Living Cationic Ring-Opening Homo- and Copolymerization of Cyclohexene Oxide by "Dormant" Species Generation Using Cyclic Ethers as Lewis Basic Additives

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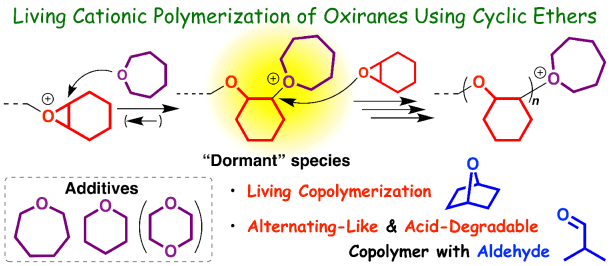


Abstract

The living cationic ring-opening polymerization of cyclohexene oxide (CHO) was demonstrated to proceed using cyclic ethers as Lewis basic additives that potentially form "dormant" species through a reaction with the CHO-derived propagating species. The polymers obtained under suitable conditions had molecular weights close to the theoretical values and narrow molecular weight distributions. The formation of the dormant species was strongly supported by the generation of chain ends consisting of a cyclic ether additive and a quencher fragment, which was confirmed by ^{1}H NMR and ESI-MS analysis of the product polymers. The use of additives with appropriate basicity, such as hexamethylene oxide and tetrahydropyran, is of considerable importance for living polymerization. In addition, the living copolymerization of CHO and 1,4-epoxycyclohexene and the synthesis of alternating-like acid-degradable polymers with aliphatic aldehydes were also achieved.

Introduction

To control the functions and physical properties of polymers, the precise design of polymer structures, including their molecular weight (MW), molecular weight distribution (MWD), polymer chain ends, and monomer sequences, is of considerable importance. Living polymerization, which proceeds with negligible side reactions, has been studied to both control the MW and synthesize polymers with well-defined structures such as block, graft, end-functionalized, and star-shaped polymers[1–3]. In addition, living polymerization has also found industrial applications to synthesize products such as adhesives, resin modifiers, and pigment dispersants. After the initial development of living anionic polymerization of styrene by Szwarc[4] in 1956, living polymerization of various monomers has been achieved. Living polymerization mediated by inherently stable propagating species, such as a carbanion derived from styrene and an oxonium ion derived from tetrahydrofuran (THF)[5–7], was achieved through the efficient generation of initiating species and rigorous removal of impurities such as adventitious water because side reactions such as chain transfer and spontaneous termination are negligible at the stable propagating ends. However, in the cationic and radical polymerization of vinyl monomers, side reactions originating from the active, unstable propagating species need to be suppressed to achieve living polymerization. To achieve this suppression, various methods have been devised. They are mainly classified into three categories[8]: dissociation-combination mechanism, atom transfer mechanism, and degenerative chain transfer mechanism, which correspond to nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) polymerization, respectively, in radical polymerization. In cationic polymerization, living polymerization of vinyl monomers such as vinyl ethers, isobutene, and styrene derivatives has become feasible by using appropriate counteranions and additives[7,9–16].

Oxirane-derived polymers constitute an important class of materials used in both daily life and industry. For example, polyethylene oxide, which is obtained by the ring-opening polymerization of ethylene oxide, is used in a very wide range of products, such as pharmaceuticals, cosmetics, skincare products, detergents, tablets, and food additives[17,18], due to its amphiphilicity and biocompatibility. In the

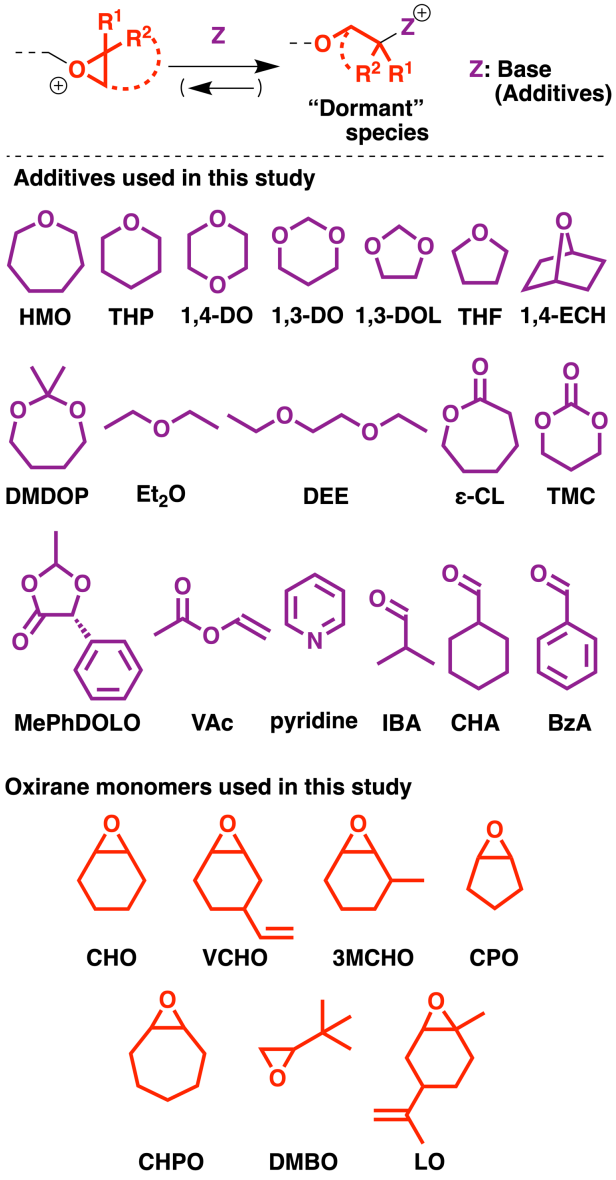
ring-opening polymerization of oxiranes, living polymerization occurs mainly by anionic or coordination mechanisms[7,19–25]. Various strategies have been devised to enable living polymerization of oxiranes[22,25–34]. In contrast, in the cationic polymerization of oxiranes, side reactions such as backbiting reactions frequently occur, which results in low-MW oligomers[35–38], and living polymerization is usually difficult. The controlled polymerization of oxiranes by the activated monomer mechanism was developed[39–44]; however, problems remain, such as minimizing the monomer concentration and a very long polymerization time.

To achieve living cationic ring-opening polymerization of oxiranes, we propose a strategy that allows "stabilization" of the propagating end by the formation of a dormant species with an additive. This strategy was inspired partly by the living cationic polymerization of vinyl ethers using a sulfide as an additive that reacts with the vinyl ether-derived propagating carbocation to form a stable cationic species[45]. This method corresponds to the dissociation-combination mechanism described above. In addition, the cationic ring-opening polymerization of oxetane, which is a four-membered cyclic ether, was reported to proceed in a living manner when the propagating ends were transiently deactivated with 1,4-dioxane (1,4-DO) as an additive[46,47].

In this study, various weak Lewis bases, such as cyclic ethers, acyclic ethers, amine, and carbonyl compounds, which potentially form dormant species (Scheme 1) through reaction with oxirane-derived propagating species, were examined as additives in cationic ring-opening polymerization to achieve living polymerization. Cyclohexene oxide (CHO) is mainly used as an oxirane monomer because it exhibits high reactivity and produces high-MW polymers[48–55]. In addition, CHO is often used as a monomer in photoinitiated polymerization systems due to its high reactivity[54,56–58]. As a result of systematic investigation, the living cationic ring-opening polymerization of CHO was achieved by using suitable cyclic ethers such as hexamethylene oxide (HMO) and tetrahydropyran (THP) as additives. The livingness of the reaction was confirmed by several experiments, such as the production of polymers with theoretical MWs, the incorporation of a quencher fragment into the ω-ends, monomer-addition experiments, and polymerization at different $[\text{monomer}]_0/[\text{initiator}]_0$ ratios. We also demonstrated the

living cationic copolymerization of CHO with other cyclic ethers and the synthesis of alternating-like acid-degradable copolymers with aliphatic aldehydes.

