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A Ruthenium-Catalyzed Hydrosilane-Induced Polymerization of 3-Alkyl-3-hydroxymethyloxetane Derivatives: Facile Access to Functionalized Polyoxetanes by Virtue of Organosilyl Groups

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Ring-opening polymerization of 3-alkyl-3-alkoxymethyl- or 3-alkyl-3-siloxymethyloxetanes is catalyzed by a triruthenium cluster, $[\text{Ru}_3\{\mu_3-(\eta^2, \eta^3, \eta^5\text{-C}_{12}\text{H}_8)\}(\text{CO})_7]$, in the presence of trialkylsilanes, providing a novel accessible method for functionalized polyoxetanes of $M_n = 10^3\text{--}10^5$. Oxetanes having alkoxy-, fluoroalkoxy-, triethyleneglycoloxy-, and trialkylsiloxy functions undergo polymerization and copolymerization. Consumption rates of two monomers in the copolymerization of 3-benzyloxymethyl- and 3-trimethylsiloxymethyl-3-alkyloxetanes are almost the same, indicating formation of random copolymers. The organosilyl group in the polymer and copolymers with siloxymethyl side chains is converted to CH_2OH or CH_2OCOR groups by hydrolysis or silyl/acyl exchange. These protocols give the way to access polymers or copolymers bearing OH and OCOR side chains. A ruthenium-catalyzed reaction of 3-ethyl-3-hydroxymethyloxetane with trialkylsilanes results in dehydrogenative silylation to give 3-ethyl-3-siloxymethyloxetane, which is followed by ring-opening polymerization. Combination of tandem dehydrogenative silylation/ring-opening polymerization/the silyl/acyl exchange realizes one-pot synthesis of polymers with CH_2OCOR side chains from 3-ethyl-3-hydroxymethyloxetane. DSC analyses of the formed polymers provided T_g and T_m data, which are a good example showing that the polymer properties are controlled by appropriate selection of functional groups at the side chain.

A discovery by Chalk in 1970 of the ring-opening polymerization of THF by combination of Et_3SiH and $[\text{Co}_2(\text{CO})_8]$,¹ which was later expanded by Crivello and co-workers by using RSiH_3 ,² was the start of a series of hydrosilane-induced polymerization of cyclic ethers and vinyl ethers catalyzed by transition-metal catalysts. The polymerization of these monomers usually proceeds by the action of cationic initiators, however, the Chalk–Crivello polymerization is initiated smoothly by a species generated from neutral hydrosilanes and $[\text{Co}_2(\text{CO})_8]$. A ruthenium carbonyl cluster, $[\text{Ru}_3\{\mu_3-(\eta^2, \eta^3, \eta^5\text{-C}_{12}\text{H}_8)\}(\text{CO})_7]$ (**1**) (Chart 1), discovered in our laboratory has several advantages over $[\text{Co}_2(\text{CO})_8]$ as the catalyst for the hydrosilane-induced polymerization:³ (1) Handling of $[\text{Co}_2(\text{CO})_8]$ is not easy due to its air- and temperature sensitivity. The ruthenium complex **1** is stable to air and moisture and can be stored under aerobic conditions over years; (2) The complex **1** produces highly active species

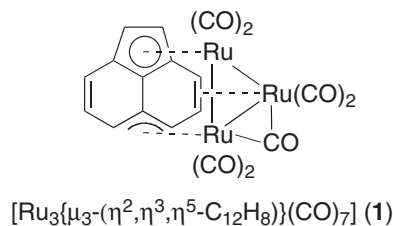
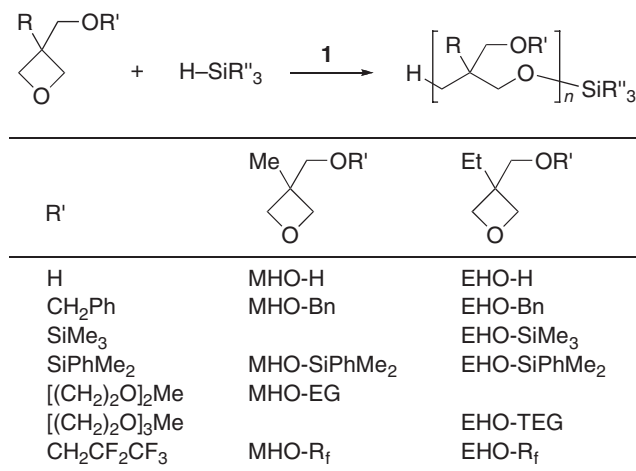


Chart 1.

in contact with R_3SiH , which shows good catalytic activity toward the polymerization of cyclic ethers, a cyclic siloxane, and vinyl ethers with R_3SiH : (3) a $\text{R}_3\text{Si-}$ group, which has potential for further chemical transformation of the formed polymers, was introduced at one of the polymer ends.

In our efforts to apply the ruthenium-catalyzed, hydrosilane-induced polymerization to highly functionalized polymers, we



Scheme 1. Hydrosilane-induced polymerization of 3-alkyl-3-alkoxyoxetanes.

were interested in 3-alkyl-3-hydroxymethyloxetanes, which are easily prepared by dehydration of trihydroxymethylalkanes and even available from commercial sources.⁴ Although polymerization of 3-alkyl-3-hydroxymethyloxetanes is expected to be promoted by Brønsted or Lewis acid with ease, reports in the literature are not straightforward: polymerization of 3-alkyl-3-hydroxymethyloxetanes initiated by strong Lewis acid does not give the corresponding linear polymer but branched or hyper-branched polyoxetanes.⁵ Although the cationic polymerization operating at low temperature reportedly contributes to reduce the number of polymer branches, completely linear polymer has never been synthesized from 3-alkyl-3-hydroxymethyl-oxetanes to our best knowledge.^{5g,5j,5n,5o} Several 3-alkyl-3-alkoxymethyloxetanes were subjected to cationic polymerization and copolymerization to give the linear polymers and copolymers, however, molecular weight of the formed polymer is M_n of several thousands.⁶

In this paper, we wish to report that these oxetane monomers are polymerized by contact with hydrosilanes and the ruthenium complex **1** (Scheme 1). Notable features compared with the cationic polymerization are: (1) Silane-induced polymerization of a series of 3-alkyl-3-alkoxymethyloxetanes shown in Scheme 1 successfully took place to give the corresponding polyoxetanes of $M_n = 10^3$ – 10^5 ; (2) copolymerizations of two different oxetanes were investigated by two experiments; there is significant difference in reactivity between two monomers in the copolymerization of a fluorinated monomer and a monomer having a glycol unit, whereas reaction profiles of two monomers in copolymerization of a 3-ethyl-3-benzyloxymethyloxetane (EHO-Bn) and 3-ethyl-3-trimethylsiloxymethyl-oxetane (EHO-SiMe₃) are almost the same to give a completely random polymer; (3) the organosilyl group in the polymer and copolymers bearing siloxymethyl side chains undergoes acid-promoted hydrolysis or silyl/acyl exchange by treatment with acyl chlorides or anhydrides. This gives a way for further transformation of the polymers or copolymers obtained: (4) Polymerization of 3-alkyl-3-hydroxymethyloxetanes was preceded by dehydrogenative silylation of the hydroxy group by catalysis of **1** to form 3-alkyl-3-siloxymethyloxetanes, which subsequently underwent silane-induced polymerization to form

the linear polymer in the reaction medium; (5) one-pot synthesis of polymer and copolymers with CH₂OCOR side chains from 3-ethyl-3-hydroxymethyloxetane was achieved by three tandem reactions consisting of the dehydrogenative silylation, the ring-opening polymerization, and the silyl/acyl exchange. By virtue of these, the present method is able to produce polyoxetane with a variety of pendant functional groups. As an example of a property controllable by the pendant group, DSC analyses were performed.

Results and Discussion

Polymerization of 3-Alkyl-3-alkoxymethyloxetane and 3-Alkyl-3-siloxymethyloxetane. The ruthenium complex **1** is stable under aerobic conditions, but produces a highly active species in contact with trialkylsilanes.³ In a typical example, generation of active species by treatment of **1** with excess PhMe₂SiH (100 equiv to **1**) was followed by addition of 3-ethyl-3-benzyloxymethyloxetane [EHO-Bn; 1000 equiv to **1**] at room temperature. Exothermic reaction took place and all of the monomer was polymerized in minutes. As shown in Entry 1, Table 1, the corresponding polyoxetane with $M_n = 4.9 \times 10^4$, $M_w/M_n = 2.0$ was isolated in 88% yield after precipitation from methanol. Besides the signals due to the phenyl group, five ¹H resonances due to CH₂Ph, CH₂–OBn, CH₂–O of the polymer chain, C–CH₂CH₃, and C–CH₂CH₃ appeared at δ 4.39 (s), 3.30 (s), 3.25–3.16 (broad AB pattern), 1.39 (q), and 0.79 (t) in CDCl₃, of which integral ratio was 2:2:4:2:3. The ¹³C NMR spectrum showed two signals at δ 71.8 and 43.6 which are assignable to methylene and quaternary carbons of the polymer chain. Signals derived from the pendant groups were observed at δ 73.4 (CH₂Ph), 71.5 (CH₂–OBn), 23.4 (C–CH₂CH₃), and 7.82 (C–CH₂CH₃) besides the phenyl carbons. These spectroscopic data are consistent with those expected from poly(EHO-Bn) with a linear polymer chain. Since signals due to the terminal PhMe₂SiO group were visible in ¹H NMR, the number of the repeated monomer units was estimated by comparison of the integral ratio of the peak due to the Si–CH₃ moiety and the peaks derived from the polymer. ¹H NMR spectra of poly(EHO-Bn) of $M_n = 2.7 \times 10^4$ determined by GPC ($M_w/M_n = 2.3$) showed two sharp singlets due to the Si–CH₃ groups at δ 0.31 and 0.29 in CDCl₃. Since the polymerization is not stereospecific, it is likely that dual Si–CH₃ peaks appeared. The number of repeated monomer units was calculated to be 47, which corresponds to M_n (NMR) = 9.7×10^3 . In contrast, that of poly(EHO-Bn) (M_n (GPC) = 1.4×10^4 , $M_w/M_n = 1.8$) gave a broad signal around 0.60–0.33 ppm in CDCl₃, and the number of repeated monomer units was calculated to be 18, which corresponds to M_n (NMR) = 3.7×10^3 . Although the molecular weights determined by NMR contain large experimental error, they are approximately one of third of M_n (GPC) in both cases; similar tendency was also reported in the silane-induced polymerization of THF.^{3a,7}

