Title	Controlled cationic copolymerization of vinyl monomers and cyclic acetals via concurrent vinyl-addition and ring-opening mechanisms
Author(s)	Shirouchi, Tomoka; Kanazawa, Arihiro; Kanaoka, Shokyoku et al.
Citation	Macromolecules. 2016, 49(19), p. 7184-7195
Version Type	AM
URL	https://hdl.handle.net/11094/100927
rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in Macromolecules, © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://doi.org/10.1021/acs.macromol.6b01565
Note	

Controlled Cationic Copolymerization of Vinyl Monomers and Cyclic Acetals via Concurrent Vinyl-Addition and Ring-Opening Mechanisms

Tomoka Shirouchi, Arihiro Kanazawa, Shokyoku Kanaoka, and Sadahito Aoshima**

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

E-mail: kanazawaa11@chem.sci.osaka-u.ac.jp, aoshima@chem.sci.osaka-u.ac.jp

Abstract

Vinyl monomers and cyclic acetals were demonstrated to copolymerize with sufficient crossover propagation reactions in a controlled manner via the generation of long-lived species. Such unusual propagation reactions, mediated by the active species derived from different types of monomers, were shown to require an appropriate dormant–active equilibrium, achieved via the elaborate design of the initiating systems. The controlled copolymerization of 2-chloroethyl vinyl ether (CEVE) and 1,3-dioxepane (DOP) proceeded using $SnCl_4$ as a catalyst in conjunction with ethyl acetate and 2,6-di-*tert*-butylpyridine, yielding multiblock-like copolymers as a result of several rounds of crossover reactions per chain. Under the same conditions, when 2-methyl-1,3-dioxolane (MDOL) was used instead of DOP, the polymerization proceeded in a highly controlled manner and involved more frequent crossover reactions. In addition, MDOL underwent almost no homopropagation reactions, unlike DOP. The nature of the

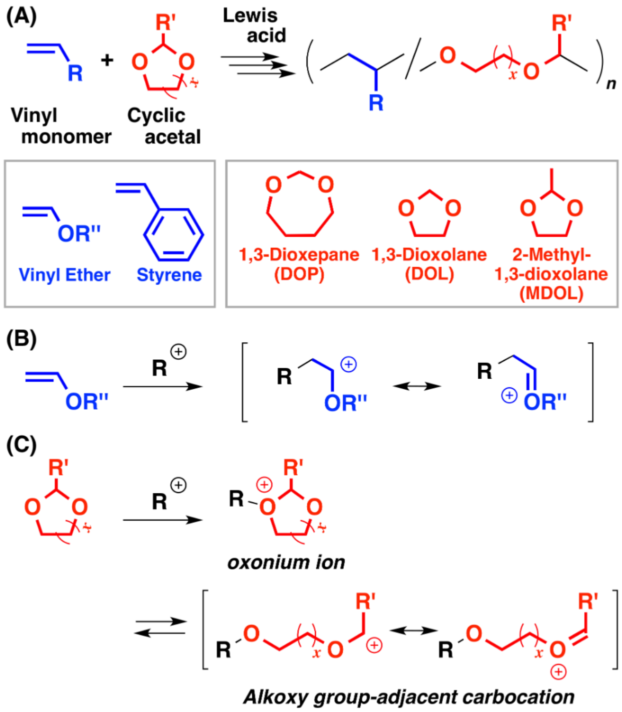
cyclic acetal-derived propagating species is most likely responsible for the difference in the copolymerization behavior. Long-lived species were also generated in the copolymerization of styrene and 1,3-dioxolane (DOL), although measurable amounts of cyclic oligomers were produced via backbiting reactions.

Introduction

The control of polymerization depends critically on the design of the growing active center, especially for an inherently unstable active species. The continued efforts of growing-end design have been highly successful in the development of controlled polymerization through a variety of mechanisms, which has allowed the precise synthesis of well-defined polymers, including block, gradient, graft, end-functionalized, and star-shaped polymers. A typical, guiding strategy is the establishment of the dormant–active equilibrium, which contributed significantly to the development of controlled polymerization reactions via cationic and radical mechanisms.[1,2] Specifically, the concentration of the active species is kept sufficiently low through the reversible formation of dormant species with covalent carbon–heteroatom bonds. The reversible generation of active species enables even propagation reactions of all chains, resulting in control over the molecular weight and molecular weight distribution (MWD) of the product polymers. In addition, bimolecular termination reactions are suppressed by diminishing the encounter ratio of two radical species via the dormant–active equilibrium in a controlled radical polymerization. To construct an appropriate dormant-active equilibrium, the reaction conditions, including initiators, catalysts, and additives, need to be specifically designed according to the reactivity of the active species.

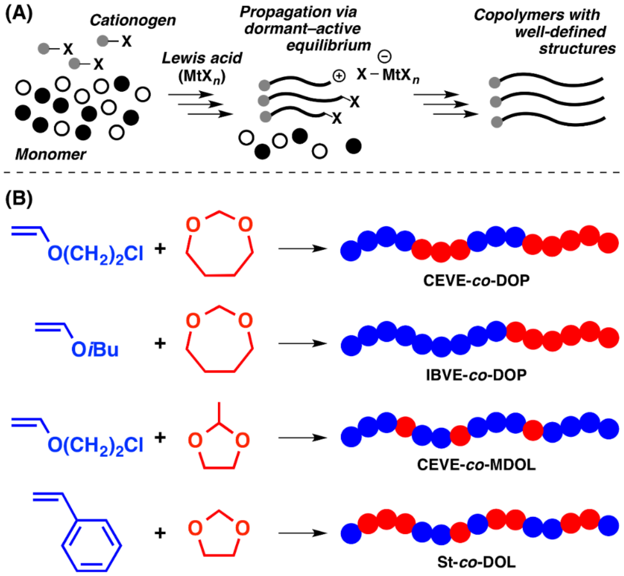
The structural design of a propagating species is also critical to the copolymerization of different types of monomers, such as vinyl and cyclic monomers,[3−11] which is expected to yield copolymers with new functions from general-purpose monomers. However, crossover reactions between different types of monomers are generally difficult because of sharp difference in the nature and/or reactivity of the propagating species. For example, vinyl monomers cannot react with oxonium ions derived from cyclic ethers, which has been the main cause for the difficulty in copolymerizing vinyl monomers and cyclic ethers via the cationic mechanism.[8−11] Our group has recently achieved concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl ethers (VEs) and oxiranes through the use of both appropriate catalysts and oxirane monomers with suitable substituents.[12,13] In this type of copolymerization, oxiranes that generate carbocations via the ring-opening reaction of oxonium ions were indispensable for the crossover reaction from the oxirane-derived propagating species to a VE monomer. Although successful crossover reactions were achieved using the correct combinations of VEs and oxiranes, controlling the propagation reactions mediated by long-lived species remained difficult because generating dormant species with comparable reactivities from a VE and an oxirane under identical conditions is a formidable challenge because the carbocationic species derived from VEs and common oxiranes have substantially different reactivities.

Carefully choosing the monomer structure should permit achieving suitable dormant-active equilibria from vinyl and cyclic monomers and, thus, generate active species with comparable reactivities. One reasonable possible strategy was demonstrated by our recent findings that an alkoxyoxirane, an oxirane monomer that generates an alkoxy group-adjacent, VE-type carbocation through the ring-opening reaction, was exceptionally effective for the generation of long-lived species in the copolymerization of VEs, although the polymerization proceeded via unique mechanisms accompanying intramolecular alkoxy group transfer reactions.[14] Encouraged by this finding, we focused on cyclic formals[15] as candidate monomers for controlled cationic copolymerization with vinyl monomers (Scheme 1A). Cyclic formals are known to generate alkoxy group-adjacent carbocations (Scheme 1C), which are structurally similar to the carbocation derived from a VE (Scheme 1B), through ring-opening reactions. Conventional cationic copolymerization with VEs or styrene using BF_3OEt_2 as a Lewis acid catalyst has been previously reported.[8,9] However, polymerization with such a conventional initiating system proceeds without generating the dormant–active equilibrium.



Scheme 1. (A) Concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl monomers and cyclic acetals (compounds shown in squares are monomers used in this study), and propagating species that generate at (B) VE- and (C) cyclic acetal-derived propagating ends (R' = H or Me).

Because a cyclic acetal is transformed into a carbocation with a similar structure to the carbocation derived from a VE, initiating systems based on the living cationic polymerization of vinyl monomers may favor the controlled copolymerization of a vinyl monomer and a cyclic acetal.[1] Diverse options for initiating systems exist, and we have developed a wide variety of metal halides as Lewis acid catalysts with Lewis basic additives having suitable basicity. In this study, we investigated the cationic vinyl-addition and ring-opening copolymerization of VEs or styrene with three cyclic acetals: 1,3-dioxepane (DOP), 2-methyl-1,3-dioxolane (MDOL), and 1,3-dioxolane (DOL). Vinyl monomers used for the copolymerization with each cyclic acetal was chosen based on the reactivity balance of monomers. In fact, inappropriate combinations of the vinyl and cyclic monomers resulted in exclusive homopolymerization of either monomer or the generation of only oligomeric products. As a result of the construction of a suitable dormant–active equilibrium, long-lived species-mediated copolymerization reactions were demonstrated to proceed with sufficient crossover reactions between vinyl and cyclic monomers (Scheme 2A). Moreover, the sequence distribution of monomer units in the copolymers determined by nuclear magnetic resonance (NMR) differed depending on the monomers used (Scheme 2B). The factors that affected the distribution are discussed, particularly in terms of the nature of the cyclic acetal-derived propagating species.