Scheme 1. Cationic Polymerization of Oxirane Monomers Using Various Additives.[a]



[a] Some additives also functioned as a comonomer and were incorporated into a main chain.

Experimental Section

Materials. CHO (TCI, >98.0%), cyclopentene oxide (CPO; Sigma-Aldrich, 98%), 3,3-dimethyl-1,2-butylene oxide (DMBO; Alfa Aesar, 95%), HMO (TCI, >98.0%), THP (TCI, >98.0%),

1,4-DO (Nacalai Tesque, >99.5%), 1,3-dioxane (1,3-DO; TCI, >98.0%), 1,3-dioxolane (1,3-DOL; TCI, >98.0%), THF (Wako, >99.5%), 1,4-epoxycyclohexane (1,4-ECH; Sigma-Aldrich, 98%), diethyl ether (Et_2O; Wako, >99.5%), 1,2-diethoxyethane (DEE; Sigma-Aldrich, 98%), vinyl acetate (VAc; Nacalai Tesque, >98.0%), and isobutyraldehyde (IBA; TCI, >98.0%) were distilled twice over calcium hydride. 4-Vinyl-1,2-cyclohexene oxide (VCHO; TCI, >98.0%), (+)-limonene oxide (LO; mixture of *cis* and *trans*; Sigma-Aldrich, 97%, ee: 98%), *ε*-caprolactone (ε-CL; TCI, >99.0%), pyridine (Sigma-Aldrich, >99.0%), cyclohexanecarbaldehyde (CHA; TCI, >98%), and benzaldehyde (BzA; Wako, >98%) were distilled twice under reduced pressure over calcium hydride. Trimethylene carbonate (TMC; TCI, >98.0%) was recrystallized from toluene. 3-Methylcyclohexene oxide (3MCHO)[59] and cycloheptene oxide (CHPO)[60] were synthesized by the epoxidation of 3-methylcyclohexene (TCI, >93.0%) and cycloheptene (TCI, >96.0%), respectively, with monoperoxyphthalic acid magnesium salt hexahydrate (TCI, >65.0%)[61] and then distilled twice under reduced pressure over calcium hydride. 2,2-Dimethyl-1,3-dioxepane (DMDOP) was synthesized and purified as reported in our previous study[62]. 2-Methyl-5-phenyl-1,3-dioxolan-4-one (MePhDOLO) was synthesized by condensation of D-(–)-mandelic acid (TCI, >99.0%) with paraldehyde (TCI, >98.0%) using *p*-toluenesulfonic acid (monohydrate; TCI, >98.0%) and purified in a manner similar to the purification of the 1,3-dioxolan-4-one derivatives[63,64]. Triphenylmethylium tetrakis(pentafluorophenyl)borate ($Ph_3CB(C_6F_5)_4$; TCI, >98.0%), triphenylmethylium hexafluorophosphate (Ph_3CPF_6; Sigma-Aldrich), triphenylmethylium tetrafluoroborate (Ph_3CBF_4; Sigma-Aldrich), and triethyloxonium hexafluorophosphate (Et_3OPF_6; Sigma-Aldrich, containing diethyl ether (10–20%) as a stabilizer) were used as received. Commercially available TfOH (Aldrich, ≥99.0%) and Tf_2NH (Wako, 98.0+%) were used without further purification after preparing their stock solutions in dichloromethane. Dichloromethane (Wako, superdehydrated) and hexane (Wako, 96.0%) were dried by passage through a solvent purification column (Glass Contour).

Preparation of PhONa[65]. Phenol (Nacalai Tesque, >99.0%) was added to 1,4-DO (Wako, >99.5%) or

ethylene glycol dimethyl ether (Nacalai Tesque, >99.0%), and then an excess amount of metallic sodium (Nacalai Tesque) was added. The mixture was left to stand for several hours at room temperature.

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 air temperature was approximately 450 °C) under dry nitrogen. Dichloromethane, hexane (internal standard for gas chromatography), HMO, and CHO were sequentially added to the tube using dry syringes. Polymerization was initiated by the addition of a prechilled $Ph_3CB(C_6F_5)_4$ solution in dichloromethane to the monomer solution at –20 °C. After a predetermined time, the reaction was terminated by the addition of PhONa. The quenched mixture was diluted with hexane and then washed with an aqueous sodium hydroxide solution and then with water. The volatiles were then removed under reduced pressure. The monomer conversion was determined by gas chromatography (column packing material: PEG-20M-Uniport HP; GL Sciences Inc.) using hexane as an internal standard.

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

Characterization. The MWD of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [TSKgel GMH_{HR}-M × 2 (exclusion limit MW = 4×10^6; bead size = 5 μm; column size = 7.8 mm id × 300 mm); flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive index detector. The number-average MW (M_n) and polydispersity ratio [weight-average MW/number-average MW (M_w/M_n)] were calculated from the chromatograms of the samples with respect to those of 16 polystyrene standards (Tosoh; MW = 5.0×10^2 to 1.09×10^6, $M_w/M_n < 1.2$). The absolute

M_n values were determined with a GPC system composed of a Viscotek VE 1122 pump, polystyrene gel columns (TSKgel GMH_{HR}-M × 2; flow rate = 0.7 mL/min; eluent: tetrahydrofuran), and a Viscotek TDA 305 triple detector [refractive index, laser light scattering (λ = 670 nm; 90° RALS and 7° LALS), and differential pressure viscometer]. The purification of the polymerization products by preparative GPC was conducted in chloroform at room temperature with a polystyrene gel column [TSKgel $G3000H_{HR}$ (exclusion limit MW = 6×10^4; bead size = 5 μm; column size = 21.5 mm id × 300 mm); flow rate = 2.0 mL/min] connected to a JASCO PU-2086 Plus pump, a JASCO UV-2075 ultraviolet detector, and a Tosoh RI-8020 refractive index detector. The NMR spectra were recorded using a JEOL JNM-ECA 500 spectrometer (500.16 MHz for ^{1}H and 125.77 MHz for ^{13}C) in dichloromethane-d_2 or chloroform-d at 25 °C. Electrospray ionization mass spectrometry (ESI-MS) data were recorded on an LTQ Orbitrap XL (Thermo Scientific) spectrometer.

Results and Discussion

Cationic Ring-Opening Polymerization of CHO with Various Additives

To construct a living cationic ring-opening polymerization system, we examined various additives (Scheme 1) that may form dormant species through interactions with the propagating end. Table 1 summarizes the results of the polymerization of CHO using $Ph_3CB(C_6F_5)_4$ as an initiator in dichloromethane at –78 to –20 °C in the presence of various additives. The amount of additive and the polymerization temperature were changed depending on the effectiveness of the additives. For example, when polymerization was extremely fast with one additive, the reaction was conducted at a lower temperature and/or at a higher additive concentration. In addition, as a control experiment, polymerization of CHO in the absence of any additives was conducted at –50 ºC (entry 1 in Table 1; Figure 1) or –20 ºC (entry 2). In this case, polymerization was completed in a few seconds, and the obtained polymers had broad MWDs and significantly higher M_n values than the theoretical values. The high MWs likely suggest that chain transfer reactions are inherently infrequent in the cationic polymerization of CHO.

