The Cationic Polymerizability of Vinyl Acetate: Alternating Copolymerization with 1,3-Dioxolan-4-ones and Branched Copolymer Formation with Cyclic Acetals

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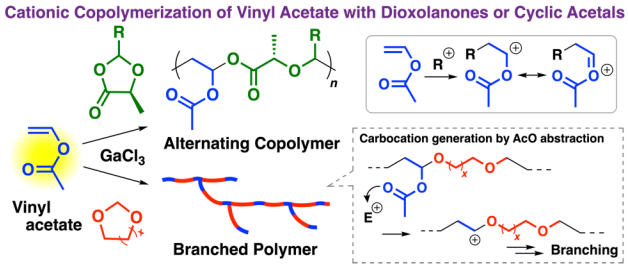


Abstract

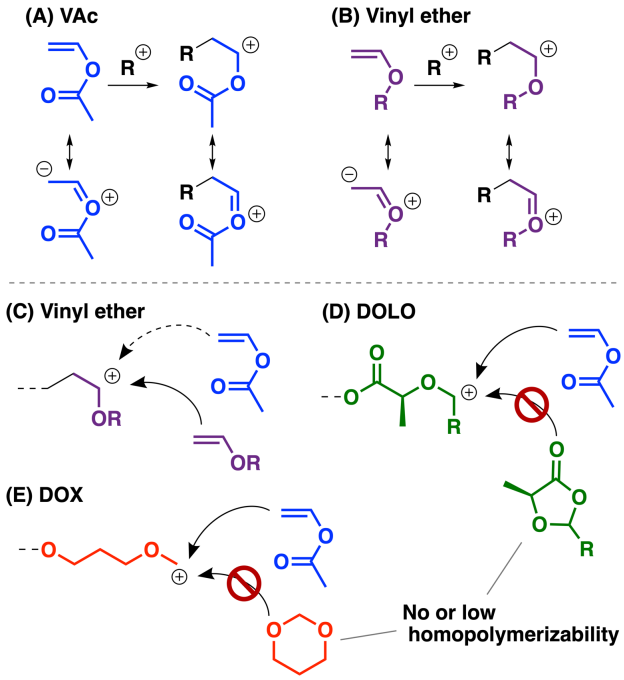
Vinyl acetate (VAc) potentially exhibits cationic polymerizability due to electron donation from the oxygen atom adjacent to the vinyl group through resonance. In this study, cationic copolymerizations of VAc and comonomers with little or no homopolymerizability were shown to proceed with very frequent crossover reactions. Alternating copolymers were produced when 1,3-dioxolan-4-ones, which generate a carbocation adjacent to oxygen via ring opening and exhibited no homopolymerizability, were used as comonomers in copolymerizations with VAc catalyzed by $GaCl_3$. An alternating copolymer with an M_n of 6.4×10^3 was obtained in the copolymerization of VAc and 2,5-dimethyl-1,3-dioxolan-4-one. Moreover, branched copolymers containing a portion with molecular weights over 10^5 were generated in copolymerizations of VAc with cyclic acetals exhibiting appropriate structures. Specifically, abstraction of the VAc-derived acetoxy group from the hemiacetal ester moiety in the main chain most likely resulted in carbocation generation and subsequent reaction with a monomer to form branched structures. The reaction of a hemiacetal ester moiety did not occur likely due to the rigid cyclic structure

when α-angelicalactone was used instead of VAc, resulting in an alternating copolymer with an M_n of 10.4×10^3 in the copolymerization with 1,3-dioxane. The copolymerization mechanisms generating such copolymer structures were discussed based on detailed analyses of the polymerization products by NMR spectroscopy.

Introduction

Cationic polymerization is an effective method for obtaining polymers from vinyl monomers with a high electron density on the vinyl group.[1–7] Representative monomers for cationic polymerizations include vinyl ethers, styrene derivatives, and isobutene. For example, electron donation from the oxygen atom to the vinyl group of vinyl ethers through the resonance effect contributes to the high reactivity of vinyl ethers toward cationic species (Scheme 1B). The carbocation generated from a vinyl ether is also stabilized due to electron donation through the resonance effect. The effects in both the monomer and the carbocation are responsible for the high polymerizability of vinyl ethers via the cationic mechanism.

Scheme 1. Carbocations Generated from (A) VAc or (B) Vinyl Ether. Possible Reactions of VAc with (C) Vinyl Ether-, (D) DOLO-, or (E) DOX-Derived Carbocations.



Poly(vinyl acetate) (poly(VAc)) is an industrially important material used for various purposes, such as in adhesives, emulsifiers, and precursors for poly(vinyl alcohol), and is produced by radical polymerization of vinyl acetate (VAc). VAc has an oxygen atom adjacent to the vinyl group and is structurally similar to vinyl ethers; hence, VAc potentially exhibits a resonance effect in a manner similar to vinyl ethers (Scheme 1). Specifically, electron donation from the oxygen atom to the vinyl group contributes to the high electron density on the vinyl group of the monomer and to stabilization of the carbocation, which potentially enables cationic polymerization of VAc. Indeed, the *e* value of VAc, which is an index of electron-donating and electron-withdrawing effects of vinyl monomers in the *Q*-*e* scheme, is –0.88, a promising value when compared with the values for cationically polymerizable

monomers; these include –1.27 for isobutyl vinyl ether, –0.80 for styrene, –1.20 for isobutene, and –1.29 for *N*-vinylcarbazole.[8] However, cationic homopolymerization of VAc was reported to be difficult in past studies.[9,10]

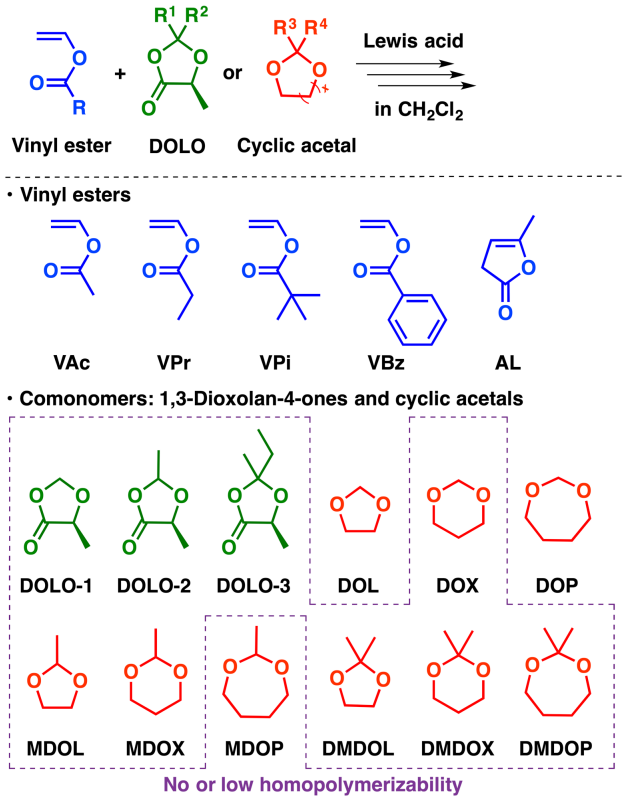
Insufficient reactivity of the VAc monomer and ineffcient generation of the VAc-derived carbocation in VAc homopropagation reactions are possible reasons for the inertness of VAc in cationic polymerization. Therefore, we sought ways to achieve cationic copolymerization of VAc and other monomers. Importantly, in past studies, cationic copolymerization of styrene and VAc was reported, although the composition of the products was analyzed by elemental analysis; thus, structural features of the polymers were not revealed.[9,10] Comonomers that exhibit high reactivity and/or generate a very reactive carbocation are required for efficient copolymerization. However, if a monomer exhibiting high homopolymerizability is used as a comonomer, a homopolymer of the comonomer is preferentially produced, and only negligible amounts of VAc are incorporated into the polymer chains, as expected for copolymerization of VAc and vinyl ethers (Scheme 1C). In the above example, styrene was preferentially consumed instead of VAc due to the cationic homopolymerizability of styrene.[9,10]