Scheme 2. Brief summary of this study: (A) Controlled cationic copolymerization mediated by the dormant-active equilibrium, and (B) illustrations for the structures of copolymers obtained from vinyl monomers and cyclic acetals

Experimental Section

Materials. 2-Chloroethyl VE (CEVE; TCI, >97.0%) and isobutyl VE (IBVE; TCI, >99.0%) were washed with a sodium hydroxide solution and then water and then distilled twice over calcium hydride. Styrene was distilled over calcium hydride under reduced pressure. DOP was synthesized through the reaction of 1,4-butanediol (TCI; >99.0%) and paraformaldehyde (Sigma-Aldrich; 95%) according to a previously reported procedure.[16] Ethyl acetate (Wako; >99.5%) and heptane (Nacalai Tesque; >99.0%) were distilled twice over calcium hydride. MDOL (TCI; >98.0%), DOL (Wako; >99.0%), 1,4-dioxane (Wako; >99.5%), and tetrahydrofuran (THF; Wako; >99.5%) were distilled over calcium hydride and then lithium aluminum hydride. 2,6-Di-*tert*-butylpyridine (DTBP; Wako; 97%) and (1-chloroethyl)benzene (St–HCl; TCI; >97.0%) were 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 with HCl or acetic acid, respectively.[17,18] $TiCl_4$ (Sigma-Aldrich; 1.0-M solution in toluene) and $SnCl_4$ (Sigma-Aldrich; 1.0-M solution in heptane) were used without further purification. A stock solution of $GaCl_3$ in hexane was prepared from anhydrous $GaCl_3$ (Sigma-Aldrich; >99.999%). 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, and hexane were stored in brown ampules under dry nitrogen.

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 approximately 450 ºC) under dry nitrogen. Dichloromethane, toluene, heptane (as an internal standard for gas chromatography), ethyl acetate, a DTBP solution in dichloromethane, and an IBEA solution in hexane were added into the tube using dry medical syringes. After cooling the solution to 0 ºC for 10 min, a $TiCl_4$ solution in toluene was added to the tube. After 15 min, the solution was cooled to –78 ºC. A $SnCl_4$ solution in toluene was added to the tube, and then, a mixture of CEVE and DOP was used to initiate the polymerization. After a predetermined interval, the reaction was terminated with methanol containing a small amount of aqueous ammonia solution. The quenched mixture was diluted with dichloromethane and hexane and washed with water. The volatiles were then removed under reduced pressure at 50 ºC to yield a polymer. Monomer conversion was determined by gas chromatography (or, for some reactions, by gravimetry and NMR).

Measurements. The polymers' MWDs were measured by gel permeation chromatography (GPC) in chloroform at 40 ºC with polystyrene gel columns (TSKgel GMH_{HR}-M × 2 or 3 with 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 a 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 polystyrene standards (Tosoh; $M_n = 577—1.09 \times 10^6$, $M_w/M_n \leq 1.1$). 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 spectra (ESI–MS) were recorded using a LTQ Orbitrap XL (Thermo Scientific) spectrometer. Polymer solutions in dichloromethane/methanol (1/1 v/v) were used for the ESI–MS analysis.

Results and Discussion

Copolymerization of CEVE and DOP

As a vinyl comonomer, IBVE was previously reported to copolymerize with DOP;[9] however, its reaction with DOP was inefficient under the conditions employed, as discussed below. Thus, we first investigated the copolymerization of DOP with CEVE, a VE monomer less reactive than IBVE due to the electron-withdrawing effect of the chlorine atom in the side chain, specifically focusing on the feasibility of achieving controlled copolymerization of these monomers through the design of initiating systems based on those for living cationic polymerization of VEs.

The cationic copolymerization of CEVE and DOP was examined under various reaction conditions for both the generation of long-lived propagating species and the suppression of side reactions, such as chain transfer reactions. Among the conditions investigated, the reaction using an IBEA/$TiCl_4$/$SnCl_4$ initiating system in the presence of ethyl acetate and DTBP at –78 ºC was demonstrated to be highly effective for the controlled copolymerization (in this study, the word *controlled copolymerization* was used for polymerization reactions that proceeded via the propagation reactions by long-lived species and involved unnoticeable side reactions). The copolymerization of CEVE and DOP under these conditions proceeded smoothly and reached moderately high conversion of both monomers (entries 1—3 in Table 1; Figure 1A). The product polymers had unimodal MWDs, although the M_w/M_n values were relatively large ($M_w/M_n > 2$). Most notably, the MWD peak shifted to the high-molecular-weight region as monomer conversion increased, indicating the generation of long-lived propagating species. This initiating system was designed on the basis of the reaction conditions suitable for the living cationic polymerization of CEVE.[19] The reaction of IBEA and $TiCl_4$ generates an HCl adduct of IBVE (IBVE–HCl) in situ, and subsequent smooth propagation reactions are catalyzed by $SnCl_4$.[20] The homopolymerization of CEVE under the same conditions proceeded in a highly controlled manner, yielding products with very narrow MWDs (entries 4 and 5). The homopolymerization of DOP, however, produced polymers with broad MWDs (entries 6 and 7), similar to the copolymerization with CEVE.

Table 1. Cationic copolymerization of vinyl monomers and cyclic acetals[a]

entry	vinyl monomer	cyclic acetal	catalyst	temp (°C)	time	conv (%)[b]		M_n ×10^{-3} [c]	M_w/M_n[c]	crossover per chain[d]	
						vinyl monomer	cyclic acetal			V to A[e]	A to V[e]
1	CEVE	DOP	$TiCl_4$/$SnCl_4$	–78	30 min	9	21	1.6	2.20	0.9	0.5–0.9[f]
2					23 h	31	74	5.8	2.20	3.9	3.9–6.3[f]
3					44 h	73	91	7.1	2.45	7.6	8.7–10.3[f]
4	CEVE	–	$TiCl_4$/$SnCl_4$	–78	10 s	77	–	7.6	1.11	–	–
5					30 s	98	–	9.3	1.09	–	–
6	–	DOP	$TiCl_4$/$SnCl_4$	–78	1 h	–	7	2.5	2.51	–	–
7					20 h	–	45	8.4	2.29	–	–
8	CEVE	DOP	$TiCl_4$/$SnCl_4$	0	20 s	19	17	1.0	1.76	1.2	0.8
9					3 min	91	54	2.0	2.82	3.0	3.4–5.4[f]
10	CEVE	DOP	$GaCl_3$	–78	2 min	4	80	4.8	12.8	n.d.[h]	n.d.[h]
11					21 h	9	92	3.6	14.7	n.d.[h]	n.d.[h]
12	CEVE	DOP	$GaCl_3$	0	3 min	27	29	1.5	3.39	1.2	1.4–2.0[f]
13					15 min	90	53	1.9	3.34	1.8	2.3–3.8[f]
14	IBVE	DOP	$TiCl_4$/$SnCl_4$	–78	7 h	74	32	9.3	1.56	(<1)[i]	(~0)[i]
15	IBVE	DOP	$GaCl_3$	–30	1 min	87	32	4.3	3.74	(<1)[i]	(~0)[i]
16	CEVE	MDOL	$TiCl_4$/$SnCl_4$	–78	2 h	22	8[g]	2.5	1.36	15.9	15.2
17					70 h	64	18[g]	5.2	1.48	29.4	26.9
18	–	MDOL	$TiCl_4$/$SnCl_4$	–78	70 h	–	2[g]	–	–	–	–
19	styrene	DOL	$SnCl_4$	0	9 h	34	41	1.2	2.71	n.d.[j]	n.d.[j]
20					480 h	77	70	1.5	3.14	n.d.[j]	n.d.[j]
21	–	DOL	$SnCl_4$	0	24 h	–	41	1.8	3.92	–	–

[a] Entries 1–9, entry 14 and 16—18: [vinyl monomer]$_0$ = 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 (except for entries 8 and 9) or 50 (entries 8 and 9) mM in toluene/dichloromethane (9/1 v/v; except for entries 8, 9, and 14) or toluene (entries 8, 9, and 14). Entries 10—13 and 15: [vinyl monomer]$_0$ = 0.51 M, [cyclic acetal]$_0$ = 0.51 M, [IBVE–HCl]$_0$ = 5.0 mM, [$GaCl_3$]$_0$ = 5.0 mM, [1,4-dioxane] = 0.50 (entries 10 and 11), 1.0 (entries 12 and 13) M or [THF] = 1.0 M (entry 15), in toluene (entries 10—13) or dichloromethane (entry 15). Entries 19–21: [styrene]$_0$ = 0 or 1.5 M, [DOL]$_0$ = 1.5 M, [St–HCl]$_0$ = 20 mM, [$SnCl_4$]$_0$ = 100 mM, [$n$$Bu_4NCl$]$_0$ = 40 mM, in dichloromethane. [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] Relatively wide ranges of values were estimated, because the peak for the structure resulting from the crossover reaction from DOP to CEVE overlapped with other peaks on the ^{1}H NMR spectra. [g] Determined by gravimetry and ^{1}H NMR analysis of products. [h] Not determined. [i] Estimated by GPC and ^{1}H NMR analysis of acid hydrolysis products. [j] Not determined because the products may include non-negligible amounts of cyclic oligomers.

