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Cationic Ring-Opening Co- and Terpolymerizations of Lactic Acid-Derived 1,3-Dioxolan-4-ones with Oxiranes and Vinyl Ethers: Nonhomopolymerizable Monomer for Degradable Co- and Terpolymers

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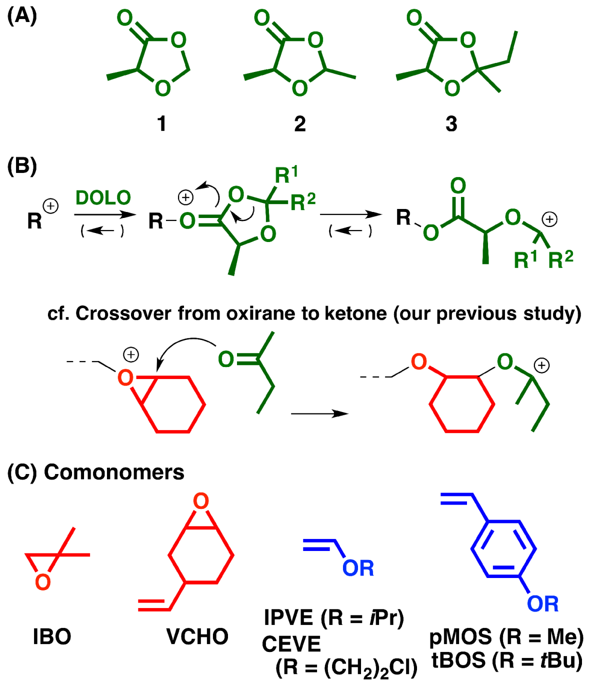
ABSTRACT: Lactic acid-derived 1,3-dioxolan-4-ones (DOLOs), which do not undergo cationic homopolymerization, were demonstrated to yield copolymers with oxiranes through a cationic copolymerization via frequent crossover reactions. Acetal and ester moieties were generated in the main chain of the copolymers via crossover reactions from DOLO to oxirane and from oxirane to DOLO, respectively, which is in contrast to the unsuccessful generation of hemiacetal ester moieties in the homopropagation of DOLO. In addition, the terpolymerization of DOLO, oxirane, and vinyl ether (VE) proceeded via crossover reactions, while copolymers could not be generated from VE and DOLO in the absence of oxirane. The obtained co- and terpolymers could be degraded under acidic conditions due to the acetal moieties in the main chain. The strategy devised in this study shows a promising avenue for employing plant-derived "nonhomopolymerizable" compounds as building blocks for the synthesis of degradable co- and terpolymers with general-purpose monomers.

The polymerizability of vinyl or cyclic compounds generally depends on factors such as the reactivity of the generated propagating species and the stability of the structures resulting from the propagation reaction. For example, vinyl monomers with a bulky group at the α-position, such as 1,1-diphenylethylene, do not polymerize due to the thermodynamic instability of the resulting homosequences due to steric hindrance. Six-membered cyclic ethers, such as tetrahydropyran and 1,4-dioxane, do not yield homopolymers due to the low ring strain. Copolymerization is an alternative and attractive way to polymerize these nonhomopolymerizable monomers because the thermodynamic disadvantage is mitigated through crossover reactions with different monomers. Indeed, 1,1-diphenylethylene has been copolymerized with styrene derivatives via both anionic and cationic mechanisms.[1,2] Tetrahydropyran and 1,4-dioxane were incorporated into polymer chains via ring-opening polymerization (ROP) reactions with other cyclic ethers, such as oxetane derivatives.[3,4] Moreover, nonhomopolymerizable monomers, such as cyclic anhydrides,[5] bicyclic bis(γ-lactone),[6] 3,4-dihydrocoumarin,[7] carbon dioxide,[8] and conjugated aldehydes,[9] have been employed in alternating copolymerization reactions with different types of monomers. Recently, we reported that ketones could be used as monomers in cationic terpolymerizations with vinyl ether (VE) and oxirane.[10] A ketone reacted with an oxirane-derived oxonium ion via a nucleophilic attack by the carbonyl group (Scheme 1B, below), which was followed by the generation of an oxygen atom-adjacent carbocation that subsequently reacts with a VE monomer. Therefore, co- or terpolymerizations can employ compounds that are not generally regarded as polymerizable, such as ketones, as monomers through the mitigation of the drawbacks. Furthermore, some structures resulting from crossover reactions between different monomers are useful for achieving desirable properties such as degradability and stimuli responsiveness.

