Title	Concurrent Cationic Vinyl-Addition and Coordination Ring-Opening Copolymerization via Orthogonal Propagation and Transient Merging at the Propagating Chain End
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Concurrent Cationic Vinyl-Addition and Coordination Ring-Opening Copolymerization via Orthogonal Propagation and Transient Merging at the Propagating Chain End

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Supporting Information Placeholder

ABSTRACT: Controlled cationic vinyl-addition polymerization of an alkyl vinyl ether (VE) and ring-opening polymerization of ε-caprolactone (CL) simultaneously proceeded using $HfCl_4$/$Hf(OBu)_4$ as a dual-role catalyst for both mechanisms, yielding a graft copolymer consisting of a poly(VE) main chain and several poly(CL) side chains. The copolymer of conventionally incompatible monomers was generated via the unprecedented mechanisms consisting of orthogonal propagating reactions and transient merging. Specifically, the poly(CL) chains were incorporated into a poly(VE) chain through an exchange reaction between the VE-derived alkoxy group and the propagating poly(CL) chain at the acetal moiety of the propagating end of the poly(VE) chain. An appropriate ratio of $HfCl_4$ and $Hf(OBu)_4$ was indispensable for both the simultaneous vinyl-addition and ring-opening polymerizations and the alkoxy group exchange reaction.

Simultaneous copolymerization via different mechanisms or intermediates has great potential to produce copolymers with novel properties in one step from conventionally incompatible monomers. To accomplish these types of reactions,[1–6] each polymerization must proceed without significantly interfering with the other reactions. For example, reversible addition–fragmentation chain transfer polymerization of styrene and ring-opening polymerization (ROP) of ε-caprolactone (CL) simultaneously proceeded to yield a block copolymer using a bifunctional initiator that generates propagating species for the two orthogonal polymerization reactions.[1] Concurrent polymerization that proceeds via common propagating ends or dormant species is also attractive because copolymers with diverse structures that cannot be synthesized via completely orthogonal reactions are produced from typically incompatible monomers. These copolymerization reactions that proceed via different mechanisms generally require an astute strategy to generate efficient crossover propagation reactions.[7,8]

A reversible equilibrium between the dormant and active species plays a central role in most living chain-growth polymerization reactions.[9,10] In living cationic polymerization of vinyl monomers, the concentration of the propagating carbocationic species is kept extremely low via reversible deactivation with anionic species such as halogen anions.[10] In our systematic study on the cationic polymerization of vinyl ether (VE) using alcohols as a cationogen, the alcohol-derived alkoxy group was incorporated into the side chains of the resulting poly(VE)s via alkoxy group exchange (AGE) reactions in the dormant–active equilibrium.[11] In this system, the metal chloroalkoxide catalysts, generated in situ by the reaction of alcohols and metal chlorides, provide the active species with the chloride anion (Figure 1, path A') or the alkoxide anion (path B'), producing two types of dormant species. The acetal end generated via path B' contains two alkoxy groups; hence, the alcohol-derived alkoxy group is incorporated into the side chain of the poly(VE)s through the abstraction of the VE-derived alkoxy group (path C) and the subsequent propagation reactions. Metal catalysts with an optimum balance between chlorophilicity and oxophilicity were indispensable for enabling the unique mechanisms.

In this study, we sought to develop a new type of concurrent copolymerization reaction consisting of the simultaneous cationic vinyl-addition polymerization of VE and the coordination ROP of cyclic esters. Because the ROP of cyclic esters using metal alkoxide catalysts proceeds via the generation of the growing alkoxide ends attached to the central metal,[12] a metal chloroalkoxide that exhibits catalytic activity for both cationic vinyl-addition polymerization and ROP enables copolymerization via unique pathways (Figure 2). Specifically, given that both propagation reactions proceed orthogonally to each other under the same conditions, exchange reactions between the alkoxy group of a polyester chain end and the alkoxy group derived from a VE side chain will occur occasionally at the acetal moiety of the propagating ends via the AGE mechanism (path B', C). Repetitive propagation and AGE reactions are expected to generate a graft copolymer via the incorporation of several polyester chains into the side chains of the backbone poly(VE) chain.

We designed an initiating system using a mixture of $HfCl_4$ and $Hf(OBu)_4$ as catalysts for the copolymerization of ethyl VE (EVE) and CL. Hafnium compounds were chosen because hafnium chloroalkoxides are effective for controlled cationic polymerization via the AGE reactions due to an appropriate balance between oxophilicity and chlorophilicity[11] and because hafnium catalysts with alkoxy ligands catalyze the living coordination ROP of CL.[13] Most importantly, an appropriate balance of the chloride and alkoxide contents was found to be essential for the simultaneous consumption of both monomers.