A strategy for avoiding homopolymer generation from a comonomer is to employ comonomers with little or no homopolymerizability. As candidates for this purpose, we focused on 1,3-dioxolan-2-ones (DOLOs) and cyclic acetals (Scheme 1D and 1E). Unlike their six-membered counterparts, DOLOs do not exhibit cationic homopolymerizability,[11] but copolymers are produced by cationic copolymerization when DOLOs are combined with oxiranes, as reported in our previous study.[12] Cyclic acetals with low ring strain are not homopolymerizable due to their low ceiling temperature (for high

equilibrium concentration),[13–22] whereas copolymerizations proceed when suitable comonomers are added, as in the cases of 1,3-dioxane (DOX) copolymerizations with cyclic acetals or cyclic ethers.[23–25] These nonhomopolymerizable monomers potentially react with VAc to generate copolymers via the cationic pathway. It should be noted that α-angelicalactone (AL), which is a five-membered cyclic vinyl ester, was reported to yield a copolymer via cationic copolymerization with 1,3-dioxolane (DOL).[26,27]

In this study, cationic copolymerizations of VAc with DOLOs or cyclic acetals were investigated (Scheme 2), and the polymerization products were analyzed in detail by NMR spectrometry. DOLOs were demonstrated to undergo very frequent crossover reactions in copolymerizations with VAc, which resulted in alternating copolymers with the highest M_n of 6.4×10^3 under suitable conditions. Furthermore, cyclic acetals with suitable structures underwent cationic copolymerizations with VAc via a mechanism consisting of crossover reactions and side-chain abstraction, and the latter led to formation of branched structures. In addition, the copolymerization of AL and DOX resulted in an alternating copolymer with an M_n of 10.4×10^3.

Scheme 2. Cationic Copolymerization of Vinyl Esters with DOLOs or Cyclic Acetals.[a]



[a] The homopolymerizability of comonomers is judged based on past studies (references 12–21).

Experimental Section

See the Supporting Information for the Materials and Characterization subsections.

Polymerization Procedure. The following is a typical polymerization procedure. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki, PJ-206A; the temperature was approximately 450 °C) under dry nitrogen. Dichloromethane, VAc, and DOLO-1 were sequentially added to the tube using dry syringes. Polymerization was initiated by addition of a prechilled dichloromethane solution of $GaCl_3$ to the monomer solution at –40 °C. After a predetermined time, the

reaction was terminated by addition of methanol containing a small amount of triethylamine. The quenched mixture was diluted with dichloromethane and then washed with aqueous sodium hydroxide solution and water. The volatiles were then removed under reduced pressure to yield the product. Monomer conversion was determined by a gravimetric method and ^{1}H NMR analysis. More specifically, the molar ratio of VAc and comonomer in the copolymerization product was determined by ^{1}H NMR analysis, and subsequently, conversion was calculated from this ratio and the weight of the product.

Acid-Catalyzed or Base-Catalyzed Degradation. Acid-catalyzed degradation of the copolymer was conducted with 0.5 M HCl(aq) in *n*-propanol or *n*-butanol at room temperature for three days. Base-catalyzed degradation of the copolymer was conducted with K_2CO_3 (1.0 eq with respect to ester groups) in diethyl ether/methanol (1/1 v/v) for three days. All reactions were conducted at room temperature with a polymer concentration of 10 mg/mL. The quenched mixtures were diluted with dichloromethane and then successively washed with an aqueous sodium hydroxide solution and water. The volatiles were evaporated to yield the product.

Results and Discussion

Cationic homopolymerization of VAc and copolymerizations with vinyl ethers or styrene

Cationic homopolymerizations of VAc[9,10] were conducted with $GaCl_3$, $SnCl_4$, or BF_3OEt_2 as Lewis acid catalysts. However, monomer conversions were very low (≤ 3%) under the conditions

examined, as listed in Table 1. The molecular weights (MWs) of the products were also low. ^{1}H NMR analysis of the product obtained with $GaCl_3$ at 0 °C suggested that side reactions, such as cleavage of the acetoxy pendants, occurred in addition to propagation by vinyl addition (Figure S1).

Table 1. Cationic Homopolymerization of VAc[a]

entry	Lewis acid	temp. (°C)	time	VAc conv. (%) [b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]
1	$GaCl_3$ (20 mM)	0	216 h	3	1.5	2.14
2	$GaCl_3$ (20 mM)	–40	816 h	1	0.9	1.67
3	$SnCl_4$ (50 mM)	–40	168 h	<1	–	–
4	BF_3OEt_2 (50 mM)	0	24 h	2	0.5	1.65

[a] $[VAc]_0$ = 3.2 (entries 1–3) or 0.80 (entry 4) M, in CH_2Cl_2. [b] Determined by gravimetry and ^{1}H NMR analysis of products. [c] By GPC using polystyrene standards.

Cationic copolymerizations of VAc with vinyl ethers were also examined (Table S1); however, homopolymers of the vinyl ethers were produced. VAc was negligibly incorporated into the polymer chains. The results indicated that the propagating species derived from the vinyl ethers exclusively reacted with a vinyl ether monomer due to the low reactivity of VAc, as expected from Scheme 1C. Moreover, VAc was also negligibly incorporated into polymer chains in the copolymerizations of VAc and styrene, in contrast with past studies.[9,10] The difference in reaction conditions could be responsible for the different results.

Cationic copolymerizations of VAc and 1,3-dioxolan-4-ones

As a promising comonomer, 5-methyl-1,3-dioxolan-4-one (DOLO-1) was employed in a cationic copolymerization with VAc using $GaCl_3$ as the catalyst in dichloromethane at 0 °C (entry 1 in

Table 2). Both monomers were consumed after a long reaction time, although the monomer conversion was low. A product with a M_n of 1.3×10^3 was obtained under these conditions. After optimization to achieve higher-MW products, the reaction was run at –40 °C and with a higher concentration of VAc than of DOLO-1 (entry 3), and this resulted in a product with a M_n of 3.4×10^3 (Figure 1A). The high concentration of VAc was adopted because we thought that the crossover reaction from the DOLO-derived propagating species to a VAc monomer would be a hurdle due to the low reactivity of VAc. This product was subjected to detailed structural analysis. The use of $EtAlCl_2$, $SnCl_4$, or $B(C_6F_5)_3$ as catalysts instead of $GaCl_3$ resulted in ineffective polymerizations (entries 4–6). Homopolymerization of DOLO-1 did not proceed (entry 9) as in the case of our previous study.[12]

Table 2. Cationic Copolymerization of VAc and DOLO[a]

entry	VAc conc.	DOLO (conc.)	Lewis acid	temp (ºC)	time	VAc conv. (%) [b]	DOLO conv. (%) [b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]	average number of units per block [d]	
										VAc	DOLO
1	1.2 M	DOLO-1 (1.2 M)	$GaCl_3$	0	120 h	13	7	1.3	1.97	—	—
2	1.2 M	(1.2 M)	$GaCl_3$	–40	192 h	9	7	1.5	1.93	1.2	1.1
3	3.2 M	(0.80 M)	$GaCl_3$	–40	816 h	9	32	3.4	2.20	1.1	1.0
4	1.2 M	(1.2 M)	$EtAlCl_2$	–40	192 h	0	0	—	—	—	—
5	1.2 M	(1.2 M)	$SnCl_4$	–40	192 h	2	2	0.5	1.69	—	—
6	1.2 M	(1.2 M)	$B(C_6F_5)_3$	–40	192 h		4[e]	0.3	1.55	—	—
7	3.2 M	DOLO-2 (0.80 M)	$GaCl_3$	–40	216 h	25	92	6.4	3.00	1.0	1.0
8	3.2 M	DOLO-3 (0.80 M)	$GaCl_3$	–40	192 h	4	19	0.6	1.48	—	—
9	none	DOLO-1 (1.2 M)	$GaCl_3$	–40	96 h	—	0	—	—	—	—
10	none	DOLO-2 (1.2 M)	$GaCl_3$	–40	96 h	—	0	—	—	—	—

[a] $[\text{Lewis acid}]_0$ = 10 (entry 6) or 20 (except for entry 6) mM in CH_2Cl_2. [b] Determined by gravimetry and ^{1}H NMR analysis of products. [c] By GPC using polystyrene standards. [d] Calculated by ^{1}H NMR. [e] Total conversion determined by gravimetry.

