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Note	

Degradable Silyl Ether Polymers Synthesized by Sequence-Controlled Cationic Terpolymerization of 1,3-Dioxa-2-Silacycloalkanes with Vinyl Ethers and Aldehydes

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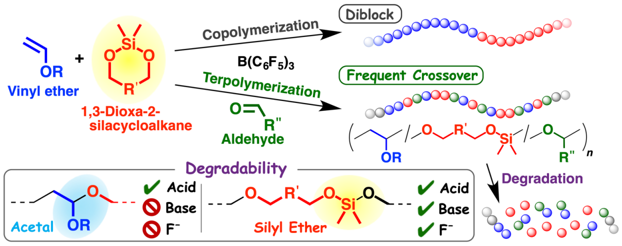


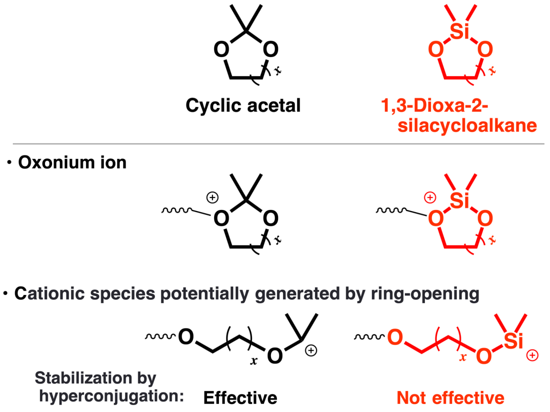
ABSTRACT: Polymers with silyl ether moieties have been gaining considerable interest due to both the properties derived from silicon-oxygen linkages and the acid-, base-, and fluoride ion-triggered degradability. In this study, 1,3-dioxa-2-silacycloalkanes were demonstrated to function as promising monomers for the synthesis of silyl ether polymers when combined with vinyl ethers and aldehydes in cationic terpolymerization with $B(C_6F_5)_3$ as a catalyst. Importantly, all three monomers were indispensable for efficient terpolymerization via frequent crossover reactions. For example, a degradable terpolymer with an M_n of 29×10^3 was obtained from a six-membered 1,3-dioxa-2-silacycloalkane, 2-chloroethyl vinyl ether, and pivalaldehyde, which was superior to both the silyl monomer homopolymerization yielding a product with an M_n of 3.3×10^3 and the inefficient copolymerizations in the absence of either the silyl monomer, vinyl ether, or aldehyde. Moreover, the terpolymers likely had ABC-type, pseudo-periodic sequences as a result of frequent and selective crossover reactions. The resulting terpolymers have acetal and silyl ether moieties in the main chain, thus exhibiting acid-, base-, or fluoride ion-triggered degradability. Indeed, the terpolymer with an M_n of 29×10^3 was smoothly degraded into a product with an M_n of 0.3×10^3 under acidic conditions. The key to the terpolymerization reaction was the reaction of an aldehyde with the silyl monomer-derived oxonium ion to generate a carbocation that can react with a vinyl ether because a vinyl ether does not react with the silyl monomer-derived oxonium ion.

INTRODUCTION

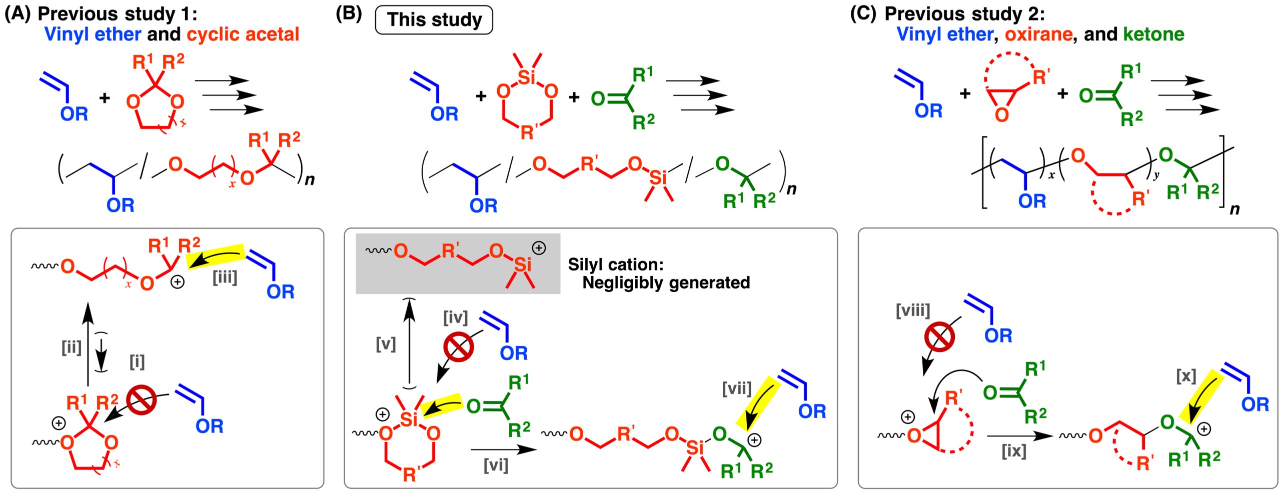
Silicon-containing polymers exhibit various excellent properties.[1] For instance, polysiloxanes[2–6] exert great heat and chemical resistance due to the strong main chain consisting of Si-O bonds, which contributes to a wide range of applications, such as elastomer, grease, oil, and biomedical devices. In addition, poly(silyl ether)s,[7–18] which have silyl ether (Si-O-C) moieties in the main chain, were shown to exhibit flexibility at low temperature and thermal stability. These properties are suitable for gas-permeable membranes and biocompatible coatings. Various methods have been developed to synthesize poly(silyl ether)s. Furthermore, silyl ether moieties are attractive as degradable units that can be easily cleaved by acids, bases, or fluoride ions. Low-molecular-weight (low-MW) compounds are obtained by the scission of the silyl ether moieties in the polymer main chain. A silyl ether moiety is also attractive as a protecting group of a hydroxy group. Poly(vinyl alcohol) can be synthesized by desilylation of poly(trimethylsilyl vinyl ether).[19]

To synthesize new silicon-containing polymers, we focused on 1,3-dioxa-2-silacycloalkanes (Scheme 1), which are silicon-counterparts of cyclic acetals and have a silicon atom instead of a carbon atom at the 2-position. Syntheses of various 1,3-dioxa-2-silacycloalkanes have been investigated for several decades.[20–34] A typical synthetic procedure of 1,3-dioxa-2-silacycloalkanes is the condensation of a diol and a silyl compound such as dimethoxydimethylsilane by an acid catalyst.[20,21] Interestingly, it was reported that five-membered monomers form dimers,[20] while six-membered monomers spontaneously polymerize.[22] In addition, seven-membered monomers are generally stable, and eight- or more-membered monomers are significantly less stable unless oxygen or nitrogen atoms or aromatic rings are introduced into the ring.[21] Nevertheless, detailed studies on the polymerization of 1,3-dioxa-2-silacycloalkanes have not been conducted. Homo- and copolymerization of 1,3-dioxa-2-silacycloalkanes potentially yield polymers that are both degraded by acids, bases, or fluoride ions and exhibit properties derived from alkyl groups and silyl ether moieties. We are very interested in the copolymerization of 1,3-dioxa-2-silacycloalkanes with other types of monomers because of the potential developments of copolymers that exhibit properties derived from each monomer.

Scheme 1. Cyclic Acetal (2,2-Dimethyl Type as an Example) and 2,2-Dimethyl-1,3-dioxa-2-silacycloalkane: Oxonium Ions and Cationic Species Generated via Ring-Opening.