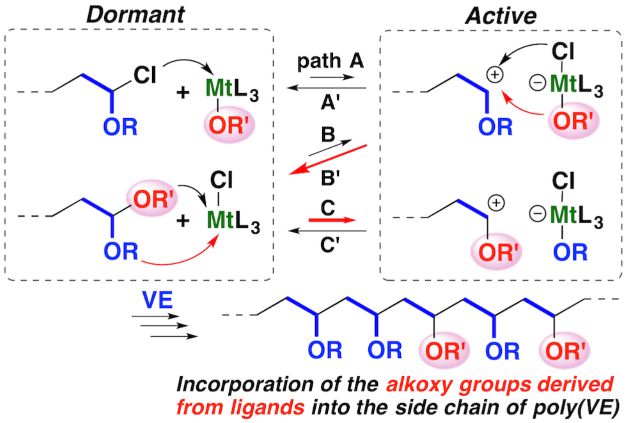

Figure 1. Propagation reaction of VE using $MtCl_x(OR')_y$ catalysts via AGE mechanisms (L: chloride or alkoxide group).

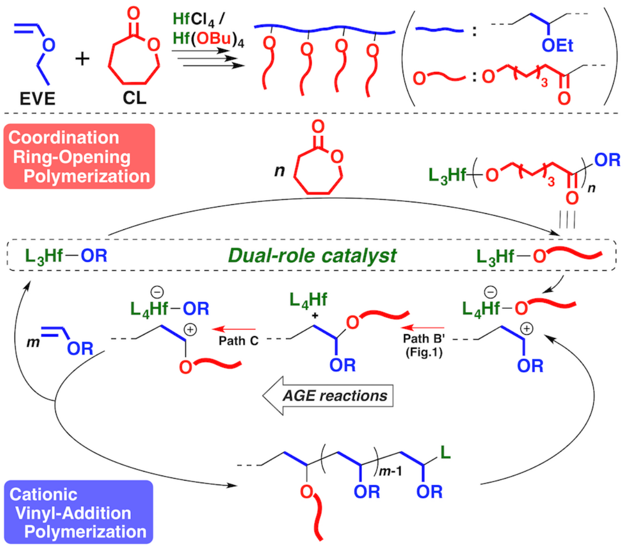

Figure 2. Copolymerization of EVE and CL using $HfCl_4/Hf(OBu)_4$ catalysts via AGE mechanisms (L: chloride or alkoxide group).

First, reactions using either $HfCl_4$ or $Hf(OBu)_4$ in dichloromethane at 30 ºC resulted in homopolymerization of either monomer (Table 1, entries 3 and 4). Only EVE was consumed when $HfCl_4$ was used, while only CL was consumed using $Hf(OBu)_4$. The reaction using a mixture of these catalysts, however, allowed for the consumption of both monomers. In particular, both monomers were consumed at similar rates with an appropriate ratio of both catalysts (entries 1 and 2). The product polymer had a unimodal molecular weight (MW) distribution (Figure 3A). Moreover, the peak shifted to the high molecular weight region as the monomer conversion values increased, indicating the generation of long-lived species. Hafnium species $HfCl_x(OR)_{4-x}$, generated in situ from $HfCl_4$ and $Hf(OBu)_4$ in a manner similar to that of the Ti and Zr counterparts,[14] were likely responsible for catalyzing the copolymerization, as deduced from the ^1H NMR spectrum of the catalyst mixture (Figure S1 in the Supporting Information). The catalytic activity of the $HfCl_x(OR)_{4-x}$ species for both polymerization reactions appeared to be moderated compared to the original tetrachloride and tetrabutoxide.[15]

