the ring-opening, causes frequent elimination of the cyclic acetal from the propagating end, leading to an increase in the homopropagation of CEVE and decreasing the frequency of the crossover reaction to the cyclic acetal. The improvement in the stability of the carbocation generated by the ring-opening of the oxonium ion contributes to the decrease in the rate of the reverse reaction from the oxonium ion to the CEVE-derived carbocation, which

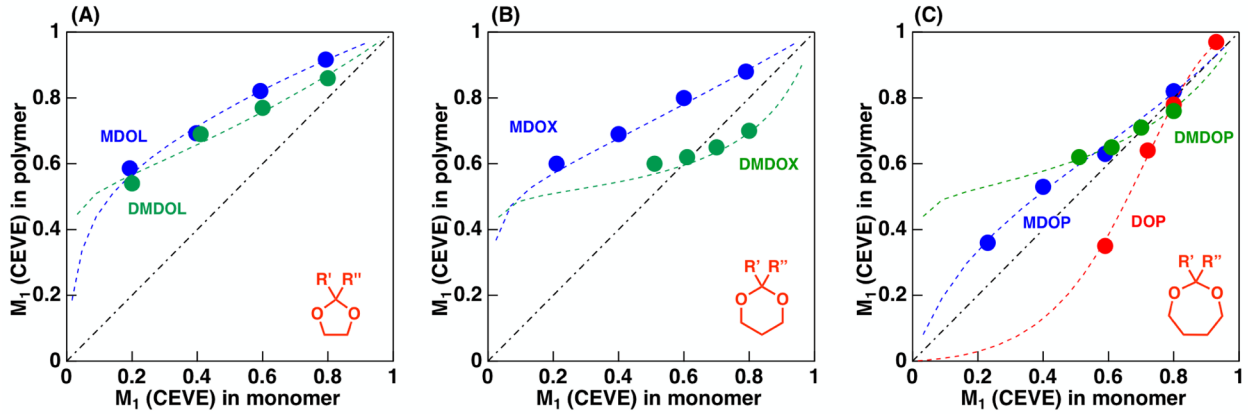


Fig. 6 Copolymer compositions for the cationic copolymerizations of CEVE and (A) five-, (B) six-, or (C) seven-membered cyclic acetals (broken curves: curves that were drawn using the *r* values obtained by the Kelen–Tüdős method; dashed-dotted lines: azeotropic lines). Polymerization conditions: $[CEVE]_0$ + $[cyclic\ acetal]_0$ = 1.0 M, $[IBEA]_0$ = 4.0 mM, $[TiCl_4]_0$ = 5.0 mM, $[SnCl_4]_0$ = 20 mM, [ethyl acetate] = 20 mM, $[DTBP]_0$ = 10 mM, in toluene/dichloromethane (9/1 v/v) at –78 °C. The data for DOP and MDOL are the same to those shown in reference 16.