The polymerization of EHO-Bn is followed by a mechanism proposed in the ruthenium-catalyzed ring-opening polymerization of THF as described in the final part of this paper.^{3a} Although catalyst **1** is stable to air and moisture, highly active species $R_3Si^+ \cdots [Ru_3H]^-$ is generated in contact with excess PhMe₂SiH; the R_3Si^+ species initiates the ring-opening

Table 1. Homopolymerization of 3-Ethyl-3-benzyloxymethyloxetane (EHO-Bn) Using Various Hydrosilanes^{a)}

Entry	Hydrosilane	Time	Conv./% ^{b)}	Yield/% ^{c)}	$M_n^{d)}$ ($\times 10^{-3}$)	$M_w/M_n^{d)}$
1	Me ₂ PhSiH	1 min	92	88	49	2.0
2	Me ₂ EtSiH	5 min	92	79	59	2.0
3	Me ₂ (EtO)SiH	5 min	88	87	52	2.2
4	Me ₃ SiOSiMe ₂ SiHMe ₂	10 min	88	76	77	2.0
5 ^{e)}	MeEt ₂ SiH	10 min	73	73	42	2.5
6 ^{e)}		10 min	75	67	99	2.1
7 ^{e)}	(Me ₃ Si) ₃ SiH	6 h	73	73	23	2.8
8 ^{e)}		23 h	84	83	55	2.3
9 ^{e)}	Et ₃ SiH	100 h	0	0	—	—
10 ^{e)}		100 h	50	45	100	1.9
11 ^{e)}		3 h	44	40	26	2.2

a) All reactions were carried out in the presence of the catalyst (3.3 μ mol), the silane (0.33 mmol), and EHO-Bn (3.3 mmol), and 1,4-dioxane (56 μ L) under an argon atmosphere at room temperature. b) Determined by ¹H NMR. c) Isolated yield of the polymer after precipitation. d) Determined by GPC (polystyrene standard). e) Among several experiments we performed, two or three extreme examples are listed.

polymerization of cyclic ethers whereas the [Ru₃H][−] terminates the propagation by hydride transfer to the carbocation at the polymer end. As shown in Entries 1–4, Table 1, PhMe₂SiH, EtMe₂SiH, Me₂(EtO)SiH, and Me₃SiOSiMe₂SiHMe₂ effectively initiated the polymerization of EHO-Bn to give poly(EHO-Bn) of $M_n = 10^4$ – 10^5 . Since sterically more hindered hydrosilanes have difficulty in generating active species from **1**, the reaction was not very reproducible. There were three cases observed for the nonreproducible polymerization with hindered hydrosilanes; the first case was unsuccessful generation of the active species leading to no reaction. In the second case, the reaction of **1** with the hydrosilane was slow and the polymerization was initiated with low concentration of active species; this provided higher monomer/active species ratio and slower termination, giving rise to formation of poly(EHO-Bn) with relatively higher molecular weights. The third case is polymerization giving similar results to that observed for polymerization with PhMe₂SiH; this occurs especially when monomers and solvents are highly purified, and the catalyst is activated very carefully to generate enough amounts of the active species prior to the addition of the monomer. Among several experiments with Et₂MeSiH, Et₃SiH, and (Me₃Si)₃SiH under the same conditions, two extreme examples in each case selected are listed in Entries 5–11. The results with Et₂MeSiH or (Me₃Si)₃SiH giving significant differences in molecular weights of the formed polymer suggest not steady generation of active species from **1** and these hydrosilanes (cases 2 and 3). We experienced all of the above three cases in the reactions with Et₃SiH as shown in Entries 9–11.

Above results showed that PhMe₂SiH is a good hydrosilane for the polymerization. In Table 2 are summarized representative results of polymerization of EHO-Bn with PhMe₂SiH. In a ratio of **1**/PhMe₂SiH/monomer = 1:10:1000 (Entry 2), the reaction took place to give poly(EHO-Bn) with $M_n =$

8.4×10^4 . Attempted polymerization in a ratio of **1**/PhMe₂SiH/monomer = 1:10:5000 was unsuccessful; this is presumably due to the deactivation of the catalyst species in diluting the catalyst solution by large amounts of monomers (Entry 1). In a ratio of PhMe₂SiH/**1** = 100:1, active species was reproducibly generated to give the polymer in high yields as shown in Entries 3–5. The reactions were complete in minutes in the experiments shown in Entries 3 and 4, whereas addition of larger amounts of the monomer caused decreased concentration of the catalyst leading to the longer reaction time as shown in Entry 5. The molecular weight is likely to be affected by the ratio of the active species with the monomer, with larger amounts of monomer providing polymer with higher molecular weight [M_n : 1.0×10^4 (Entry 3) < 4.9×10^4 (Entry 4) < 9.6×10^4 (Entry 5)]. The molecular weight is not precisely controllable by changing the ratio of **1**/PhMe₂SiH/EHO-Bn due to the difficulties in quantitative generation of the active species as well as the temperature control of the exothermic reaction. Nevertheless, it should be noted that the ratio of active species with the monomer shown in these experiments is a rough but successful control factor for the molecular weight in a range of 10^3 – 10^6 . In Entries 6–9 are listed the results of solution polymerization by increase of the amount of the solvent from 56 μ L (other entries) to 670 μ L. In diluted solutions, the reaction required longer reaction time for completion. The temperature of 0 °C was too low to initiate the active species in a dilute solution, whereas the reaction smoothly occurred at 30, 40, and 60 °C. The molecular weight seemed to decrease at higher temperature; but the effect was not significant.

In Table 3 is summarized polymerization of several 3-alkyl-3-alkoxymethyl- or 3-alkyl-3-siloxymethyloxetanes with a **1**/PhMe₂SiH/monomer ratio of 1:100:1000. In the cases of benzyloxy or siloxy derivatives, the reaction rapidly proceeded

Table 2. Homopolymerization of 3-Ethyl-3-benzyloxymethyloxetane (EHO-Bn) Using HSiPhMe₂^{a)}

Entry	1/Si-H/monomer	<i>T</i> /°C	Time	Conv./% ^{c)}	Yield/% ^{d)}	<i>M_n</i> ^{e)} ($\times 10^{-3}$)	<i>M_w</i> / <i>M_n</i> ^{e)}
1	1/10/5000	rt	3 d	trace	—	—	—
2	1/10/1000	rt	10 min	80	78	84	2.1
3	1/100/100	rt	5 min	94	88	10	1.7
4	1/100/1000	rt	1 min	92	88	49	2.0
5	1/100/5000	rt	18 h	80	78	96	2.1
6 ^{b)}	1/100/1000	0	6 h	0	—	—	—
7 ^{b)}	1/100/1000	30	3 h	69	67	38	2.1
8 ^{b)}	1/100/1000	40	1 h	89	84	34	2.2
9 ^{b)}	1/100/1000	60	1 h	90	77	28	2.2

a) All reactions were carried out in the presence of the catalyst (3.3 μ mol), H-SiPhMe₂, EHO-Bn, and 1,4-dioxane (56 μ L; Entries 1–5). b) The amount of 1,4-dioxane was 670 μ L. Entries 6–9 under an argon atmosphere. c) Determined by ¹H NMR. d) Isolated yield of the polymer after precipitation. e) Determined by GPC (polystyrene standard).