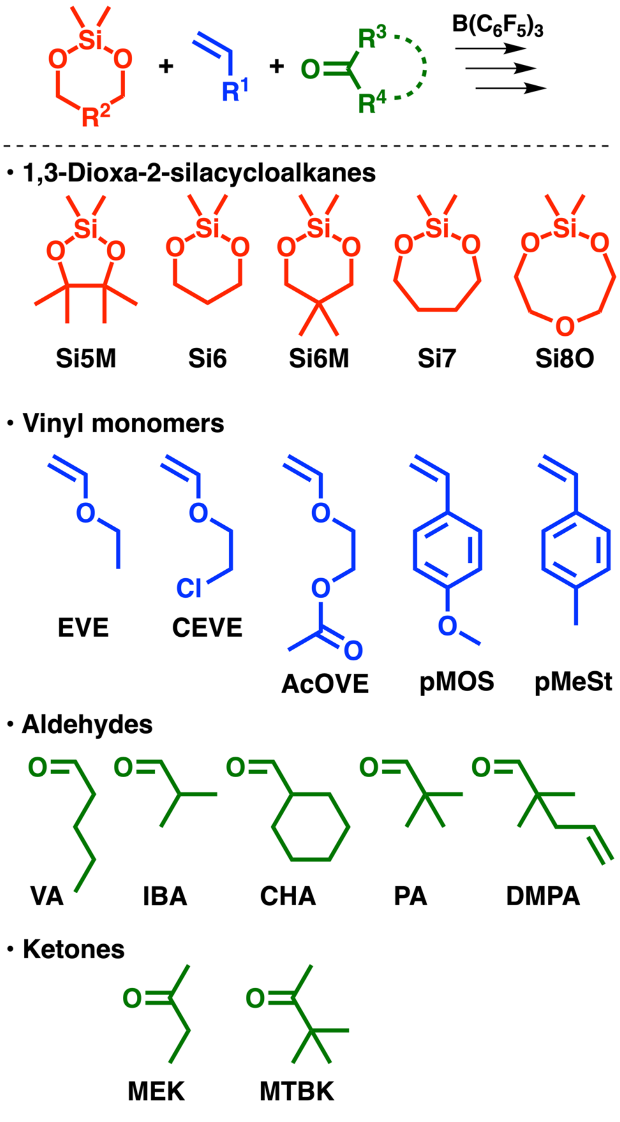
Scheme 2. Propagation Reactions and Strategy to Encourage Crossover Reactions: The Outcomes of Our Previous Studies (left and right) and the Strategy of This Study (center).



Cyclic acetals with suitable substituents and ring structures undergo cationic copolymerizations with vinyl monomers such as vinyl ethers (VEs) and styrene derivatives.[35–38] A key to copolymerization via crossover reactions is the generation of a carbocation through ring-opening of a cyclic acetal-derived oxonium ion ([ii] and [iii] in Scheme 2A). This is because vinyl monomers do not react with the oxonium ion ([i] in Scheme 2A). We have demonstrated that cyclic acetals with suitable substituents, which contribute to carbocation stabilization, at the 2-position (a 2,2-dimethyl type is shown in Scheme 1 as an example) are effective for cationic copolymerizations with vinyl monomers via frequent crossover reactions.[37,38] In the case of 1,3-dioxa-2-silacycloalkanes, however, silyl cations are considered to be negligibly generated by ring-opening of the oxonium ion ([v] in Scheme 2B) due to the instability associated with inefficient hyperconjugation with alkyl groups (Scheme 1, right).[39,40] Therefore, copolymerization of vinyl monomers and 1,3-dioxa-2-silacycloalkanes is probably hard to occur due to inefficient crossover reactions from the Si monomer to a vinyl monomer ([iv] in Scheme 2B).

The use of a carbonyl compound as the third monomer is a promising strategy for terpolymerization with vinyl monomers and 1,3-dioxa-2-silacycloalkanes via crossover reactions. A carbonyl compound such as aldehydes and ketones potentially reacts with the 1,3-dioxa-2-silacycloalkane-derived oxonium ion via nucleophilic attack onto the silicon atom to generate the carbonyl compound-derived carbocation, which is structurally similar to the VE-derived carbocation and is stabilized by conjugation with the adjacent oxygen atom ([vi] in Scheme 2B). This carbocation is expected to react with a vinyl monomer ([vii] in Scheme 2B). Indeed, we have reported that ketones undergo cationic terpolymerization with VEs and oxiranes via frequent crossover reactions.[41,42] Specifically, a ketone reacts with the oxirane-derived oxonium ion to generate an oxygen-adjacent, ketone-derived carbocation ([ix] in Scheme 2C), which is followed by the reaction with a VE ([x] in Scheme 2C). In addition, the cationic polymerization of VEs was reported to occur from a carbocation generated from the reaction of a ketone or an aldehyde and trimethylsilyl chloride.[43,44]

Scheme 3. Cationic Co- and Terpolymerization of 1,3-Dioxa-2-silacycloalkanes with Vinyl Monomers and/or Carbonyl Compounds (upper). Monomers Used in This Study (lower).



Thus, in this study, we investigated the cationic polymerization of 1,3-dioxa-2-silacycloalkanes. Various vinyl monomers and carbonyl compounds were employed for the coand terpolymerization with 1,3-dioxa-2-silacycloalkanes (Scheme 3). The copolymerizations of 1,3-dioxa-2-silacycloalkanes with vinyl monomers resulted in diblock copolymers due to inefficient crossover reactions from the silyl monomer to a vinyl monomer, as expected above. In contrast, the cationic terpolymerizations of 1,3-dioxa-2-silacycloalkanes, VEs, and appropriate aldehydes successfully proceeded via frequent crossover reactions, resulting in terpolymers with ABC-type, pseudo-periodic sequences. The terpolymers have both acetal and silyl ether moieties in the main chain; hence, the terpolymers were degraded into low-MW compounds by acids, bases, and fluoride ions. The cationic copolymerizations of 1,3-dioxa-2-silacycloalkanes with cyclic ethers were also investigated.

EXPERIMENTAL SECTION

See the Supporting Information for the Materials and Characterization subsections.

Synthesis of 1,3-dioxa-cycloalkanes.

2,2-Dimethyl-1,3-dioxa-cycloalkanes were synthesized by the condensation of dimethoxydimethylsilane (TCI, >98.0%) and diol[20,21] using indium(III) trifluoromethanesulfonate (Sigma–Aldrich) as a catalyst at room temperature. After condensation, the reaction mixture was concentrated to remove methanol, which was generated as a byproduct.

2,2,4,4,5,5-Hexamethyl-1,3-dioxa-2-silacyclopentane (Si5M). Synthesized from dimethoxydimethylsilane and pinacol (Sigma–Aldrich, 98%) and purified by distillation from calcium hydride and sodium under reduced pressure after the removal of residual diol by the reaction with sodium. Colorless liquid. Final yield after distillation: 9%. ^{1}H NMR (CDCl$_3$; 500

MHz): δ 1.25 (s, 12H), 0.24 (s, 6H). ^{13}C NMR (CDCl$_3$; 125 MHz): δ 81.2, 25.5, 0.63. MS (ESI) *m*/*z* [M + Na]$^+$, calcd: 197.0968, found: 197.0969.

2,2-Dimethyl-1,3-dioxa-2-silacyclohexane (Si6). Synthesized from dimethoxydimethylsilane and 1,3-propanediol (TCI, >98.0%). Purified by distillation from calcium hydride under reduced pressure. Colorless liquid. Final yield after distillation: 29%. ^{1}H NMR (CDCl$_3$; 500 MHz): δ 4.06 (m, 4H), 1.87 (m, 2H), 0.19 (s, 6H). ^{13}C NMR (CDCl$_3$; 125 MHz): δ 63.8, 31.8, –1.70. MS (ESI) *m*/*z* [M + H]$^+$, calcd: 133.0679, found: 133.0678.

2,2,5,5-Tetramethyl-1,3-dioxa-2-silacyclohexane (Si6M). Synthesized from dimethoxydimethylsilane and 2,2-dimethyl-1,3-propanediol (TCI, >98.0%). Purified by distillation from calcium hydride under reduced pressure. Colorless liquid. Final yield after distillation: 36%. ^{1}H NMR (CDCl$_3$; 500 MHz): δ 3.66 (s, 4H), 0.96 (s, 6H), 0.20 (s, 6H). ^{13}C NMR (CDCl$_3$; 125 MHz): δ 73.7, 35.3, 22.0, –2.5. MS (ESI) *m*/*z* [M + Na]$^+$, calcd: 183.0812, found: 183.0811.