On the basis of these previous works, we focused on 1,3-dioxolan-4-ones (DOLOs; Scheme 1A) as candidate monomers for cationic copolymerizations via crossover reactions. DOLOs have been synthesized via the condensation of α-hydroxy acids, such as lactic acid, glycolic acid, and mandelic acid, with aldehydes or ketones since the late 1800s.[11—14] However, to the best of our knowledge, cationic polymerizations of DOLOs have not been reported. We thought that a DOLO monomer could potentially react with a cationic species through an attack by a carbonyl group in a manner similar to that seen with ketones[10] and subsequently undergo a ring-opening reaction to generate an oxygen-adjacent carbocation, which would be structurally similar to a VE-derived carbocation, as shown in Scheme 1B. Important examples of polymerizations of DOLOs include the coordination-insertion ROP using a metal catalyst; however, this polymerization was accompanied by the elimination of a carbonyl compound and resulted not in poly(DOLO)s but in poly(α-hydroxy acid)s.[15] The copolymerization of DOLOs with lactide was also reported to yield polymers.[16] In addition, a six-membered cyclic ester acetal, which has an additional carbon atom in its ring compared to DOLOs, was homopolymerized via a cationic mechanism.[17] 6,8-Dioxabicyclo[3.2.1]octan-7-one, which has a DOLO moiety in its bicyclic structure, was also reported to undergo cationic polymerization.[18]

In this study, we examined cationic homo-, co-, and terpolymerizations of DOLOs. The homopolymerizations of DOLOs did not proceed probably due to both the low ring strain in DOLOs and the inefficient generation of the hemiacetal ester structure in a polymer chain. Importantly, the crossover reactions from and to the different types of monomers (Scheme 1C) were key to the incorporation of DOLOs into the polymers. The copolymerization with oxiranes and terpolymerization with oxiranes and VEs successfully proceeded via crossover reactions and generated acid-degradable polymers with acetal and ester moieties in the main chains.

Scheme 1. (A) 1,3-Dioxolan-4-ones Used in This Study, (B) the Reaction of a Cation with a DOLO Monomer (the Crossover from Oxirane to Ketone; Reference 10), and (C) the Examined Comonomers



The cationic homopolymerization of DOLOs did not proceed under any of the examined conditions. DOLO monomers with no (**1**), one (**2**), or two (**3**) alkyl groups at the 2-position (Scheme 1A; **2** and **3** are mixtures of diastereomers) were synthesized via the condensation of lactic acid with paraformaldehyde, paraldehyde, or methyl ethyl ketone, respectively, according the literature method.[11—14,19] Negligible amounts of these DOLOs were consumed in the reactions using $B(C_6F_5)_3$ as a strong Lewis acid catalyst in dichloromethane at −78 ºC (entries 1—3 in Table 1). Polymerizations using cationic initiators and Lewis acids such as $Ph_3C^+B(C_6F_5)_4^-$, $Et_3O^+PF_6^-$, and $Ga(OTf)_3$ or reactions at higher temperatures were also ineffective (Table S1). The balance of several factors, such as the lability of the hemiacetal ester moiety[20] of the DOLO–DOLO homosequence, the low reactivity of the oxygen atom-adjacent carbocation, and the low ring strain of the DOLO monomer, is likely responsible for the inertness (Scheme 2A).