Table 3. Homopolymerization of Various 3-Alkyl-3-alkoxyxymethyloxetanes Using HSiPhMe₂^{a)}

Entry	R ¹	R ²		<i>T</i> /°C	Time	Conv./% ^{b)}	Yield/% ^{c)}	<i>M_n</i> ^{d)} ($\times 10^{-3}$)	<i>M_w</i> / <i>M_n</i> ^{d)}
1	Me	CH ₂ Ph	MHO-Bn	rt	30 min	97	78	42	2.6
2	Me	SiMe ₂ Ph	MHO-SiMe ₂ Ph	rt	5 min	96	92	66	3.6
3	Me	[(CH ₂) ₂ O] ₂ Me	MHO-EG	rt	1 h	99	83	15	2.1
4	Me	CH ₂ CF ₂ CF ₃	MHO-R _f	rt	4 h	87	78	97	2.0
5	Et	CH ₂ Ph	EHO-Bn	rt	1 min	92	86	49	2.0
6	Et	SiMe ₂ Ph	EHO-SiMe ₂ Ph	rt	5 min	95	88	57	2.4
7	Et	SiMe ₃	EHO-SiMe ₃	rt	5 min	>99	95	31	2.9
8	Et	[(CH ₂) ₂ O] ₃ Me	EHO-TEG	rt	5 h	96	72	19	2.1
9	Et	CH ₂ CF ₂ CF ₃	EHO-R _f	80	8 h	95	71	35	2.3

a) All reactions were carried out in the presence of the catalyst (3.3 μ mol), PhMe₂SiH (0.33 mmol), and monomer (3.3 mmol), and 1,4-dioxane (56 μ L) under an argon atmosphere. b) Determined by ¹H NMR. c) Isolated yield of the polymer after precipitation. d) Determined by GPC (polystyrene standard).

to give the corresponding polymer of $M_n = 4.0 \times 10^4$ – 6.0×10^4 with regardless of alkyl group at the 3-position being methyl or ethyl as shown in Entries 1, 2, and 5–7. Oxetanes having CH₂O(CH₂CH₂O)₂CH₃ or CH₂OCH₂CF₂CF₃ moieties at the 3-position polymerized slower than their benzyloxy homologs. The rate was sensitive to the 3-alkyl group; 3-methyl derivatives underwent the polymerization within several hours, whereas 3-ethyl derivatives were apparently slower.

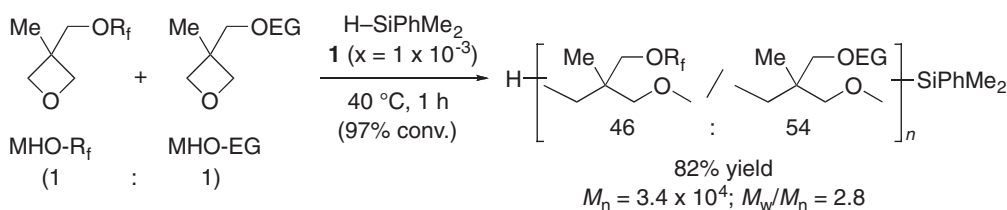
Two-Step Conversion of 3-Alkyl-3-hydroxymethyloxetanes to Polymers and Copolymers Bearing Siloxy Pendants. An OH bearing monomer, MHO-H and EHO-H, is different from alkoxy derivatives in giving hyperbranched polymers with the aid of BF₃·OEt₂.⁵ Thus, linear polymerization to form polyoxetanes with OH groups at the side chains is difficult to achieve by cationic initiators. The ruthenium-

catalyzed, silane-induced polymerization is able to solve this problem, since **1** is a good catalyst for dehydrogenative silylation of alcohols, which is faster than the ring-opening polymerization. In a typical example, EHO-H was treated with PhMe₂SiH (2.0 equiv) in the presence of **1** in dioxane or THP (Table 4, Entries 1 and 2). The reaction showed vigorous evolution of H₂ gas at the initial stage, being complete after 1 h to give poly(EHO-SiPhMe₂) of $M_n = \text{ca. } 2.0 \times 10^4$ and $M_w/M_n = \text{around } 2.5$. ¹H and ¹³C NMR of the formed polymer were identical to those of poly(EHO-SiPhMe₂) prepared by the ruthenium-catalyzed polymerization of EHO-SiPhMe₂; this suggests that there was no side reaction leading to hyperbranched polymers.⁸ As shown in the scheme in Table 4, the results can be explained by rapid dehydrogenative silylation of EHO-H to EHO-SiPhMe₂, which is preceded by the ring-opening polymerization.

Table 4. Homopolymerization of 3-Ethyl-3-hydroxymethyloxetane (EHO-H)^{a)}

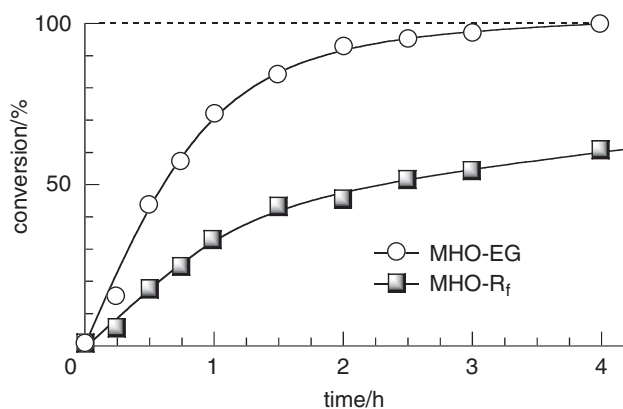
Entry	1/Si-H/monomer	Solvent	<i>T</i> /°C	Time/min	Conv./% ^{b)}	Yield/% ^{c)}	<i>M_n</i> ^{d)} ($\times 10^{-3}$)	<i>M_n</i> / <i>M_w</i> ^{d)}
1	1:2000:1000	dioxane	rt	60	99	96	18	2.5
2	1:2000:1000	THP	rt	60	99	81	22	2.6
3	1:1100:1000	dioxane	rt	15	93	91	14	4.3
4	1:1100:1000	THP	rt	15	96	78	18	3.7
5 ^{e)}	1:1100:1000	THP	-60 → rt	45	89	83	55	2.3

a) All reactions were carried out in the presence of the catalyst (3.3 μ mol) dissolved in 1,4-dioxane or tetrahydropyran (56 μ L) under an argon atmosphere. b) Determined by ^1H NMR. c) Isolated yield of the polymer after precipitation. d) Determined by GPC (polystyrene standard). e) The reaction temperature was slowly raised from -60 to 11 °C. Dehydrogenative silylation of hydroxy groups was completed after 8.5 h. When the mixture was warmed to room temperature, polymerization was started and complete after 45 min.

**Scheme 2.** Copolymerization of MHO-EG and MHO-R_f.

Copolymerization Studies. Copolymerization behavior of 3-alkyl-3-alkoxymethyloxetane is an interesting subject in considering the effect of side chains. Since the 3-position of oxetane is remote from the oxygen atom of oxetanes which can be activated by proton or Lewis acid to initiate the polymerization, it is not likely that substituents at the 3-position strongly affect the initiation. There is a possibility of interaction of the alkoxymethyl group at the 3-position with the cationic polymer terminus waiting for another molecule of oxetane monomer; however, molecular modeling studies do not suggest such interactions. Nevertheless, Wynne and co-workers reported that there is substantial difference in reactivity between MHO-EG and MHO-R_f.⁶¹ In contrast, Feng and co-workers examined the copolymerization of 3-methyl-3-(methoxyethoxyethoxyethoxymethyl)oxetane [MHO-(CH₂CH₂O)₃-CH₃] and 3-methyl-3-(2-cyanoethoxy)methyloxetane (MHO-CH₂CH₂CN).⁶² They reported that the monomer component ratio in the polymer obtained was similar to the charged monomer ratio. This implies that there is little difference in reactivity between MHO-(CH₂CH₂O)₃CH₃ and MHO-CH₂CH₂CN.

Studies on the ruthenium-catalyzed, silane-induced copolymerization of MHO-EG and MHO-R_f revealed that substantial difference in the reactivity of comonomers as deduced from the reaction rate of homopolymerization of these monomers as shown in Table 3. A 1:1 mixture of MHO-EG and MHO-R_f (5 equiv each to PhMe₂SiH) was treated with PhMe₂SiH in the presence of a catalytic amount of **1** (1 mol % to PhMe₂SiH)

**Figure 1.** Copolymerization behavior of MHO-EG and MHO-R_f at room temperature.

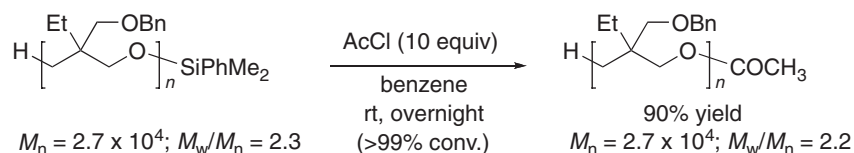
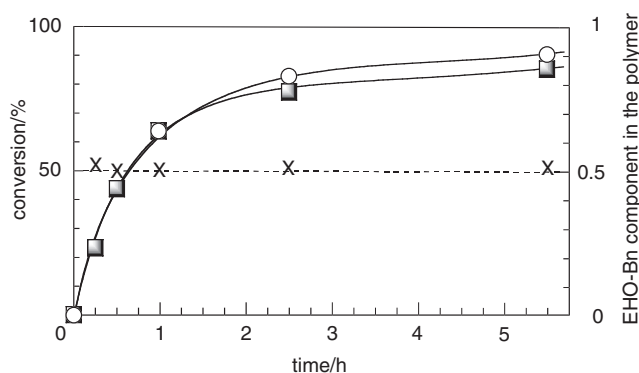
at 40 °C. After 1 h, conversion of the monomers reached >97% to give poly(MHO-EG-co-MHO-R_f) (MHO-EG/MHO-R_f = 54:46) (Scheme 2). At room temperature, the reaction was slower, and conversion of the monomer vs. reaction time is depicted in Figure 1. The monomer reactivity of MHO-EG > MHO-R_f is similar to that observed in literature.⁶¹