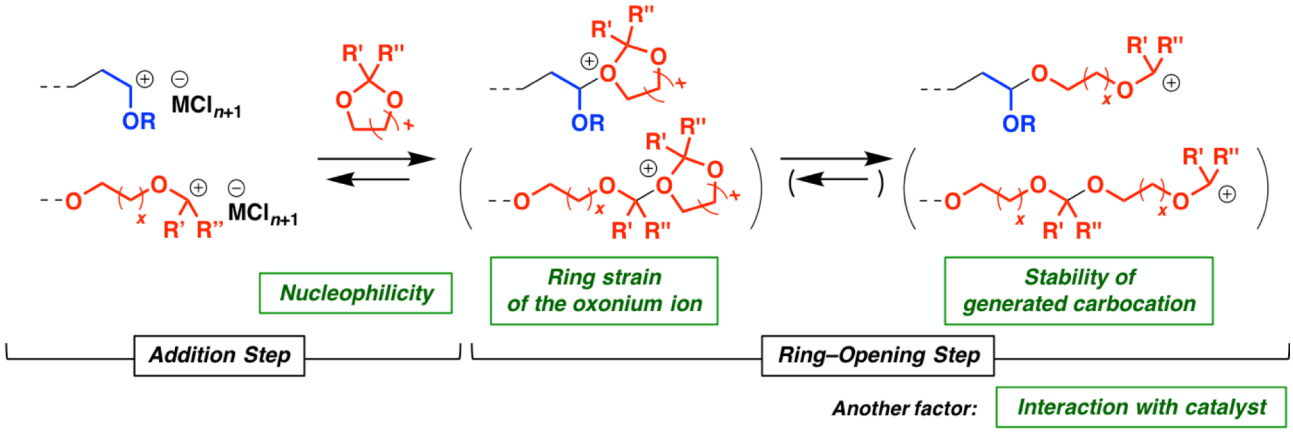


Fig. 7 Factors affecting the copolymerization behavior

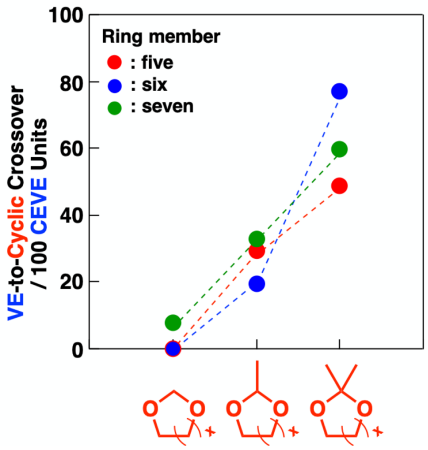


Fig. 8 Frequencies of crossover reactions per chain: By ^1H NMR analysis. The values were calculated from the data shown in entries 1, 3, 6, 8, 10, 12, 14, 16, and 18 in Table 1.

enhances the efficiency of the crossover reaction. This discussion is based on the assumption that cyclic acetals with the same ring member have comparable nucleophilicities and ring strain regardless of the number of methyl groups at the 2-position.

(b) Effects of the ring member.

The ring member of the cyclic acetal is related to its ring strain. In the reaction mechanism shown in Fig 7, the ring-opening of the oxonium ion is most likely facilitated by higher ring strain (six- < five- ~ seven-membered ring).[32–39] However, the copolymerization of MDOX, a six-membered cyclic acetal, was the fastest among the three cyclic acetals with one methyl substituent (MDOL: 40 h, MDOX: 1 h, and MDOP: 2 h, for 50% conversion of CEVE). These results suggest that factors other than ring strain also affect the copolymerization behavior.

The difference in the Lewis basicities of the five- and six-membered cyclic acetals, which interact with a Lewis acid catalyst, had a noticeable effect on the polymerization rates. Cyclic acetals are used as an additive to moderate the Lewis acidity of the catalyst in controlled cationic polymerizations of VEs. In our previous report, cyclic acetals were an efficient additive in a manner similar to weak Lewis bases such as ethyl acetate, 1,4-dioxane, and tetrahydrofuran.[40] To examine the abilities of cyclic acetals to serve as Lewis basic additives, the polymerization of IBVE was conducted in the presence of DOL, MDOL, DMDOL, or MDOX (Table 3; Fig. S9). In all cases, the incorporation of the cyclic acetal into the polymer chains under the examined conditions was negligible. Notably, the polymerization of IBVE in the presence of MDOX proceeded much faster than that in the presence of MDOL (entries 2 and 3 in Table 3), suggesting that MDOL is more Lewis basic than MDOX. This tendency is consistent with the polymerization rates of the copolymerizations with CEVE. In addition, the order of the basicities (six < five-membered [DOX < DOL]) is consistent with the previous report.[41,41] Moreover, the polymerization rates of IBVE were comparable regardless of the number of substituents (entries 1, 2, and 4; DOL, MDOL, and DMDOL). These results indicate that not only the ring strain but also the Lewis basicity of the cyclic acetal affects the copolymerization rate.

Table 3 Homopolymerization of IBVE in the presence of cyclic acetals as an additive[a]

			conv. (%)	
entry	cyclic	time	vinyl[b]	cyclic[c]
1	DOL	60 s	12	0
2	MDOL	60 s	24	0
3	MDOX	60 s	75	0
4	DMDOL	60 s	18	1

[a] Polymerization conditions: $[IBVE]_0$ = 0.76 M, $[cyclic\ acetal]_0$ = 1.0 M, $[IBVE\text{-}HCl]_0$ = 4.0 mM, $[SnCl_4]_0$ = 5.0 mM, in toluene at –78 °C. See Fig. S9 for time–conversion curves. [b] Determined by gas chromatography. [c] By gravimetry and ^{1}H NMR analysis of products.