2,2-Dimethyl-1,3-dioxa-2-silacycloheptane (Si7). Synthesized from dimethoxydimethylsilane and 1,4-butanediol (TCI, >99.0%). Purified by distillation from calcium hydride under reduced pressure. Colorless liquid. Final yield after distillation: 44%. ^{1}H NMR (CDCl$_3$; 500 MHz): δ 3.85 (m, 4H), 1.75 (m, 4H), 0.14 (s, 6H). ^{13}C NMR (CDCl$_3$; 125 MHz): δ 64.4, 32.6, –2.6. MS (ESI) *m*/*z* [M + Na]$^+$, calcd: 169.0655, found: 169.0655.

2,2-Dimethyl-1,3,6-trioxa-2-silacyclooctane (Si8O). Synthesized from dimethoxydimethylsilane and diethylene glycol (Wako, >99.0%). Purified by distillation from calcium hydride under reduced pressure. Colorless liquid. Final yield after distillation: 46%. ^{1}H NMR (CDCl$_3$; 500 MHz): δ 3.85 (m, 4H), 3.71 (m, 4H), 0.18 (s, 6H). ^{13}C NMR (CDCl$_3$; 125 MHz): δ 74.2, 64.0, –2.8. MS (ESI) *m*/*z* [M + Na]$^+$, calcd: 185.0604, found: 185.0605.

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, vinyl monomer, 1,3-dioxa-2-silacycloalkane, and carbonyl compound were sequentially added into the tube using dry medical syringes. The polymerization reaction was initiated by the addition of a prechilled solution of $B(C_6F_5)_3$ in dichloromethane to the monomer solution at –78 °C. After a predetermined time, the reaction was terminated by the addition of methanol containing a small amount of aqueous ammonia. The quenched mixture was diluted with dichloromethane or hexane and then washed with water. The volatiles were removed under reduced pressure. The monomer conversion was determined by ^{1}H NMR analysis of a product polymer and/or gravimetry.

Degradation.

Acid hydrolysis of the polymers was conducted with 0.5 M HCl (aq) in 1,2-dimethoxyethane at 60 °C for 3 h or 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. Degradation by base was conducted with 0.5 M K_2CO_3 in diethyl ether/methanol (1/1 v/v) at room temperature. The reaction mixture was diluted with dichloromethane and washed with water. Degradation by fluoride ions was conducted with tetrabutylammonium fluoride (TBAF; TCI, 1 M in THF; 2 eq with respect to Si-O bonds) in tetrahydrofuran at room temperature for 30 min. The reaction mixture was diluted with dichloromethane and washed with saturated aqueous ammonium chloride and then water. The products were obtained after removing solvents and volatile products by evaporation.

RESULTS AND DISCUSSION

Homopolymerizations of 1,3-dioxa-2-silacycloalkanes and copolymerizations with VEs.

Cationic homopolymerizations of 1,3-dioxa-2-silacycloalkanes were conducted using $B(C_6F_5)_3$ as a Lewis acid catalyst in dichloromethane at –78 °C (Table 1). Cationogens were not used; hence, the initiation reaction occurs through proton generation from adventitious water and $B(C_6F_5)_3$ and/or an interaction of a silyl monomer and $B(C_6F_5)_3$. Among a series of silyl monomers with five-membered (Si5M; entry 13), six-membered (Si6; entries 5 and 6), seven-membered (Si7; entry 10), or eight-membered (Si8O; entry 15) rings, Si6 exhibited promising polymerizability and yielded a polymer with an M_n of 2.0×10^3. However, the polymerization proceeded spontaneously[22] even during storage of the Si6 monomer in a nitrogen-filled glass ampule in a freezer, producing a stretchable solid that was insoluble in chloroform. Even when stored in dichloromethane in an ampule, the polymerization occurred spontaneously, yielding a soluble polymer with an M_n of approximately 10^4. Therefore, Si6M, which has two extra methyl groups at the 4-position, was synthesized to prevent spontaneous polymerization. The substituents on the ring contribute to decreasing the ring-opening ability.[45] As a result, this monomer was successfully stored in an ampule for a long time. Si6M underwent homopolymerization to yield a polymer with an M_n of 3.3×10^3 (entry 2; Figure 1A). From these results, Si6M was mainly used in the co- and terpolymerization demonstrated below.

Table 1. Cationic Homo- and Copolymerizations 1,3-Dioxa-2-silacycloalkanes with VEs[a]

	monomer (M)					conv.[b]			
entry	VE		silyl monomer		time	VE	Si	$M_n \times 10^{-3}$ [c] [$M_n \times 10^{-3}$ (hydrolysis)]	M_w/M_n [c] [M_w/M_n (hydrolysis)]
1	None		Si6M	0.80	93.5	–	3	0.2	1.23
2			Si6M	2.4	22.5	–	8	3.3	1.20
3	CEVE	0.80	Si6M	0.80	93.5	2	2	10	8.96
4		2.4	Si6M	2.4	20 h	25	35	7.1 [4.5]	5.09 [5.21]
5	None		Si6	0.80	19 h	–	26	0.6	6.12
6			Si6	2.4	20.5	–	82	2.0	2.13
7	CEVE	0.80	Si6	0.80	3.5	16	47	7.5 [4.9]	1.21 [1.23]
8		2.4	Si6	2.4	19 h	2	67	0.9	2.08
9	EVE	0.80	Si6	0.80	1.5	71	37	29 [26]	1.66 [1.59]
10	None		Si7	0.80	210	–	14	0.5	1.40
11	CEVE	0.80	Si7	0.80	1.5	31	9	30 [27]	1.18 [1.20]
12	EVE	0.80	Si7	0.80	0.5	73	<1	18	1.74
13	None		Si5M	2.4	22 h	–	70	0.2	1.04
14	CEVE	2.4	Si5M	2.4	22 h	3	63	0.2	1.03
15	None		Si8O	0.80	23 h	–	<1	–	–
16	CEVE	0.80	Si8O	0.80	20 h	53	44	2.4	2.76
17	EVE	0.80	Si8O	0.80	1 h	65	<1	6.5	2.84

[a] $[B(C_6F_5)_3]_0$ = 5.0 mM, in dichloromethane at –78 °C. [b] Determined by ^{1}H NMR analysis. Si: 1,3-dioxa-2-silacycloalkane. [c] Determined by GPC (polystyrene standards).

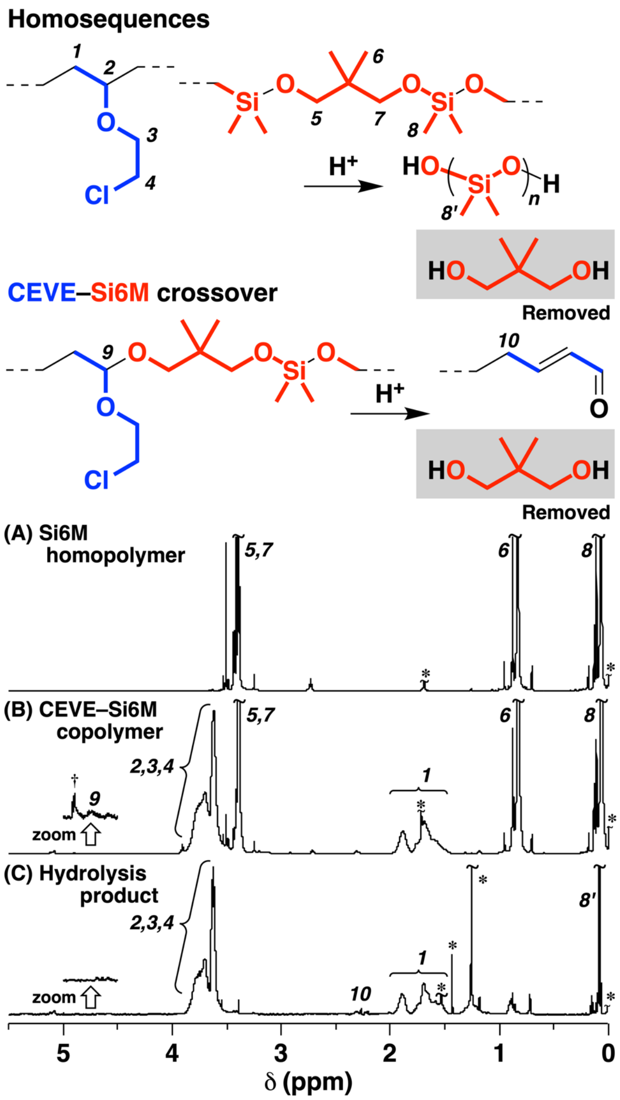


Figure 1. ^{1}H NMR spectra of (A) the Si6M homopolymer (entry 2 in Table 1), (B) the CEVE–Si6M copolymer (entry 4), and (C) the product obtained by acid hydrolysis of the copolymer; in $CDCl_3$ at 30 °C; * TMS, water, or stabilizer. † The acetal moieties of the CEVE-derived byproducts.