In contrast to the significant difference in monomer reactivity between MHO-EG and MHO-R_f, PhMe₂SiH-induced homopolymerization of benzyloxy monomers, MHO-Bn and EHO-Bn, and siloxy monomers, MHO-SiPhMe₂, EHO-SiPhMe₂, and EHO-SiMe₃ showed similar polymerization

Table 5. Copolymerization of EHO-SiMe₃ and EHO-Bn^{a)}

Entry	<i>m/n</i> ^{b)}	<i>t</i> /min	Conv./% ^{c)}	Yield/% ^{d)}	<i>M_n</i> ^{e)} ($\times 10^{-3}$)	<i>M_w</i> / <i>M_n</i> ^{e)}	PhCH ₂ /Me ₃ Si ^{f)}	<i>T_g</i> /°C
1	8:2	5	98	98	22	2.4	80:20	−24.9
2	6:4	5	99	98	22	2.3	61:39	−25.1
3	5:5	15	99	97	22	2.2	50:50	−24.5
4	4:6	5	98	92	24	2.5	43:57	−25.4
5	2:8	5	97	87	17	2.2	24:76	−25.0

a) All reactions were carried out in the presence of the catalyst (3.3 μmol), H-SiPhMe₂ (0.33 mmol), and monomers (EHO-Bn + EHO-SiMe₃ = 3.3 mmol), and 1,4-dioxane (56 μL) at room temperature under an argon atmosphere. b) Charged molar ratio of two monomers. c) Determined by ¹H NMR. d) Isolated yield of the polymer after precipitation. e) Determined by GPC (polystyrene standard). f) Ratios of two monomer components in the polymer determined by ¹H NMR.

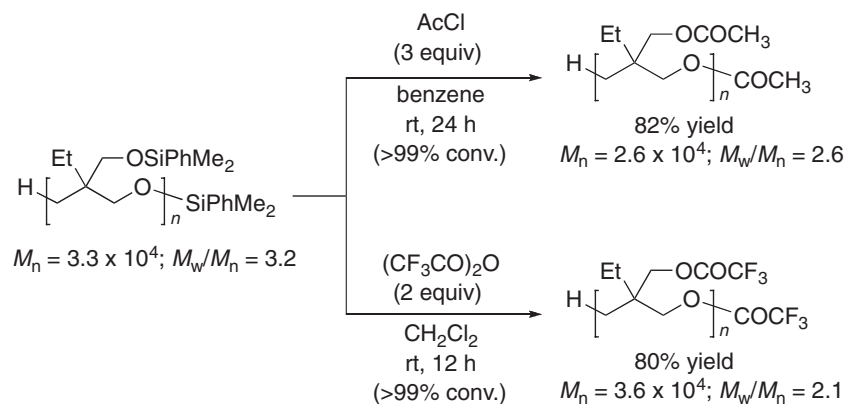
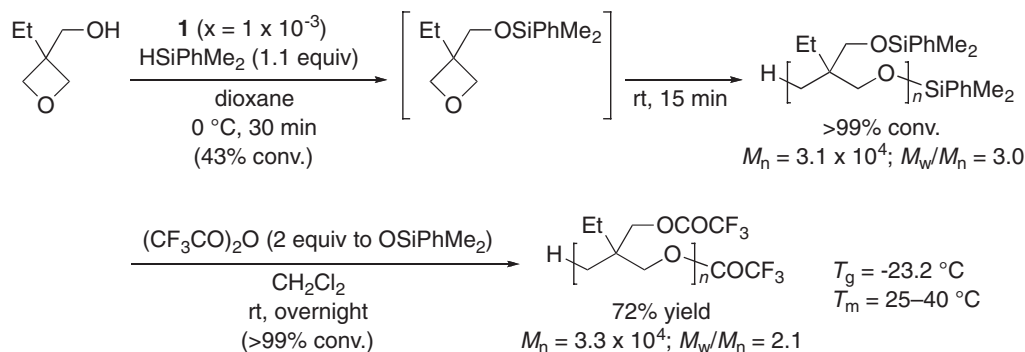
**Scheme 3.** Chemical transformation of the poly(EHO-Bn).**Figure 2.** Copolymerization behavior of EHO-Bn and EHO-SiMe₃: conversion of EHO-Bn (○) and EHO-SiMe₃ (■), and EHO-Bn component in the polymer (X).

behavior by catalysis of **1**, suggesting not very different monomer reactivity in the copolymerization of either of two monomers. As a representative example, we carried out the copolymerization of EHO-Bn and EHO-SiMe₃ in detail. Treatment of a 1:1 mixture of EHO-Bn and EHO-SiMe₃ (5 equiv each to PhMe₂SiH) with PhMe₂SiH and a catalytic amount of **1** ($x = 1 \times 10^{-2}$ to PhMe₂SiH) resulted in formation of the corresponding copolymer in several minutes at room temperature. In Table 5 are summarized the results of copolymerization changing the ratio of two monomers from 1:4–4:1. In all cases, the copolymers have $M_n = 1.7\text{--}2.4 \times 10^4$, $M_w/M_n = 2.2\text{--}2.5$. ¹H NMR and ¹³C NMR spectra of the copolymer, poly(EHO-SiMe₃-co-EHO-Bn) are in coincidence with sum of those of poly(EHO-Bn), poly(EHO-SiMe₃).⁹ All of the copolymerization proceeded quantitatively, and the component ratios of two monomer units in the produced polymers are close to the charged ratios of two monomers. The reaction was slowed by diluting with dioxane [EHO-SiMe₃ (1.65 mmol) and EHO-Bn (1.65 mmol) in 670 μL of dioxane]; this made possible observation of the reaction profile seeing consumption rate of the monomers as shown in Figure 2. The reaction profile

of copolymerization of a 1:1 mixture of EHO-SiMe₃ and EHO-Bn indicates that there is no difference in the consumption rate of two monomers regardless of the reaction time. Similarly, the component ratio of an EHO-SiMe₃ unit with an EHO-Bn moiety in the formed copolymer was 1:1, which is independent on the reaction time. These clearly indicates that monomer reactivity ratio between EHO-SiMe₃ and EHO-Bn was close to one, giving a random copolymer.

Acylation of the Siloxy Group.^{10,11} As reported earlier, the hydrosilane-induced polymerization of cyclic ethers is effectively catalyzed by **1** to form the polyether, R₃SiO–[(CH₂)_nO]_m–H.^{3a} There is an R₃SiO group derived from the hydrosilane, R₃SiH, as an end group of the polymer, which is assigned by NMR spectroscopy. The polyoxetane described in this paper also has a PhMe₂SiO group at the polymer terminus; in a typical example, poly(EHO-Bn) showed a ¹H and a ¹³C resonances at δ 0.31 and 0.29 for SiCH₃ and δ −1.84 (br) for SiCH₃ in CDCl₃, respectively. The terminal PhMe₂Si group can be transformed to an acetyl moiety by treatment with AcCl (Scheme 3).¹⁰ For instance, a benzene solution of poly(EHO-Bn) bearing a OSiMe₂Ph terminus [M_n (GPC) = 2.7×10^4 , $M_w/M_n = 2.3$] was treated with AcCl (10 equiv to the PhMe₂Si group) at room temperature overnight. ¹H and ¹³C resonances due to the AcO group appeared in regions expectable [¹H NMR: δ 1.93 (CH₃), ¹³C NMR: δ 20.8 (CH₃) and 170.9 (C=O)], and a typical $\nu_{\text{C=O}}$ absorption was observed at 1742 cm^{−1}. GPC profiles before and after the acetylation did not change. The yield of the acetoxy-terminated polymer was 90% [M_n (GPC) = 2.7×10^4 , $M_w/M_n = 2.2$].⁷

In similar fashion, the siloxy groups at the side chain of the polyoxetane were converted to the acyloxy group with ease (Scheme 4). Treatment of a benzene solution of poly(EHO-SiPhMe₂) ($M_n = 3.3 \times 10^4$, $M_w/M_n = 3.2$) with AcCl (3.0 equiv) at room temperature for 24 h gave poly(EHO-Ac) ($M_n = 2.6 \times 10^4$, $M_w/M_n = 2.6$) in 82% yield. As a synthetic method for polyoxetanes having acetoxymethyl side chains, treatment of insoluble poly[3,3-bis(hydroxymethyl)oxetane] with large excess of Ac₂O at high temperature was reported.^{6b}

Scheme 4. Chemical transformations of poly(EHO-SiPhMe₂).Scheme 5. Synthesis of poly(EHO-COCF₃) from EHO-H.