Copolymerization of cyclic acetals with IBVE

The reactivity of the VE also affected the copolymerization via the concurrent vinyl-addition and ring-opening mechanism. The copolymerization of cyclic acetals with IBVE, a more reactive VE than CEVE, using the same initiating system as that used in the controlled copolymerization with CEVE yielded ill-defined copolymers (Fig. S10); hence, an initiating system was designed based on the living cationic polymerization of IBVE.[42] As a result, the controlled copolymerization was achieved using $SnCl_4$ as a Lewis acid catalyst in conjunction with IBVE–HCl as a cationogen in the presence of ethyl acetate. The copolymerization results are listed in Table 4 and Table S3. In our previous study, DOP and MDOL were shown to be inefficient comonomers for copolymerization with IBVE.[16] In sharp contrast, DMDOL, DMDOX, MDOP, and DMDOP were demonstrated to copolymerize with IBVE in a controlled manner (entries 3, 6, 8, and 9 in Table 4). For example, the sharp MWD peak (M_w/M_n < 1.2) of the DMDOP copolymer shifted to the high-molecular-weight region as the reaction progressed (Fig. 9C). The M_n values obtained by GPC analysis linearly increased in accordance with the values calculated from the monomer conversion (Fig. 9B), which indicates that the copolymerization was mediated by long-lived species. In all cases, the M_w/M_n values of the copolymers with IBVE were smaller than those with CEVE, suggesting an improvement in the controllability (Fig. S11). The occurrences of the crossover reactions were confirmed by the detection of acetal protons derived from the crossover reactions in the ^{1}H NMR spectrum of the product (Fig. S12). The acid hydrolysis products had much lower M_n values than the original copolymers (Fig. 9C), which supports the frequent occurrence of crossover reactions. Accordingly, the selection of an appropriate initiating system allowed the controlled copolymerization of VEs with different reactivities and suitable cyclic acetals.

Table 4 Cationic Copolymerization of IBVE and Various Cyclic Acetals[a]

			conv (%)[b]				crossover per chain[d]		units per block[d]	
entry	cyclic	time	vinyl	cyclic	$M_n \times 10^{-3}$ [c]	M_w/M_n[c]	V to A[e]	A to V[e]	vinyl	Cyclic
1	DOL	30 s	73	0[f]	7.1	1.10	—	—	—	—
2	MDOL	60 s	60	1[f]	6.7	1.09	—	—	—	—
3	DMDOL	3 min	84	3[f]	9.9	1.09	3	3	27	1.0
4	DOX	60 s	68	0[f]	6.4	1.18	—	—	—	—
5	MDOX	60 s	64	0[f]	6.8	1.09	—	—	—	—
6	DMDOX	30 s	98	24[f]	12.8	1.16	30	30	3.3	0.95
7	DOP	6 h	83	8	4.5	1.34	1.5	~0	29	1.5
8	MDOP	90 s	92	58	8.6	1.36	20	21	2.6	1.4
9	DMDOP	30 s	82	28[f]	13.0	1.16	28	28	2.8	1.0

[a] $[IBVE]_0$ = 0.50 M, $[cyclic\ acetal]_0$ = 0.50 M, $[IBVE\text{-}HCl]_0$ = 5.0 mM, $[SnCl_4]_0$ = 5.0 mM, [ethyl acetate] = 1.0 M in dichloromethane at –78 °C. [b] Determined by gas chromatography. [c] Determined by GPC (polystyrene standards). [d] Estimated by ^{1}H NMR analysis. [e] V: vinyl monomer; A: cyclic acetal. [f] Determined by gravimetry and ^{1}H NMR analysis of products.