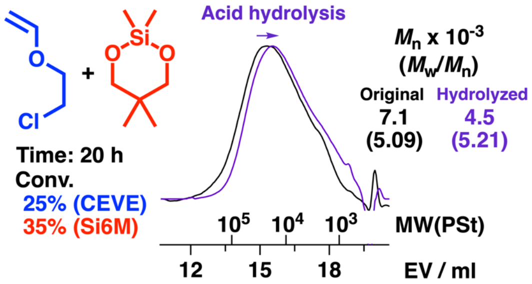
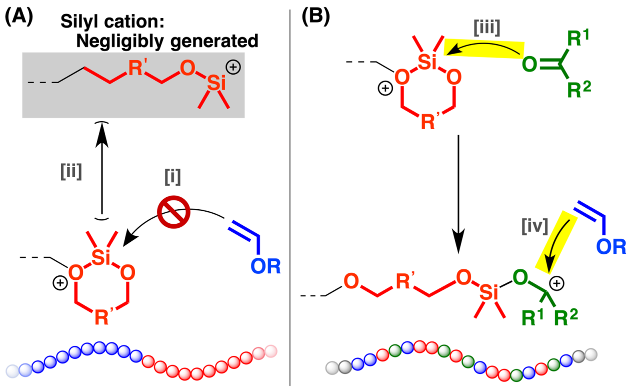


Figure 2. Molecular weight distribution (MWD) curves of the CEVE–Si6M copolymer (black; entry 4 in Table 1) and the product obtained by acid hydrolysis of the copolymer (purple) (see Table 1 for the polymerization conditions; degradation: 0.5 M HCl in 1,2-dimethoxyethane at 60 ºC for 3 h, 0.5 wt% polymer).

Cationic copolymerizations of 1,3-dioxa-2-silacycloalkanes with VEs were next examined under conditions similar to those of the homopolymerizations. The copolymerization of 2-chloroethyl VE (CEVE) and Si6M at monomer concentrations of 0.80 M resulted in very low conversion (entry 3 in Table 1), whereas both monomers were consumed to produce a polymer at 2.4 M (entry 4; Figure 2). ^{1}H NMR analysis of the product (Figure 1B) revealed that both monomers were incorporated into a polymer. However, an acetal peak assigned to the structure resulting from the crossover from CEVE to Si6M (peak 9) was very small. In addition, acid hydrolysis of the polymer resulted in an insufficient decrease in the MW (the purple curve in Figure 2). Si6M-derived diol units in the original polymer chains were completely removed during work-up after acid hydrolysis; hence, the hydrolysis product mainly consists of poly(CEVE) chains (Figure 1C). Siloxane oligomers (peak 8'), which were derived from condensation of silanol during hydrolysis, also likely existed. These results suggest that a diblock copolymer was most likely obtained by copolymerization as a result of negligible crossover reactions from Si6M to CEVE (Scheme 4A).

Scheme 4. Reactions at the 1,3-Dioxa-2-silacycloalkane-Derived End in (A) the Absence and (B) the Presence of a Carbonyl Compound.



Similar products likely consisting of diblock chains were obtained in the copolymerizations of CEVE with Si6, Si7, or Si8O (entries 7, 8, 11, and 16 in Table 1). The use of ethyl VE (EVE), which is a more reactive VE than CEVE, was inefficient for the promotion of crossover from the silyl monomers to VE (entries 9, 12, and 17). In the case of Si5M, a dimer with an O-Si-O-Si-O unit was likely produced via the condensation of a silanol in both the homopolymerization and the copolymerization with CEVE (entries 13 and 14; Figure S1).

Terpolymerization of CEVE, Si6M, and carbonyl monomers.

Both the inertness of the silyl monomer-derived oxonium ion to a VE ([i] in Scheme 4A) and negligible generation of a silyl cation[39,40] by ring-opening of the oxonium ion ([ii] in Scheme 4A) are most likely responsible for the generation of a diblock copolymer rather than a multiblock copolymer in the copolymerization of 1,3-dioxa-2-silacycloalkanes and VEs. Therefore, we employed carbonyl compounds as promising monomers that react with the oxonium ion ([iii] in

Scheme 4B), as explained in the Introduction section.[41,42] The reaction of aldehydes or ketones with the silyl monomer-derived oxonium ion potentially generates an oxygen-adjacent carbocation, which is expected to react with a VE ([iv] in Scheme 4B).

The terpolymerizations of CEVE and Si6M with various carbonyl monomers (Scheme 3) were investigated using $B(C_6F_5)_3$ as a catalyst in dichloromethane at –78 °C (Table 2). The use of aliphatic aldehydes rather than ketones was effective for terpolymerization. A polymer with an M_n of 1.7×10^3 was obtained by terpolymerization with isobutyraldehyde (IBA) (entry 1 in Table 2). Moreover, the increase in monomer concentrations resulted in an increase in the MWs of the products (entries 2–4), yielding a polymer with an M_n of 8.1×10^3 at CEVE, Si6M, and IBA concentrations of 2.4 M, 2.4 M, and 1.2 M, respectively (entry 4; see Figure S2 for ^{1}H NMR). Preferential occurrences of the propagation reactions compared to side reactions, such as the formation of cyclic products, are likely promoted at relatively high monomer concentrations. More interestingly, the use of pivalaldehyde (PA), which has a *tert*-butyl group, resulted in a terpolymer with a high MW (entry 7). A polymer with an M_n of 29×10^3 was obtained under the conditions that were appropriate for terpolymerization with IBA. The terpolymerizations with PA in other solvents (entries 8 and 9) or at a relatively low temperature (–96 °C; entry 10) also yielded polymers with high MWs, while the reaction at a relatively high temperature (–40 °C; entry 11) resulted in a decrease in the MW, likely due to the increased frequency of side reactions. From these results, the terpolymerization at high monomer concentrations at low temperature with a suitable aldehyde is of importance to obtain a polymer with a high MW.

Table 2. Cationic Ter- and Copolymerizations of CEVE, Si6M, and Carbonyl Compounds[a]

	monomer (M)					conv.[b] (%)				
entry	CEVE	Si6M	carbonyl compound		time	V	Si	C	$M_n \times 10^{-3}$ [c] [$M_n \times 10^{-3}$ (acid hydrolysis)]	M_w/M_n[c] [M_w/M_n (acid hydrolysis)]
1	0.80	0.80	IBA	0.4	22.5 h	48	27	96	1.7 [0.2]	2.00 [1.64]
2	1.6	1.6		0.8	45.5 h	32	41	96	2.2 [0.2]	2.57 [1.23]
3	2.0	2.0		1.0	23.5 h	29	53	100	4.6 [0.2]	2.15 [1.50]
4	2.4	2.4		1.2	22.5 h	26	66	90	8.1 [0.2]	2.27 [1.30]
5	2.4	–		1.2	21 h	20	–	68	1.1 [0.2]	1.99 [1.52]
6	–	2.4		1.2	21.5 h	–	2	0	–	–
7	2.4	2.4	PA	1.2	21 h	42	65	76	29 [0.3]	1.99 [1.57]
8[d]	2.4	2.4		1.2	21 h	35	41	59	25 [0.3]	1.93 [1.16]
9[e]	2.4	2.4		1.2	21 h	34	43	61	24 [0.3]	1.99 [1.32]
10[f]	2.4	2.4		1.2	22 h	39	53	71	25	2.23
11[g]	2.4	2.4		1.2	21.5 h	60	83	57	5.6	3.05
12	2.4	–		1.2	21.5 h	<1	–	<1	0.4	2.21
13	–	2.4		1.2	21 h	–	2	<1	–	–
14	2.4	2.4	DMPA	1.2	21 h	6	67	15	38 [0.3]	2.09 [1.20]
15	2.4	2.4	CHA	1.2	21.5 h	28	67	72	7.5 [0.2]	3.40 [1.48]
16	2.4	2.4	VA	1.2	21 h	8	4	46	3.4 [0.3]	1.80 [2.10]
17	2.4	2.4	MEK	1.2	23.5 h	0	59	2	–	–
18	2.4	2.4	MTBK	1.2	24 h	<1	2	0	–	–