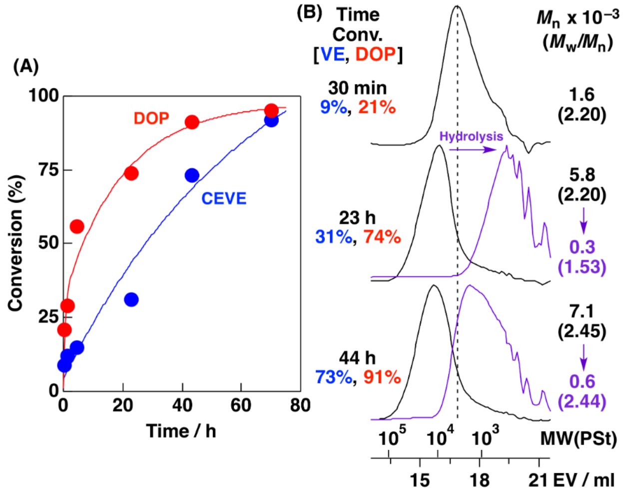


Figure 1. (A) Time–conversion curves for the copolymerization of CEVE and DOP using $TiCl_4/SnCl_4$, and (B) MWD curves of the poly(CEVE–*co*–DOP)s (black) and acid hydrolysis products (purple). Polymerization conditions: $[CEVE]_0 = 0.40$ M, $[DOP]_0 = 0.40$ M, $[IBEA]_0 = 4.0$ mM, $[TiCl_4]_0 = 5.0$ mM, $[SnCl_4]_0 = 20$ mM, [ethyl acetate] = 20 mM, [DTBP] = 10 mM in toluene/dichloromethane (9/1 v/v) at –78 °C. Hydrolysis conditions: 1.0 M HCl(aq) in 1,2-dimethoxyethane (0.5 wt% polymer) at room temperature for 3 h. The data correspond to entries 1—3 in Table 1.

^{1}H NMR analysis of the product polymers (Figure 2A) suggested that the copolymerization proceeded via several rounds of crossover reactions between both monomers in each chain to yield copolymers with multiblock-like structures. The peak at 4.8 ppm (peak 16) was assigned to the acetal proton derived from the crossover reaction from CEVE to DOP. This acetal peak was easily distinguishable from other acetal peaks, such as the acetal structures in the DOP homosequences (peak 9) and the ω-end acetals derived from CEVE (peak 34) or DOP (peak 36) with the methanol quencher. The structure derived from the crossover reaction from DOP to CEVE was reflected by the peaks at 3.4—3.5 ppm (peaks 13 and 14). Based on the integral ratios of these peaks and those for the α-end structures (peaks 31 and 33), the numbers of the crossover reactions per chain were calculated to be 0.9, 3.9 and 7.6 from CEVE to DOP and 0.5—0.9, 3.9—6.3, and 8.7—10.3 from DOP to CEVE for the products obtained after 30 min, 23 h, and 44 h, respectively (entries 1—3 in Table 1). The increase of these values as the monomer conversion increased also suggests that the copolymerization proceeded via long-lived species. In addition, 70—80% of the chains were derived from IBEA (peaks 31 and 32), whereas the other chains were most likely generated from adventitious water (peak 33). Moreover, almost no peaks corresponding to side reactions were observed in the spectra (see also Figure S1 and Scheme S1 in the Supporting Information), which suggests the occurrence of highly controlled copolymerization reactions (see the Note on page 4 in the Supporting Information for details regarding chain-end analysis). ^{13}C NMR analysis (Figure S2) also supported the successful copolymerization. ESI–MS of the product, however, indicated that backbiting reactions[15] of DOP partially occurred, generating a small amount of cyclic oligomers (Figure S3). Slight tailings on the MWD curves (Figure 1B) indicate these cyclic oligomers.

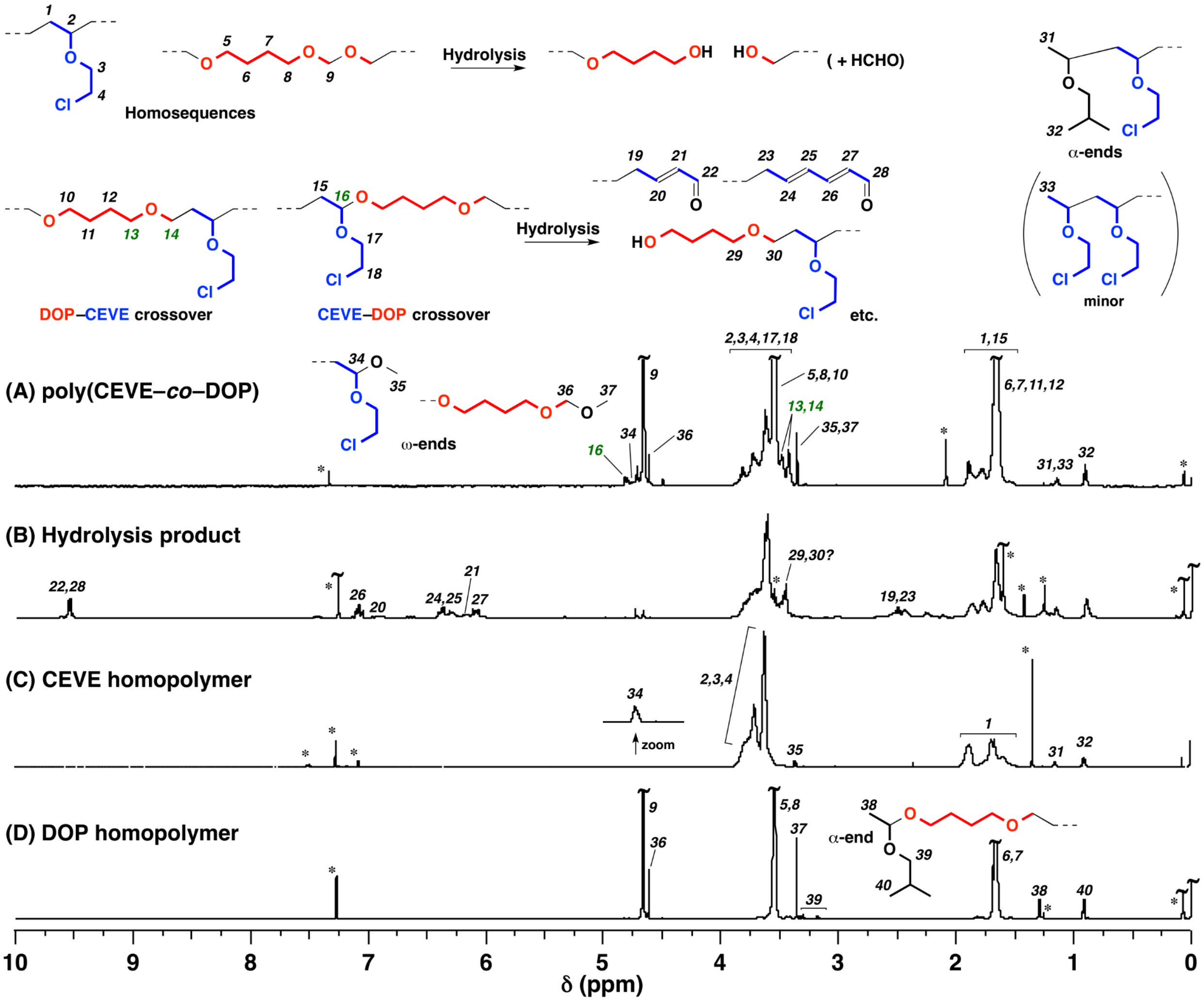
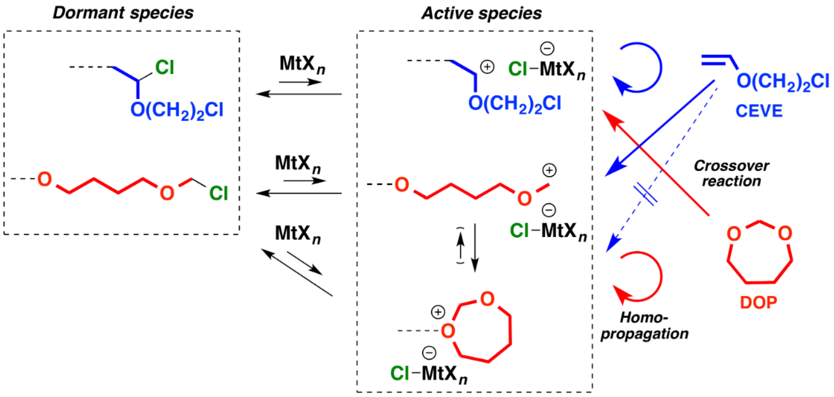


Figure 2. ^{1}H NMR spectra of (A) poly(CEVE–*co*–DOP) (entry 2 in Table 1), (B) its hydrolysis product, (C) poly(CEVE) (entry 4), and (D) poly(DOP) (entry 6) (in $CDCl_3$ at 30 °C; * water, grease, vaseline, $CHCl_3$, stabilizer, etc).

The successful copolymerization via the two-way crossover reactions was also corroborated by the structure of the hydrolysis products of the obtained copolymers. Acid-labile acetal structures generated via the crossover reactions from CEVE to DOP and via the homopropagation reactions of DOP can be hydrolyzed under acidic conditions. In the ^{1}H NMR spectrum after hydrolysis, the peak for the acetal structures disappeared, and the aldehyde peaks emerged at 9.5 ppm (Figure 2B). In addition, the hydrolysis products had unimodal MWDs and molecular weight values lower than those of the original copolymers (purple curves in Figure 1B). The difference between the middle and bottom curves of the hydrolysis products in Figure 1B is caused by the gradient sequences of both monomer units in the copolymer chains because DOP and CEVE were preferentially incorporated into chains early and late in the copolymerization, respectively, due to the difference in monomer reactivity and the change in the instantaneous concentrations of the monomers (Figure 1A).