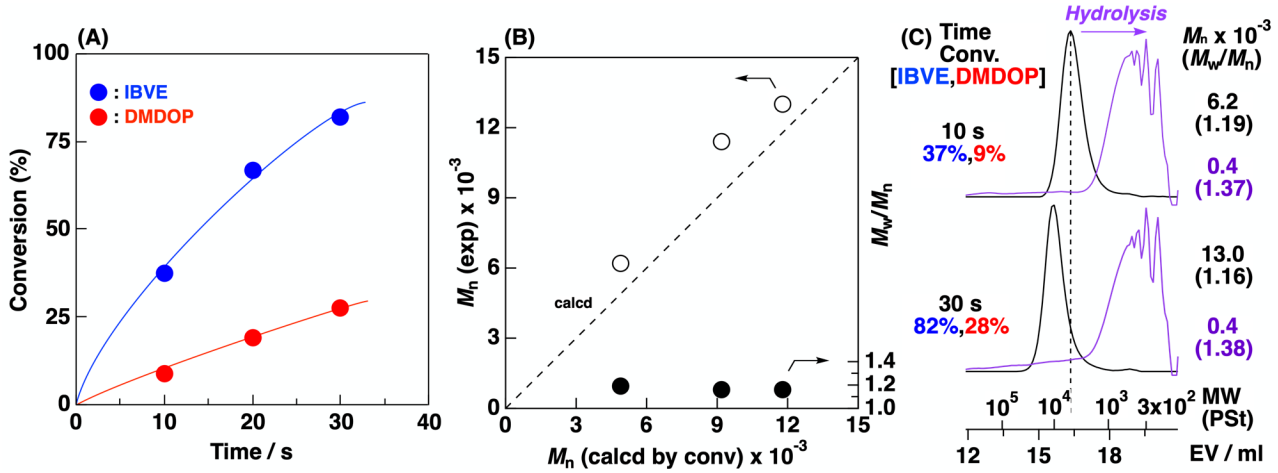


Fig. 9 (A) Time–conversion curves for the copolymerization of IBVE and DMDOP, (B) the M_n (open) and M_w/M_n (filled) values of the copolymers obtained, and (C) MWD curves of poly(IBVE-co-DMDOP)s (black) and acid hydrolysis products (purple). Polymerization conditions: $[IBVE]_0$ = 0.50 M, $[DMDOP]_0$ = 0.50 M, $[IBVE\text{-}HCl]_0$ = 5.0 mM, $[SnCl_4]_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, in dichloromethane at –78 °C. Hydrolysis conditions: 1.0 M HCl in 1,2-dimethoxyethane (0.5 wt% polymer) at room temperature for 3 h. The data correspond to entry 9 in Table 4 and entry 17 in Table S3.

The reactivities of the vinyl monomers mainly affected the frequencies of the crossover reactions. The average numbers of IBVE units per block were larger than those in the case of CEVE (Fig. 5), indicating that the crossover reactions from IBVE to the cyclic acetals were less favorable. For example, the CEVE/DMDOL units per block were calculated to be 2.1/0.96, while for IBVE this value was 27/1.0. Moreover, MDOL and MDOX, which produced copolymers with CEVE, did not copolymerize with IBVE (entries 2 and 5 in Table 4). In the case of IBVE, the homopropagation of the vinyl monomer is favored due to the high reactivity of IBVE, which disturbs the crossover reaction to the cyclic acetals. The larger r_1 values of the copolymerizations with IBVE relative to those with CEVE are consistent with the smaller ratios of the crossover reactions to the homopropagation (Table 2; Fig. S13). Suitable combinations of both vinyl and cyclic monomers based on their reactivities are crucial for copolymerizations via efficient crossover reactions.

Conclusions

In conclusion, the systematic study of the controlled cationic copolymerizations of VEs and cyclic acetals demonstrated the significant effects of both the numbers of substituents and the ring member of the cyclic acetal on the copolymerization behavior. In most cases, the copolymerizations of CEVE and cyclic acetals proceeded in a living manner, resulting in the generation of well-defined acid-degradable copolymers with acetal moieties in the main chain. The differences in the structures of the cyclic acetals significantly affected the propagation reactions. Specifically, an increase in the number of substituents at the 2-position of the cyclic acetal improved the stability of the carbocation generated from the ring-opening reaction. In addition, the ring member was responsible for the ring strain and the Lewis basicity. These factors affected both the frequency of the crossover reactions and the polymerization rates. The balance between the reactivities of the vinyl and cyclic monomers also influenced the sequence of the copolymer. The results of this study help elucidate the correlation between the structure and the copolymerization behaviors of different types of monomers. We are also presently investigating cyclic acetals with other substituents, such as cyclohexyl, phenyl, and vinyl groups, at the 2-position for the purpose of tuning the electronic and steric effects on the polymerization. Furthermore, the synthesis of well-defined, acid-degradable copolymers from a variety of cyclic acetals, which are easily synthesized from commercially available aldehyde or ketone, will enable the design of unique copolymer chains.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partially supported by JSPS KAKENHI Grant Number 18K05217.

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