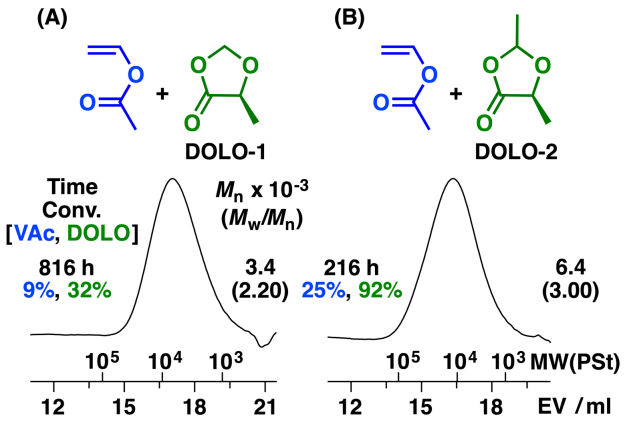


Figure 1. MWD curves of the products obtained by the copolymerization of VAc and (A) DOLO-1 (entry 3 in Table 2) or (B) DOLO-2 (entry 7). See Table 2 for the polymerization conditions.

^{1}H NMR analysis of the copolymerization product revealed that the polymer chains consisted mostly of alternating sequences of VAc and DOLO-1 (Figure 2A). A peak at 6.9 ppm (peak *e*) was assignable to the VAc-derived methine group adjacent to the acetoxy group and the DOLO-derived oxygen atom. This structure is proof of the crossover reaction from the VAc-derived carbocation to a DOLO-1 monomer. In addition, peaks at 3.5 and 3.8 ppm (peak *i*) were assignable to the DOLO-derived methylene group adjacent to the next VAc unit, which indicates that the crossover reaction from DOLO-1 to VAc also occurred. Importantly, the peaks assigned to VAc homosequences (peak *b*; see also Figure S1A) were very small, and peaks for DOLO-1 homosequences were not observed at all, which is consistent with the negligible homopolymerizabilities of these monomers.[9–12] These results indicated that the copolymer had almost alternating sequences. The integral ratios of the observed peaks were also consistent with the assignments. Moreover, the validity of the structure was supported by ^{13}C, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC, and ^{1}H–^{13}C HMBC spectra (Figures S2–S5) of the copolymer. Differential scanning calorimetry (DSC) analysis of the copolymer showed a T_g at 5 °C (Figure S6), which was lower

than the value for a VAc homopolymer obtained by radical polymerization (28 °C), although the low MW of the copolymer possibly led to the lower T_g value.

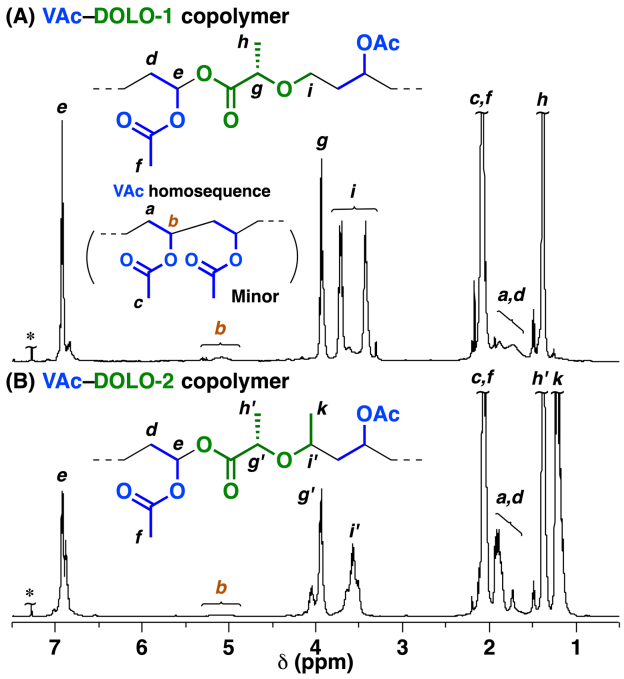
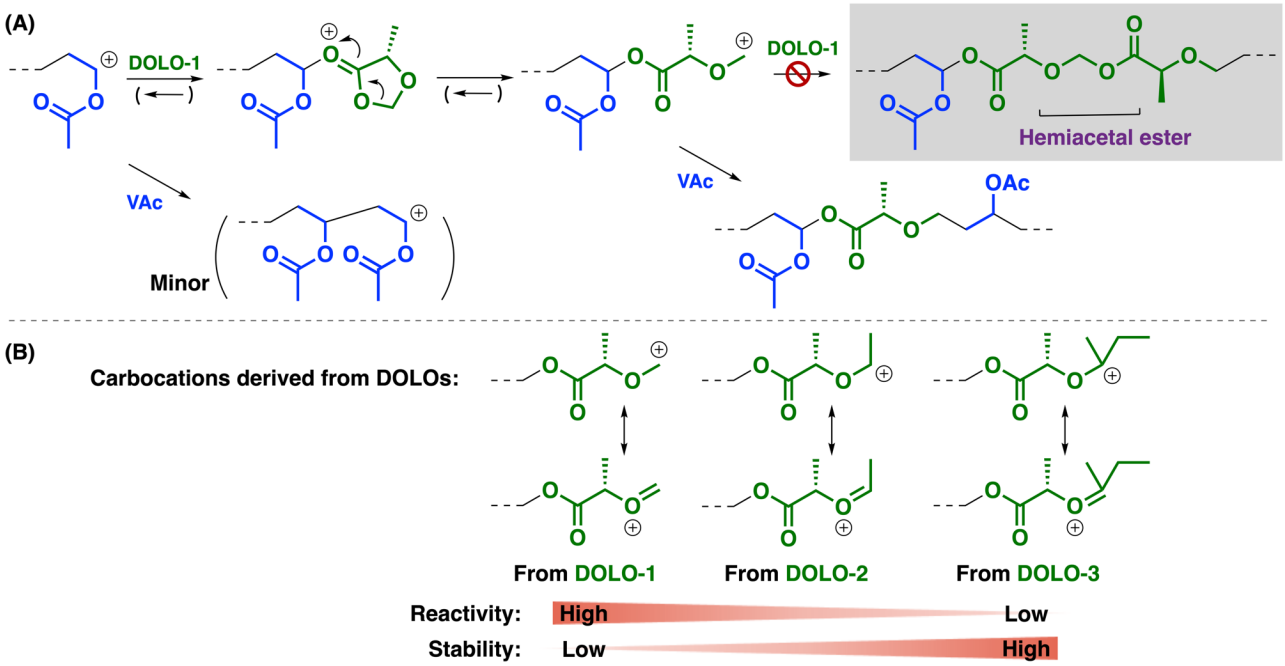


Figure 2. ^{1}H NMR spectra of the poly (VAc-*co*-DOLO)s (entries (A) 3 and (B) 7 in Table 2; after purification by preparative GPC; in $CDCl_3$ at 30 ºC; * $CHCl_3$).