The procedure presented in this paper is apparently more useful than the previous method in the points that hydrosilane-induced polymerization provides soluble siloxypolyoxetane and the subsequent PhMe₂Si/Ac exchange proceeds under mild conditions using a small amount of AcCl. Trifluoroacetylation was also possible; poly(EHO-SiPhMe₂) ($M_n = 3.3 \times 10^4$, $M_w/M_n = 3.2$) was treated with (CF₃CO)₂O (2 equiv to the polymer) in CH₂Cl₂ at room temperature for 12 h to give a polymer showing typical signals of CF₃CO groups [¹⁹F NMR: δ -78.3 (CF₃), IR: $\nu_{C=O}$ 1787 cm⁻¹] in 80% yield.¹¹

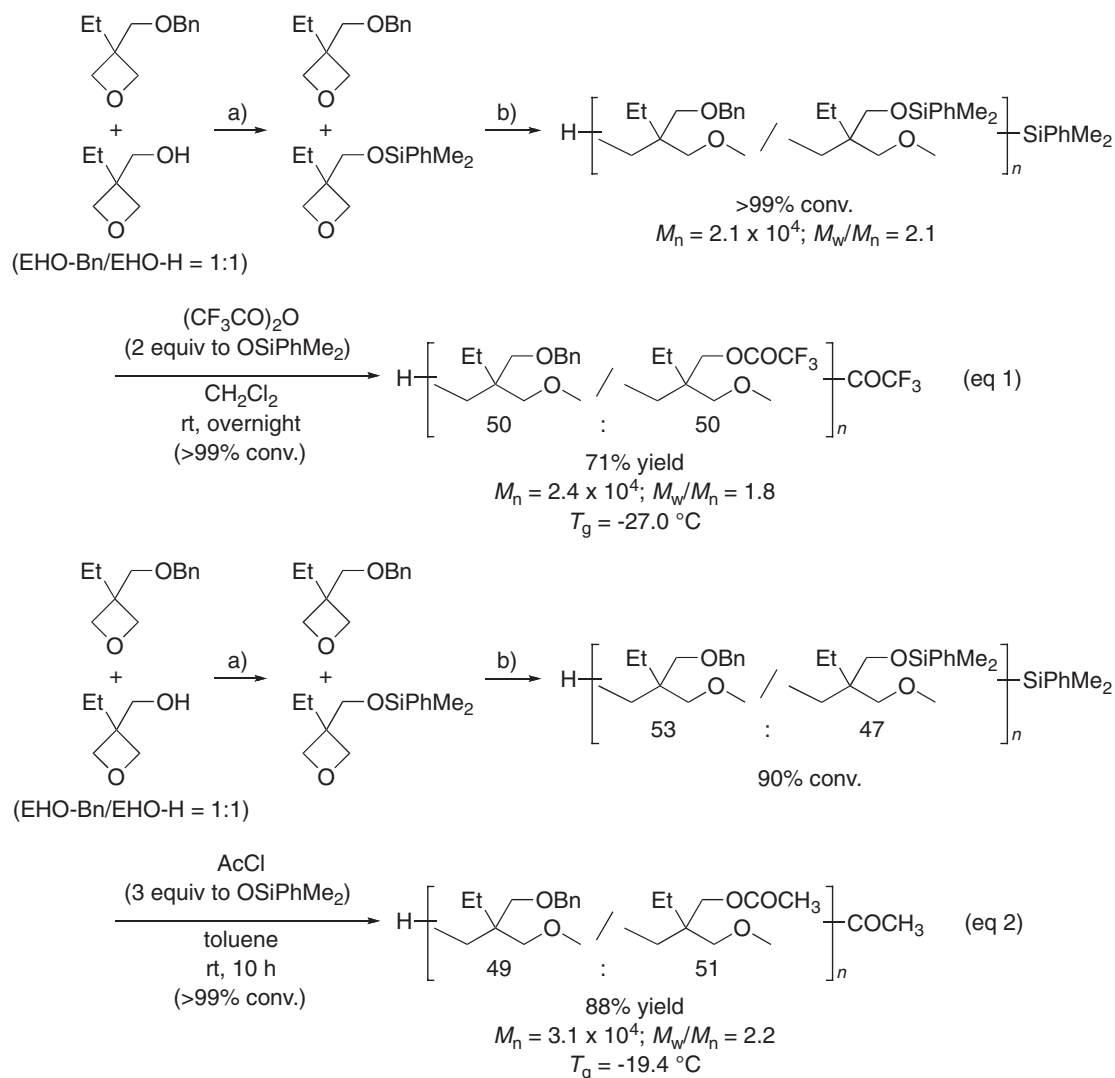
The utility of dehydrogenative silylation/ring-opening polymerization of EHO-H described above was emphasized by combination with the OSi/OCOR exchange of the formed siloxy polymers. For example, a tandem procedure consisting of dehydrogenative silylation of EHO-H (1/Si-H/monomer = 1:1100:1000) at 0 °C, polymerization at room temperature, and trifluoroacetylation in CH₂Cl₂ gave poly(EHO-COCF₃) ($M_n = 3.3 \times 10^4$, $M_w/M_n = 2.1$) in 72% yield based on the charged EHO-H (Scheme 5).

One-Pot Synthesis of Acyloxy/Benzyloxy Copolymers.

By taking advantage of almost identical reactive monomer ratio of EHO-Bn and EHO-SiPhMe₂, random copolymers of EHO-Bn and EHO-COR were also synthesized in one-pot starting from a mixture of EHO-Bn and EHO-H. The component ratio of EHO-Bn and EHO-COR was precisely controlled by the charged ratio of EHO-Bn and EHO-H. In a typical example, a 1:1 molar ratio of EHO-Bn and EHO-H was treated with a slightly excess amount of PhMe₂SiH to EHO-H at 0 °C then room temperature followed by trifluoroacetylation or acetylation to give poly(EHO-Bn-co-EHO-COCF₃) (71% isolated

yield; EHO-Bn/EHO-COCF₃ = 50:50) or poly(EHO-Bn-co-EHO-COCH₃) (88% isolated yield; EHO-Bn/EHO-COCH₃ = 49:51) as shown in Scheme 6.

Hydrolysis of Silyl Groups and Its Application to Synthesize Hydroxy/Benzyloxy Copolymer. As described above, chemical transformation of siloxy groups by acyl groups has made possible preparation of polyoxetane with acyloxy pendants. An alternative chemical transformation of siloxy groups is hydrolysis, which can produce polyoxetane polyols (Table 6). As typical examples, poly(EHO-SiMe₃) and poly(EHO-Bn-co-EHO-SiMe₃) were subjected to acid-promoted hydrolysis (Table 6). In a typical example, poly(EHO-Bn-co-EHO-SiMe₃) (EHO-Bn/EHO-SiMe₃ = 50:50, $M_n = 2.6 \times 10^4$, $M_w/M_n = 2.1$) dissolved in toluene was treated with HCl/MeOH at room temperature overnight. After removal of the solvent, the residue was purified by precipitation twice from THF/hexane to give poly(EHO-Bn-co-EHO-H) (EHO-Bn/EHO-H = 47:53) in 92% yield (Entry 3). The GPC profiles before and after the hydrolysis are almost identical; this indicates that no side reaction involving degradation of the polyoxetane chain occurred. NMR analyses of copolymers before and after the hydrolysis showed that signals due to the organosilyl groups disappeared, and change of chemical shifts suggesting CH₂OSi → CH₂OH was observed [¹H NMR: δ 3.40 to 3.51 (CH₂); ¹³C NMR: δ 63.2 to 67.6–64.5 (CH₂)]. Hydrolysis of the homo- and copolymers shown in Table 6 showed that polarity of the polymer chain was apparently increased by conversion of OSiMe₃ moieties to OH groups; this is typically seen in solubility of the polymers to organic solvents. Typically, poly(EHO-H) shown in Entry 6 is not



Scheme 6. One-pot synthesis of acyloxy/benzyloxy copolymers.

Table 6. Hydrolysis of Poly(EHO-Bn-co-EHO-SiMe₃) to Poly(EHO-Bn-co-EHO-H)^{a)}

Entry	EHO-Bn /EHO-SiMe ₃ ^{b)}	Conv./% ^{b)}	Yield/%	Before hydrolysis		After hydrolysis		
				M_n^c ($\times 10^{-3}$)	M_w/M_n^c	EHO-Bn/EHO-H ^{b)}	M_n^c ($\times 10^{-3}$)	M_w/M_n^c
1	80:20	>99	88	29	2.3	80:20	27	2.7
2	59:41	>99	90	26	2.2	59:41	22	2.3
3	50:50	>99	92	26	2.1	47:53	21	2.2
4	40:60	>99	87	29	2.3	40:60	23	2.3
5	23:77	>99	85	17	2.2	24:76	14	2.4
6	0:100	>99	90	17	2.1	0:100	— ^{d)}	— ^{d)}

a) The polymers listed in this Table were treated with HCl/MeOH (5 equiv to O-SiMe₃) in toluene at room temperature overnight.

b) Determined by ¹H NMR. c) Determined by GPC in THF calibrated by the polystyrene standard. d) GPC failed due to the low solubility of the polymer.

soluble in polar organic solvents or water presumably due to strong interchain hydrogen bonding. As described above, there is essentially no difference in monomer reactivity between EHO-Bn and EHO-SiMe₃; this gives a good preparative way to random copolymers of which component ratio is controllable

by the charged monomer ratio. Combination of this copolymerization with the hydrolysis achieves preparation of copolymers in which the nonpolar component EHO-Bn and the highly polar component EHO-H, of which ratio can be controlled, is randomly distributed.