The controlled copolymerization of CEVE and DOP most likely proceeded via a dormant-active equilibrium consisting of the reversible activation-deactivation reaction of the carbon–chlorine bonds at the propagating chain ends, as shown in Scheme 3, in a manner similar to that of living cationic polymerization of vinyl monomers.[1] The generation of dormant species from DOP was not directly evidenced but rationally deduced from the polymerization results. The successful copolymerization of CEVE and DOP indicates that the carbocations were generated through the ring-opening reaction of the oxonium ion derived from DOP because oxonium ions cannot react with vinyl monomers[8−11] (the ring-opening reaction may occur not directly but through the generation of the carbon–chlorine bond; vide infra). Once generated, the DOP-derived primary carbocation, more reactive than the secondary carbocation generated from CEVE, most probably reacts not only with vinyl and cyclic monomers but also with the counteranion, MtCl_{n+1}^{-}, to generate the dormant carbon–chlorine bond in a manner similar to the living cationic polymerization of vinyl monomers. However, the reactions generating the DOP-derived carbocation and dormant species were likely less dominant compared to the homopropagation reactions of DOP via the reaction of the oxonium ion with a DOP monomer, which was also supported by the significantly large monomer reactivity ratio for DOP (r_2 = 18) in the copolymerization of CEVE and DOP, as determined and discussed in the last part of the Results and Discussion. Therefore, the rates for the activation–deactivation cycles were most likely small in the dormant–active equilibrium involving DOP-derived propagating species, which is responsible for the relatively large MWDs of both the copolymers and the DOP homopolymers. The copolymerization results using IBVE instead of CEVE also supported the generation of dormant species from DOP, as demonstrated below. The dormant carbon–chlorine bonds thus produced were converted to carbon–methoxy bonds by quenching the reaction with methanol, as confirmed by ^{1}H NMR analysis. Approximately 80% of the dormant ends were DOP-derived species at 31% and 74% conversion of CEVE and DOP, respectively (entry 2 in Table 1), as determined based on the integral ratios of the ω-ends. The preferential generation of the dormant ends from DOP rather than CEVE possibly stemmed from the difference in the stabilities of the propagating carbocations. The difference in the reactivity of the CEVE- and DOP-derived dormant ends is also likely responsible for the broad MWDs of the copolymers, which results from uneven propagation reactions of all the chains. This is in contrast to the results using MDOL, a cyclic acetal that generates a secondary carbocation, as demonstrated below.



Scheme 3. Possible mechanisms for the cationic copolymerization of CEVE and DOP.

The copolymerization reactions at higher temperature yielded ill-defined products because of the inefficient suppression of side reactions. The reaction using the IBEA/$TiCl_4$/$SnCl_4$ initiating system at 0 ºC proceeded much faster than that at –78 ºC to produce polymers with unimodal MWDs (entries 8 and 9 in Table 1). Although long-lived species were generated, the molecular weights were smaller and the MWDs broader than those of the products obtained at –78 ºC (Figure 3A). ^{1}H NMR analysis (Figure S1B) suggested that chain transfer reactions occurred at this temperature because of the reaction of the propagating species with an alcohol derived from the CEVE side group (2-chloroethanol; Scheme S1A)[21] and/or the intramolecular transfer reactions through the reactions between the propagating carbocation with the alkoxy group in the side chain (Scheme S1B). The homopolymerization of CEVE at 0 ºC under the same conditions, however, did not generate the ω-ends with two 2-chloroethyl groups via the side reaction shown in Scheme S1A. Therefore, the intramolecular transfer reactions (Scheme S1B) were most likely to be mainly responsible for the generation of such structures in the copolymerization. In addition, relatively large amounts of low-molecular-weight portions (molecular weight < 10^3) were attributed to cyclic oligomers resulting from backbiting reactions (vide supra; Scheme S1C). Moreover, the conversion of DOP leveled off at approximately 50% at 0 ºC, which is likely related to the equilibrium monomer concentration.[22]

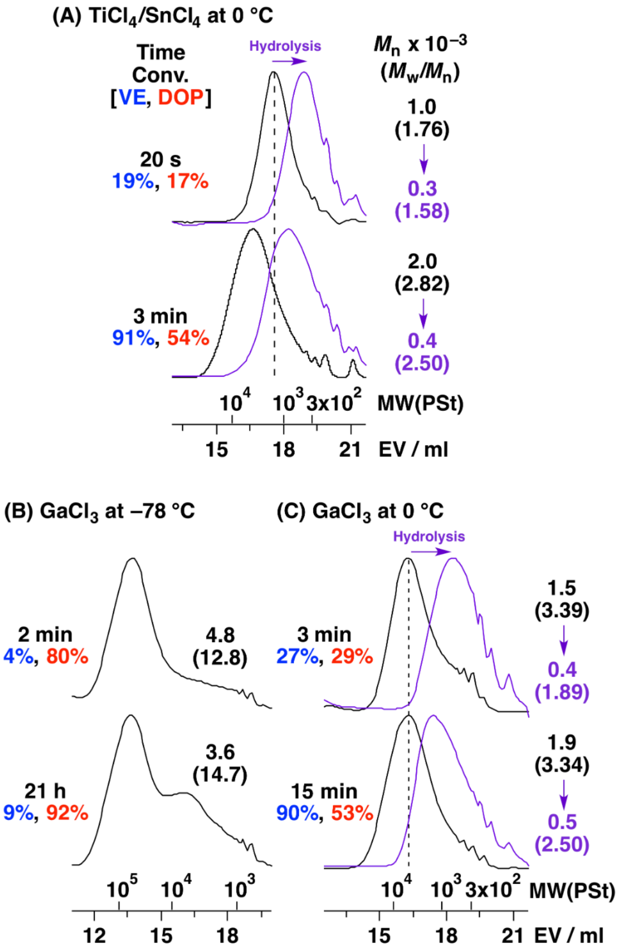


Figure 3. GPC curves of poly(CEVE–*co*–DOP)s (black) and acid hydrolysis products (purple). Polymerization conditions: (A) $[\text{CEVE}]_0$ = 0.40 M, $[\text{DOP}]_0$ = 0.40 M, $[\text{IBEA}]_0$ = 4.0 mM, $[\text{TiCl}_4]_0$ = 5.0 mM, $[\text{SnCl}_4]_0$ = 20 mM, [ethyl acetate] = 50 mM, [DTBP] = 10 mM in toluene at 0 °C. (B) and (C)

$[\text{CEVE}]_0$ = 0.50 M, $[\text{DOP}]_0$ = 0.50 M, $[\text{IBVE–HCl}]_0$ = 5.0 mM, $[\text{GaCl}_3]_0$ = 5.0 mM, [1,4–dioxane] = 0.50 (for B) or 1.0 (for C) M, in toluene at –78 (for B) or 0 (for C) °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 (A) entries 8 and 9, (B) entries 10 and 11, and (C) entries 12 and 13 in Table 1.

The initiating system was also a decisive factor in achieving controlled copolymerization reactions. In the polymerization using an IBVE–HCl/$GaCl_3$ at –78 ºC, DOP was preferentially consumed to yield products composed of DOP homopolymers and a small amount of copolymers with CEVE (entries 10 and 11 in Table 1; Figure 3B). The results suggest that the generation of dormant species through the reaction of the propagating species and the $GaCl_4^-$ counteranion did not occur efficiently. Such inefficient deactivation by tetrachloride anions, including $GaCl_4^-$, $FeCl_4^-$, and $AlCl_4^-$, was observed in our previous study on the cationic polymerization of *p*-methoxystyrene.[23] At 0 ºC, however, the copolymerization using $GaCl_3$ proceeded with crossover reactions between both monomers. Long-lived species might be partly generated as demonstrated by the slight increase of M_n values and the change in the shape of the MWD curves with the increase of monomer conversion values, although the products had low molecular weights due to frequent side reactions (entries 12 and 13 in Table 1; Figure 3C). The structures derived from the chain transfer reactions that occurred in a manner similar to the reaction using the IBEA/$TiCl_4$/$SnCl_4$ initiating system at 0 ºC (Scheme S1) were confirmed by ^{1}H NMR.

IBVE, a VE monomer with higher reactivity than CEVE, did not copolymerize efficiently with DOP under any conditions examined. The reaction using the initiating system consisting of IBEA, $TiCl_4$, and $SnCl_4$ yielded polymers with unimodal MWDs (entry 14 in Table 1; Figure S4A). However, the acetal peak resulting from the crossover reaction from IBVE to DOP was very small in the ^{1}H NMR spectrum (Figure S5A; the integral ratio was not accurately estimated because the peak overlapped with the acetal peak derived from DOP homosequences). Moreover, the MWD curve shifted only slightly to the lower-molecular-weight region after acid hydrolysis (Figure S4A), indicating that the products were composed of each homopolymer and a small amount of copolymers. By contrast, the copolymerization reaction slightly improved with the use of $GaCl_3$ as a catalyst at –30 °C (entry 15 in Table 1), unlike CEVE. The MWD curve obviously shifted to the lower-molecular-weight region after acid hydrolysis (Figure S4B), suggesting the generation of copolymers in polymerization. ^{1}H NMR analysis of the hydrolysis product (Figure S5B), however, suggested that the copolymer had a diblock structure resulting from a single crossover reaction from IBVE to DOP per chain with negligible crossover reactions from DOP to IBVE. This consequence resulted from the equality of the integral ratios of the fragment derived from the cationogen and the aldehyde structure indicated in the ^{1}H NMR spectrum of the hydrolysis product. The inefficient crossover reaction from DOP to IBVE suggests that the carbocation generation via the ring-opening reaction of the DOP-derived oxonium ion occurs not directly but through the formation of the covalent carbon–chlorine bond because IBVE, a VE that is more reactive than CEVE, should react with the carbocations more efficiently than CEVE if the carbocation is generated through the ring-opening reaction of the oxonium ion. This result indirectly indicates the generation of the dormant species with the carbon–chlorine bond at the DOP-derived propagating ends. Negligible activation of the DOP-derived carbon–chlorine end, which is less reactive than the IBVE-derived carbon–chlorine end under the conditions used, would then be responsible for the inefficient copolymerization.