Table 1. Cationic Polymerization of CHO Using Various Additives[a]

entry	type of additives	additive (pK_b; conjugated acid pK_a)[b]	conc (M)	temp (°C)	time	conv (%)[c]	$M_n \times 10^{-3}$ (calcd)	$M_n \times 10^{-3}$ (exp)[d]	M_w/M_n[d]	incorporated ratio (%)[e]
1	no additive	—	—	–50	7 s	95	18.6	56.6	1.98	—
2		—	—	–20	5 s	95	18.6	34.5	1.97	—
3	cyclic ether	HMO (4.01; –2.02)	0.090	–20	98 h	94	18.4	12.7 [19.8[g]]	1.41	<1[h]
4[f]		HMO	0.10	–20	117 h	94	18.4	4.4	1.74	<1
5		THP (4.83; –2.79)	0.10	–20	94 h	96	18.8	14.0 [20.6[g]]	1.31	<1[h]
6		1,4-DO (5.85; –3.22)	1.0	–50	243 h	94	18.4	10.6 [16.3[g]]	1.53	<1[h]
7		1,4-DO	0.10	–20	1 min	95	18.6	13.5	1.78	<1
8		1,3-DO (6.67; —)	1.0	–50	10 s	93	18.3	14.3	1.95	6
9		1,3-DOL (7.55; —)	5.0	–78	30 s	57	11.2	13.5	1.93	5
10		DMDOP	1.20	–78	30 s	89	17.5	21.3	2.25	<1[i]
11		THF (4.22; –2.08)	0.10	–20	19 h	86	18.6[j]	6.5	1.53	12
12		1,4-ECH (—; –2.80)	0.40	–50	3 h	67	20.8[j]	8.4 [10.6[g]]	1.47	37[i]
13	acyclic ether	Et_2O (—; –3.59)	1.0	–20	3 min	89	17.5	5.1	1.94	—
14		DEE	1.0	–50	4 h	23	4.5	2.4	1.60	—
15	ester	ε-CL	0.40	–20	17 h	13	2.6	0.3	1.10	—
16		TMC	0.10	–20	71 h	64	12.6	0.5	1.27	—
17		MePhDOLO	1.1	–78	30 s	82	23.9[j]	2.5	1.76	21
18		VAc	1.0	–40	1 h	97	19.0	6.4	2.36	—
19	amine	pyridine	0.10	–20	24 h	19 (<1[k])	3.7	0.3	1.02	—
20	aldehyde	IBA	3.0	–78	15 s	98	30.8[j]	12.3	1.84	45
21		CHA	3.0	–78	150 s	90	35.6[j]	2.2	1.79	47
22		BzA	3.0	–78	5 min	63	12.4	0.3	1.21	—

[a] $[CHO]_0 = 0.40$ M, $[Ph_3CB(C_6F_5)_4] = 2.0$ mM, in dichloromethane. [b] References 67 and 68. [c] Determined by gas chromatography. [d] By GPC using polystyrene standards. [e] Incorporated ratio is the percentage of each additive incorporated into the main chain, as determined by NMR. [f] In dichloromethane/hexane (1/1 v/v). [g] Absolute M_n determined by GPC equipped with a light-scattering detector. [h] Determined with high-MW parts separated by preparative GPC. [i] Determined by gas chromatography. [j] Based on the amounts of both CHO and an additive. [k] By gravimetry.

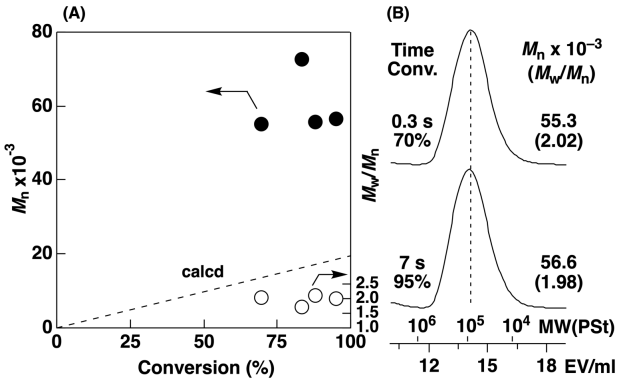


Figure 1. (A) M_n and M_w/M_n values and (B) MWD curves of the polymers obtained by the polymerization of CHO in the absence of additives ($[CHO]_0$ = 0.40 M, $[Ph_3CB(C_6F_5)_4]$ = 2.0 mM, in dichloromethane at –50 ºC).

As seen from the polymerization results in the presence of various additives, cyclic ethers were effective for the generation of long-lived species.[66] In particular, polymerization in the presence of HMO, THP, or 1,4-DO resulted in polymers with narrow MWDs and M_n values that were very close to the theoretical values (entries 3, 5, and 6 in Table 1). Living polymerization most likely proceeded with these additives, which is discussed in detail in the next subsection. In contrast, polymerization in the presence of 1,3-DO, 1,3-DOL, or DMDOP, which are cyclic ethers with lower basicity[67,68] than HMO, THP, and 1,4-DO, proceeded much faster even at high additive concentrations (1.0—5.0 M), yielding polymers with broad MWDs (entries 8—10). Various cyclic ethers and cyclic acetals are known to exhibit (co)polymerizability; hence, some cyclic ethers used in this study functioned not only as additives but also as comonomers. For example, the polymers obtained in the presence of 1,3-DO and 1,3-DOL contained 5—6% of these cyclic acetals. Larger amounts of cyclic ethers were incorporated in the cases of THF and 1,4-ECH[69,70] (entries 11 and 12). Moreover, when 1,4-ECH was used, the copolymerization proceeded in a living manner, which is discussed in detail below.

Unlike cyclic ethers, acyclic ethers were not effective at controlling the polymerization of CHO. When Et_2O was used as an additive, polymerization proceeded relatively rapidly and yielded a polymer with a lower M_n value than those obtained in the presence of cyclic ethers (entry 13). In the case of DEE, the polymerization ceased at a low monomer conversion (entry 14).

Esters and amines were also ineffective as additives. The polymerization of CHO ceased in the presence of ε-CL, TMC, or pyridine, resulting in low-MW oligomers (entries 15, 16, and 19). MePhDOLO was incorporated into a polymer chain, as in the cases of some cyclic ethers (entry 17). However, the polymerization was not controlled, and a product with a low M_n value was obtained. A polymer with a lower M_n value and a broader MWD than those of the polymers obtained with cyclic ethers was produced in the presence of VAc (entry 18; simple esters, such as ethyl acetate, were not used because of the possible function as a chain transfer agent[71,72]). Benzoates or haloacetates would be useful for more detailed investigation of the effects of basicity of ester additives.

Aliphatic aldehydes such as IBA and CHA, which exhibit poor homopolymerizability[73], functioned as comonomers when used as additives, resulting in copolymers with CHO (entries 20 and 21). In particular, polymers with high M_n values were produced in the presence of IBA. The crossover reaction from an aldehyde to CHO generated an acetal structure in the main chain. The detailed results will be discussed below. Unlike aliphatic aldehydes, an aromatic aldehyde was completely ineffective for polymerization. CHO oligomers were obtained in the presence of BzA (entry 22).

Living Polymerization Using Cyclic Ethers as Additives

As described in the previous subsection, the polymerization of CHO in the presence of cyclic ethers such as HMO, THP, and 1,4-DO resulted in polymers with M_n values close to the theoretical values and relatively narrow MWDs, which are indicative of living polymerization. The detailed results are explained here. Figure 2A shows the time–conversion plots and $\ln([M]_0/[M])$–time plots of the polymerizations. Monomer conversion reached nearly quantitative values, and the $\ln([M]_0/[M])$–time plots followed straight lines, indicating that the concentration of the propagating species was constant during the reactions and that any termination reactions did not occur. The MWD curves of the product polymers had unimodal shapes and shifted to the higher-MW region without a tailing, suggesting that long-lived species were generated (Figure 2B). The M_n values increased linearly with an increase in monomer conversion (filled circles in Figure 2C). Furthermore, the absolute M_n values determined by

GPC equipped with a light-scattering detector agreed well with the theoretical values calculated from the charged amounts of CHO and the initiator (squares in Figure 2C). These results indicate that the living polymerization of CHO proceeded with the formation of long-lived species. In the case of 1,4-DO, polymerization under conditions similar to those suitable for HMO and TMP (0.10 M at –20 °C) proceeded very rapidly, and polymers with relatively broad MWDs were obtained (entry 7 in Table 1; Figure S1). Polymerization at a high concentration of 1,4-DO (1.0 M) and a lower temperature (–50 °C) was effective in improving the controllability (entry 6; green symbols in Figure 2C), which is likely related to the basicity of the additives, as discussed below.