A plausible copolymerization mechanism is shown in Scheme 3A. A carbocation derived from VAc reacts negligibly with VAc but preferentially with DOLO-1, which is followed by ring-opening of the oxonium ion to generate a DOLO-1-derived primary carbocation. This carbocation receives electron donation from the lone pair of the adjacent oxygen atom, as in the case of a vinyl ether-derived carbocation. Subsequently, the DOLO-1-derived carbocation reacts exclusively with VAc due to the nonhomopolymerizability of DOLO-1. Repetition of these crossover reactions results in alternating sequences of the copolymer.

Scheme 3. (A) A Propagation Mechanism of the Cationic Copolymerization of VAc and DOLO-1 and (B) Carbocations Derived from DOLOs.



The copolymer chain formation was likely triggered by initiation from a proton and quenched by reactions with side products such as acetic acid and water. The polymerization starts through proton generation from the reaction of a Lewis acid with protic impurities, such as adventitious water, and/or interaction of a Lewis acid with the carbonyl group of DOLO-1. At the end of propagation, a reaction of the VAc-derived carbocation with acetic acid or water results in VAc-OAc or VAc-OH chain ends, respectively, and liberation of a proton. Indeed, peaks with *m*/*z* values corresponding to these chain-end structures were detected via electrospray ionization mass spectrometry (ESI-MS) analysis (Figure S7). The ratio of the frequencies of the crossover reactions between VAc and DOLOs and side reactions is

responsible for the MWs of the products. In addition, the VAc-OH moiety was likely transformed into an aldehyde, which was supported by detection of aldehydes via ^{1}H NMR (Figure S8).

2,5-Dimethyl-1,3-dioxolan-4-one (DOLO-2), which has a methyl group at the 2-position, also successfully underwent copolymerization with VAc and yielded an alternating copolymer with a higher MW than the copolymer of VAc and DOLO-1 (entry 7 in Table 2, Figure 1B and Figure 2B). In contrast, the use of 2-ethyl-2,5-dimethyl-1,3-dioxolan-4-one (DOLO-3), which has methyl and ethyl groups at the 2-position, resulted in oligomer formation (entry 8; Figure S9). The differences among DOLOs are likely related to the reactivities of the DOLO-derived carbocations (Scheme 3B). Primary, secondary, and tertiary carbocations are generated from DOLO-1, DOLO-2, and DOLO-3, respectively. The reactivities of the carbocations decrease while the stabilities increase in this order. DOLO-2 exhibited greater copolymerizability than the other two due to a suitable balance of reactivity and stability of the carbocation, whereas the inefficiency of DOLO-3 in copolymerization with VAc is likely due to the insufficient reactivity of the tertiary carbocation with the VAc monomer.

The copolymerizations of VAc and DOLOs were very slow probably due to several reasons, such as the suppressed Lewis acidity of the catalysts via the interaction with the ester group of the monomers, the low reactivity of a VAc monomer toward a cationic propagating species, and the somewhat inefficient ring-opening reaction of the DOLO-derived oxonium ion into the carbocation. The copolymerization of DOLO-2 was much faster than that of DOLO-1 (see Figure S10 for the time–conversion curves), which likely suggests that the ring-opening reaction of the DOLO-2-derived

oxonium ion proceeded more smoothly than that of the DOLO-1 counterpart due to the more stable DOLO-2-derived carbocation.

Other vinyl esters were also effective for the copolymerization with DOLOs. The use of vinyl pivalate (VPi) or vinyl benzoate (VBz) instead of VAc resulted in copolymers with alternating sequences in the copolymerization with DOLO-1 or DOLO-2 (Table S2 and Figure S11).

Cationic copolymerizations of VAc and cyclic acetals

Nonsubstituted five- (DOL), six- (DOX), and seven-membered (1,3-dioxepane; DOP) cyclic acetals were subsequently used as comonomers in cationic copolymerizations with VAc by using $GaCl_3$ as a Lewis acid catalyst. Both VAc and cyclic acetals were consumed in the copolymerizations, while the efficiencies of the copolymerizations obviously depended on the homopolymerizabilities of the cyclic acetals. DOP, which exhibits greater homopolymerizability (entry 13 in Table 3) than DOL (entry 11) and DOX (entry 12),[14,15] resulted in a product with a very large proportion of DOP homosequences (entry 10; Figure 3C). In contrast, DOX, which exhibits negligible homopolymerizability (entry 12),[13,15,16] was the most suitable cyclic acetal among the three for comparable consumption of both VAc and DOX (entries 3–6). In addition, as a result of investigations of various reaction conditions, copolymerizations of VAc with higher concentrations than those of cyclic acetals were effective in yielding products with higher MWs (entries 1–6). A reaction at a lower temperature resulted in a product with a MW comparable to that obtained at 0 °C (entry 7). Other catalysts were inferior to $GaCl_3$ (entries 8 and 9). Interestingly, the product obtained from VAc and DOX under the optimized conditions (entry 6) contained fractions

with MWs exceeding 10^5, as judged by gel permeation chromatography (GPC) analysis with polystyrene calibration (Figure 3B). The copolymerizations of VAc and DOX were very slow as in the cases of the DOLO counterparts likely due to similar reasons (vide supra; see Figure S12 for the time–conversion curve of the copolymerization under the conditions for entry 6).

Table 3. Cationic Copolymerization of VAc and Cyclic Acetals[a]

entry	VAc conc	cyclic acetal	Lewis acid	temp. (ºC)	time	VAc conv. (%) [b]	cyclic acetal conv. (%) [b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]	composition in copolymer (%)[d]	
										VAc	acetal
1	0.80 M	DOL (0.80 M)	$GaCl_3$ (10 mM)	0	24 h	9	24	0.7	2.06	26	74
2	3.2 M	(0.80 M)	$GaCl_3$ (20 mM)	0	216 h	23	62	1.9	3.93	46	54
3	0.80 M	DOX (0.80 M)	$GaCl_3$ (10 mM)	0	24 h	5	7	1.2	5.53	42	58
4	0.80 M	(1.6 M)	$GaCl_3$ (10 mM)	0	24 h	8	6	0.8	4.37	37	63
5	1.6 M	(0.80 M)	$GaCl_3$ (10 mM)	0	24 h	5	11	1.3	5.06	48	52
6	3.2 M	(0.80 M)	$GaCl_3$ (20 mM)	0	216 h	14	47	2.7	9.17	54	46
7	3.2 M	(0.80 M)	$GaCl_3$ (20 mM)	–40	816 h	13	43	2.8	5.87	55	45
8	3.2 M	(0.80 M)	$SnCl_4$ (100 mM)	0	264 h	68	100	1.6	3.56	70	30
9	0.80 M	(0.80 M)	BF_3OEt_2 (50 mM)	0	24 h	2	4	0.6	2.32	33	67
10	3.2 M	DOP (0.80 M)	$GaCl_3$ (20 mM)	0	168 h	5	86	1.0	2.28	19	81
11	none	DOL (0.80 M)	$GaCl_3$ (10 mM)	0	24 h	—	5	0.5	1.53	—	—
12	none	DOX (0.80 M)	$GaCl_3$ (10 mM)	0	24 h	—	0	—	—	—	—
13	none	DOP (0.80 M)	$GaCl_3$ (10 mM)	0	24 h	—	43	0.9	5.41	—	—

[a] In CH_2Cl_2. [b] Determined by gravimetry and ^1H NMR analysis of products. [c] By GPC using polystyrene standards. [d] Calculated by ^1H NMR.