Copolymerization of CEVE and MDOL

MDOL was next employed as a cyclic acetal monomer because a secondary carbocation, a propagating species more stable than the species derived from DOP, is expected to arise through the ring-opening reaction of the oxonium ion. The cationic copolymerization of MDOL with CEVE was conducted under the same conditions as used for the copolymerization of CEVE and DOP. The reaction using the IBEA/$TiCl_4$/$SnCl_4$ initiating system at –78 °C proceeded smoothly (entries 16 and 17 in Table 1; Figure 4A), yielding polymers with unimodal MWDs. Interestingly, the MWDs were much narrower than those of the copolymers of CEVE and DOP. Furthermore, the MWD curve clearly shifted to the higher-molecular-weight region as the reaction proceeded (Figure 4C), indicating the generation of long-lived species. The M_n values obtained by GPC analysis using polystyrene calibration increased linearly, although the values were lower than those calculated based on the monomer consumed and cationogen charged (Figure 4B).

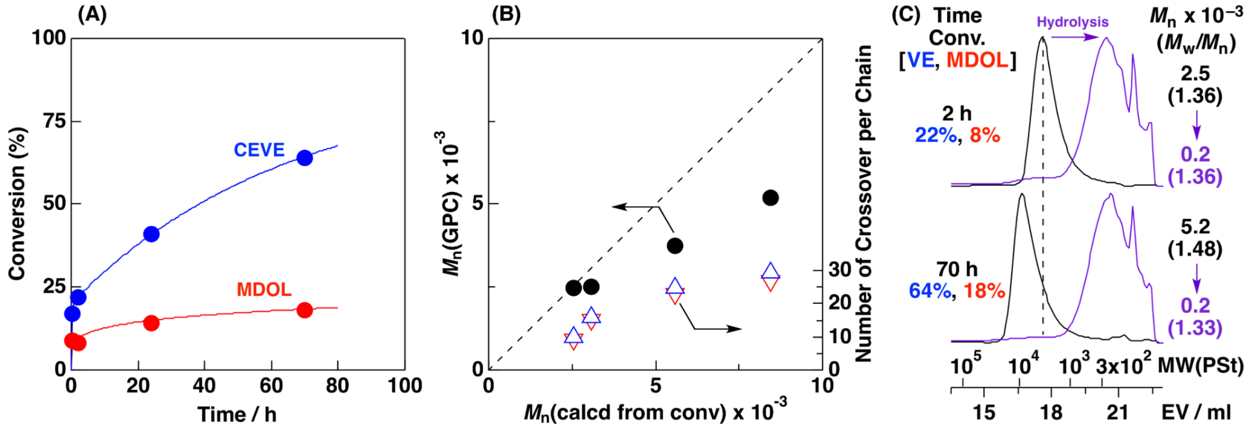


Figure 4. (A) Time–conversion curves for the copolymerization of CEVE and MDOL, (B) the relationship between M_n(GPC) (circles) or the number of crossover reactions per chain (blue triangles: from CEVE to MDOL; red inverted triangles: from MDOL to CEVE) and M_n(calcd by GC) of the polymers obtained, and (C) MWD curves of poly(CEVE–*co*–MDOL)s (black) and acid hydrolysis products (purple). Polymerization conditions: $[CEVE]_0 = 0.40$ M, $[MDOL]_0 = 0.40$ M, $[IBEA]_0 = 4.0$ mM, $[TiCl_4]_0 = 5.0$ mM, $[SnCl_4]_0 = 20$ mM, [ethyl acetate] = 20 mM, [DTBP] = 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 16 and 17 in Table 1.

The occurrence of frequent crossover reactions was confirmed through ^{1}H NMR and acid hydrolysis of the copolymerization products. The ^{1}H NMR spectrum (Figure 5A) exhibited peaks assigned to the structures derived from the crossover reactions from CEVE to MDOL (peak 42) and from MDOL to CEVE (peak 47). Peaks assigned to the α- (peaks 52, 53, 56, and 57) and ω-ends (peaks 35 and 60) derived from the cationogen and the quencher, respectively, were also observed, indicating that the copolymerization proceeded in a controlled manner through the dormant–active equilibrium (Scheme 4). The generation of long-lived species was also suggested by the increased numbers of crossover reactions per chain as copolymerization progressed [15.9 and 29.4 times from CEVE to MDOL and 15.2 and 26.9 times from MDOL to CEVE at lower (entry 16) and higher (entry 17) conversion, respectively; triangle symbols in Figure 4B]; the numbers of crossover reactions per chain were estimated from the integral ratios of the peaks assigned to the acetal (peak 42), the methyl group of the MDOL units (peak 47), and the α-end (peaks 53 and 57) structures. Moreover, homopropagation reactions of MDOL hardly occurred in the copolymerization, as demonstrated by the fact that a peak assigned to the methyl group adjacent to the acetal structure of the homosequences of MDOL negligibly appeared at 1.3 ppm (a chemical shift similar to those of peaks 54 and 58). The negligible occurrence of the homopropagation reaction was also supported by the failure of the homopolymerization of MDOL to proceed (entry 18 in Table 1), as also previously reported.[24,25] The copolymer was hydrolyzed under acidic conditions because of the degradation of the acetal structures, resulting in the generation of very low-molecular-weight compounds (purple curves in Figure 4C; Figure 5B).

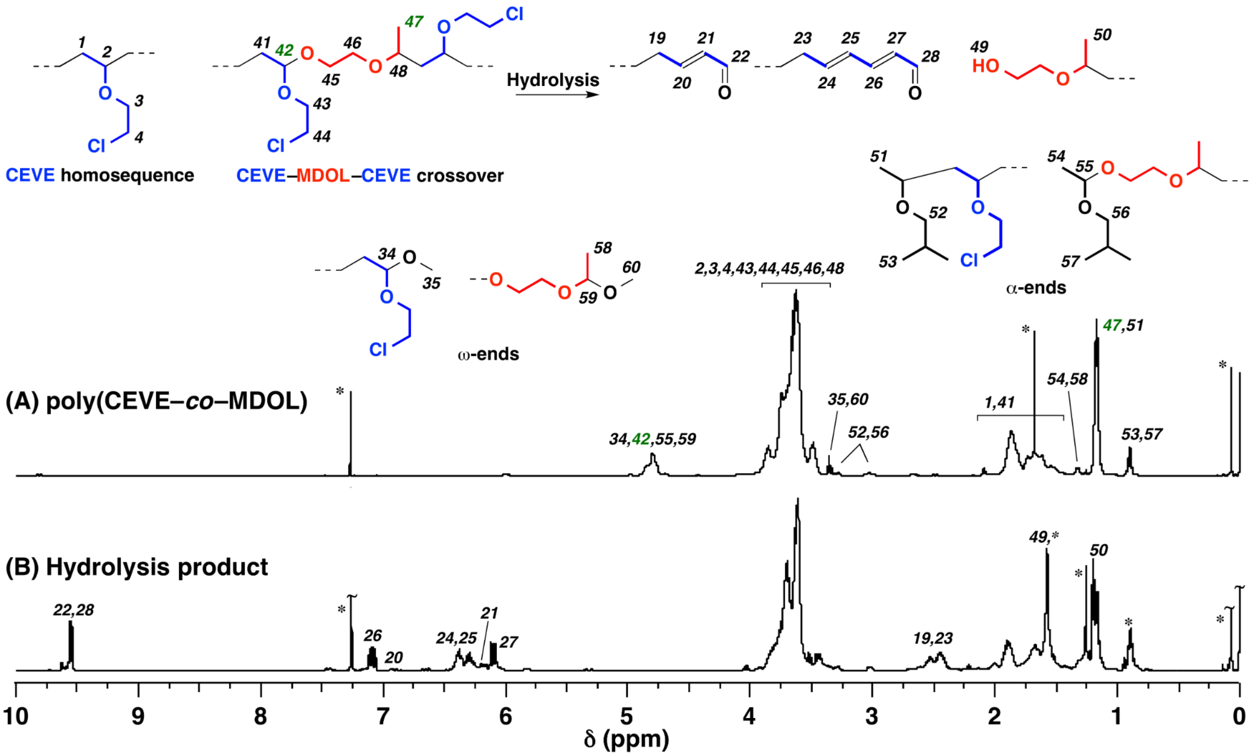
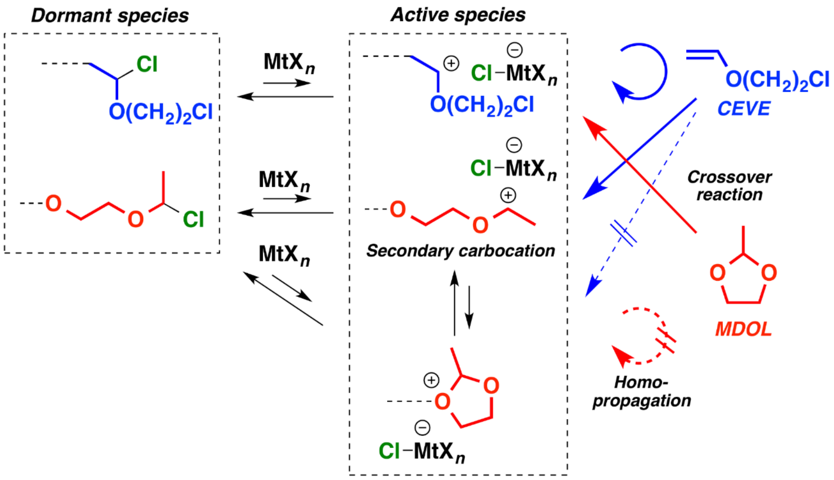


Figure 5. ^{1}H NMR spectra of (A) poly(CEVE–*co*–MDOL) (entry 16 in Table 1) and (B) its hydrolysis

product (in $CDCl_3$ at 30 °C; * water, grease, vaseline, $CHCl_3$, and stabilizer).