Unlike the negligible DOLO homopolymerization, the copolymerization with oxiranes proceeded efficiently via frequent crossover reactions between the two different types of monomers. The cationic copolymerization of **2** with isobutylene oxide (IBO) using $B(C_6F_5)_3$ yielded a polymer with an M_n value of 4.5×10^3 (entry 5 in Table 1; Figure 1A). The ^1H NMR spectrum of the product (Figure 2A) had an acetal peak at 4.8 ppm (peak 5) derived from the crossover from **2** to IBO and peaks at 4.1–4.2 ppm (peak 3) assigned to the methine proton between the carbonyl group and the ether oxygen of **2**, which indicates that **2** was incorporated into polymer chains. In addition, peaks assigned to the methylene protons of the DOLO-adjacent IBO units were observed at 3.3–3.7 ppm (peaks 1, 7, and 9) due to the effects of the adjacent ester and acetal moieties, and peaks were not observed at these positions in the spectrum of the homopolymer of IBO (Figure 2C). These assignments were confirmed by analyses of the ^{13}C and 2D NMR spectra (Figures S1–S4). The average numbers of units of IBO and **2** per block were estimated to be 2.7 and 1.0, respectively, from the ^1H NMR spectrum (Figure 2A), which indicates that crossover reactions occurred very frequently and that homopropagation of DOLO did not occur. Peaks attributable to a hemiacetal ester, which would have appeared at approximately 6 ppm, were not observed (Figure S5),[20] confirming that homosequences of DOLOs were not generated. The copolymerizations of IBO with **1** or **3** also proceeded under similar conditions (entries 4 and 6; Figure S6); however, the molecular weights were very low [$< 10^3$; larger amounts of $B(C_6F_5)_3$ (6.0 mM) were used than the other entries because the reactions negligibly proceeded at 3.0 mM]. We are presently examining suitable reaction conditions, such as monomer concentrations and solvents.

Scheme 2. Homopropagation and Crossover Reactions of DOLOs (Counteranions Are Omitted)

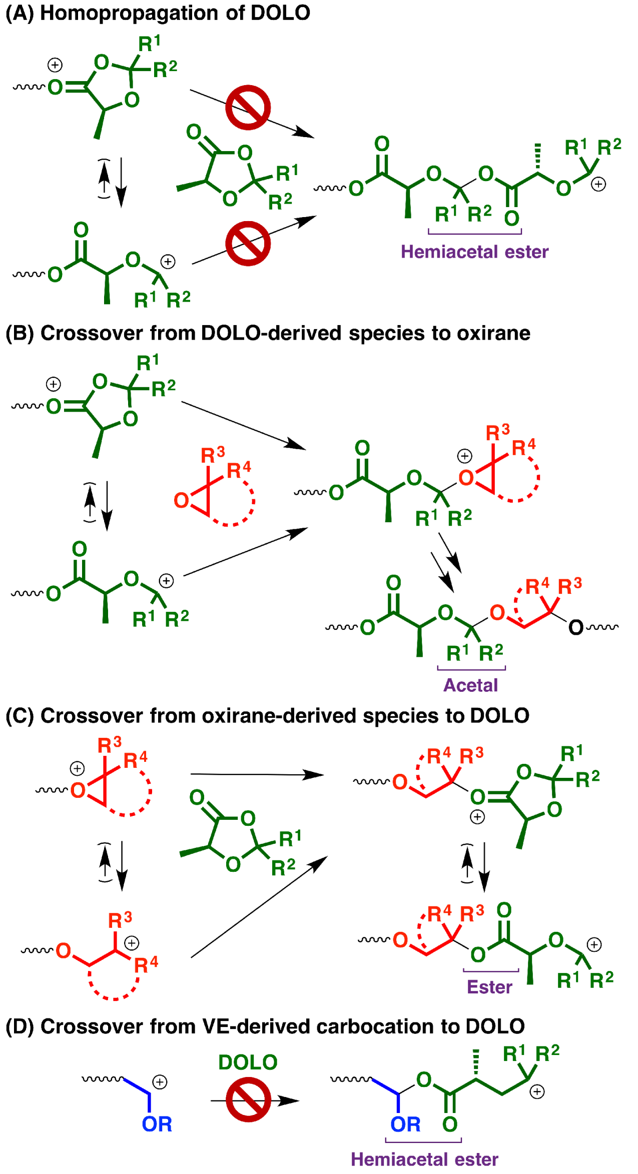


Table 1. Cationic Homo- and Copolymerization of DOLOs [a]