The ^1H NMR analyses of the obtained polymers confirmed that the copolymerization successfully proceeded via the AGE mechanism to yield graft copolymers consisting of a poly(EVE) main chain and several poly(CL) side chains. The structure of the product was elucidated from several key structures, such as the absence of a hydroxy group at the ω-end of a poly(CL) chain, the presence of ethoxy groups at the α-end of poly(CL) chains, and residual CL-derived structures after alkali hydrolysis, as explained below. The graft density and the lengths of VE and CL homosequences were determined by simultaneous equations of integral ratios. In the spectrum of the copolymerization product (Figure 4A), there was no peak assigned to the hydroxy group-adjacent methylene protons of the ω-end of a CL homopolymer at 3.6-3.7 ppm (peak 19 in Figure 4D), indicating the incorporation of the poly(CL) growing chains into the side chains of poly(EVE). In addition, the generation of the EVE-derived ethoxy groups at the α-end of poly(CL) (peaks 15 and 16) indicated the occurrence of the initiation reaction of CL polymerization from the Hf-OEt bonds generated via AGE reactions. The average structure of the copolymer, deduced from the integral ratios of peaks 11, 15, and 4 to the peak for the ω-end of poly(EVE) (peak 17), was composed of 59 units of EVE in the main chain and approximately 5 branch chains with 10 units of CL in each branch (Figure 3B). ^{13}C NMR spectra of the products also suggested the graft copolymer formation (Figure S2). The molecular weight estimated from this structure, approximately 10 × 10^3, was comparable to the value from GPC [14.1 × 10^3 by polystyrene calibration and 13.7 × 10^3 by a system equipped with refractive index, light scattering, and viscosity detectors (the *dn/dc* value of the product was 0.064 in THF)]. The Mark-Houwink-Sakurada constant, determined by the GPC analysis via light scattering and viscometric detections, was 0.54. The chain length and grafting density of the produced copolymers changed depending on polymerization conditions such as concentrations of the monomers and the catalysts (Table S1).

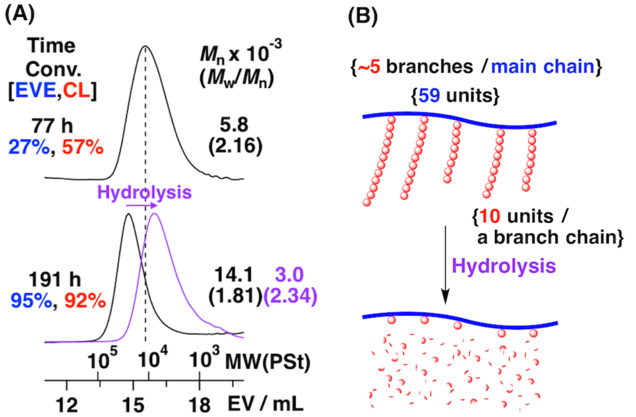

Figure 3. (A) MWD curves for poly(EVE-*co*-CL) (black; Table 1, entries 1 and 2) and its alkali hydrolysis product (purple). (B) Illustrations of the obtained graft copolymer (entry 2) and its alkali hydrolysis product.

Table 1. Concurrent cationic vinyl-addition and coordination ring-opening copolymerization of VE and CL[a]

entry	VE	$HfCl_4$ (mM)	$Hf(OBu)_4$ (mM)	time	conv.[b] (%) VE	conv.[b] (%) CL	$M_n \times 10^{-3}$ [c]	M_w/M_n[c]	grafting density (per 100 VE units)[d]
1	EVE	12	10	77 h	27	57	5.8	2.16	9
2	EVE	12	10	191 h	95	92	14.1	1.81	10
3	EVE	20	–	4.5 min	99	0	6.0	2.73	–
4	EVE	–	20	60 h	0	100	3.4	1.15	–
5	IPVE	12	8.0	70 h	67	44	3.2	2.66	<1 [e]

[a] $[VE]_0$ = 1.52 (entries 1–4) or 0.75 (entry 5) M, $[CL]_0$ = 1.52 (entries 1–4) or 0.76 (entry 5) M, in dichloromethane (entries 1–4) or in toluene (entry 5) at 30 ºC. [b] Determined by gas chromatography. [c] Determined by GPC (polystyrene standards). [d] Estimated by ^{1}H NMR. [e] Except for the linkage of poly(IPVE) and poly(CL) chains at the ω-end of the poly(IPVE) chain.