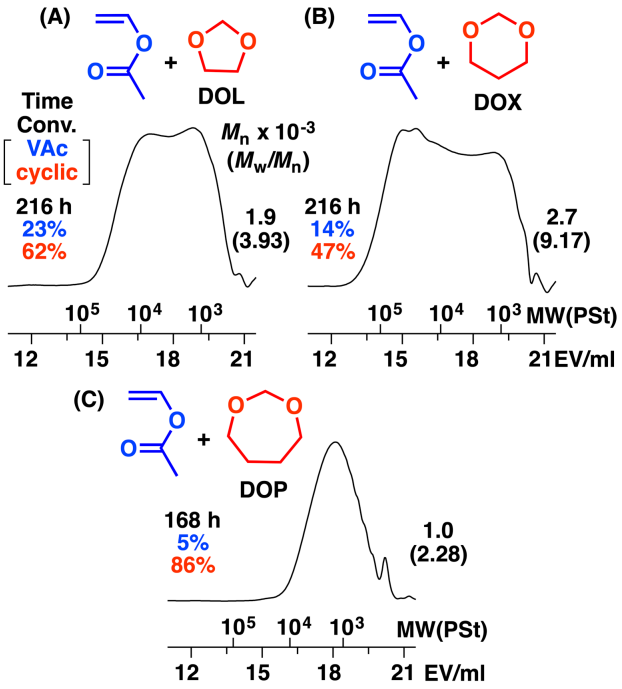


Figure 3. MWD curves of the products obtained by the copolymerizations of VAc with (A) DOL (entry 2 in Table 3), (B) DOX (entry 6), or (C) DOP (entry 10). See Table 3 for the polymerization conditions.

NMR analysis of the product obtained from VAc and DOX revealed that the copolymerization proceeded via crossover reactions and branching reactions triggered by abstraction of an acetoxy moiety derived from VAc. The ^{1}H NMR spectrum (Figure 4) exhibited large peaks at 2.0 and 3–4 ppm, which were assigned to the methyl groups of VAc units and the oxygen-adjacent methylene groups of DOX units, respectively. However, a peak at 5–6 ppm, which was assigned to a hemiacetal ester produced via reaction crossover from VAc to DOX ([iii] in Figure 4; peak *h*), was obviously small. Instead, noticeable peaks were present at several chemical shifts, such as 1.4, 3.7, 4.1, 4.7, 5.3, and 6.9 ppm. These peaks were assigned to hemiformal ester ([iv]; peak *k*), diacetoxymethine ([v]; peak *l*), ester ([vi]; peak *m*), and six-membered cyclic acetal[28] ([vii]; peaks *o*, *o'*, *p*, and *p'*) structures. These assignments were consistent with the ^{13}C, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC, and ^{1}H–^{13}C HMBC spectra (Figures S13–S16). The ^{1}H NMR

spectrum of the product obtained by $SnCl_4$ (entry 8 in Table 3) also exhibited similar peaks (Figure S17), indicating that similar copolymerization occurred irrespective of the catalysts used.

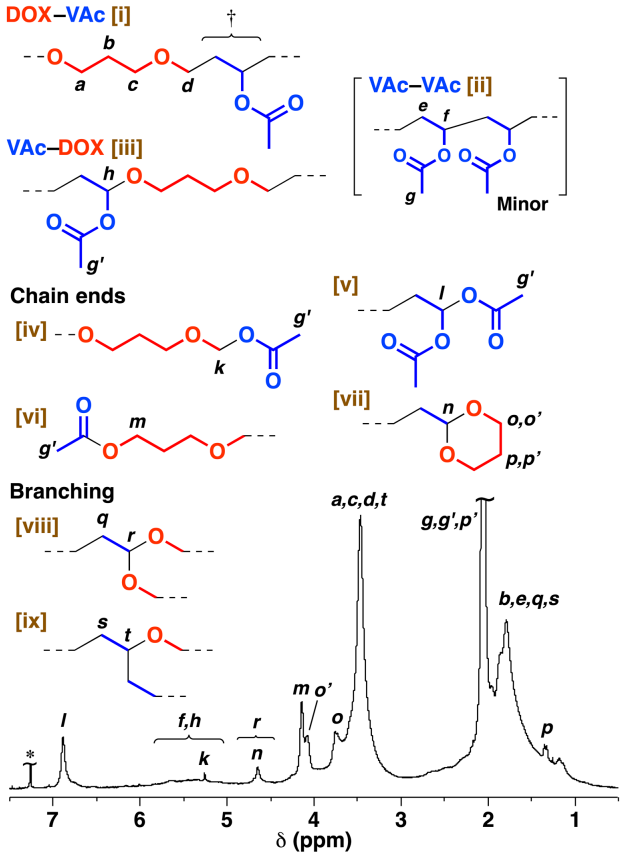
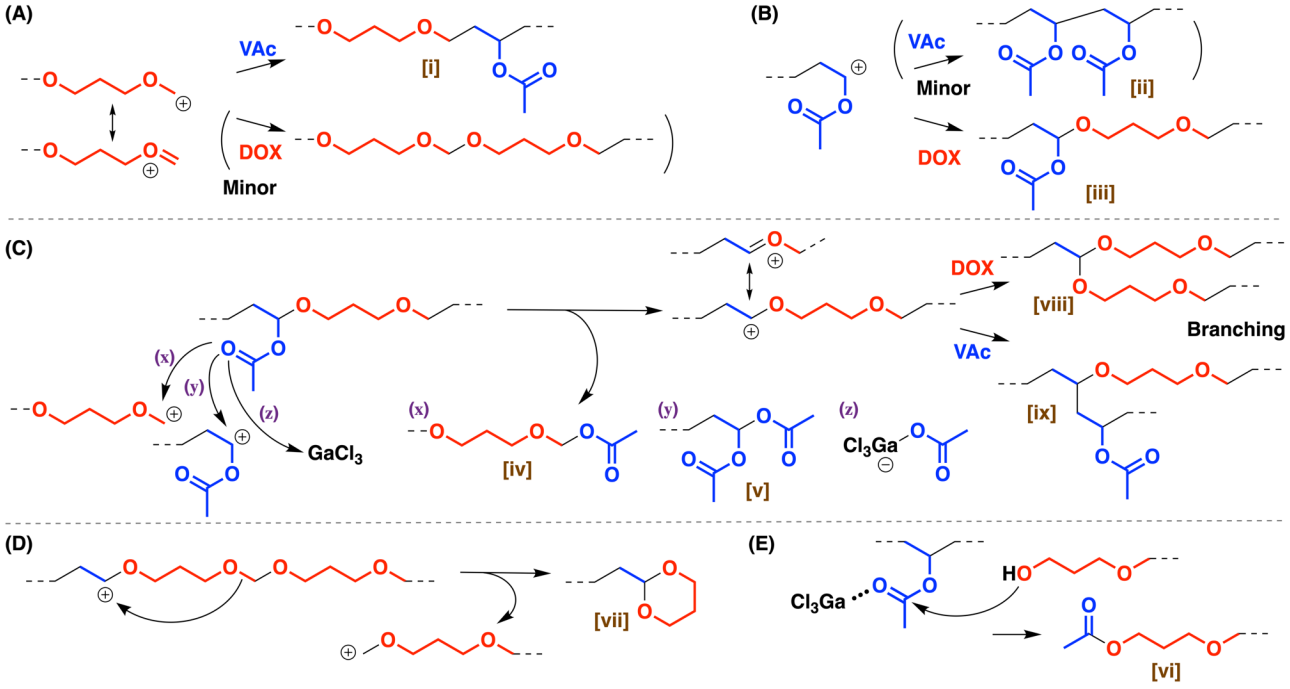


Figure 4. ^{1}H NMR spectrum of the poly(VAc-*co*-DOX) (entry 6 in Table 3; a high-MW portion separated by preparative GPC; in $CDCl_3$ at 30 ºC; * $CHCl_3$). † Some of the VAc units adjacent to the DOX unit were transformed into other units, such as structures [vii], [viii], and [ix], as a result of the abstraction of the acetoxy moiety. Peaks *o*, *o'*, *p*, and *p'* are consistent with the chemical shifts of a 2-substituted 1,3-dioxane (ref 28).