entry	comonomer (M)		DOLO (M)		time	comonomer conv (%)	DOLO conv (%)	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]	average numbers of units per block [c]	
										comonomer	DOLO
1	None		**1**	0.70	141 h	—	0	—	—	—	—
2			**2**	1.2	42 h	—	0	—	—	—	—
3			**3**	1.2	49 h	—	0	—	—	—	—
4[d]	IBO	0.75	**1**	0.75	97 h	84	22	0.4	1.31	—	—
5		0.75	**2**	0.75	3 h	31	12	4.5	1.83	2.7	1.0
6[d]		0.80	**3**	1.2	72 h	81	25	0.5	1.58	—	—
7	VCHO	0.75	**1**	0.75	1 min	83	9	13.6	2.24	11	1.0
8		0.75	**2**	0.75	6.5 min	76	10	18.8	2.21	6.7	0.95
9		0.75	**3**	0.75	3 min	67	16	6.9	1.62	9.9	1.0
10	CEVE	0.75	**1**	0.75	24 h	87	0	65.7	2.28	—	—
11		0.80	**2**	0.80	24 h	25	0	54.5	2.99	—	—
12		0.78	**3**	0.78	14 h	100	0	53.9	3.00	—	—
13	pMOS	0.75	**2**	0.75	1 h	19	0	>10^2 [e]	n.d.[e]	—	—
14	tBOS	0.78	**3**	0.78	20 h	65	0	39.6	4.98	—	—

[a] $[B(C_6F_5)_3]_0$ = 3.0 mM (except for entries 4 and 6), in dichloromethane at –78 °C. [b] By GPC (polystyrene calibration). [c] Calculated by ^{1}H NMR. [d] $[B(C_6F_5)_3]_0$ = 6.0 mM. The reactions negligibly proceeded at 3.0 mM. [e] Not determined. The peak partly exceeded the exclusion limit of the GPC columns.

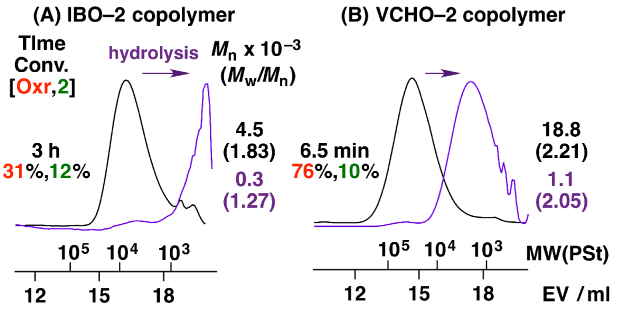


Figure 1. MWD curves of (A) IBO–**2** (entry 5 in Table 1) and (B) VCHO–**2** (entry 8) copolymers (black) and their hydrolysis products (purple). See Table 1 for polymerization conditions.

4-Vinyl-1,2-epoxycyclohexane (VCHO), which is more reactive than IBO and unlike IBO does not generate a carbocation via ring-opening,[10,21] underwent copolymerization with **1**, **2**, and **3** (entries 7—9 in Table 1; Figures 1B and S7). Copolymers with longer oxirane blocks than what were seen in the analogous reactions with IBO were generated due to the higher reactivity of VCHO. Crossover reactions occurred in both directions, as confirmed by the appearance of peaks from ester and acetal moieties in the ^{1}H NMR spectra (Figure S8). Notably, ketal structures were generated in the main chain via the crossover from **3** to VCHO (Figures S9–S11), unlike the negligible generation of ketal structures that occurred in the copolymerization of an oxirane and a ketone in our previous study.[10] The electron-withdrawing effect of the ester group derived from the DOLO monomer may have helped stabilize the ketal structure.[22]