[a] $[B(C_6F_5)_3]_0$ = 5.0 mM, in dichloromethane (except for entries 8 and 9), at –78 ºC (except for entries 10 and 11). [b] Determined by ^{1}H NMR analysis. V: CEVE, Si: Si6M, C: carbonyl compound. [c] Determined by GPC (polystyrene standards). [d] In toluene. [e] In hexane/dichloromethane (5/5 v/v). [f] At –96 ºC. [g] At –40 ºC.

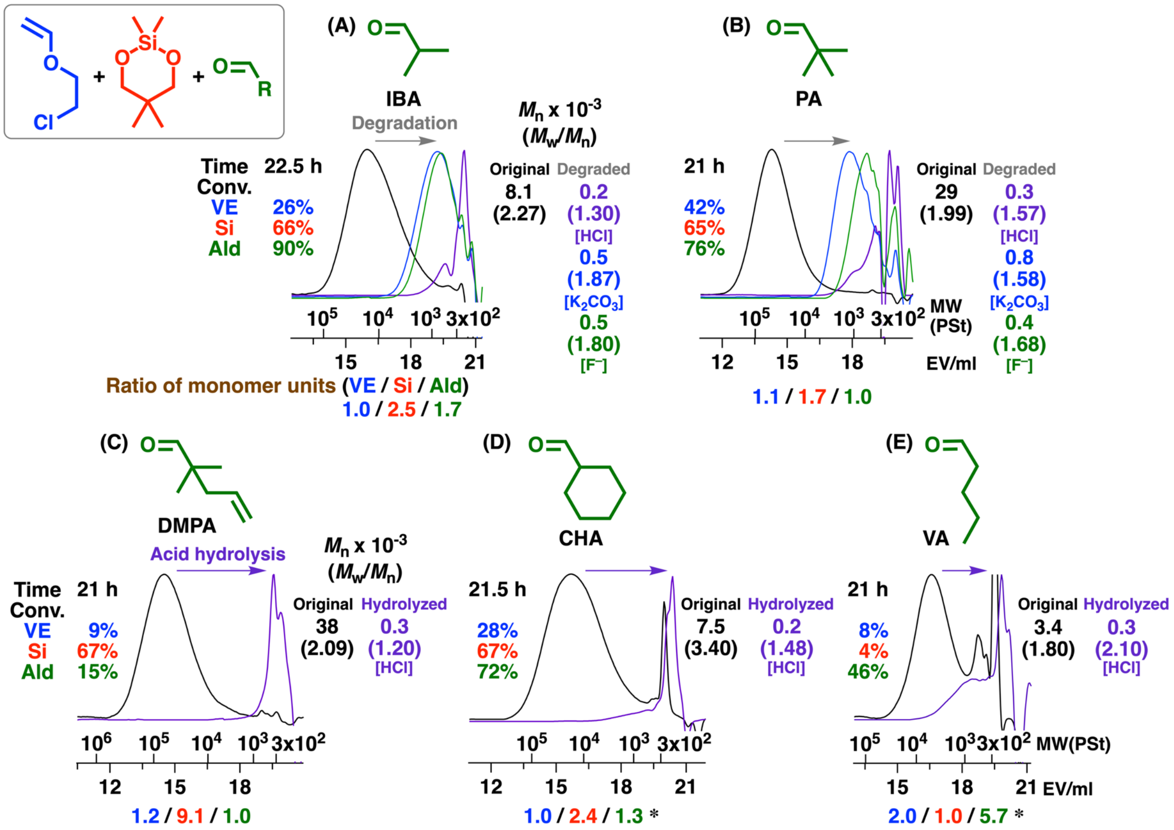


Figure 3. MWD curves of the CEVE–Si6M–aldehyde terpolymers (black; (A) entry 4 in Table 2, (B) entry 7, (C) entry 14, (D) entry 15, and (E) entry 16) and the products obtained by degradation under acidic (purple), basic (blue), or F^- (green) conditions (see Table 2 for the polymerization conditions; degradation (0.5 wt% polymer): 0.5 M HCl in 1,2-dimethoxyethane at 60 ºC for 3 h; 0.5 M K_2CO_3 in diethyl ether/methanol (1/1 v/v) for (A) 2 h or 22 h; or two equimolar amounts of TBAF with respect to the Si-O bonds in tetrahydrofuran for 30 min). * Values containing oligomers.

The occurrences of very frequent crossover reactions in the terpolymerization were confirmed by ^{1}H NMR analysis of the product (Figure 4A). Peaks assigned to an acetal moiety derived from the crossover from CEVE to Si6M were observed at 4.5–5.0 ppm (peak 9; other possible acetals by CEVE to PA and PA to Si6M crossover reactions were likely negligibly generated under the conditions employed, as judged from inefficient copolymerizations in the absence of either Si6M (entry 12 in Table 2) or CEVE (entry 13)).[46] Peaks 10 and 11 were assigned to PA units in polymer chains. The assignments of the peaks are supported by ^{13}C, DEPT 135, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC, and ^{1}H–^{13}C HMBC NMR spectra (Figures S3–S6). The CEVE/Si6M/PA unit ratios were estimated to be 1.1/1.7/1.0 from the integral ratios in the ^{1}H NMR spectrum. Given that the homopropagation of PA did not occur (vide infra; Figures S6 and S7), this ratio corresponds to the average number of each monomer unit per block, which indicates that preferential crossover reactions compared to homopropagations occurred in the terpolymerization reaction. The degradation of the terpolymer into very low-MW compounds by acid, base, or fluoride ions (Figure 3B), which is discussed in detail below, also supports the very frequent crossover reactions.

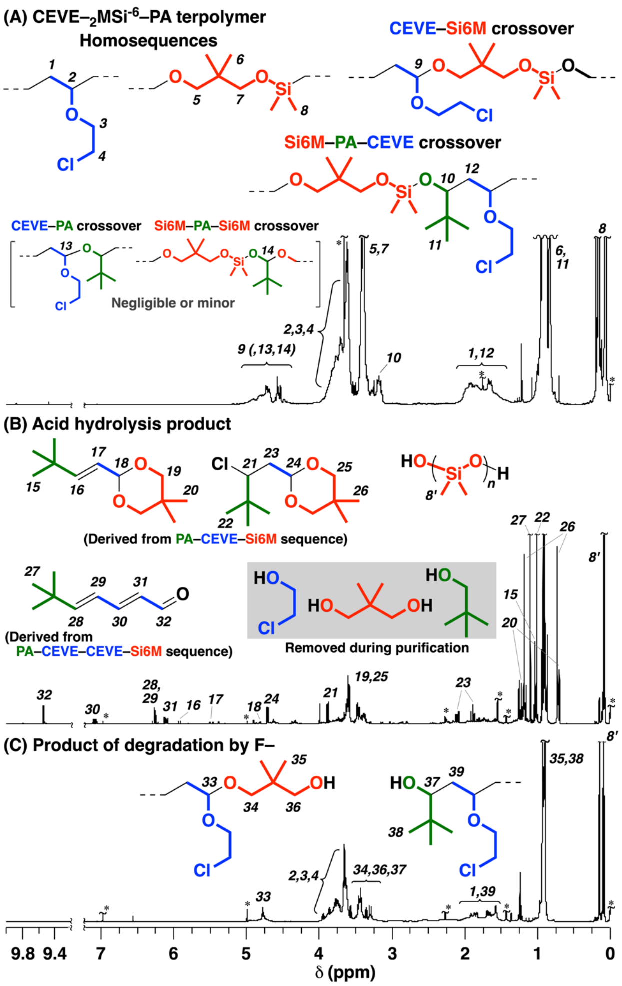


Figure 4. ^{1}H NMR spectra of (A) the CEVE–Si6M–PA terpolymer (entry 7 in Table 2), (B) the product obtained by acid hydrolysis of the terpolymer (the assignments of the degradation products are partly based on references 48–51), and (C) the product obtained by degradation with F$^-$; in $CDCl_3$ at 30 °C; * TMS, residual monomer, water, or stabilizer.