DSC Studies of the Homopolymers and Copolymers. As described above, a feature of the polymers and copolymers of substituted oxetanes formed by hydrosilane-induced polymerization catalyzed by **1** is facile introduction of siloxy or alkoxy groups as substituents of the polyoxetane side chain. It is important that the siloxy group can be transformed to either acyloxy or hydroxy group; this emphasizes the utility of the silane-induced polymerization as a preparative method for polyoxetane having a variety of pendant groups. The pendant groups are expected to give interesting properties to the polymers. As introductory experiments to access desired properties of polyoxetanes, we carried out DSC analyses of the homo- and copolymers synthesized in this study. DSC measurements of several polyoxetanes have appeared in literature.^{12,13} Parent polyoxetane with no side chains reportedly shows a change of DSC curve with a reflection point at -71°C , an exothermic peak at -30°C , an endothermic peak at 20°C at heating rate of $10^\circ\text{C min}^{-1}$, which are assignable to T_g , cold crystallization, and T_m , respectively.¹² DSC analyses of poly(3,3-dialkylloxetane), where alkyl = Me, Et, *n*-Pr, *n*-Bu, and *t*-Bu, showed glass transition in temperature range from -50 to -4°C ;¹³ the T_g values of these polyoxetanes are higher when the alkyl groups in the side chain are bulky. As DSC studies on polymers of EHO and MHO derivatives, homo- and copolymers of MHO-(CH₂O)₃OCH₃ and MHO-CH₂CH₂CN were investigated; T_g of these were observed in a temperature range of -52 to -18°C .^{6j} T_g of the copolymers are according to the Fox equation ($T_{g(\text{cal})}^{-1} = w_1 T_{g1}^{-1} + w_2 T_{g2}^{-1}$).¹⁴ In DSC of the homo- and copolymers of MHO-(CH₂O)₂OCH₃ and MHO-R_f (R_f = CH₂CF₂CF₃), T_g was observed from -67.3 to -43.5°C (heating rate: $20^\circ\text{C min}^{-1}$).⁶ⁱ

In Figure 3 and Table 7 are summarized DSC data (heating rate: $10^\circ\text{C min}^{-1}$) of homopolymers of EHO and MHO prepared by the present method. A change of DSC curve with a reflection point assignable to T_g was observed on DSC of homopolymers, in which T_g was dependent on the functional groups of the side chain; T_g of polyEHO; R² = CH₂Ph and SiMe₃ (ca. -20°C) > SiMe₂Ph and CH₂CF₂CF₃ (ca. -35°C) > TEG (-77.2°C). There was no significant difference in T_g between polyEHO and polyMHO as long as the functional group of the side chain is identical. In contrast to the fact that the siloxy or alkoxy polyoxetanes did not show a peak suggesting melting point, the polymers having OH, OCOCH₃, and OCOCF₃ groups showed a strong endothermic peak assignable to T_m . DSC of poly(EHO-H) showed a broad strong endothermic peak at 132°C assignable to T_m besides two small changes of DSC curve with a reflection point at 46.9 and 87.9°C . Poly(EHO-Ac) is interesting in showing only one strong T_m peak at 66.7°C . In several runs of DSC measurements of poly(EHO-COCF₃), a change of DSC curve with a reflection point at -23.2°C , presumably due to T_g , always appeared, whereas a weak peak which may be assignable to T_m seen at 25 – 40°C was observed (not always reproducible). These features in DSC can be roughly explained by considering the interaction of functional group–functional group between polymer chains. The high melting point observed for poly(EHO-H) may be explained by the interpolymer chain hydrogen bonding of OH groups, while weak polar acetoxy–acetoxy interaction may be the

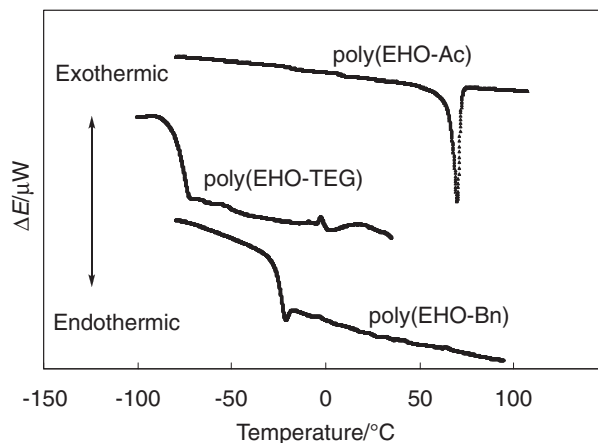


Figure 3. DSC curves of poly(EHO-Ac), poly(EHO-TEG), and poly(EHO-Bn). The measurements were done by raising the temperature from -100 to 100°C with the heating rate of $10^\circ\text{C min}^{-1}$.

Table 7. DSC Data of EHO- and MHO-Derived Homopolymers

Entry	R ¹	R ²	M_n ($\times 10^{-3}$) ^{a)}	M_w/M_n ^{a)}	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$
1	Et	CH ₂ Ph	27	2.3	-24.7	— ^{b)}
2		SiMe ₂ Ph	25	3.6	-33.8	— ^{b)}
3		SiMe ₃	31	2.9	-22.3	— ^{b)}
4		TEG	10	3.2	-77.2	— ^{b)}
5		CH ₂ CF ₂ CF ₃	35	2.3	-36.6	— ^{b)}
6		H	— ^{c)}	— ^{c)}	$46.9, 87.9$	131.9
7		COCH ₃	26	2.6	— ^{b)}	66.7
8		COCF ₃	36	2.1	-23.2	25 – 40 ^{d)}
9	Me	CH ₂ Ph	42	2.6	-22.7	— ^{b)}
10		SiPhMe ₂	66	3.6	-34.3	— ^{b)}
11		EG	8.7	3.1	-74.1	— ^{b)}
12		CH ₂ CF ₂ CF ₃	97	2.0	-46.6	— ^{b)}

a) M_n , M_w/M_n of copolymer was calculated by GPC (solvent was THF; polystyrene standard). b) Not detected. c) GPC was not measurable because of low solubility of the formed polymer in THF. d) T_m changed in the range from 25 to 40°C in some measurements.

reason for the T_m of poly(EHO-Ac). In the case of poly(EHO-COCF₃), the polar interaction due to the $\delta^+\text{C}=\text{O}^{\delta-}\cdots\delta^+\text{C}=\text{O}^{\delta-}$ is mitigated by CF₃–CF₃ repulsion to give T_g instead of T_m .

The DSC studies on copolymers are summarized in Tables 8 and 9. Poly(EHO-Ac-co-EHO-Bn) (EHO-Ac/EHO-Bn = 50:50) showed T_g at -19°C . The $\delta^+\text{C}=\text{O}^{\delta-}\cdots\delta^+\text{C}=\text{O}^{\delta-}$ interaction giving strong interpolymer chain interaction is mitigated by introduction of Bn groups. Poly(EHO-COCF₃-co-EHO-Bn) (EHO-COCF₃/EHO-Bn = 50:50) showed T_g at -27°C . The data of poly(MHO-R_f-co-MHO-TEG) (heating rate: $10^\circ\text{C min}^{-1}$) are similar to those reported by Wynne (heating rate: $20^\circ\text{C min}^{-1}$) in considering the difference in the heating rates. They are also in accord with T_g (-61.4°C) calculated from the Fox equation.¹⁴ The DSC data of copolymers, poly(EHO-Bn-co-EHO-H), are dependent on the copolymer ratio; as expected, the increased ratio of OH resulted in

Table 8. DSC Data of Copolymers

Entry	R ¹	R ²	R ³	R ² /R ^{3a)}	M _n ^{b)} (×10 ⁻³)	M _w /M _n ^{b)}	T _g /°C	T _m /°C
1	Et	COCH ₃	CH ₂ Ph	51:49	31	2.2	-19.4	— ^{c)}
2	Et	COCF ₃	CH ₂ Ph	50:50	24	1.8	-27.0	— ^{c)}
3	Me	CH ₂ CF ₂ CF ₃	EG	46:54	34	2.8	-65.2	— ^{c)}
4 ^{d)}	Me	CH ₂ CF ₂ CF ₃	EG	50:50	3.7–4.5	1.9–2.8	-56.9	— ^{c)}

a) Determined by ¹HNMR. b) M_n, M_w/M_n of copolymer was calculated by GPC (solvent was THF; polystyrene standard). c) Not detected. d) Ref. 6i.

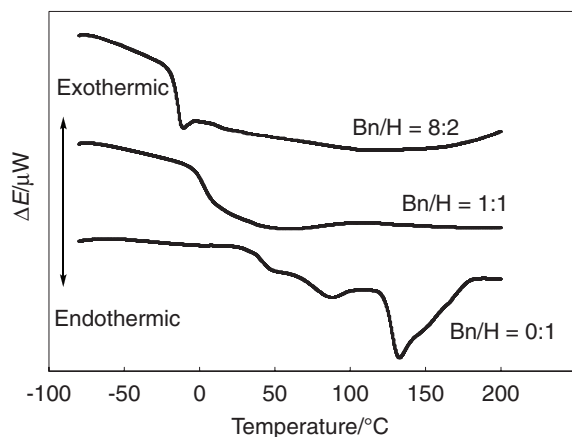


Figure 4. DSC curves of poly(EHO-Bn-co-EHO-H) copolymers. The measurements were done by raising the temperature from -100 to 220 °C with the heating rate of 10 °C min⁻¹.

increase of *T_g* as shown in Figure 4 and Table 9, Entries 1 (EHO-Bn/EHO-H = 100:0)–5 (40:60). Copolymers of (EHO-Bn/EHO-H = 24:76) showed *T_m* at 131 °C. Similar to the result of poly(EHO-Ac-co-EHO-Bn), interchain hydrogen bonding in poly(EHO-Bn-co-EHO-H) possibly gives *T_m*; however, it was not seen in poly(EHO-Bn-co-EHO-H) of (EHO-Bn/EHO-H = 80:20–40:60) because the hydrogen bonding is prevented by benzyloxy groups in the copolymer.