The secondary carbocation generated from MDOL is most likely responsible for the higher degree of control over this copolymerization than that using DOP (Scheme 4). Even activation of both the CEVE- and MDOL-derived dormant ends occurred efficiently because both ends generate secondary carbocations, unlike the copolymerization events of CEVE and DOP. In addition, cyclic oligomerization did not occur, possibly because of MDOL's negligible homopropagating ability. The copolymerization of MDOL with IBVE (Figure S6) resulted in inefficient incorporation of MDOL units (less than a few units per chain) due to the large difference in reactivity of both monomers. Moreover, copolymerization reactions using styrene derivatives, such as styrene, *p*-methylstyrene, *p*-chlorostyrene, and α-methylstyrene, produced oligomers with M_n values of $<10^3$ under the conditions employed. We are presently investigating the copolymerization with those styrene derivatives in more detail, particularly focusing on the design of suitable initiating systems.



Scheme 4. Possible mechanisms for the cationic copolymerization of CEVE and MDOL.

Copolymerization of Styrene and DOL

The initiating system designed according to the living cationic polymerization of styrene[26] was efficient for the cationic copolymerization of styrene and DOL. The reaction was conducted using $SnCl_4$ as a catalyst in conjunction with St–HCl and $n$$Bu_4NCl$ as a cationogen and an added salt, respectively, in dichloromethane at 0 ºC. The polymerization proceeded at a slow rate, yielding polymers with relatively broad MWDs (entries 19 and 20 in Table 1; Figure 6A). However, the peak of the MWD curves of the products shifted to the higher-molecular-weight region as the monomer conversion increased, indicating the generation of long-lived species. Moreover, acid hydrolysis yielded products with lower molecular weights than the original polymers. Because the crossover reaction from styrene to DOL does not generate an acetal structure, unlike copolymerizations using VEs, the degradation was attributed to the cleavage of acetal structures in the homosequences of DOL. Thus, these results indicate the successful generation of copolymers of styrene and DOL. However, the products exhibited large tailings in the low-molecular-weight regions on the MWD curves, suggesting the occurrence of undesired reactions.

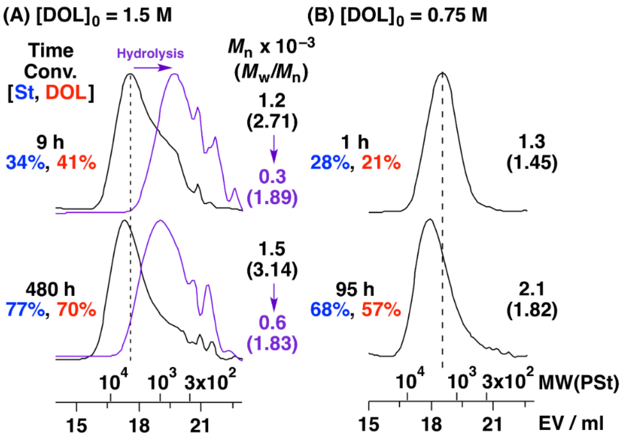


Figure 6. MWD curves of poly(styrene–*co*–DOL)s (black) and acid hydrolysis products (purple). Polymerization conditions: $[styrene]_0$ = 1.5 M, $[DOL]_0$ = 1.5 (for A) or 0.75 (for B) M, $[St–HCl]_0$ = 20 mM, $[SnCl_4]_0$ = 100 mM, [$n$$Bu_4NCl$] = 40 mM, in dichloromethane at 0 °C. Hydrolysis conditions: 1.0 M HCl in 1,2-dimethoxyethane (0.5 wt% polymer) at room temperature for 3 h. The data for (A) correspond to entries 19 and 20 in Table 1.

Analyzing the product polymers after separation into high- and low-molecular-weight portions by preparative GPC (Figure S7) demonstrated that chain transfer reactions hardly occurred and that cyclic oligomerization was responsible for the broad MWDs and low-molecular-weight values of the products. ^{1}H NMR analysis of the high-molecular-weight portion showed negligible peaks assigned to structures resulting from side reactions, such as β-proton elimination reactions (Figure 7A). In addition, peaks for α-end structures were detected at 1.0—1.3 ppm (peaks 73 and 74), indicating that a linear copolymer was obtained. The ESI–MS analysis of the low-molecular-weight portion revealed the generation of cyclic oligomers consisting of only styrene or both styrene and DOL (Figure 8). Peaks assigned to the structure with a proton (or a fragment derived from St–HCl) at the α-end and a chlorine atom at the ω-end were absolutely negligible (Figure S8). Linear structures with an olefinic end resulting from the β-proton elimination reaction also have the same *m*/*z* values as cyclic oligomers; however, the amount of these olefin structures was most likely very small, as confirmed by ^{1}H NMR analysis (Figure S9C), indicating that the major products were cyclic oligomers. The formation of cyclic oligomers indicates frequent backbiting reactions[15] in the copolymerization.

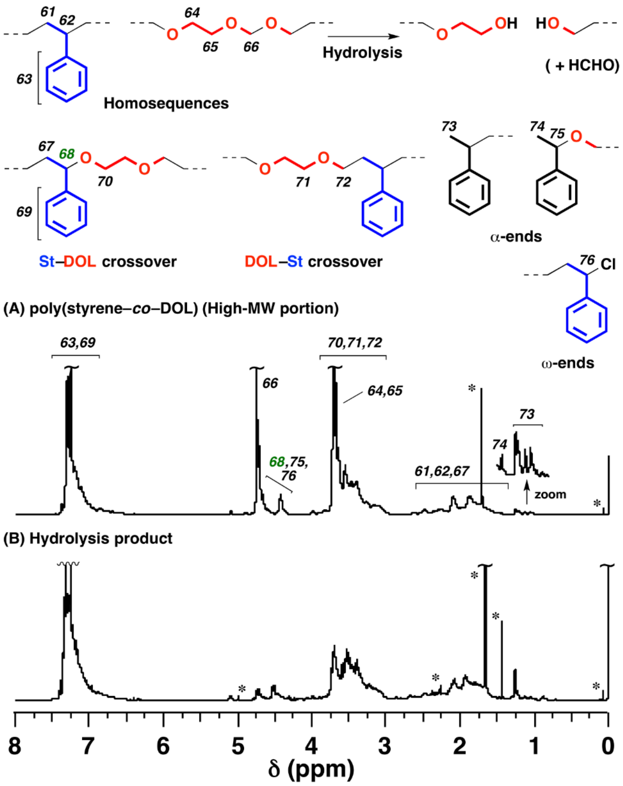


Figure 7. (A) ^{1}H NMR spectra of the high-molecular-weight portion of poly(styrene–*co*–DOL) [entry 19 in Table 1; separated by preparative GPC (a red curve shown in Figure S7)] and (B) its hydrolysis product (in $CDCl_3$ at 30 °C; * water, grease, vaseline, $CHCl_3$, and stabilizer).

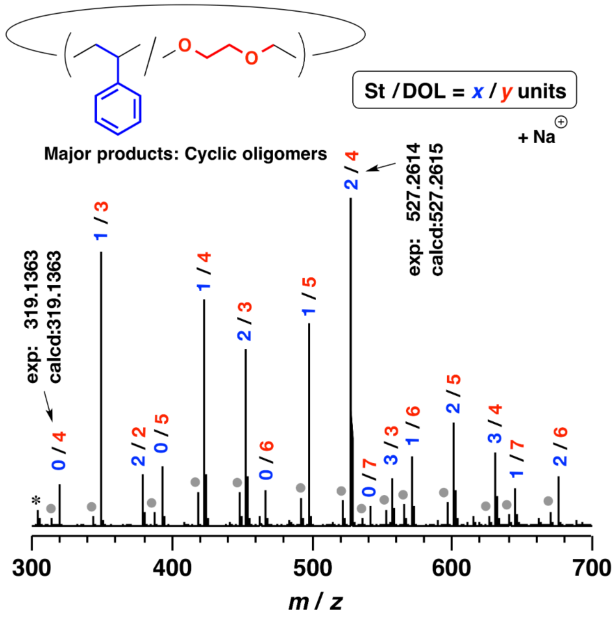
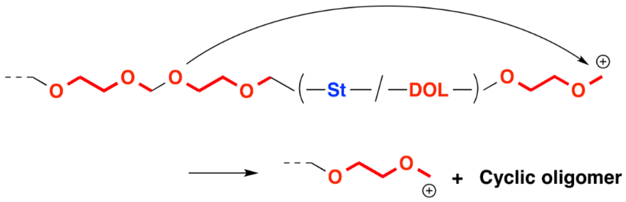


Figure 8. ESI–MS spectrum of the low-molecular-weight portion of poly(styrene–*co*–DOL) [entry 19 in

Table 1; separated by preparative GPC (a blue curve shown in Figure S7)]. Peaks labeled with gray circles are assigned to NH_4^+ adducts. Assignments for minor peaks are shown in Figure S8; * contamination.



Scheme 5. Backbiting reaction in the copolymerization of styrene and DOL (counteranions are omitted). Styrene-derived carbocations or DOL-derived oxonium ions may also induce similar backbiting reactions.