The copolymerization most likely proceeds via the propagation of the DOLO- or oxirane-derived oxonium ions and carbocations. It is hypothesized that the polymerization is initiated by a proton generated by the reaction of adventitious water and the catalyst and/or the direct interaction between the catalyst and a DOLO or an oxirane. The DOLO-derived propagating species, which is generated via the attack of the carbonyl group of a DOLO monomer to the oxirane-derived species, is directly attacked by an oxirane monomer or undergoes a ring-opening reaction to generate a carbocation (Scheme 2B). The

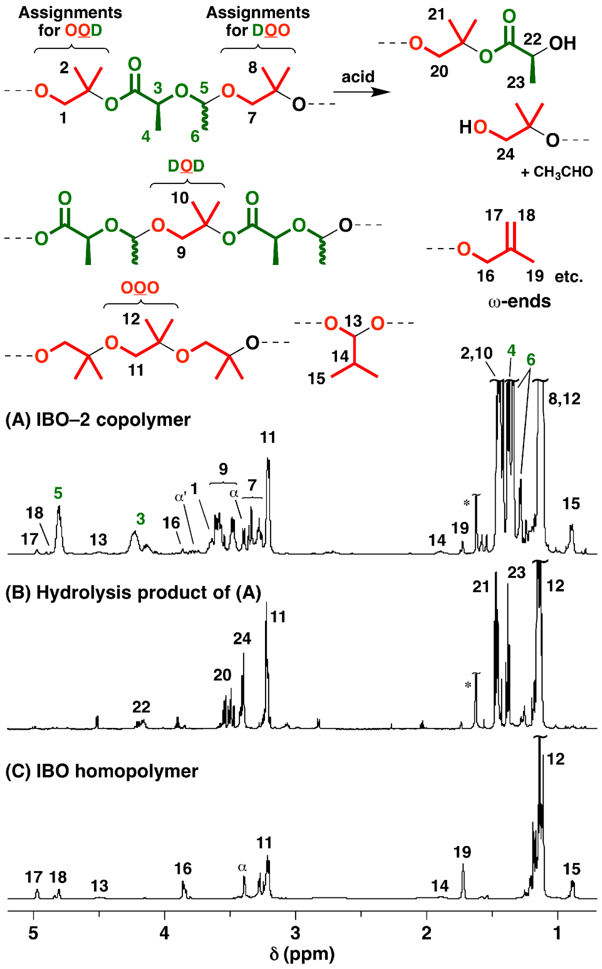


Figure 2. ^{1}H NMR spectra of (A) the copolymer of IBO and **2** (entry 5 in Table 1; Figure 1A), (B) its hydrolysis product (purple curve in Figure 1A), and (C) IBO homopolymer (the same spectrum to that reported in reference 21). Peaks α and α' are likely assigned to the methylene groups at the α-ends with H–<u>IBO</u>–IBO– and H–<u>IBO</u>–**2**–sequences (the former corresponds to peak 24), respectively. Whether the **2**-derived α-ends exist or not is unclear. See Figure S5 for other ω-ends; * water.

carbocation also reacts with an oxirane monomer. Subsequently, the oxirane-derived oxonium ion is attacked either by a DOLO monomer or an oxirane monomer (Scheme 2C). In the case of IBO, the carbocation is also likely generated via a ring-opening reaction and subsequently attacked by a monomer.[21] In addition, the IBO-derived oxonium ion likely cleaved mostly via the α-scission even when the crossover reaction to a DOLO monomer occurred without the generation of the carbocation.[23–26] The generation of acetal or ester moieties, which are more stable than a hemiacetal ester structure, is likely responsible for the efficiency of the crossover reactions from and to a DOLO monomer. The polymer chain terminates via β-proton elimination from the oxirane- or the DOLO-derived propagating ends (Figure S5). The proton generated by this reaction generates a new propagating chain. These chain transfer reactions and relatively slow initiation compared to the propagation are probably responsible for the broad molecular weight distributions (MWDs) of the products.