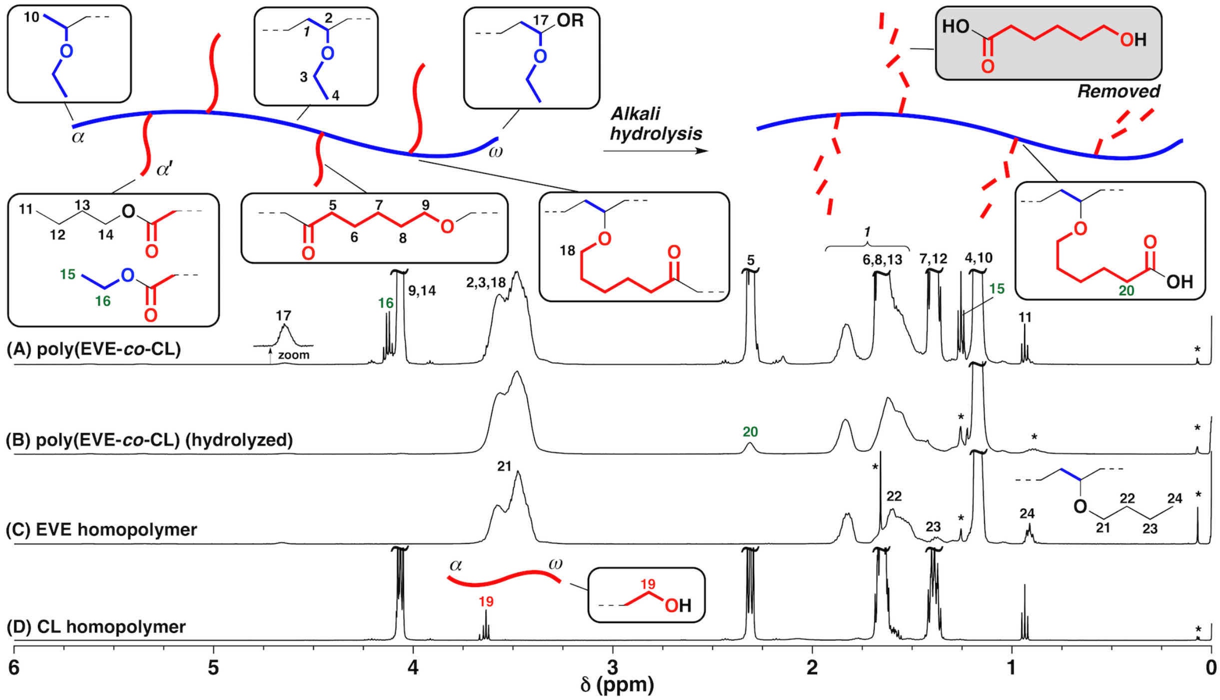

Figure 4. ^{1}H NMR spectra of (A) poly(EVE-*co*-CL) (Table 1, entry 2), (B) poly(EVE-*co*-CL) after alkali hydrolysis, (C) EVE homopolymer {$[EVE]_0$ = 0.76 M, $[HfCl_4]_0$ = 14 mM, $[Hf(OBu)_4]_0$ = 6.0 mM, [EtOAc] = 1.4 M, in dichloromethane at 0 ºC. M_n(GPC) = 6.4 × 10^3}, and (D) CL homopolymer {$[CL]_0$ = 0.81 M, $[HfCl_4]_0$ = 22 mM, $[Hf(OBu)_4]_0$ = 11 mM, in toluene at 30 ºC. M_n(GPC) = 2.4 × 10^3} recorded in $CDCl_3$ at 30 ºC. Peaks with an asterisk are due to grease, vaseline, and water.

Cleavage of the ester linkages of the poly(CL) segments by alkali hydrolysis also provided evidence for the generation of graft copolymers. Peaks for the protons adjacent to the ester moiety (Figure 4A, peaks 9, 14, and 16) completely disappeared after hydrolysis, as shown in the ^{1}H NMR spectrum(Figure 4B). In contrast, a small peak assigned to the methylene group adjacent to the carbonyl group of a CL unit (peak 20) remained, suggesting that the original copolymer structureconsisted of a poly(EVE) backbone and poly(CL) side chains. In addition, the MW distribution curve of the original copolymer shifted to the lower MW region after hydrolysis while maintaining a unimodal shape (Figure 3, purple). The M_n value of the degradation product was 3.0 × 10^3, which is consistent with the value expected from the remaining poly(EVE) chain (59 units; MW ~ 4 × 10^3).

From these results, the polymerization mechanisms are rationally explained as follows. The ROP of CL is initiated through the coordination of CL to the Hf center and the insertion of CL into the Hf-oxygen bond through the ring-opening reaction. The propagation reaction of CL smoothly proceeds ina manner similar to that of the initiation reaction.[12,13] The cationic polymerization of EVE appeared to occur via the initiation reaction from a proton derived from adventitious water or alcohol impurities, although the details are currently unclear.[16] The propagation reaction of EVE subsequently proceeds via the dormant-active equilibrium involving both the carbon–chlorine and carbon–alkoxy dormant ends, as explained above (Figure 1). During these orthogonal reactions, the incorporation of poly(CL) chains into a poly(EVE) chain transiently occurs through the following sequential procedures: the addition reaction of a poly(CL) chain into the carbocation at the growing ends of poly(EVE) to form an acetal moiety (Figure 5, path B'), the abstraction of the EVE-derived ethoxy group from the acetal end by the Hf catalyst (path C), and the addition reaction of EVE to the resulting carbocation. In addition, new poly(CL) chains are continuously generated via the initiation reaction from the resulting Hf-OEt catalyst, which was also confirmed by the incorporation of the ethoxy group into the chain end of poly(CL) segments. The graft copolymers are produced by the repetition of these reactions. These mechanisms were also suggested by the copolymerization via the addition of the EVE monomer into the reaction solution of ROP of CL at the later stage of the polymerization (Figures S4 and S5).