Using the characteristic structures revealed by NMR analyses, a copolymerization mechanism was deduced (Scheme 4). The DOX-derived carbocation reacts preferentially with VAc due to the very low homopolymerizability (Scheme 4A). Subsequently, the VAc-derived carbocation reacts negligibly with VAc monomer due to the inefficient homopropagation, so it reacts with DOX (Scheme 4B).

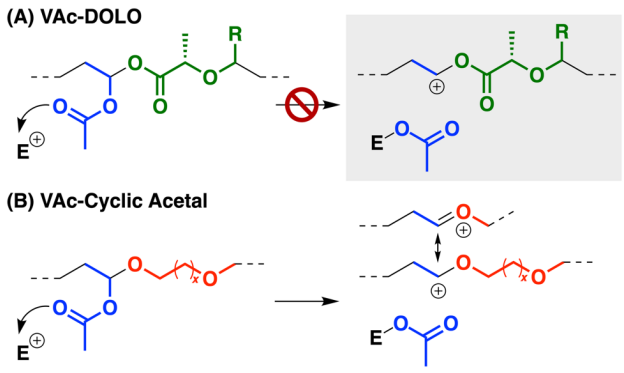
Importantly, the VAc–DOX sequence ([iii] in Figure 4) obtained by crossover from VAc to DOX undergoes abstraction of an acetoxy moiety via reaction with the DOX-derived carbocation or the VAc-derived carbocation ((x) and (y) in Scheme 4C), resulting in the hemiformal ester ([iv]) or diacetoxymethine ([v]) structures, respectively, that were detected by NMR analysis. $GaCl_3$ also abstracts an acetoxy unit ((z) in Scheme 4C). Acetoxy abstraction occurs because a carbocation is generated which is stabilized by electron donation from the lone-pair electrons of the oxygen atom and has a structure similar to the carbocation derived from a vinyl ether. This carbocation subsequently reacts with DOX or VAc, resulting in branched structures ([viii] and [ix]). It is important to note that this type of branching does not occur in copolymerizations of VAc and DOLOs because a carbocation with sufficient stability is not generated (Scheme 5). The six-membered cyclic acetal ([vii]) structure is generated via the reaction shown in Scheme 4D. The ester moiety ([vi]) is derived from a reaction between the acetoxy moiety and the hydroxy group, which results from a proton and DOX (Scheme 4E). The structures explained here were also supported by ESI-MS analyses of the copolymerization product (Figure S18 and Scheme S1). In addition, the absolute M_n values of the poly(VAc-*co*-DOX)s determined by GPC with a light-scattering detector were much higher than the values determined by polystyrene calibration (Table S3 and Figure S19), which is consistent with the formation of branched structures. Interestingly, the products obtained by the copolymerizations of VAc with DOL or DOX exhibited multimodal and broad MWDs (Figures 3A, 3B, and Figure S12B). The reason of such MWDs is unclear; however, coupling reactions between polymer chains via some reactions, such as the reaction between a carbocation and a chain end hydroxy group, might occur and be responsible for such MWDs.

Scheme 4. Plausible Mechanisms of the Cationic Copolymerization of VAc and DOX.[a]



[a] Counteranions are omitted.

Scheme 5. The Difference of the Copolymerizations of VAc with (A) DOLO or (B) a Cyclic acetal.[a]



[a] E^+ represents a cationic species or a Lewis acid.

Similar reactions occurred in copolymerizations of VAc with DOL (entries 1 and 2 in Table 3; Figure 3A). Peaks assignable to the chain end structures described above were detected in the ^{1}H, ^{13}C,

^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC, and ^{1}H–^{13}C HMBC spectra of the copolymerization products (Figures S20–S24). Unlike the DOX case, however, DOL homosequences were also generated in polymer chains due to the sufficient homopolymerizability of DOL. The copolymerization of VAc and DOP also likely occurred via a similar mechanism, although the DOP homosequences were much longer (entry 10; Figure S25).

The copolymerization product was degraded into low-MW compounds under acidic or basic conditions. Degradation by acid was conducted in butanol or propanol. The hemiacetal ester and the diacetoxymethine moieties were cleaved and transformed into butanol or propanol-derived acetal structures (Figure 5B), which was confirmed by both ^{1}H NMR (Figures S26) and the shift of the molecular weight distribution (MWD) curve in GPC analysis into the lower-MW region (Figure 5A). The copolymer was also degraded by base (K_2CO_3) due to hydrolyses of the hemiacetal ester moieties into hemiacetal moieties, which were subsequently cleaved spontaneously to give aldehydes.

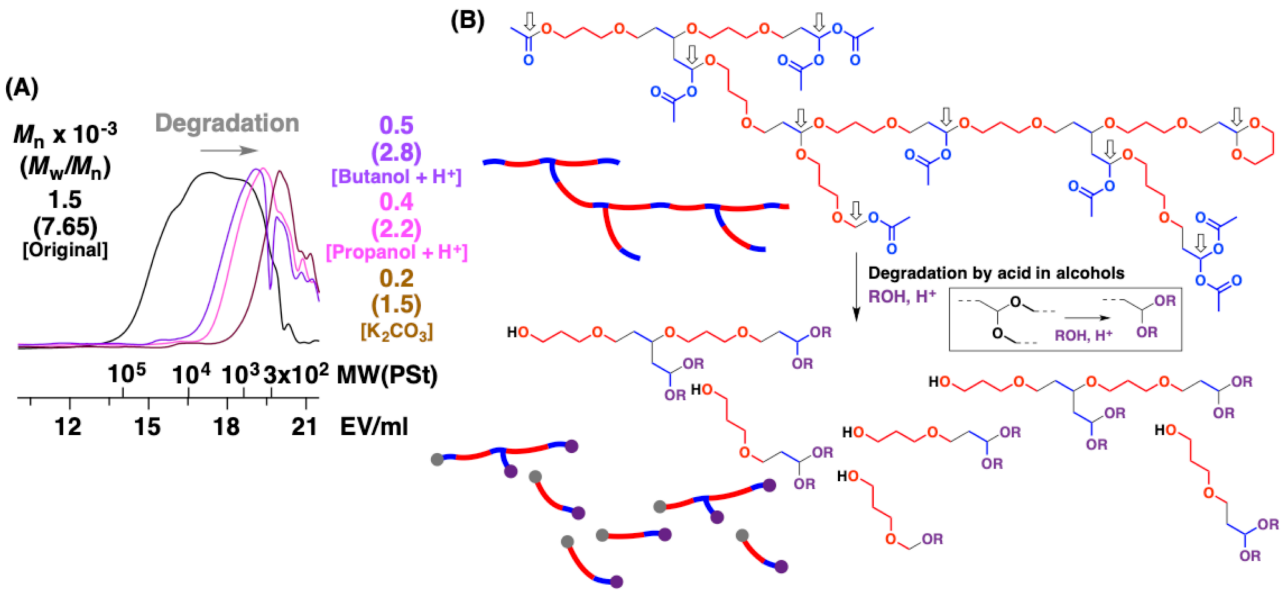


Figure 5. (A) MWD curves of the products obtained by the copolymerization of VAc and DOX (black; obtained under the same conditions as those for entry 6 in Table 3) and the acid (red and purple) or base (blue) degradation products. (B) A representative structure of a copolymer chain obtained by the cationic copolymerization of VAc and DOX (upper) and the structures resulting from degradation by acid in an alcohol (lower).