Mechanistic Consideration. As noted earlier, the polymerization mechanism for the ruthenium-catalyzed ring-opening polymerization of hydrosilanes was proposed in our previous papers.³ As evidenced by isolation of intermediary ruthenium clusters having Ru–Si and Ru–H bonds, the reaction of **1** with R₃SiH results in activation of the Si–H bond to give a catalytically active species, R₃Si[Ru₃H], which generates ion pair, R₃Si⁺...[Ru₃H]⁻, in solution. The R₃Si⁺ species activates the oxetane monomer to initiate the polymerization. The termination occurs by hydride transfer from the [Ru₃H]⁻ to the cationic species at the polymer end (Figure 5). The catalyst **1** is a stable solid and can be stored over years under aerobic conditions. In contact with excess R₃SiH, air- and moisture-sensitive R₃Si[Ru₃H] was generated in dioxane, which promotes exothermic polymerization of the oxetane under the standard conditions. The stability of **1** has the advantage of easy handling, but is not good for instant and quantitative generation of the active species, especially when sterically hindered compounds are used as a hydrosilane. Since the active species is sensitive toward air and moisture, purification of the monomer and the solvent and careful generation of the active

Table 9. DSC Data of Poly(EHO-Bn-co-EHO-H)^{a)}

Entry	EHO-Bn/EHO-H ^{b)}	M _n ^{b)} (×10 ⁻³) ^{c)}	M _w /M _n ^{c)}	T _g /°C	T _m /°C
1	100:0	27	2.3	-24.7	— ^{d)}
2	80:20	27	2.7	-15.2	— ^{d)}
3	59:41	22	2.3	0.9	— ^{d)}
4	47:53	21	2.2	2.2	— ^{d)}
5	40:60	23	2.3	12.4	— ^{d)}
6	24:76	14	2.4	35.3	131.0
7	0:100	— ^{e)}	— ^{e)}	46.9, 87.9	131.9

a) The measurements were done from -100 to 220 °C (10 °C min⁻¹). b) Determined by ¹HNMR. c) M_n, M_w/M_n of copolymer was calculated by GPC (solvent was THF; polystyrene standard). d) Not detected. e) Low solubility of the formed polymer in THF made GPC difficult.

species are necessary for reproducible polymerizations in dilute solutions and those of lower **1**/Si–H ratio. The molecular weight of the formed polymer is dependent on the concentration of R₃Si⁺ species as the initiator and that of [Ru₃H]⁻ as the terminator. The propagation is competitive with the hydride transfer from the [Ru₃H]⁻ species; however, it is fast enough to produce the polymer of M_n = 10³–10⁵ under the standard conditions. The results shown in Entries 3–5 of Table 2 suggest that the molecular weight would become higher in increasing the monomer concentration, if uniform amounts of R₃Si⁺...[Ru₃H]⁻ species can be generated in the reaction medium. Since the polymerization is not living, precise control of the molecular weight by appropriate choice of the monomer, the hydrosilane, and the catalyst is impossible. The molecular weight was determined by the concentration of the active species, which is affected by both initiation and termination steps, and by that of monomer. In an ideal case, in which active species equal to the amount of the catalyst is generated, the rate of the initiation and termination would be stable. Thus, the monomer concentration is a key to determine the molecular weight. In a real system, the active species is generated by treatment of the Ru₃ cluster and the hydrosilane. The Ru₃ cluster is stable and the reaction with the hydrosilane is slow even if large excess amounts of hydrosilane is used for the initiation. Under the circumstances, the concentration of the active species is not always the same at the initiation of polymerization. Thus, the molecular weight of the polymer is roughly controllable by changing the ratio of the monomer and the hydrosilane, but contains large experimental errors. At present stage, the molecular weight control is roughly accomplished by the choice of **1**/R₃SiH/monomer ratio; however, the results implicate that discovery of the catalyst

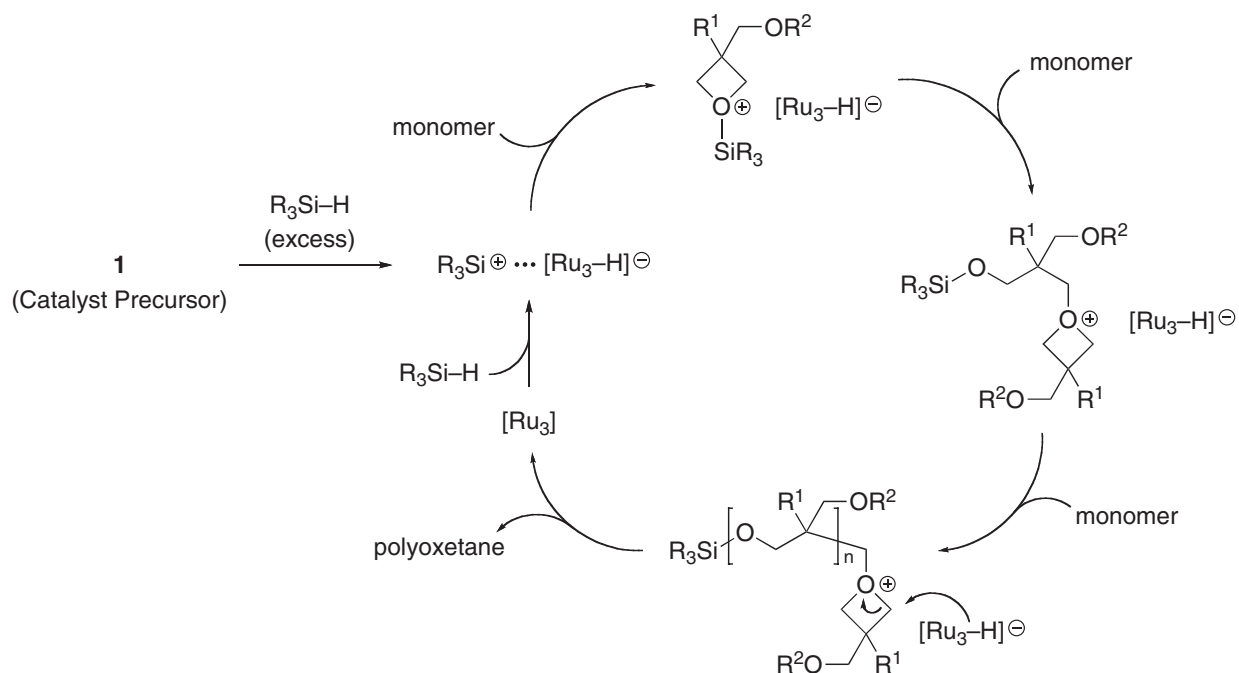


Figure 5. Proposed catalytic cycle.

precursor which generates the active species quantitatively as soon as contact with the hydrosilane leads to more precise control of the molecular weight.

Conclusion

The present polymerization procedure initiated by hydrosilane and a catalytic amount of a triruthenium cluster **1** has provided a convenient and reliable method for synthesis of polyoxetane with a variety of pendant functional groups. In contrast to the fact that conventional cationic polymerization of EHO-R and MHO-R (R = alkyl group) gives polymer of relatively low molecular weight, the present method gave polymer of $M_n = 10^3$ – 10^5 . Application of the present reaction to polymerization of EHO-H gave a linear polymer EHO-SiR₃; this is interesting in that cationic polymerization of EHO-H gives hyperbranched polymers. An interesting result was obtained from copolymerization of EHO-Bn and EHO-SiMe₃, in which there is no difference in monomer reactivity ratio to give random copolymers with a component ratio identical to the charged monomer ratio. This is particularly important in producing copolymers with interesting properties in combination with facile chemical transformation of organosilyl functional groups to others. Typical two examples are OSiR₃/OCOR exchange by treatment with RCOCl and hydrolysis of OSiR₃ moieties to OH groups. Nonpolar OSiR₃ group is converted to polar OCOR or OH groups by this chemical transformation. These polar polymers and copolymers can be prepared in one-pot connecting the silane-induced polymerization and chemical transformation of OSiR₃ groups. The results described in this paper suggest that chemists can synthesize polyoxetanes having a variety of properties which are available by appropriate design of the pendant functional groups. As the simplest examples of design of polymer property, DSC analyses of the polymers and copolymers

obtained were investigated, showing that this polymerization is an interesting and useful entry to polyoxetane-based polymer materials.¹⁵