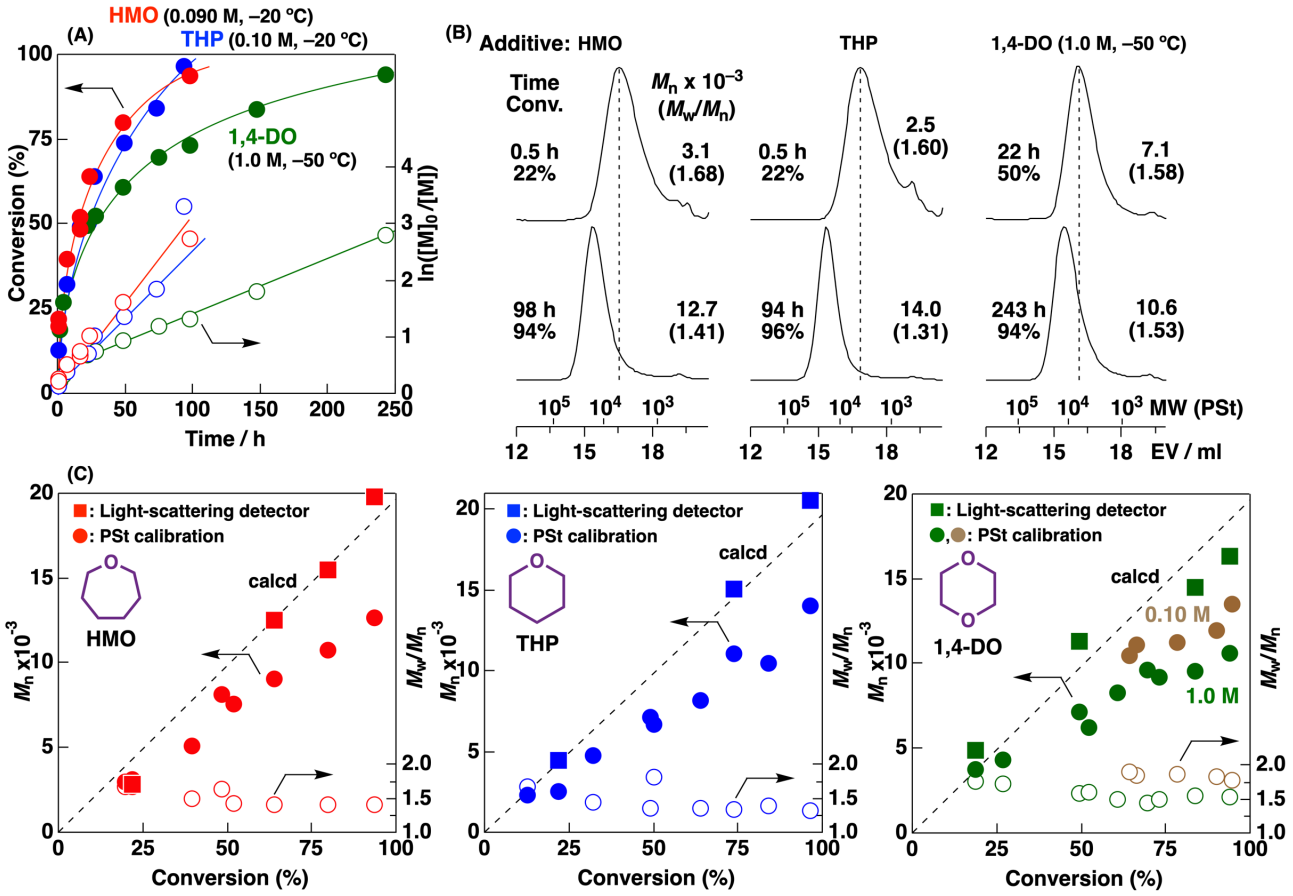


Figure 2. (A) Time-conversion curves and first order plot of the polymerization of CHO in the presence of HMO, THP, or 1,4-DO, (B) MWD curves, and (C) M_n and M_w/M_n values of the obtained polymers ($[CHO]_0$ = 0.40 M; $[HMO]_0$ = 0.090 M, $[THP]_0$ = 0.10 M, or $[1,4\text{-DO}]_0$ = 1.0 (green) or 0.10 (brown) M; $[Ph_3CB(C_6F_5)_4]$ = 2.0 mM; in dichloromethane at –20 (HMO, THP, 1,4-DO [0.10 M]) or –50 (1,4-DO [1.0 M]) ºC. Filled squares: Absolute M_n determined by GPC equipped with a light-scattering detector. Filled circles: M_n determined by GPC with polystyrene calibration.

^{1}H NMR analysis of the polymers obtained in the presence of HMO, THP, or 1,4-DO using PhONa as a quencher[65] (Figure 3) strongly suggested that these additives formed dormant species during polymerization. Peaks attributed to the phenoxy group were observed at 6.8 and 7.2 ppm (peaks 12—14), which indicates that the quencher was successfully incorporated into a polymer chain. Interestingly, the phenoxy group was most likely attached not to a CHO-derived unit but to HMO-, THP-, or 1,4-DO-derived units, as suggested by the triplet peaks at 3.86, 3.87, or 4.02 ppm (peaks 11, 15, and 16), respectively. The integral ratios of the triplet peaks and the peaks of the *o*- and *p*-protons of the phenoxy group (peaks 12 and 14) were approximately 2/3, which also supports the assignments. Moreover, in the ESI-MS analysis of the polymers, main peaks with *m*/*z* values consistent with structures consisting of CHO units and one HMO, THP, or 1,4-DO unit were detected (Figures S2—S4). These results suggest that cyclic ether-derived propagating ends were generated in the polymerization and that the quencher reacted with the cyclic ether-derived propagating ends. Most of the polymer chains obtained under suitable conditions likely had quencher-derived ω-ends, as concluded from the comparison of the M_n values determined by ^{1}H NMR with those determined by GPC equipped with a light-scattering detector (vide infra). Unlike those of the ω-ends, the incorporation ratios of a trityl group (peaks 1—3) derived from the initiator into the α-ends were 20—30%. The α-end of the other chains was a hydroxy group (peak 7; the assignment was supported by the spectrum recorded with one drop of D_2O (Figure S5)). This hydroxy group was likely generated either by the loss of the trityl group during the purification process or by initiation from a proton derived from the reaction between the initiator and adventitious water.