Cyclic acetals with methyl groups at the 2-position (2-methyl-1,3-dioxolane (MDOL), 2-methyl-1,3-dioxane (MDOX), and 2-methyl-1,3-dioxepane (MDOP)) also underwent copolymerization with VAc in a manner similar to the nonsubstituted cyclic acetals (entries 1–3 in Table 4). Structures similar to those shown in Scheme 4 were confirmed by ^{1}H, ^{13}C, and 2D NMR analyses of the copolymerization products (Figures S27–S34). However, the MWs of the products were very low. The lower reactivity of the secondary carbocations derived from the methyl-substituted cyclic acetals than that of the primary carbocations derived from the nonsubstituted counterparts is possibly responsible for the low MWs due to inefficient crossover reactions from the methyl-substituted cyclic acetals to VAc. Indeed, dimethyl-substituted cyclic acetals (2,2-dimethyl-1,3-dioxolane (DMDOL), 2,2-dimethyl-1,3-dioxane (DMDOX), and 2,2-dimethyl-1,3-dioxepane (DMDOP)), which generate tertiary carbocations, were completely ineffective in copolymerizations with VAc (entries 4–6).

Table 4. Cationic Copolymerization of VAc and 2-Substituted Cyclic Acetals[a]

entry	cyclic acetal	VAc conv. (%) [b]	cyclic acetal conv. (%) [b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]	composition in copolymer (%)[d]	
						VAc	cyclic acetal
1	MDOL	15	44	0.5	2.04	58	42
2	MDOX	11	29	0.5	2.14	60	40
3	MDOP	8	38	0.4	1.37	46	54
4	DMDOL	1	6	0.3	1.38	–	–
5	DMDOX	<1	4	0.3	1.41	–	–

6	DMDOP	<1	1	0.3	1.34	–	–

[a] $[VAc]_0$ = 3.2 M, [cyclic acetal]$_0$ = 0.80 M, $[GaCl_3]_0$ = 20 mM, in CH_2Cl_2 at 0 ºC. Polymerization time = 168 h. [b] Determined by gravimetry and ^{1}H NMR analysis of products. [c] By GPC using polystyrene standards. [d] Calculated by ^{1}H NMR.

Cationic copolymerizations of vinyl esters and DOX

To validate the copolymerization mechanism proposed above, vinyl esters other than VAc were used in cationic copolymerizations with DOX. Copolymerizations of DOX with vinyl propionate (VPr), VPi, or VBz, which have an ethyl, *tert*-butyl, or phenyl group, respectively, instead of the methyl group of VAc, yielded products with MWs and MWDs similar to those of poly(VAc-*co*-DOX) resulting under similar reaction conditions (Table S4 and Figure S35). ^{1}H NMR analyses of the products (Figure 6) showed that chain ends consisted of structures such as hemiformal ester ([iv]), diacetoxymethine ([v]), ester ([vi]), and six-membered cyclic acetal ([vii]) structures; these were similar to the structures detected in poly(VAc-*co*-DOX), indicating that the copolymerizations proceeded via abstraction of the side chains and subsequent branching reactions, as in the case of VAc.

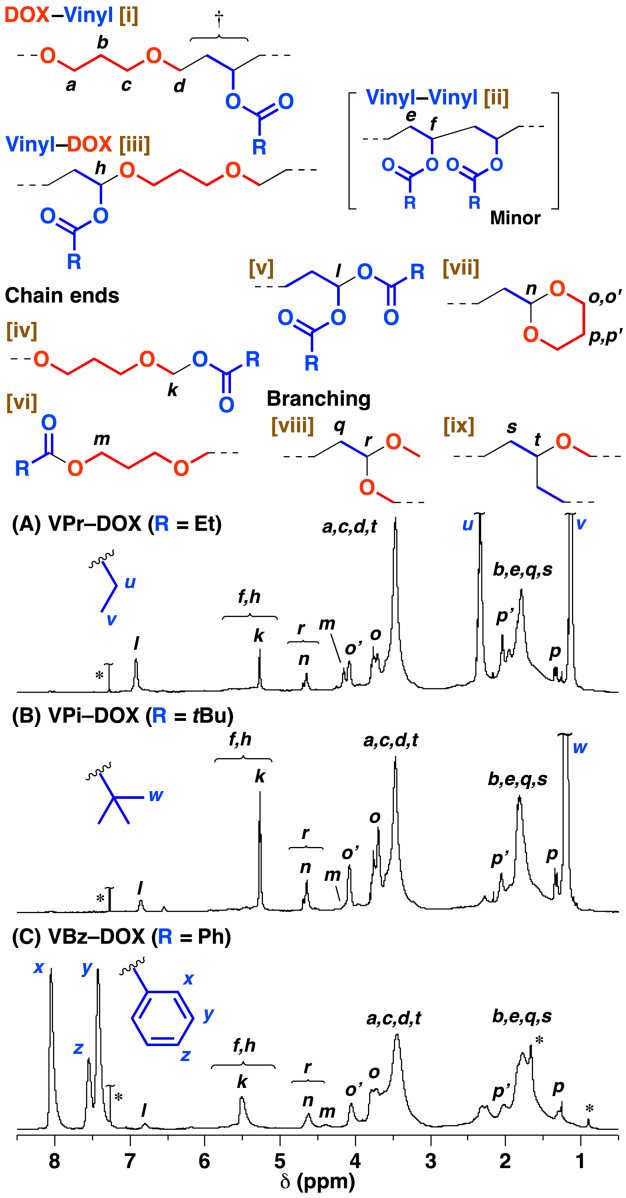


Figure 6. ^{1}H NMR spectra of the poly(vinyl ester-*co*-DOX)s (entries (A) 2, (B) 5, and (C) 7 in Table S4; $[\text{vinyl ester}]_0$ = 3.2 M, $[\text{DOX}]_0$ = 0.80 M, $[GaCl_3]_0$ = 20 mM, in CH_2Cl_2 at 0 ºC. Polymerization time = 264 h. After purification by preparative GPC). In $CDCl_3$ at 30 ºC. * $CHCl_3$, water, or vaseline. † Some of the vinyl ester units adjacent to the DOX unit were transformed into other units, such as structures [vii], [viii], and [ix], as a result of the abstraction of the acetoxy moiety.

Cationic copolymerizations of AL and cyclic acetals

As explained in the Introduction section, AL, which is a five-membered cyclic vinyl ester, was reported to undergo cationic copolymerization with DOL in a past study.[26,27] To investigate the reaction

of AL in detail and compare the results with those of VAc, cationic polymerizations of AL were also examined in this study.