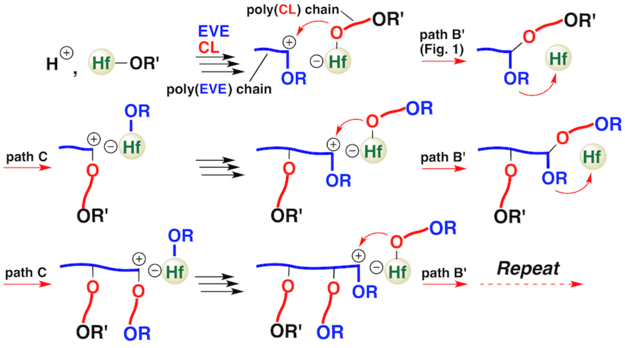

Figure 5. Illustrative drawing of the copolymerization of EVE and CL via the AGE mechanisms.

Considering these mechanisms, the selectivity in abstracting alkoxy groups at the acetal chain ends is responsible for the grafting density. This selectivity appears to depend on the stability of the resulting carbocation and/or the affinity of a metal catalyst for alkoxy groups. In fact, the use of isopropyl VE (IPVE), a VE with a secondary alkoxy group, instead of EVE resulted in the negligible generation of graft copolymers (Table 1, entry 5). The AGE mechanism rarely operated (Figure S6) to mainly produce the CL homopolymer and diblock copolymer (Figures S7 and S8). The selective abstraction of the poly(CL) chain from the acetal moiety consisting of the isopropoxy group and the poly(CL) chain is consistent with several reports on the Lewis acid-catalyzed activation of acetals containing primary and secondary alkoxy groups.[17] Thus, a higher grafting efficiency will be attained using appropriate monomers, which is currently under investigation. In addition, a metal catalyst that exhibits sufficient affinity to alkoxy groups is indispensable for efficient copolymerization; hence, the reaction using catalysts with various central metals will also be investigated in our group.

In conclusion, the copolymerization of VEs and CL was achieved via AGE mechanisms using a mixture of $HfCl_4$ and $Hf(OBu)_4$ as a dual-role catalyst. Most importantly, both the cationic vinyl-addition and the ring-opening polymerization reactions orthogonally proceeded without interfering with the other reactions, while the different types of propagating chains transiently merged to yield graft copolymers consisting of a poly(VE) main chain with several poly(CL) side chains. An appropriate ratio of $HfCl_4$ and $Hf(OBu)_4$ was essential for the propagation reactions of both monomers at similar rates. Further optimization of the polymerization conditions, including catalyst design, will allow for precise control over the frequency of the AGE reactions and the MWs of the backbone and branch chains. The characteristic strategy demonstrated in this study will be applied to the synthesis of graft copolymers and other highly branched copolymers from a wide variety of commercially available VEs and cyclic esters.

ASSOCIATED CONTENT

Supporting Information

Experimental section and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

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(15) Cationic homopolymerization of EVE using $HfCl_x/(OBu)_{4-x}$ in the presence of ethyl acetate proceeded much slower (90% conversion in 70 h at $[HfCl_4]_0/[Hf(OBu)_4]_0$ = 14 mM/6 mM) compared to that using $HfCl_4$ alone (97% in 11 min at $[HfCl_4]_0$ = 20 mM) due to the decrease of the Lewis acidity through the replacement of chlorine atoms to alkoxy groups. The polymerization rate of CL with $HfCl_4/Hf(OBu)_4$ (entries 1 and 2) was approximately one-third of that with $Hf(OBu)_4$ (entry 4) likely due to the difference of the abilities to coordinate a CL monomer and to involve the alkoxy group in the propagation reaction.

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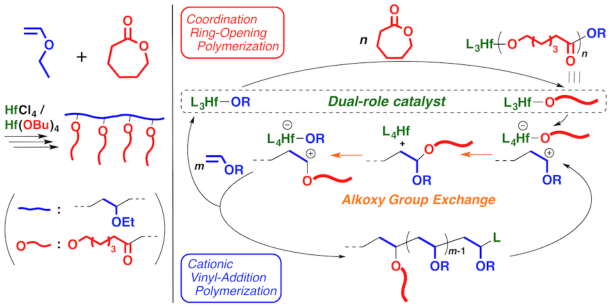

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