The reaction using a smaller amount of DOL exhibited improved control over the polymerization with fewer side reactions. The MWDs of the products obtained with 0.75-M DOL had smaller tailings than when 1.5-M DOL was used (Figure 6B), suggesting that the products included fewer cyclic oligomers. The decreased DOL units in the copolymer chains are responsible for the partial suppression of backbiting reactions.

The use of vinyl monomers more reactive than styrene resulted in exclusive homopolymerization reactions of the vinyl monomers. The reactions of DOL with CEVE or *p*-methylstyrene using $GaCl_3$ as a catalyst did not efficiently proceed, generating CEVE or *p*-methylstyrene homopolymers. DOL was gradually consumed after the complete consumption of the vinyl monomers although it was not clear whether block copolymers were partly generated. The higher reactivity of the vinyl monomers compared to DOL and/or the smaller reactivity of the carbocations generating from the vinyl monomers than that from styrene were likely responsible for the negligible crossover reactions from the vinyl monomer-derived propagating species to DOL monomers.

Overview of the Copolymerization Results: Prerequisites for Controlled Copolymerization and Discussion of the Frequency of Crossover Reactions

The experimental results shown above demonstrate that a prerequisite for the controlled cationic copolymerizations of vinyl monomers and cyclic acetals is to design suitable reaction conditions with particular emphasis on the suppression of side reactions, such as chain transfer reactions. Specifically, the propagation reactions of both monomers via a suitable dormant–active equilibrium at low temperature contributed to the copolymerization reactions that proceeded through the generation of long-lived species. In particular, the initiating systems that were designed based on the living cationic polymerization of vinyl monomers were efficient for controlled copolymerization.

Another essential factor for controlled copolymerization is the efficient generation of crossover reactions between the vinyl and cyclic monomers. The crossover reaction from a vinyl monomer-derived species to a cyclic formal appears to depend on both the nucleophilicity of the cyclic formal and the subsequent ring-opening reaction of the oxonium ion through either attack by the next monomer or the generation of a carbocation, as discussed in our previous study on the copolymerization of VEs and oxiranes.[13] Cyclic acetals with suitable reactivities were required, depending on the reactivity of propagating carbocationic species derived from vinyl monomers; hence, DOP and MDOL, which are cyclic acetals with relatively large reactivities, were copolymerized with CEVE, whereas DOL, a less reactive cyclic acetal, was copolymerized with styrene. The crossover reaction in the other direction, from a cyclic acetal to a vinyl monomer, required the generation of carbocationic species through the ring-opening reactions of cyclic acetal-derived oxonium ions. This requirement was satisfied because cyclic acetals generate carbocations with an adjacent alkoxy group, which serves as an electron-donating moiety. The frequency of the carbocation generation via the ring-opening reaction is considered to depend on the ring strain of cyclic acetals and the stability of the carbocations generated.

The difference in the frequency of the crossover reactions or the sequence distributions in copolymer chains among cyclic formals was also explained by the monomer reactivity ratios for the copolymerization reactions. Table 2 shows the monomer reactivity ratios calculated by the Kelen–Tüdõs method[27,28] using the data shown in Figure 9. The r_1 and r_2 values larger than 1.0 were obtained for the copolymerization of CEVE and DOP (r_1 = 4.8 and r_2 = 18), suggesting that homopropagation reactions preferentially occurred compared to crossover reactions at propagating ends derived from both monomers.

In particular, the significantly large r_2 value suggests that the carbocation generation via the ring-opening reaction of the oxonium ion does not occur frequently and that the homopropagation reaction of DOP preferentially proceeded via the reaction of DOP monomers with the propagating oxonium ion. In contrast, a very small r_2 value ($r_2 = 0.06$) was obtained in the copolymerization of CEVE and MDOL, in agreement with the experimental results showing that the homopropagation reaction of MDOL hardly occurred. The stability of the secondary carbocation derived from MDOL and the negligible homopolymerizability of MDOL resulted in very efficient preferential crossover reactions to a VE monomer at the MDOL-derived propagating end. The values for the copolymerization of styrene and DOL ($r_1 = 2.4$ and $r_2 = 2.7$) were different from those for copolymerization by the conventional system using BF_3OEt_2 as a catalyst at 0 ºC ($r_1 = 0.65$ and $r_2 = 6.5$ in toluene, $r_1 = 1.4$ and $r_2 = 3.8$ in nitrobenzene[8,29]). This difference probably stemmed from solvent polarity and/or the catalysts used. In particular, the generation of the dormant species through the reaction of the DOL-derived oxonium ion with the chloride anion may have affected the r_2 value.

Table 2. Monomer reactivity ratios[a]

M_1	M_2	r_1	r_2
CEVE	DOP	4.8	18
CEVE	MDOL	2.6	0.06
styrene	DOL	2.4	2.7

[a] Determined by the Kelen–Tüdõs method. The values were calculated from the data shown in Figure 9. The plots for the determination of the monomer reactivity ratios are shown in Figure S10.

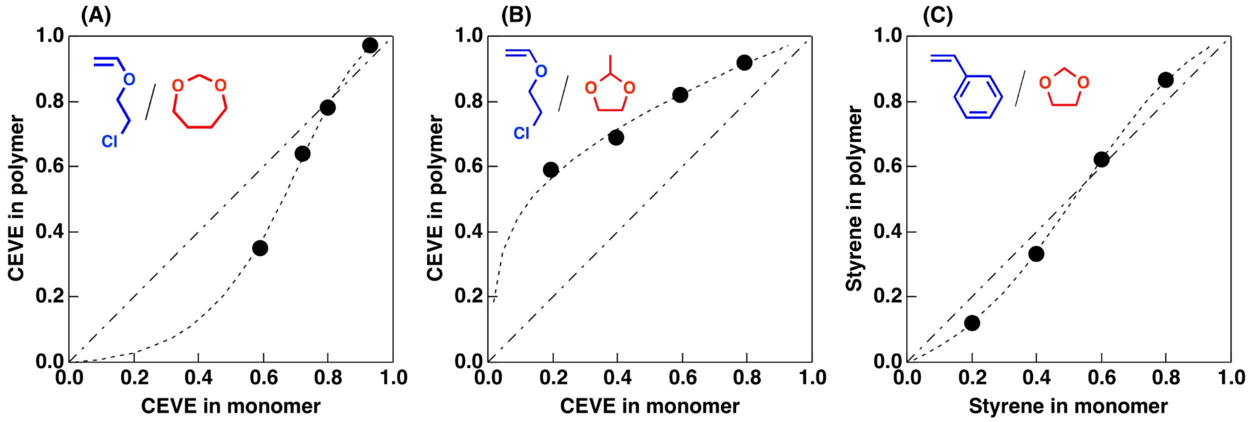


Figure 9. Copolymer compositions for the cationic copolymerizations of (A) CEVE and DOP, (B) CEVE and MDOL, and (C) styrene and DOL (broken curves: curves that were drawn using the *r* values obtained by the Kelen–Tüdõs method; dashed-dotted lines: azeotropic lines). Polymerization conditions: (A) and (B) [CEVE]$_0$ + [cyclic acetal]$_0$ = 0.80 M, [IBEA]$_0$ = 4.0 mM, [$TiCl_4$]$_0$ = 5.0 mM, [$SnCl_4$]$_0$ = 20 mM, [ethyl acetate] = 20 mM, [DTBP] = 10 mM, in toluene/dichloromethane (9/1 v/v) at –78 ºC. (C) [styrene]$_0$ + [DOL]$_0$ = 2.0 M, [St–HCl]$_0$ = 20 mM, [$SnCl_4$]$_0$ = 100 mM, [*n*Bu_4NCl]$_0$ = 40 mM, in dichloromethane at 0 ºC.

Conclusion

In conclusion, concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl monomers and cyclic acetals was demonstrated to proceed via the crossover propagation reactions and long-lived species under suitable reaction conditions. In particular, initiating systems designed based on the living cationic polymerization of vinyl monomers were highly important for the controlled copolymerization reactions. In addition, the difference in the distributions of the monomer units in copolymer chains most likely stemmed from the reactivity balance between the vinyl and cyclic monomers and the nature of the cyclic acetal-derived propagating species. The results obtained in this study will surely contribute to the development of initiating systems that allow for the controlled copolymerization of different types of monomers, such as vinyl, cyclic, and carbonyl compounds.

Associated Content

Additional data including NMR, ESI–MS, and GPC analyses. The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxx.

Acknowledgments

This work was partially supported by JSPS KAKENHI Grant Number JP26708014.

References

1. For reviews on controlled cationic polymerization: (a) Sawamoto, M. Modern Cationic Vinyl Polymerization. *Prog. Polym. Sci.* **1991**, *16*, 111—172. (b) Kennedy, J. P.; Ivan, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser: New York, 1992. (c) Matyjaszewski, K.; Sawamoto, M. In *Cationic Polymerizations*; Matyjaszewski, K., Ed.; Marcel Dekker; New York, 1996; Chapter 4. (d) Kennedy, J. P. Living Cationic Polymerization of Olefins. How Did the Discovery Come About? *J. Polym. Sci., Part A: Polym. Chem.* **1999,** *37,* 2285—2293. (e) Puskas, J. E.; Kaszas, G. Living Carbocationic Polymerization of Resonance-Stabilized Monomers. *Prog. Polym. Sci.* **2000**, *25*, 403—452. (f) De, P.; Faust, R. In *Macromolecular Engineering. Precise Synthesis, Materials Properties, Applications.*; Matyjaszewski, K.; Gnanou, Y.; Leibler, L., Eds.; WILEY-VCH GmbH & Co. KGaA, Weinheim, 2007; Chapter 3. (g) Goethals, E. J.; Prez, F. D. Carbocationic Polymerizations. *Prog. Polym. Sci.* **2007**, *32*, 220—246. (h) Aoshima, S.; Yoshida, T.; Kanazawa, A.; Kanaoka, S. New Stage in Living Cationic Polymerization: An Array of Effective Lewis Acid Catalysts and Fast Living Polymerization in Seconds. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1801—1813. (i) Aoshima, S; Kanaoka, S. A Renaissance in Living Cationic Polymerization. *Chem. Rev.* **2009**, *109*, 5245—5287. (j) Kanazawa, A.; Kanaoka, S.; Aoshima, S. Recent Progress in Living Cationic Polymerization of Vinyl Ethers. *Chem. Lett.* **2010**, *39*, 1232—1237.