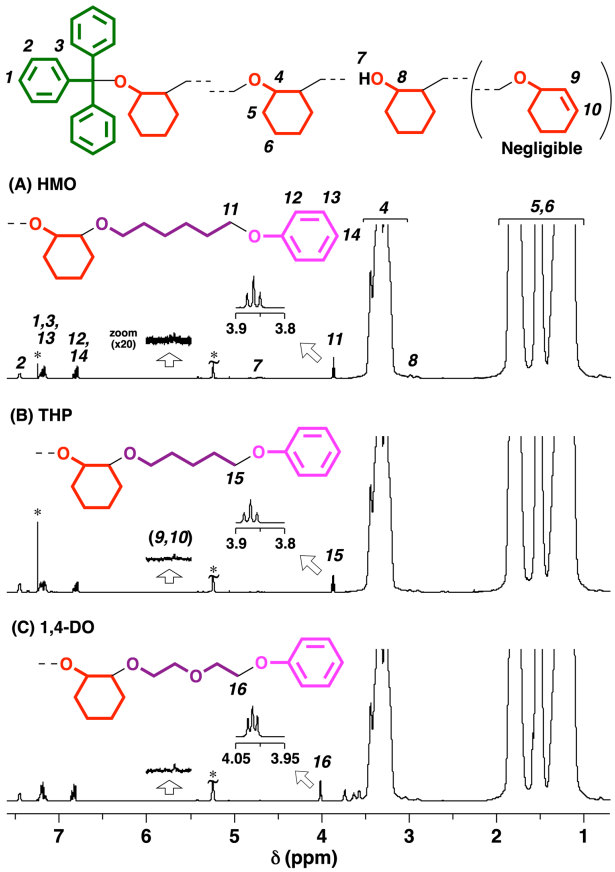


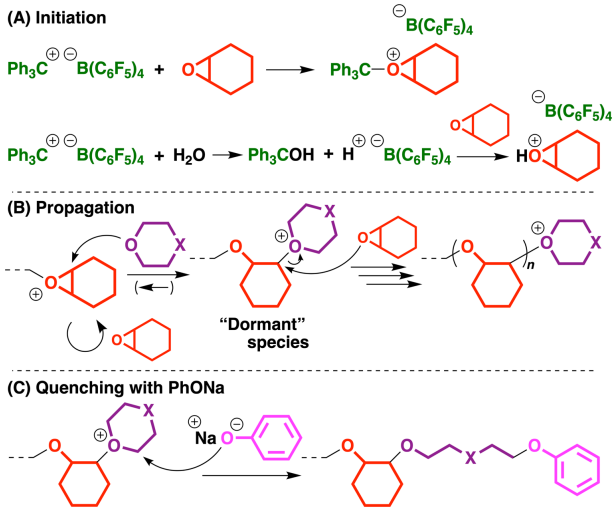
Figure 3. ^{1}H NMR spectra of the poly(CHO)s obtained in the presence of (A) HMO (conv = 94%; entry 3 in Table 1), (B) THP (conv = 96%; entry 5), or (C) 1,4-DO (conv = 68%; obtained under the same conditions to those for entry 6) (in dichloromethane-d_2 at 25 ºC; * dichloromethane or $CHCl_3$). See the caption of Figure 2 for the polymerization conditions. After purification by preparative GPC. See Figure S6 for the ^{13}C NMR spectrum of the product obtained in the presence of HMO.

Plausible Mechanism of Cationic Ring-Opening Polymerization of CHO

A series of plausible mechanisms of polymerization in the presence of cyclic ethers is shown in Scheme 2. There are two main possible mechanisms for the initiation reaction. One is the reaction of a monomer with the trityl cation of the initiator [$Ph_3CB(C_6F_5)_4$], and the other is initiation via a proton generated by the reaction of the initiator with adventitious water (Scheme 2A). During the propagation reactions, the propagating end is "stabilized" by the formation of dormant species through the reaction of the CHO-derived species with a cyclic ether (Scheme 2B). This mechanism is strongly supported by the analyses of the product polymers by ^{1}H NMR and ESI-MS, as described above. The propagation reaction mainly occurs via nucleophilic attack of a monomer molecule onto the CHO-derived methine carbon

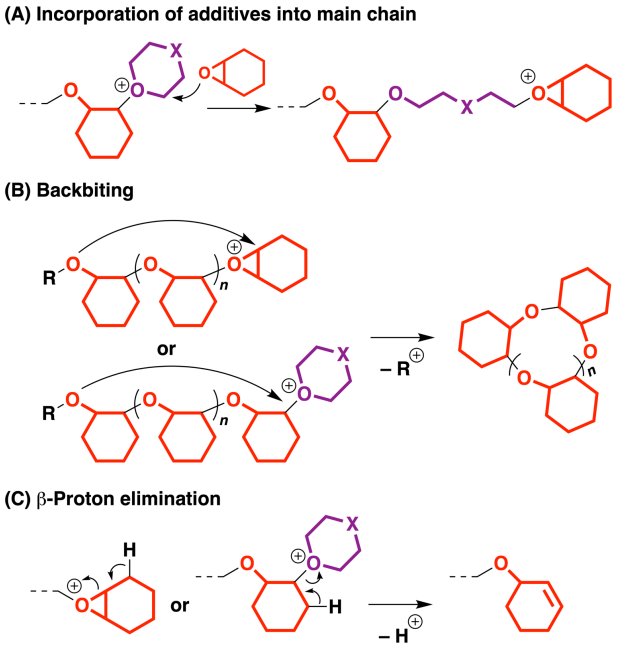
adjacent to the cyclic ether-derived positively charged oxygen atom of the dormant species at the propagating end. Quenching of the polymerization by a PhONa quencher[65] proceeds by the attack of the cyclic ether-derived methylene group of the dormant species by a phenoxy anion (Scheme 2C; it is unclear why the phenoxy anion selectively reacts with not the methine group of the oxonium center-adjacent CHO unit but the methylene group of the cyclic ether unit). In addition, during the propagation reactions, a monomer molecule occasionally attacks not the CHO-derived methine but the cyclic ether-derived methylene group of the dormant species, resulting in the incorporation of a cyclic ether into the main chain (Scheme 3A). Indeed, peaks with *m*/*z* values consistent with structures consisting of CHO units and more than one cyclic ether unit were detected by ESI-MS analysis (Figures S2—S4). However, the incorporation ratios of the cyclic ether units in the product polymers were very low (<1%), as confirmed by ^{1}H NMR analysis. Other side reactions include backbiting cyclization and β-proton elimination (Schemes 3B and 3C), although the frequency of the side reactions was very low, as suggested by the analyses of the product polymers by ^{1}H NMR and ESI–MS.

Scheme 2. The Plausible Mechanism of Cationic Polymerization of CHO in the Presence of Cyclic Ether (X = CH_2CH_2 (HMO), CH_2 (THP), or O (1,4-DO)).[a]



[a] Counteranions are omitted in B and C.

Scheme 3. Possible Side Reactions: (A) Incorporation of Cyclic Ethers into the Main Chain, (B) Backbiting Reaction, and (C) β-Proton Elimination Reaction.



The formation of the dormant species most likely contributed to the well-controlled M_n and the relatively narrow MWDs of the products by allowing the even propagation of all the propagating chains. Polymers with very high M_n values were obtained in the additive-free system (Figure 1), suggesting that both chain transfer reactions by backbiting cyclization or β-proton elimination (Schemes 3B and 3C) and termination reactions are inherently infrequent in the cationic ring-opening polymerization of CHO. The M_n values that were much higher than the theoretical values in the additive-free system likely resulted from propagation reactions that were significantly faster than the initiation reaction. Therefore, the propagation reactions were moderated and decelerated through the formation of the dormant species in the polymerization in the presence of cyclic ethers. As a result, all the propagating chains propagated evenly, resulting in polymers with theoretical M_n values and narrow MWDs. The "stabilization" of the propagating species by cyclic ethers means that cyclic ethers react with the CHO-derived propagating end to form a dormant species and do not induce undesired reactions such as β-proton elimination.

Experiments to Confirm the Livingness of the Polymerization

To confirm the livingness of the polymerization of CHO in the presence of cyclic ethers, a

monomer addition experiment was conducted. When a fresh aliquot of CHO was added at a late stage of the reaction in the presence of HMO, the polymerization continued to proceed smoothly (Figure 4A). The obtained polymers had narrow MWDs, and the M_n values were relatively consistent with the theoretical values (Figure 4B and C). These results suggest that the polymerization proceeded in a living manner.