Cationic homopolymerization of AL was first examined with $GaCl_3$ used as a Lewis acid catalyst; however, no polymer was obtained (entry 1 in Table 5). Subsequently, the cationic copolymerization of AL and DOL was conducted under similar conditions. Copolymerization proceeded with frequent crossover reactions to yield a copolymer with average numbers of AL and DOL units per block of 1.1 and 1.4, respectively, (entry 2; Figures 7A and 8A). This result is similar to that for a previously reported reaction using $SnCl_4$ as the catalyst. [26,27]

Table 5. Cationic Copolymerization of AL with Cyclic acetals or DOLO-1[a]

entry	AL conc (M)	comonomer	temp (°C)	time	AL conv. (%)[b]	comonomer conv. (%)[b]	$M_n \times 10^{-3}$[c]	M_w/M_n[c]	average number of units per block[d]	
									AL	comonomer
1	3.2	–	–40	216 h	29[e]	–	–	–	–	–
2	1.6	DOL (1.6 M)	–40	96 h	55	72	5.5[f]	2.54[f]	1.1	1.4
3	0.80	DOX (0.80 M)	–78	384 h	36	42	10.4	1.57	1.0	1.0
4	1.0	DOLO-1 (1.0 M)	–40	288 h		6[g]	–	–	–	–

[a] $[GaCl_3]_0 = 10$ (entries 1 and 4) or 20 (entries 2 and 3) mM, in CH_2Cl_2. [b] Determined by gravimetry and ^{1}H NMR analysis of products. [c] By GPC using polystyrene standards. [d] Calculated by ^{1}H NMR. [e] The product mainly consists of a ring-opened product resulting from the reaction with methanol, used as a quencher. [f] The value for the polymer peak. [g] Total conversion determined by gravimetry.

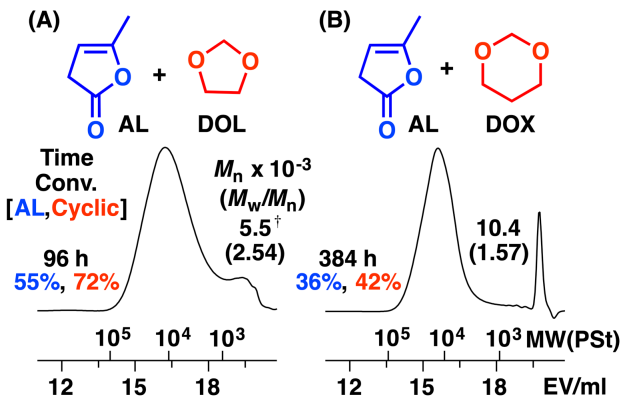


Figure 7. MWD curves of the products obtained by the copolymerization of AL with (A) DOL (entry 2 in Table 5; † Values for the polymer peak) or (B) DOX (entry 3). A sharp peak in the low-MW region in Figure 7B is likely assigned to a cyclic oligomer consisting of AL and DOX although the exact structure has not been confirmed yet.

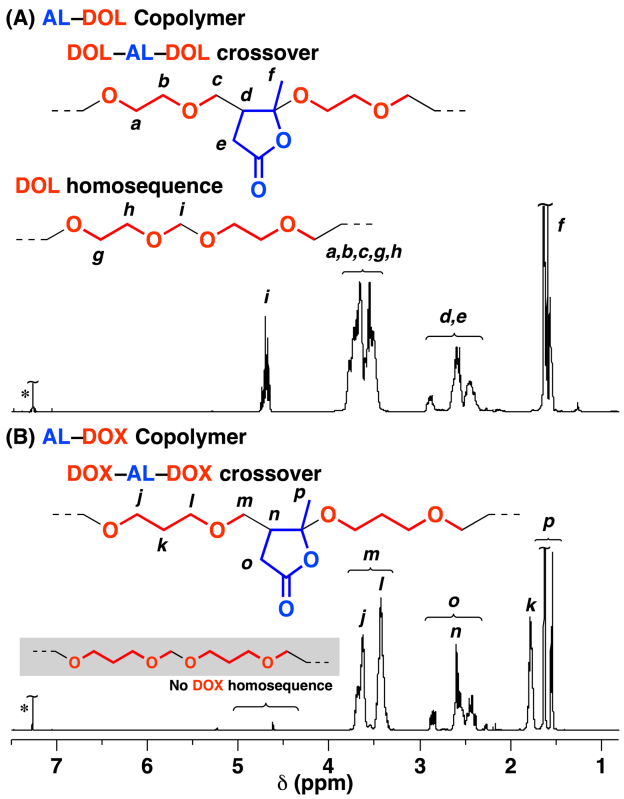


Figure 8. ^{1}H NMR spectra of the products obtained by the copolymerization of AL with (A) DOL (entry 2 in Table 5) or (B) DOX (entry 3) (after purification by preparative GPC; in $CDCl_3$ at 30 ºC; * $CHCl_3$).

As far as we know, copolymerizations of AL with DOX or DOLO were examined for the first time in this study. Interestingly, an alternating copolymer was produced in the copolymerization of AL and DOX (entry 3 in Table 1; Figures 7B and 8B; see Figures S36–S39 for the ^{13}C and 2D NMR spectra). The negligible homopolymerizabilities of both AL and DOX are responsible for the absence of homopropagation reactions. In contrast, in the case of DOLO-1, copolymerization with AL did not proceed (entry 4). The lower reactivity of the tertiary carbocation derived from AL relative to the

secondary carbocation derived from VAc would be insufficient for reaction crossover from AL to DOLO-1.

In the copolymerizations of AL and cyclic acetals, abstraction of the side chain did not occur, in contrast to the copolymerizations of VAc and cyclic acetals. The rigid five-membered structure is most likely responsible for this inertness.

A copolymer of AL and DOX was subjected to DSC analysis. The alternating copolymer likely has a T_g at 2 ºC (Figure S40).

Conclusions

Cationic copolymerizations of VAc with comonomers exhibiting little or no homopolymerizability proceeded successfully with $GaCl_3$ as the Lewis acid catalyst to yield alternating or branched copolymers (Chart 1). Copolymerizations of VAc with DOLOs that generate a primary or secondary carbocation through ring-opening proceeded with frequent crossover reactions to give alternating copolymers with M_ns of 3.4×10^3 or 6.4×10^3, respectively. DOX, which exhibits no homopolymerizability, also underwent copolymerization with VAc via frequent crossover reactions, while abstraction of the acetoxy group from the VAc-to-DOX crossover-derived structure subsequently occurred. The abstraction most likely resulted in branch formation via reaction of a generated carbocation with VAc or DOX. The copolymerization of VAc with DOL or DOP, which, unlike DOX, exhibits homopolymerizability, also proceeded via a mechanism similar to that proposed for DOX. The branching

reaction did not occur when AL was used instead of VAc, resulting in the alternating copolymer with an M_n of 10.4×10^3 in the copolymerization with DOX. The results obtained in this study demonstrated that cationic copolymerizations of VAc, which is a vinyl monomer expected to be susceptible to cationic polymerization, were possible with suitable comonomers. Future studies on VAc will pursue cationic homopolymerization of VAc and cationic copolymerizations of VAc with various comonomers so as to obtain VAc-based copolymers exhibiting characteristics derived from VAc and the comonomers.

Chart 1. Summary of the Copolymerizations of VAc or AL with DOLOs or Cyclic Acetals

Comonomer	VAc	AL
DOLO-1 DOLO-2	Alternating copolymer	Inefficient
DOLO-3	Inefficient (Oligomers)	–
DOL	Branched copolymer (DOL homosequences exist)	Copolymer (Frequent crossover)
DOX	Branched copolymer (No DOX homosequences)	Alternating copolymer
DOP	Similar reactions to DOL and DOX cases (Long DOP homosequences)	–
MDOL MDOX MDOP	Similar reactions to DOL and DOX cases (Oligomers)	–
DMDOL DMDOX DMDOP	Inefficient	–

Associated Content

Supporting Information

Polymerization data, NMR and ESI-MS spectra of polymerization products, and DSC profiles of polymers.

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Notes
The authors declare no competing financial interest.

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

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