2. For reviews on controlled radical polymerization: (a) Kamigaito, M.; Ando, T.; Sawamoto, M. Metal-Catalyzed Living Radical Polymerization. *Chem. Rev.* **2001**, *101*, 3689—3745. (b) Ouchi, M.; Terashima, T.; Sawamoto, M. Transition Metal-Catalyzed Living Radical Polymerization: Toward Perfection in Catalysis and Precision Polymer Synthesis. *Chem. Rev.* **2009**, *109*, 4963—5050. (c) Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. *Chem. Rev.* **2001**, *101*, 2921—2990. (d) Rosen, B. M.; Percec, V. Single-Electron Transfer and Single-Electron Transfer Degenerative Chain Transfer Living Radical Polymerization. *Chem. Rev.* **2009**, *109*, 5069—5119. (e) Hawker, C. J.; Bosman, A. W.; Harth, E. New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations. *Chem. Rev.* **2001**, *101*, 3661—3688. (f) Moad, G.; Rizzardo, E.; Thang, S. H. Radical Addition-Fragmentation Chemistry in Polymer Synthesis. *Polymer* **2008**, *49*, 1079—1131. (g) Yamago, S. Precision Polymer Synthesis by Degenerative Transfer Controlled/Living Radical Polymerization Using Organotellurium, Organostibine, and Organobismuthine Chain-Transfer Agents. *Chem. Rev.* **2009**, *109*, 5051—5068.
3. Simionescu, C. I.; Grigoras, M.; Bicu, E.; Onofrei, G. Spontaneous Copolymerization of 2-Methyl-2-Oxazoline and *N*-Phenyl Maleimide. *Polym. Bull.* **1985**, *14*, 79—83.
4. Rivas, B. L.; Pizarro, C.; Canessa, G. S. Copolymerization via Zwitterion. 11. *N*-Phenylmaleimide with 2-Ethyl-2-Oxazoline. *Polym. Bull.* **1988**, *19*, 123—128.
5. Hagiwara, T.; Takeda, M.; Hamana, H.; Narita, T. Copolymerization of *N*-Phenylmaleimide and Propylene Oxide Initiated with Organozinc Compounds. *Macromolecules* **1989**, *22*, 2025—2026.
6. Ikeda, Y.; Yoshida, Y.; Ishihara, K.; Hamana, H.; Narita, T.; Hagiwara, T. Copolymerization of 3,3,3-Trifluoro-1,2-Epoxypropane with *N*-Phenylmaleimide Using Organozinc Initiators. *Macromol. Rapid. Commun.* **1996**, *17*, 713—721.
7. Yang, H.; Xu, J.; Pispas, S.; Zhang, G. Hybrid Copolymerization of ε-Caprolactone and Methyl Methacrylate. *Macromolecules* **2012**, *45*, 3312—3317.
8. Okada, M.; Yamashita, Y.; Ishii, Y. Cationic Copolymerization of 1,3-Dioxolane with Styrene.

Makromol. Chem. **1966**, *94*, 181—193.

9. Okada, M.; Yamashita, Y. Cationic Copolymerization of Cyclic Formals and Vinyl Ethers. *Makromol. Chem.* **1969**, *126*, 266—275.
10. Aoki, S.; Fujisawa, K.; Otsu, T.; Imoto, M. The Copolymerization of the Vinyl Monomer with a Cyclic Compound. III. the Cationic Copolymerization of Styrene with Substituted Ethylene Oxides. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 729—733.
11. Solaro, R.; D'Antone, S.; Orsini, M.; Andruzzi, F.; Chiellini, E. Hybrid Copolymerization of Alkyl Vinyl Ethers with Glycidyl Ethers. *J. Appl. Polym. Sci.* **1983**, *28*, 3651—3663.
12. Kanazawa, A.; Kanaoka, S.; Aoshima, S. Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization Using $B(C_6F_5)_3$ as a Catalysts: Copolymerization of Vinyl Ethers and Isobutylene Oxide via Crossover Propagation Reactions. *J. Am. Chem. Soc.* **2013**, *135*, 9330—9333.
13. Kanazawa, A.; Kanaoka, S.; Aoshima, S. Rational Design of Oxirane Monomers for Efficient Crossover Reactions in Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization with Vinyl Ethers. *Macromolecules* **2014**, *47*, 6635—6644.
14. Kanazawa, A.; Kanda, S.; Kanaoka, S.; Aoshima, S. Alkoxyoxirane, a Unique Cyclic Monomer: Controlled Cationic Homopolymerization Mediated by Long-Lived Species and Copolymerization with Vinyl Ether via Alkoxy Group Transfer. *Macromolecules* **2014**, *47*, 8531—8540.
15. Kubisa, P.; Vairon, J. P. In *Polymer Science: A Comprehensive Reference*; Matyjaszewski, K., Möller, M., Eds.; Elsevier B.V.: Amsterdam, 2012; Vol. 4.10.
16. Pattison, D. B. Seven-Membered Cyclic Acetals. *J. Org. Chem.* **1957**, *22*, 662—664.
17. Higashimura, T.; Kamigaito, M.; Kato, M.; Hasebe, T.; Sawamoto, M. Living Cationic Polymerization of α-Methylstyrene Initiated with a Vinyl Ether-Hydrogen Chloride Adduct in Conjunction with Tin Tetrachloride. *Macromolecules* **1993**, *26*, 2670–2673.
18. Aoshima, S.; Higashimura, T. Living Cationic Polymerization of Vinyl Monomers by

Organoaluminum Halides. 3. Living Polymerization of Isobutyl Vinyl Ether by $EtAlCl_2$ in the Presence of Ester Additives. *Macromolecules* **1989**, *22*, 1009—1013.

19. (a) Kimura, R.; Yamada, M.; Kanazawa, A.; Kanaoka, S.; Aoshima, S. Monomer-Selective Domino Living Cationic Copolymerization of a Variety of Vinyl Ethers and Styrene Derivatives. *Polym. Prepr., Jpn.* **2013**, *62*, 2412. (b) Yoshizaki, T.; Kanazawa, A.; Kanaoka, S.; Aoshima, S. to be submitted.
20. Shinke, Y.; Kanazawa, A.; Kanaoka, S.; Aoshima, S. Living Cationic Polymerization of Vinylnaphthalene Derivatives. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 4828—4834. (b) Yoshida, T.; Kanazawa, A.; Kanaoka, S.; Aoshima, S. Instant Living Cationic Polymerization Using $SnCl_4/EtAlCl_2$ with a Weak Lewis Base: Ultrafast Polymerization in Seconds. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4288—4291.
21. Rahman, M. D.; Hashimoto, T.; Kodaira, T. Cationic Polymerization of Vinyl Ether with a Benzoate Pendant: The Formation of Long-Lived Polymers and the Identification of Side Reactions. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4362—4372.
22. Pantiru, M.; Vuluga, D. M.; Vasilescu, D. S.; Abadie, M. J. M. Study of the Cationic Photopolymerization Kinetics of Cyclic Acetals. *Polym. Bull.* **2002**, *47*, 485—492.
23. Kanazawa, A.; Shibutani, S.; Yoshinari, N.; Konno, T.; Kanaoka, S.; Aoshima, S. Structure Effects of Lewis Acids on the Living Cationic Polymerization of *p*-Methoxystyrene: Distinct Difference in Polymerization Behavior from Vinyl Ethers. *Macromolecules* **2012**, *45*, 7749—7757.
24. Okada, M.; Yamashita, Y.; Ishii, Y. Polymerization of 1,3-Dioxolane. *Makromol. Chem.* **1964**, *80*, 196—207.
25. Firat, Y.; Plesch, P. H. Oligomers from 2-Methyl-1,3-Dioxolan. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 135—136.
26. Higashimura, T.; Ishihama, Y.; Sawamoto, M. Living Cationic Polymerization of Styrene: New Initiating Systems Based on Added Halide Salts and the Nature of the Growing Species. *Macromolecules* **1993**, *26*, 744—751.

27. Kelen, T.; Tüdõs, F. A New Improved Linear Graphical Method for Determining Copolymerization Reactivity Ratios. *React. Kinet. Catal. Lett.* **1974**, *1*, 487—492.

28. Kennedy, J. P.; Kelen, T.; Tüdõs, F. Analysis of the Linear Methods for Determining Copolymerization Reactivity Ratios. II. A Critical Reexamination of Cationic Monomer Reactivity Ratios. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2277—2289.

29. Okada, M.; Yamashita, Y. Cationic Copolymerization of Cyclic Formals with Styrene. *Kogyo Kagaku Zasshi* **1966**, *69*, 506—510.

TOC Graphic

"Controlled Cationic Copolymerization of Vinyl Monomers and Cyclic Acetals via Concurrent Vinyl-Addition and Ring-Opening Mechanisms"

Tomoka Shirouchi, Arihiro Kanazawa*, Shokyoku Kanaoka, and Sadahito Aoshima*