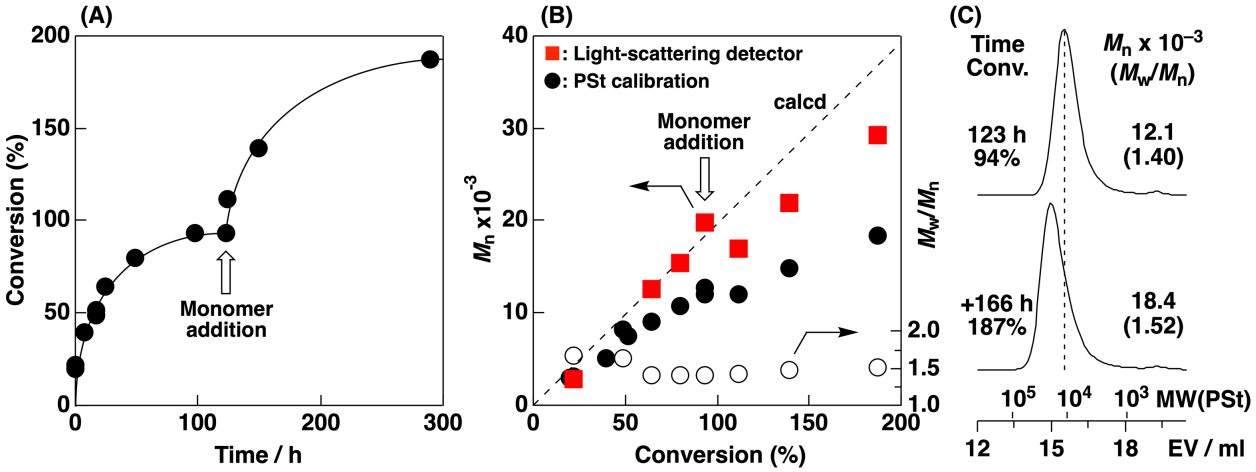


Figure 4. Monomer-addition experiment: (A) Time–conversion curve, (B) M_n and M_w/M_n values, and (C) MWD curves of the obtained polymers ($[CHO]_0$ = $[CHO]_{added}$ = 0.40 M, $[HMO]_0$ = 0.090 M, $[Ph_3CB(C_6F_5)_4]_0$ = 2.0 mM, in dichloromethane at –20 ºC).

Polymerization at different monomer/initiator ratios was also conducted. Polymerization using different amounts of the initiator proceeded, yielding polymers with M_n values relatively close to the theoretical values calculated from the ratios of $[CHO]_0$ to $[Ph_3CB(C_6F_5)_4]_0$ (Figure 5). This result suggests that the initiation reaction occurred in a relatively quantitative manner.

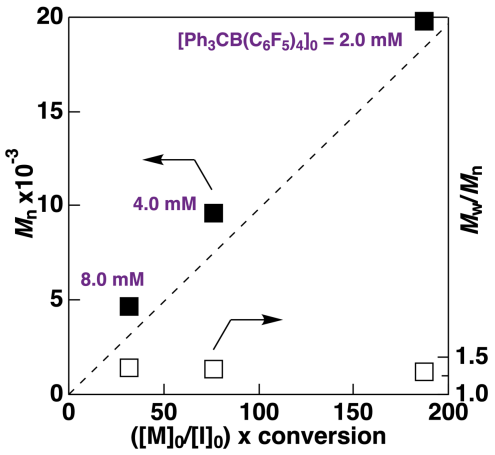


Figure 5. The M_n–$[M]_0/[I]_0$ plot in the polymerization of CHO at different concentrations of the initiator ($[CHO]_0$ = 0.40 M, $[HMO]_0$ = 0.090 M, $[Ph_3CB(C_6F_5)_4]_0$ = 2.0, 4.0, or 8.0 mM, in dichloromethane at –20 ºC; M: monomer, I: initiator). The M_n values are absolute M_n determined by GPC equipped with a light-scattering detector. See Figure S7 for the M_n–conversion plots.

The incorporation ratios of the quencher into the ω-ends were examined to estimate the number of living propagating chains. The incorporation ratios (Figure 6) were calculated from a comparison between the absolute M_n values determined by GPC with a light-scattering detector and the M_n values determined from the integral ratios of the peaks of the main chain and the phenoxy group in ^{1}H NMR spectra. The results indicate that over 80% of the polymer chains were living even at the late stage of polymerization in the presence of HMO or THP (red and blue symbols in Figure 6). 1,4-DO is likely inferior to HMO and THP in terms of controllability (green symbols) even at a higher concentration of 1,4-DO (1.0 M) and a lower temperature (–50 ºC), which was also consistent with the results of the monomer addition experiments in the presence of 1,4-DO (Figure S8). Chain transfer reactions via backbiting (Scheme 3B) and/or β-proton elimination (Scheme 3C) might occur as judged from the gradual plateauing of the M_n–conversion plot. The integral ratios of the peaks of the quencher derived end (peak 16 in Figure 3C) and the β-proton elimination-derived end (peaks 9 and 10) were 1.0/0.02; hence, the contribution of β-proton elimination is likely small. Backbiting and/or other undetected chain transfer reactions would be a main cause.

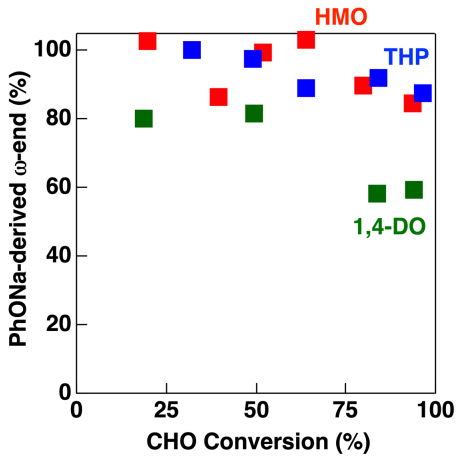
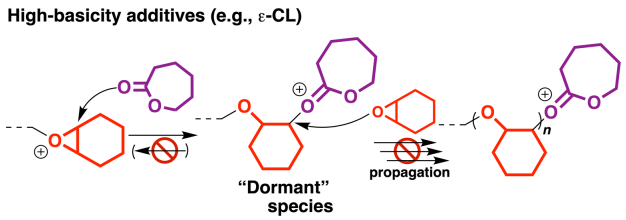


Figure 6. The ratios of the PhONa-derived ω-ends ($[CHO]_0$ = 0.40 M; $[HMO]_0$ = 0.090 M (red), $[THP]_0$ = 0.10 M (blue), or $[1,4\text{-DO}]_0$ = 1.0 M (green); $[Ph_3CB(C_6F_5)_4]_0$ = 2.0 mM; in dichloromethane at –20 (red and blue) or –50 ºC (green)). The ratios are based on the absolute M_n values determined by GPC equipped with a light-scattering detector and the M_n(NMR) values calculated from the integral ratios of the peaks of the main chain and the phenoxy group of the ^{1}H NMR spectra. The samples were analyzed after purification by preparative GPC. The samples correspond to entries 3, 5, and 6 in Table 1 and Figure 2.

The difference among the cyclic ethers in terms of controllability of the polymerization is most likely attributed to the basicity of cyclic ethers. HMO and THP have higher basicity than 1,4-DO (reported pK_b values[67] and pK_a values of the conjugated acids[68] are listed in Table 1); hence, HMO and THP form stronger bonds with the CHO-derived propagating species and thus generate a more appropriate dormant species than 1,4-DO does. Indeed, smaller amounts of HMO or THP than of 1,4-DO and lower temperatures were sufficient for the controlled polymerization. The suitable basicity of HMO and THP resulted in livingness. In contrast, polymerization in the presence of 1,3-DO or 1,3-DOL, which are less basic than 1,4-DO, proceeded much faster and produced polymers with broader MWDs (entries 8 and 9 in Table 1; Figure S9), probably because less stable dormant species were generated. Unlike cyclic ethers, additives such as ε-CL and pyridine were not effective for polymerization (entries 15 and 19 in Table 1). Excessively stable (and almost inactive) dormant species and/or deactivated species were probably generated with these additives (Scheme 4).

Scheme 4. The Plausible Mechanism of Cationic Polymerization of CHO in the Presence of ε-CL.



Investigation of a Suitable Initiator and Solvent for Living Polymerization

To find a suitable initiator for living polymerization of CHO, we conducted polymerizations using Ph_3CPF_6, Ph_3CBF_4, Et_3OPF_6, Tf_2NH, and TfOH (Table 2, Figure S10). The polymerization using Ph_3CPF_6 proceeded at a rate similar to that using $Ph_3CB(C_6F_5)_4$; however, the M_n values of the obtained polymers were smaller than those of the polymers obtained with $Ph_3CB(C_6F_5)_4$ (entry 2 in Table 2; Figure S10A). Polymers with bimodal MWDs were generated when Ph_3CBF_4 was used (entry 3; Figure S10B), although the reason is unclear. Et_3OPF_6, Tf_2NH, and TfOH were also ineffective for polymerization, resulting in low-MW products and/or cessation of the reaction at very low conversion (entries 4—6; Figure S10C—E). On the basis of these results, it was concluded that $Ph_3CB(C_6F_5)_4$ was appropriate as an initiator.