The monomer reactivity ratios of IBO and **2** corresponded to the negligible homopropagation of DOLO and the frequency of the crossover reactions ($r_1 = 2.3$ and $r_2 \sim 0$ for IBO and **2**, respectively; Figure S12). The value of **2** was almost zero, indicating the inability of **2** to homopolymerize. In addition, the relatively small value of IBO agreed well with the average numbers of units per block of the copolymer generated by the frequent crossover reactions. The sequence distributions of the copolymers are potentially controlled via the design of reaction conditions, such as monomer concentrations, solvent polarity, and additives.

The substituents at the 2-position of DOLOs influenced the frequency of the crossover reactions. Among the three DOLOs, the mono-substituted DOLO, **2**, underwent crossover reactions with VCHO most frequently, as confirmed by the resulting copolymer having the smallest number of VCHO units per block (6.7). The stabilities of the DOLO-derived carbocations and the resulting sequences were likely responsible for the differences in the crossover frequency. The **1**-derived primary carbocation is less stable and less frequently generated via ring-opening than the secondary and the tertiary carbocations derived from **2** and **3**, respectively, which resulted in less frequent crossover in the copolymerization of **1**. Monomer **3** generated a stable tertiary carbocation but underwent less frequent crossover compared to **2**, potentially due to the less efficient generation of a ketal via the crossover to an oxirane. The effects of the substituents on the reactivity are currently being investigated in detail.

The thermal properties of the copolymers were examined by differential scanning calorimetry (DSC) analysis (Figure S13). The copolymer of IBO and **2** had T_g of –47 °C, while peaks indicative of crystallinity were not detected, which is in contrast to the crystallinity of the IBO homopolymer.

Unlike oxiranes, VEs did not copolymerize with DOLOs [entries 10–12 in Table 1; other VEs such as ethyl VE, which are more reactive than 2-chloroethyl VE (CEVE), were also inefficient] due to the negligible crossover from VE to DOLO (Scheme 2D). The hemiacetal ester structure was likely difficult to generate via the crossover from the VE-derived, low-reactive carbocation, which is similar to the negligible homopropagation of DOLO. Styrene derivatives [*p*-methoxystyrene (pMOS) and *p*-*tert*-butoxystyrene (tBOS)] were also inefficient in copolymerizations with DOLOs (entries 13 and 14), although the structure derived from the crossover is not a hemiacetal ester but a benzyl-type ester.

Instead, VEs were incorporated into polymer chains in terpolymerizations with a DOLO and an oxirane. A polymer with an M_n value of 19.9 × 10^3 was produced in the terpolymerization of isopropyl VE (IPVE), IBO, and **2** under conditions similar to those used for the copolymerization of IBO and **2** (Figure 3A). ^{1}H NMR analysis indicated that all three monomers were incorporated into the polymer chains (Figure S14). The average numbers of monomer units per acetal, which correspond to the average numbers of each monomer per block, were 6.3, 1.6, and 1.0 for IPVE, IBO, and **2**, respectively. The crossover reactions that could occur in the terpolymerization are shown in Figure 3B. IPVE was incorporated into the polymer via crossover from the IBO-derived carbocation and from the **2**-derived carbocation. The crossover from the latter to a VE monomer was also confirmed by terpolymerization using VCHO, which does not undergo crossover to VE, instead of IBO (Figures S15 and S16). The VE-derived carbocation reacts with an oxirane monomer to generate an acetal moiety. A suitable choice of monomers will lead to sequence control, such as the crossover via one direction,[10] in the terpolymerization.