Aldehydes with a bulky substituent at the position adjacent to the formyl group are most likely indispensable for efficient terpolymerization yielding high-MW polymers. The terpolymerization reaction with 2,2-dimethyl-4-pentenal (DMPA), which has a quaternary carbon-adjacent formyl group as in the case of PA, also resulted in a high-MW terpolymer ($M_n = 38 \times 10^3$) via crossover reactions (entry 14 in Table 2; Figure S8). A difference between the reactions with PA and DMPA is the larger incorporated amounts of Si6M in the DMPA case, which is likely due to less efficient reactions of DMPA with the Si6M-derived oxonium ion than that with PA. The use of cyclohexanecarboxaldehyde (CHA; entry 15; Figure S9), which has a structure similar to that of IBA, resulted in a polymer with an MW comparable to that of the IBA-derived terpolymer. Interestingly, a relatively low-MW product was obtained in the terpolymerization reaction with valeraldehyde (VA), which has a primary alkyl group (entry 16; Figure S10). These results suggest that the structures of aldehydes are likely related to side reactions that lead to a decrease in the MWs of the products. A possible reaction is the backbiting cyclization from the aldehyde-derived carbocation and/or to the aldehyde-derived silyl ether units. Unlike aldehydes, ketones were completely ineffective for terpolymerization (entries 17 and 18). In our previous study, ketones functioned as a very effective monomer in terpolymerization with VEs and oxiranes;[41,42] hence, the species resulting from the reaction between the silyl monomer-derived oxonium ion and a ketone may be inefficiently produced due to instability.

Initiators and catalysts other than $B(C_6F_5)_3$ were examined for the terpolymerization of CEVE, Si6M, and PA. The polymerization proceeded with $Ph_3C^+B(C_6F_5)_4^-$ (entry 1 in Table 3), although the MW of the product was much smaller than that obtained by $B(C_6F_5)_3$. BF_3OEt_2 was not effective, resulting in negligible consumption of monomers (entry 2). $SnCl_4$ and $GaCl_3$, which are effective for the living cationic polymerization of VEs, induced terpolymerization to yield polymers with an M_n value of several thousand (entries 3–5). The activity of the metal chloride catalysts was comparable to that of $B(C_6F_5)_3$ (entry 7 in Table 2) as judged from the monomer conversions. The availability of metal chlorides potentially leads to the development of living terpolymerization, which will be examined in a future study.

The terpolymerization of CEVE, Si6M, and PA is considered to proceed via a one-way cycle of crossover reactions via the CEVE→Si6M, Si6M→PA, and PA→CEVE directions (Scheme 5). The crossover reactions via the opposite directions (Si6M→CEVE, CEVE→PA, and PA→Si6M) hardly occurred under the adopted conditions, which is suggested by inefficient copolymerizations in the absence of either of the three monomers (entry 4 in Table 1; entries 12 and 13 in Table 2).[46,47] The CEVE-derived carbocation reacts with CEVE and Si6M ([i] and [ii] in Scheme 5), while it hardly reacts with PA ([iii] in Scheme 5). The Si6M-derived oxonium ion does react with CEVE ([iv] in Scheme 5), while it reacts with Si6M and PA ([v] and [vi] in Scheme 5). The PA-derived carbocation reacts with CEVE ([vii] in Scheme 5) rather than Si6M ([viii] in Scheme 5). The homopropagation of PA is thought to be inefficient ([ix] in Scheme 5); however, two consecutive PA units might be generated (see a note for Figures S6 and S7). The average number of CEVE/Si6M/PA units per block was estimated to be 1.1/1.7/1.0 given that PA homopropagation did not occur, while the value was 1.6/2.6/1.5 if the acetal peak at 4.6 ppm was assigned to the two consecutive PA units. In all cases, however, the terpolymerization of CEVE, Si6M, and PA proceeded via very frequent crossover reactions, likely resulting in an ABC-type pseudo-periodic terpolymer.

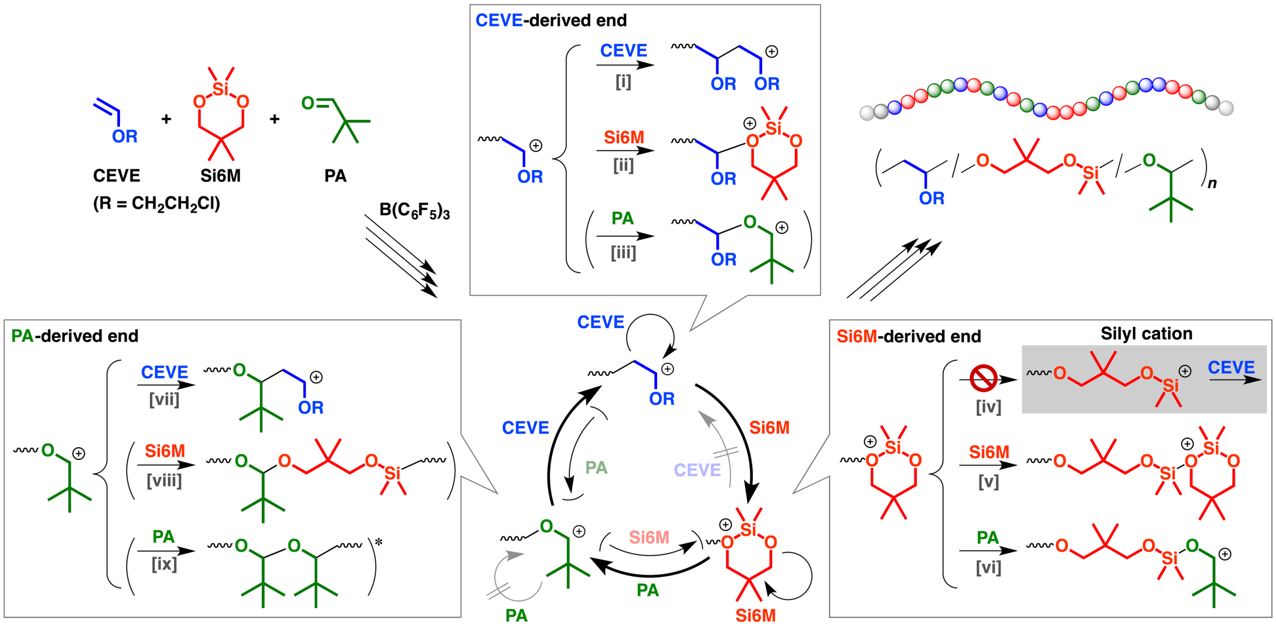
Table 3. Cationic terpolymerizations of CEVE, Si6M, and PA with different cationogens and/or catalysts[a]

entry	cationogen and/or (mM)	catalyst	time	conv.[b] (%) V	Si	C	$M_n \times 10^{-3}$ [c]	M_w/M_n[c]
1	$Ph_3C^+B(C_6F_5)_4^-$	5.0	19 h	77	11	33	1.9	2.60
2	BF_3OEt_2	5.0	21.5 h	<1	3	1	1.2	1.41
3	IBVE–HCl/$SnCl_4$	5.0/20	21 h	62	72	49	7.1	1.92
4	IBVE–HCl/$GaCl_3$	5.0/20	22 h	93	76	49	5.4	2.33