Polymerization in less polar solvents was also examined; however, the reaction yielded ill-defined products. The polymerization in dichloromethane/hexane (1/1 v/v; entry 4 in Table 1; Figure S11) yielded polymers with M_n values smaller than those obtained for the reaction in dichloromethane alone. Therefore, polymerization in this study was conducted mainly in dichloromethane.

Table 2. Cationic Polymerization of CHO[a] Using Various Initiators

entry	initiator	temp (°C)	time	conv[b] (%)	$M_n \times 10^{-3}$ (GPC)[c]	M_w/M_n (GPC)[c]	polymerization
1[d]	$Ph_3CB(C_6F_5)_4$	–50	243 h	94	10.6	1.53	long-lived species-mediated
2	Ph_3CPF_6	–50	173 h	66	7.4	1.57	long-lived species-mediated
3	Ph_3CBF_4	–50	173 h	47	2.0	3.55	bimodal
4	Et_3OPF_6	–40	96 h	50	5.3	1.76	not long-lived species-mediated
5	Tf_2NH	–50	144 h	41	2.5	1.64	not long-lived species-mediated
6	TfOH	–50	528 h	10	0.3	1.20	oligomer

[a] $[CHO]_0$ = 0.40 M, $[1,4\text{-DO}]_0$ = 1.0 M, [initiator] = 2.0 mM, in dichloromethane. [b] Determined by gas chromatography. [c] By GPC using polystyrene standards. See Figure S10 for the time–conversion plots and M_n–conversion plots. [d] The same data as entry 6 in Table 1.

Polymerization of Various Oxiranes Other than CHO

Polymerization of various oxiranes other than CHO was examined using HMO or 1,4-DO as an additive (Scheme 1, Chart 1). When VCHO was used as a monomer (entries 1 and 2 in Table 3; Figure S12), the product polymers had M_n values that increased in proportion to the monomer conversion. The peak top of the MWD curve shifted toward the high-MW region as the polymerization proceeded. These results indicate that the living polymerization of VCHO proceeded as in the case of CHO. Indeed, when a fresh aliquot of VCHO was added at a late stage of the polymerization of CHO in the presence of HMO, the copolymerization proceeded smoothly to yield a block copolymer (Figure S13). In contrast, when 3MCHO was used as a monomer, the M_n values did not increase at the late stage of polymerization (entries 3 and 4; Figure S14). The methyl group at the 3-position potentially hindered efficient formation of the dormant species due to steric hindrance. Polymerization of LO also yielded products with low M_n values (entry 5; Figure S15), as in the case of 3MCHO. Unlike oxiranes with a six-membered fused ring, CPO, which has a five-membered fused ring, did not yield polymers during polymerization; instead, oligomers with M_n of 0.3×10^3 were produced (entries 6 and 7; Figure S16). ESI-MS analysis (Figure S17) suggested that cyclic oligomers were mainly generated. Poly(CPO)s with M_n values over 10^4 could be produced under other conditions (e.g., $B(C_6F_5)_3$ as a catalyst in dichloromethane at –78 °C, unpublished data); hence, the initiating system used in this study is likely related to cyclic oligomer formation. In the case of CHPO, which is an oxirane with a seven-membered fused ring, polymerization proceeded faster than that of oxiranes with a six-membered fused ring. However, the M_n values increased little as the monomer conversion increased (entries 8 and 9; Figure S18). The polymerization of DMBO, which does not have an alicyclic skeleton, resulted in low monomer conversion and oligomer formation (entries 10 and 11; Figure S19). Polymers could be obtained under other conditions; hence, the initiating system used is likely unsuitable, as in the case of CPO.

Table 3. Cationic Polymerization of Various Oxirane Monomers Using HMO or 1,4-DO [a]

entry	monomer	additive	temp (°C)	time	conv[b] (%)	$M_n \times 10^{-3}$ (GPC)[c]	M_w/M_n (GPC)[c]
1	VCHO	HMO	–20	72 h	75	9.4	1.47
2		1,4-DO	–40	4 h	58	10.1	1.44
3	3MCHO	HMO	–20	3.5 h	49	5.7	1.65
4		1,4-DO	–40	3.5 h	88	7.4	1.86
5	LO	1,4-DO	–50	0.5 h	95	2.2	1.64
6	CPO	HMO	–20	147 h	87	0.3	1.25
7		1,4-DO	–50	100 h	84	0.3	1.05
8	CHPO	HMO	–20	2 h	84	5.3	1.72
9		1,4-DO	–50	1 h	94	7.7	1.86
10	DMBO	HMO	–20	459 h	17	0.5	1.76
11		1,4-DO	–50	117 h	5.7	0.5	1.40

[a] $[monomer]_0$ = 0.40 M; $[HMO]_0$ = 0.10 M or $[1,4\text{-DO}]_0$ = 1.0 M; $[Ph_3CB(C_6F_5)_4]$ = 2.0 mM; in dichloromethane. [b] Determined by gas chromatography. See Figures S12, S14-S16, S18, S19 for the time–conversion plots and M_n–conversion plots. [c] By GPC using polystyrene standards.

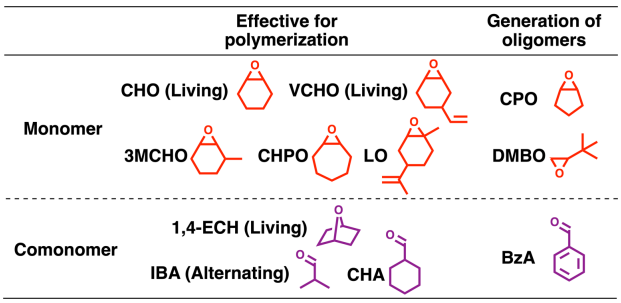


Chart 1. Effectiveness of monomers and comonomers in cationic polymerization

Copolymerization of CHO and 1,4-ECH Mediated by Living Species

The basicity of 1,4-ECH is similar to that of HMO, THP, and 1,4-DO[68], and unlike these cyclic ethers, 1,4-ECH exhibits homopolymerizability[69,70], probably due to its large ring strain; hence, 1,4-ECH functioned as both an effective additive and a highly reactive comonomer in the polymerization of CHO (entry 12 in Table 1). Figure 7 shows the results of the cationic copolymerization of CHO and 1,4-ECH

using $Ph_3CB(C_6F_5)_4$ as an initiator in dichloromethane at –50 °C. CHO was consumed twice as fast as 1,4-ECH (Figure 7A). The M_n values of the obtained polymers increased in proportion to the monomer conversion, although the values were smaller than the theoretical values (Figure 7B). Moreover, it was also confirmed that the quencher (PhONa) was incorporated into the ω-end (see Figure S21 for ^{1}H NMR) at a relatively high ratio in the early stage of polymerization (Figure 7D). The results demonstrated that the copolymerization of CHO and 1,4-ECH proceeded in a living manner. 1,4-ECH most likely formed a dormant species in the same way as other cyclic ethers, such as HMO, THP, and 1,4-DO, while functioning as a comonomer due to its high polymerizability (Scheme 5). When a fresh aliquot of 1,4-ECH was added in the middle stage of the polymerization of CHO, a block copolymer consisting of CHO block and statistical CHO–1,4-ECH block was successfully obtained (Figure S22). The glass transition temperatures (T_g) of the obtained copolymers are shown in Figure S23.