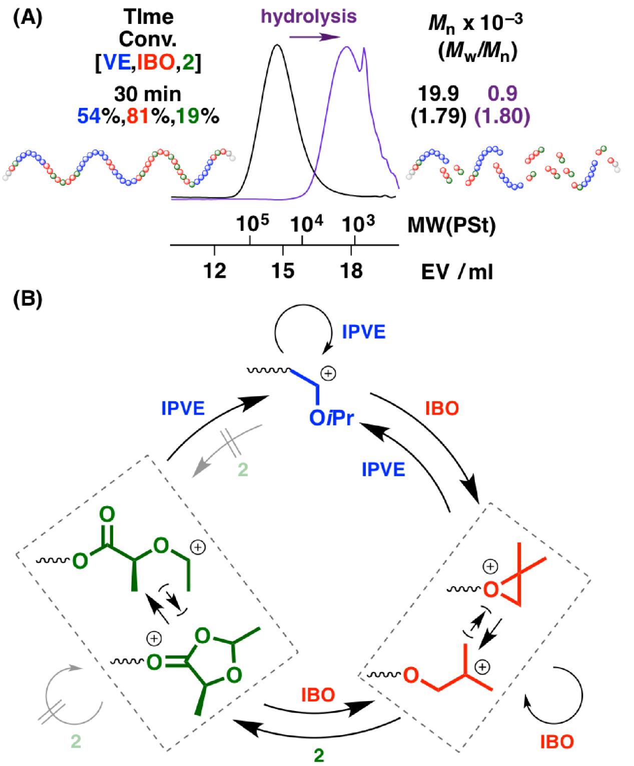


Figure 3. (A) MWD curves of the terpolymerization product (black) and its hydrolysis product (purple) (polymerization conditions: $[\text{IPVE}]_0$ = 0.78 M, $[\text{IBO}]_0$ = 0.44 M, $[\mathbf{2}]_0$ = 0.78 M, $[\text{B}(\text{C}_6\text{F}_5)_3]_0$ = 3.0 mM, in dichloromethane at –78 °C) and (B) the propagation reactions in the terpolymerization of IPVE, IBO, and **2** (counteranions are omitted).

The DOLO–oxirane copolymers were hydrolyzed into low-molecular-weight products under acidic conditions via the cleavage of the acid-labile acetal moieties in the main chain. A peak assigned to the acetal moieties in the ^{1}H NMR spectrum disappeared after acid hydrolysis (Figure 2B and Figure S8; a portion of the ester moieties may have also been degraded). The products of the hydrolysis of the copolymers had unimodal MWDs (purple curves in Figure 1), which indicated that the copolymerization products were not mixtures containing oxirane homopolymer, but they were copolymer alone. In addition, the M_n value of the hydrolysis product was comparable to the value estimated from the average numbers of monomer units per block. The terpolymer with VE was also hydrolyzed under acidic conditions via the cleavage of the acetal moieties (a purple curve in Figure 3A).

In conclusion, DOLOs were successfully copolymerized with oxiranes via frequent crossover reactions by a cationic mechanism. DOLOs did not undergo cationic homopolymerization under any of the conditions examined. Thus, the drawbacks causing the inefficient homopropagation of DOLOs were overcome by the crossover reactions from and to oxiranes, which generated ester and acetal moieties, respectively, in the main chain. In addition, the co- and terpolymers could be degraded under acidic conditions due to acid lability of the acetal moieties. The method demonstrated in this study opens up a new method for employing plant-derived α-hydroxy acids, such as lactic acid, as a building block for the synthesis of acid-degradable co- and terpolymers with oxiranes and vinyl monomers. We are presently investigating the polymerization of DOLO derivatives with various substituents and copolymerizations with other monomers to elucidate the effects of the substituents on the polymerization behavior and on the properties of the co- and terpolymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental section, additional polymerization data, and NMR spectra (PDF).

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Notes

The authors declare no competing financial interest.

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22. However, cyclohexene oxide, which is an oxirane with a similar structure to VCHO, was inefficient for the copolymerization with **3**. A subtle difference of the stability is likely responsible for the generation of the ketal structure.
23. A peak assigned to the ester oxygen-adjacent methylene protons should exist at the lower field than peaks 1 and 9 in the ^{1}H NMR spectrum when the β-scission occurred; however, no large peak exists at this region. The acid-catalyzed ring-opening reaction of IBO was reported to occur mainly

via the α-scission except when strong or sterically hindered nucleophiles are used (references 24–26).

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