5	$GaCl_3$	20	22 h	66	88	88	9.5	2.99

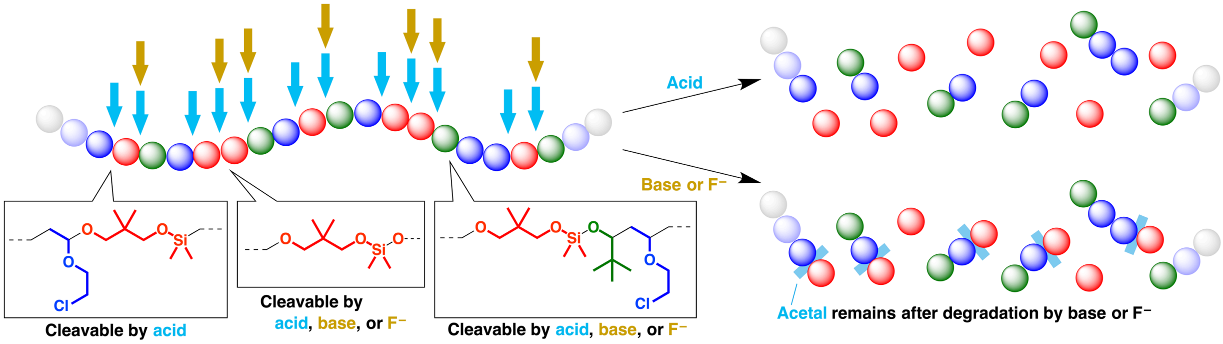
[a] $[CEVE]_0$ = 2.4 M, $[Si6M]_0$ = 2.4 M, $[PA]_0$ = 1.2 M, in dichloromethane at –78 °C. [b] Determined by ^1H NMR analysis. V: CEVE, Si: Si6M, C: PA. [c] Determined by GPC (polystyrene standards).

Scheme 5. Cationic Terpolymerization of CEVE, Si6M, and PA via Crossover Reactions.



* Two consecutive PA units may exist.

Scheme 6. Cleavages of Acetal and Silyl Ether Moieties in the Main Chain by Acids, Bases, or Fluoride Ions

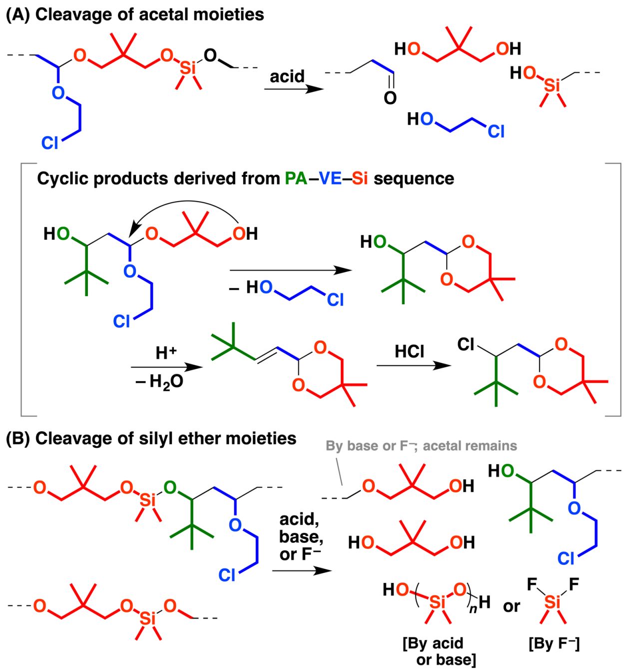


Degradation of terpolymers by acids, bases, and fluoride ions.

The obtained terpolymers are degradable because acetal and silyl ether moieties exist in the main chain. Acetal moieties are cleavable by acids, while silyl ether moieties are cleavable by acids, bases, or fluoride ions (Scheme 6); hence, different degradation products are expected to occur depending on the degradation conditions.

Degradation of the terpolymers by hydrochloric acid yielded a product via the cleavage of both acetal and silyl ether moieties. Analysis of the degradation products by GPC exhibited peaks in very low-MW regions (purple curves in Figure 3; M_ns of the products = 0.2—0.3 × 10^3), indicating that many degradable units existed in the main chain of the original terpolymer. The ^{1}H NMR spectrum of the product obtained by the hydrolysis of the CEVE–Si6M–PA terpolymer (Figure 4B) exhibited peaks assigned to structures[48–51] consistent with those expected from the degradation pathway (Scheme 7). Notably, products with a six-membered ring structure (peaks 15—26 in Figure 4B) correspond to the presence of the PA–CEVE–Si6M unit in the original terpolymer. Alcohols generated by degradation were removed by washing with water. In addition, an aldehyde derived from one PA and one CEVE was likely removed by drying. The products with a six-membered ring structure and the aldehyde derived from one PA and two CEVE, which were detected by ^{1}H NMR, can also be probably removed by drying under vacuum at high temperature. Therefore, the degradable terpolymers obtained in this study would be useful for applications that require clean degradation.

Scheme 7. Structures Generated after the Degradation of the CEVE–Si6M–PA Terpolymer.[a]



[a] Minor or negligible structures are not shown.

Degradation of the terpolymers by bases or fluoride ions resulted in the preservation of acetal moieties and exclusive cleavages of silyl ether moieties (Scheme 7B). Indeed, the MWs of the degradation products by bases or fluoride ions (green and blue curves in Figure 3) were higher than those of the acid hydrolysis product. A peak of the acetal moieties was observed in the ^{1}H NMR spectrum of the product (Figure 4C).

Thermal properties of the terpolymers.

DSC measurements of the CEVE–Si6M–aldehyde terpolymers and the Si6M homopolymer demonstrated that the terpolymers exhibited higher glass transition temperatures (T_g) than the Si6M homopolymer (Figure 5). In addition, a melting point (T_m) was observed in the case of the CEVE–Si6M–DMPA terpolymer, which was likely due to the existence of Si6M homosequences with sufficient lengths (entry 14 in Table 2; Figure 3C). The terpolymers obtained from IBA or

PA did not exhibit T_m because of the very short Si6M homosequences. The TGA measurements (Figure S11) demonstrated that the terpolymers started to decompose at approximately 200 °C, which was comparable to the degradation temperature of the Si6M homopolymer.

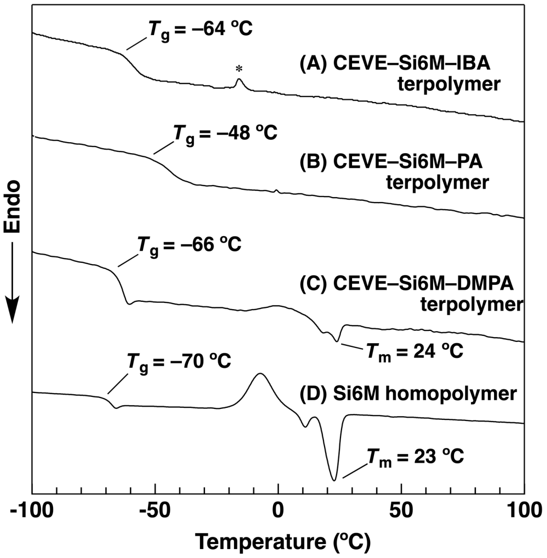


Figure 5. DSC curves of (A) the CEVE–Si6M–IBA terpolymer (entry 4 in Table 2), (B) the CEVE–Si6M–PA terpolymer (obtained by the same conditions as those for entry 7 in Table 2, M_n(GPC) = 15×10^3), (C) the CEVE–Si6M–DMPA terpolymer (entry 14 in Table 2), and (D) the Si6M homopolymer (entry 2 in Table1) (the second heating scan; heating rate: 10 ºC/min, * noise).