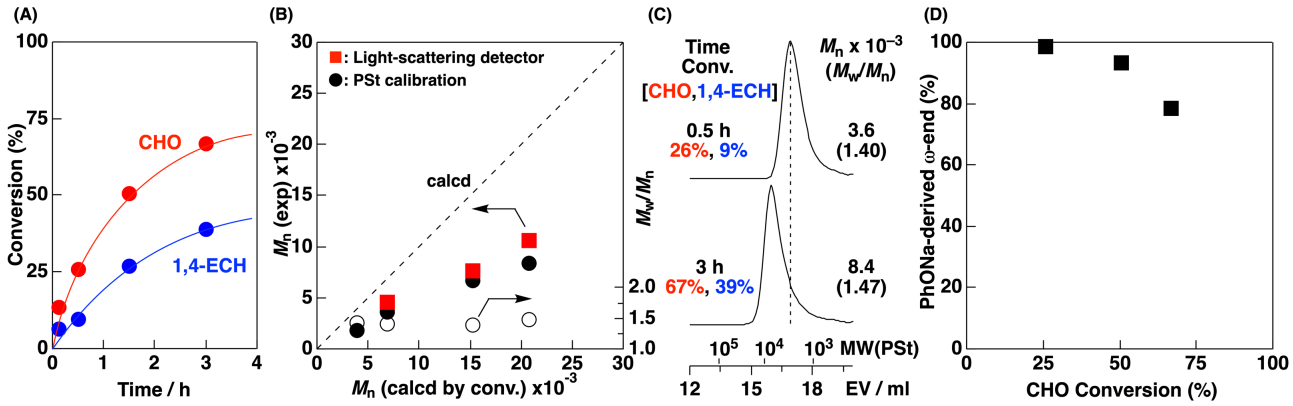
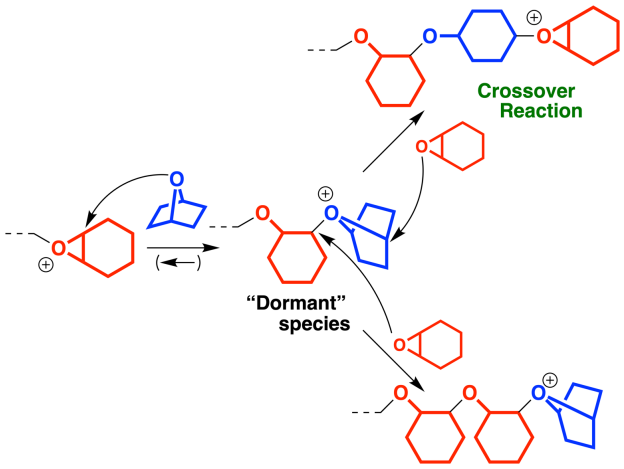


Figure 7. (A) Time–conversion curves of the copolymerization of CHO and 1,4-ECH, (B) M_n and M_w/M_n values, (C) MWD curves of the obtained polymers, and (D) the ratios of the PhONa-derived ω-ends ($[CHO]_0$ = 0.40 M, $[1,4\text{-ECH}]_0$ = 0.40 M, $[Ph_3CB(C_6F_5)_4]$ = 2.0 mM, in dichloromethane at –50 ºC). See Figure S20 for the ESI-MS spectrum of the product.

Scheme 5. The Plausible Mechanism of Cationic Copolymerization of CHO and 1,4-ECH.



Synthesis of Acid-Degradable Alternating-Like Copolymers of CHO and Aliphatic Aldehyde

As briefly explained above, aliphatic aldehydes were successfully copolymerized with CHO (entries 20 and 21 in Table 1; Figure S24A). Aliphatic aldehydes exhibit poor homopolymerizability (Scheme 6A) due to their very low ceiling temperature;[73] hence, copolymerization was conducted at a higher concentration of IBA (3.0 M) than of CHO (0.40 M) to facilitate crossover reactions. The copolymerization proceeded very rapidly even at a very low temperature (–78 °C), resulting in near quantitative conversion of CHO. As a result, a polymer with an alternating-like sequence consisting of 1.2 and 1.0 units of CHO and IBA per block, respectively, was generated (Figures 8 and S25). Since the polymerization was extremely fast, the livingness of the polymerization was not confirmed. The polymer could be degraded into a low-MW compound by acid hydrolysis (purple curve in Figure 8) through the cleavage of the acetal structures (Scheme 6) that were generated in the main chain via crossover from IBA to CHO.

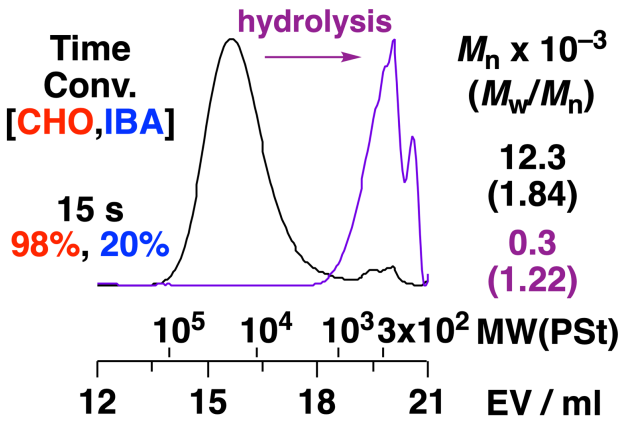
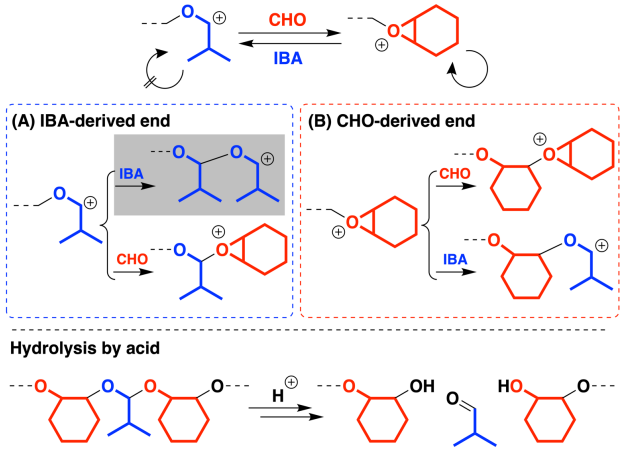


Figure 8. MWD curves of the copolymer consisting of CHO and IBA (black) and its acid hydrolysis product (purple) ($[CHO]_0$ = 0.40 M, $[IBA]_0$ = 3.0 M, $[Ph_3CB(C_6F_5)_4]_0$ = 2.0 mM, in dichloromethane at –78 ºC).

Scheme 6. Crossover Reactions That Generate from (A) IBA- and (B) CHO-Derived Propagating Species (Reactions with Gray Shadow Negligibly Occur).



Conclusion

In conclusion, the living cationic polymerization of CHO proceeded in the presence of cyclic ethers such as HMO and THP. The linear increase of M_n–conversion plots, the linearity of $\ln([M]_0/[M])$–time plots, the successful monomer-addition experiment, the successful block copolymerization, the predictable MWs at different $[M]_0/[I]_0$ ratios, and efficient incorporations of a quencher fragment into chain ends demonstrated the efficient initiation reactions, the absence of termination and chain transfer reactions, and the occurrence of living polymerization. During the propagation reactions, the propagating end formed dormant species through the reaction of the CHO-derived species with cyclic ethers. This is

strongly supported by the detection of polymer structures with a quencher-attached HMO, THP, or 1,4-DO unit at the chain end. The difference in controllability of polymerization among the cyclic ethers is most likely attributed to the basicity of the cyclic ethers. Additives with greater basicity, such as HMO and THP, can form a stronger bond and generate an appropriate dormant species, which results in livingness. In addition, the copolymerization of CHO and 1,4-ECH proceeded in a living manner. 1,4-ECH functioned as both an effective additive and a reactive comonomer. The copolymerization of CHO with an aliphatic aldehyde also proceeded to yield an alternating-like copolymer with acid degradability. The results obtained in this study will allow further development of both the living cationic polymerization of oxiranes and the precise synthesis of well-defined polymers with new functions and high performance.

Associated Content

Supporting Information

Polymerization data, NMR and ESI-MS spectra, and DSC thermogram.

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Notes

The authors declare no competing financial interest.

Acknowledgments

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