Table 4. Cationic terpolymerization of vinyl monomers, 1,3-dioxa-2-silacycloalkanes, and carbonyl compounds[a]

	monomer (M)							conv.[b] (%)				
entry	VE		Si		carbonyl compound		time	V	Si	C	$M_n \times 10^{-3\,c}$ [$M_n \times 10^{-3}$ (acid hydrolysis)]	M_w/M_n [c]
1	AcOVE	2.4	Si6M	2.4	PA	1.2	18.5	36	36	52	17 [0.2]	1.88
2	EVE	2.4	Si6M	2.4	IBA	1.2	23.5	62	10	76	1.4 [0.2]	1.77
3	EVE	2.4	Si6M	2.4	PA	1.2	21.5	86	27	49	3.5 [0.4]	2.08
4	pMeSt	2.4	Si6M	2.4	PA	1.2	21.5	<1	2	<1	–	–
5	pMOS	2.4	Si6M	2.4	PA	1.2	19 h	3	1	0	–	–
6[d]	CEVE	2.4	Si6	2.4	PA	1.2	24 h	35	61	64	10.4	2.16
7	CEVE	2.4	Si7	2.4	IBA	1.2	20 h	37	10	64	2.9 [0.4]	2.29
8	CEVE	2.4	Si7	2.4	PA	1.2	21 h	17	6	27	9.2 [0.3]	1.95
9	CEVE	2.4	Si5M	2.4	PA	1.2	22 h	75	21	77	3.6	2.16
10	CEVE	2.4	Si5M	2.4	DMPA	1.2	22 h	40	47	19	2.5	2.11
11	CEVE	0.80	Si8O	0.80	IBA	1.2	4 h	35	1	39	0.8 [0.4]	1.49
12	CEVE	2.4	Si8O	2.4	PA	1.2	20 h	<1	<1	1	–	–

[a] $[B(C_6F_5)_3]_0$ = 5.0 mM in dichloromethane at –78 ºC. [b] Determined by ^1H NMR analysis. V: VE, Si: 1,3-dioxa-2-silacycloalkane, C: carbonyl compound. [c] Determined by GPC (polystyrene standards). [d] The Si6 monomer used was viscous, which suggests that the monomer partly polymerized in an ampule during storage.

Terpolymerization of various monomers and copolymerization of 1,3-dioxa-2-silacycloalkanes and cyclic ethers.

Terpolymerizations with various vinyl monomers and 1,3-dioxa-2-silacycloalkanes (Scheme 3) were investigated in conjunction with IBA, PA, or DMPA (Table 4). 2-Acetoxyethyl VE (AcOVE), which exhibits a reactivity comparable to that of CEVE, underwent efficient terpolymerization, yielding a terpolymer with an M_n of 17 × 10^3 (entry 1; Figures 6A and S12). The use of EVE, which is more reactive than CEVE and AcOVE, also yielded terpolymers, although the MWs were relatively low (entries 2 and 3; Figures 6B and S13). Unlike VEs, styrene derivatives such as *p*-methoxystyrene (pMOS) and *p*-methylstyrene (pMeSt) were completely inactive in the terpolymerization reaction (entries 4 and 5). The propagation reactions of the styrene derivatives were probably suppressed due to the Lewis basicity of aldehydes.

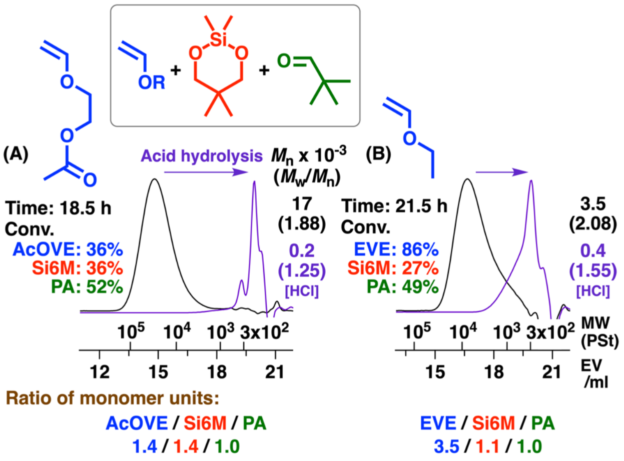


Figure 6. MWD curves of the VE–Si6M–PA terpolymers (black; entries (A) 1 and (B) 3 in Table 4) and the products obtained by degradation under acidic conditions (purple). See Table 4 for the polymerization conditions.

Silyl monomers other than Si6M were also investigated. Si6 was effective for terpolymerization via frequent crossover reactions (entry 6 in Table 4; Figure S14). Si7 also underwent terpolymerization with CEVE and aldehydes (entries 7 and 8; Figure S15). In particular, a polymer with an M_n of 9.2 × 10^3 was obtained in the terpolymerization with CEVE and PA. ^{1}H NMR analysis of the product (Figure S16) and the result of acid hydrolysis (Figure S15) suggested the occurrence of frequent crossover reactions in the terpolymerization, which was also observed for Si6M. Unlike six- and seven-membered monomers, Si5M and Si8O were not effective for terpolymerization. In the terpolymerization reaction with Si5M (entries 9 and

10; Figure S17), the same dimer as that obtained in the reaction of Si5M alone or the copolymerization of VE and Si5M (entries 13 and 14 in Table 1) was obtained. In addition, copolymers of CEVE and aldehydes, which were not obtained in the copolymerization of CEVE and PA in the absence of Si6M (entry 12 in Table 2; vide supra), were likely generated in the terpolymerization with Si5M, although the reason is unclear. In the terpolymerization with Si8O, the silyl monomer was negligibly consumed (entries 11 and 12).

From these results, monomers effective for the terpolymerization are summarized in Chart 1. VEs with relatively low reactivity, 1,3-dioxa-2-silacycloalkanes with appropriate ring structures, and aldehydes with bulky substituents were demonstrated to contribute to both frequent crossover reactions and products with high MWs.

Chart 1. Effectiveness of Monomers in Terpolymerization

	Effective for terpolymerization	Ineffective
Vinyl monomer	**CEVE, AcOVE, EVE**	**pMeSt, pMOS**
1,3-Dioxa-2-silacycloalkane	**Si6M, Si6, Si7**	**Si5M, Si8O**
Carbonyl compound	**PA, DMPA, IBA, CHA, VA**	**MEK, MTBK**

Cyclic ethers were also employed as comonomers in the cationic copolymerizations with 1,3-dioxa-2-silacycloalkanes. Copolymerization occurred when suitable cyclic ethers and 1,3-dioxa-2-silacycloalkanes were combined; however, the amounts of 1,3-dioxa-2-silacycloalkanes incorporated into polymer chains were very small compared to cyclic ethers. The detailed results are summarized in the Supporting Information (Table S1 and Figures S18–S20).

CONCLUSIONS

In conclusion, 1,3-dioxa-2-silacycloalkanes were demonstrated to be promising monomers for the design and synthesis of acid-, base-, or fluoride ion-triggered degradable polymers by cationic terpolymerization with VEs and aldehydes. The copolymerization of VEs and 1,3-dioxa-2-silacycloalkanes was ineffective due to the negligible generation of a silyl cation by ring-opening of the oxonium ion, resulting in diblock copolymers. The use of an aldehyde as the third monomer importantly contributed to highly efficient terpolymerization via very frequent crossover reactions. The key role of an aldehyde was the reaction with the silyl monomer-derived oxonium ion via attack onto the silicon atom to generate an oxygen-adjacent, aldehyde-derived carbocation. Moreover, aldehydes with a bulky substituent were indispensable for the generation of high-MW terpolymers with ABC-type, pseudo-periodic sequences. The obtained terpolymers had acetal and silyl ether moieties in the main chain; hence, the terpolymers were degraded into very low-MW compounds by acids, bases, or fluoride ions. The results obtained in this study surely contribute to the design of degradable polymers based on silicon chemistry. Furthermore, the availability of various VEs and aldehydes in sequence-controlled cationic terpolymerization with 1,3-dioxa-2-silacycloalkanes will provide a basis for material design through infinite combinations of different types of monomers. The ABC-type periodic sequence control is potentially useful for the incorporation of functional groups at regular intervals in a regular order.

ASSOCIATED CONTENT

Supporting Information

Polymerization data, NMR spectra of polymerization products, and ESI-MS spectrum of the product obtained by degradation with F^-.

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

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Notes

The authors declare no competing financial interest.

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