Experimental

¹H, ¹³C, ¹⁹F, and ²⁹Si NMR spectra were measured on a JEOL GSX-270 (270 MHz), ECA 400 (396 MHz), and ECA 600 (600 MHz) spectrometers. Chemical shifts for ¹H NMR are described in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$) in CDCl₃, unless otherwise noted. Chemical shifts for ¹³C NMR are expressed in parts per million in CDCl₃ as an internal standard ($\delta = 77.1$), unless otherwise noted. Chemical shifts for ¹⁹F NMR are described in parts per million downfield from trifluoroacetic acid as an external standard ($\delta = -79$ ppm). Chemical shifts for ²⁹Si NMR were described in parts per million downfield from tetramethylsilane as an external standard. IR spectra were measured on a JASCO FT/IR-4200 spectrometer. GPC analysis was performed with a JASCO-GPC system consisting of DG-1580-53 degasser, PU-980 HPLC pump, UV-970 UV-vis detector, RI-930 RI detector, and CO-2065-plus column oven (at 40 °C) using two connected Shodex GPC-KF-804L columns in THF (sample concentration: $w = 1 \times 10^{-2}$; flow rate = 1.0 mL min⁻¹). The molecular weight was calibrated with a commercially available polystyrene (Shodex: SM-105); seven standard solutions, of which M_n range from 1.31×10^3 to 7.36×10^5 ($M_w/M_n = 1.07$). A DSC 6220 (Seiko Instruments Inc.) was used for analyses of the thermal behavior of the polymers. The polymer samples (5–15 mg) were pretreated at 100 °C under reduced pressure (0.05 Torr) overnight and cooled to -100 °C by liquid nitrogen. The measurements were done from -100 to 100 °C in aluminum pans under N₂ flow (13–50 mL min⁻¹) with a heating rate of 10 °C min⁻¹ unless otherwise noted. $[Ru_3\{\mu_3-(\eta^2, \eta^3, \eta^5-C_{12}H_8)\}(CO)_7]$ (**1**) was

prepared according to a method reported previously.¹⁶ Hydro-silanes listed in Table 1 and HCl/MeOH reagent (ca. 5–10% HCl) are purchased from Tokyo Chemical Industry Co., Ltd. or Chisso. Monomers, EHO-H, EHO-Bn, MHO-H, and MHO-Bn were donated from Ube Industries. Other monomers shown in Scheme 1 were prepared from MHO-H or EHO-H as summarized in the Supporting Information. All reactions were carried out in a reaction vessel dried by heat gun under vacuum just before use under an argon atmosphere.

A Typical Procedure for the Silane-Induced Polymerization of 3-Alkyl-3-alkoxymethyloxetane. In a 20 mL two-necked flask, **1** (2.15 mg, 3.3 μ mol) was dissolved in a minimum amount of dioxane (typically, 60 μ L). To this solution, PhMe₂SiH (50 μ L, 0.33 mmol) was added, and the mixture was stirred at ambient temperature for 30 min. The initial orange color of the solution was darkened. Then, the monomer EHO-Bn (681 mg, 3.3 mmol) was added dropwise and the mixture was stirred at room temperature. The reaction was exothermic and viscosity of the reaction mixture was gradually increased. After the reaction was complete, the reaction mixture was dissolved in benzene (6 mL). The benzene solution was poured into MeOH (20 mL) to precipitate the polymer. Filtration followed by removal of the solvent remained in vacuo gave poly(EHO-Bn) in 86% yield (586 mg). $M_n = 4.9 \times 10^4$, $M_w/M_n = 2.0$; ¹H NMR (396 MHz, CDCl₃): δ 7.37–7.16 (m, 5H, Ph), 4.39 (s, 2H, CH₂Ph), 3.30 (s, 2H, CH₂OBn), 3.25–3.16 (brs, 4H, CH₂-O of polymer chain), 1.39 (q, $J = 7.7$ Hz, 2H, C-CH₂CH₃), 0.79 (t, $J = 7.7$ Hz, 3H, C-CH₂CH₃); ¹³C NMR (99.5 MHz, CDCl₃): δ 139.2 (*ipso*-Ph), 128.3, 127.29 (*o*- and *m*-Ph), 127.26 (*p*-Ph), 73.4 (CH₂Ph), 71.8 (CH₂-O of polymer chain), 71.5 (CH₂OBn), 43.6 (C-Et), 23.4 (C-CH₂CH₃), 7.82 (C-CH₂CH₃).

A typical example for the copolymerization is as follows: In a 20 mL Schlenk tube, **1** (2.15 mg, 3.3 μ mol) was dissolved in dioxane (60 μ L). To this solution, PhMe₂SiH (50 μ L, 0.33 mmol) was added and the mixture was stirred at room temperature for 30 min. A mixture of EHO-Bn (340 mg, 1.65 mmol) and EHO-SiMe₃ (311 mg, 1.65 mmol) was added and the mixture was stirred at room temperature. The reaction was exothermic and viscosity of the reaction mixture gradually increased. After the reaction was complete, the reaction mixture was dissolved in benzene (6 mL). The benzene solution was poured into MeOH (20 mL) to precipitate the polymer. Filtration followed by removal of the solvent remained in vacuo gave poly(EHO-SiMe₃-*co*-EHO-Bn) in 97% yield (631 mg; EHO-SiMe₃/EHO-Bn = 50:50 by ¹H NMR). $M_n = 2.2 \times 10^4$, $M_w/M_n = 2.2$; ¹H NMR (396 MHz, CDCl₃): δ 7.38–7.17 (m, 5H, Ph), 4.42 (brs, 2H, CH₂Ph), 3.40 (brs, 2H, CH₂-OSi), 3.32 (brs, 2H, CH₂OBn), 3.28–3.07 (m, 8H, CH₂-O of polymer chain), 1.46–1.24 (m, 4H, C-CH₂CH₃), 0.86–0.74 (m, 6H, C-CH₂CH₃), 0.10–0.01 (m, 9H, Si-CH₃); ¹³C NMR (67.8 MHz, CDCl₃): δ 139.3 (*ipso*-Ph), 128.3 (Ph), 127.4 (Ph), 127.3 (Ph), 73.4 (CH₂Ph), 71.9, 71.7, 71.6 (CH₂-O of polymer chain and C-OBn), 63.3 (C-OSi), 43.9 (C-Et derived from EHO-SiMe₃), 43.7 (C-Et derived from EHO-Bn), 23.5 (C-CH₂CH₃ of EHO-Bn moiety), 23.0 (C-CH₂CH₃ derived from EHO-SiMe₃), 8.0 (C-CH₂CH₃), -0.4 (Si-CH₃); ²⁹Si NMR (119 MHz, CDCl₃): δ 16.8–16.6 (O-SiMe₃), 6.8–6.6 (OSiMe₂Ph of the polymer end).

Dehydrogenative Silylation Followed by the Silane-Induced Polymerization of 3-Ethyl-3-hydroxymethyloxetane (Table 4, Entry 3). In a 20 mL two-necked flask, **1** (2.15 mg, 3.3 μ mol) was dissolved in dioxane (60 μ L). To this solution, PhMe₂SiH (495 mg, 3.63 mmol) was added and the mixture was stirred at ambient temperature for 30 min. At this point, the initial orange color of the solution darkened. Then, EHO-H (383 mg, 3.3 mmol) was added dropwise and the mixture was stirred at room temperature. The reaction was exothermic and vigorous evolution of H₂ gas was observed at the initial stage. The viscosity of the reaction mixture gradually increased. After 15 min, the reaction was complete. The reaction mixture was dissolved in benzene (6 mL). The benzene solution was poured into MeOH (20 mL) to precipitate the polymer. Yield 91% (760 mg); $M_n = 1.4 \times 10^4$, $M_w/M_n = 4.3$; ¹H NMR (396 MHz, CDCl₃): δ 7.54–7.49 (m, 2H, Ph), 7.34–7.26 (m, 3H, Ph), 3.43 (s, 2H, CH₂-OSi), 3.19–3.09 (m, 4H, CH₂-O of polymer chain), 1.32 (q, $J = 7.7$ Hz, 2H, C-CH₂CH₃), 0.76 (t, $J = 7.7$ Hz, 3H, C-CH₂CH₃), 0.29 (s, 6H, Si-CH₃); ¹³C NMR (99.5 MHz, C₆D₆): δ 139.0 (*ipso*-Ph), 134.3 (*o*-Ph), 130.3 (*p*-Ph), 128.6 (*m*-Ph), 72.5 (CH₂-O of polymer chain), 64.6 (CH₂-OSi), 45.0 (C-Et), 23.9 (C-CH₂CH₃), 8.8 (C-CH₂CH₃), -1.1 (Si-CH₃).

Chemical Transformation of the Copolymer, Poly(EHO-SiMe₃-*co*-EHO-Bn). Hydrolysis: Silylated polymers are subjected to protodesilylation with HCl in MeOH. In a typical example, the copolymer, poly(EHO-SiMe₃-*co*-EHO-Bn) (EHO-SiMe₃/EHO-Bn = 50:50, $M_n = 2.6 \times 10^4$, $M_w/M_n = 2.1$; 575 mg, 2.91 mmol, 1.46 mmol of SiMe₃ group) dissolved in dry toluene (12 mL) was treated with HCl/MeOH (5–10% HCl; 5.31 g) at room temperature overnight. After removal of the solvent, the residue was dissolved in THF (5 mL). To the THF solution, hexane (20 mL) was added to precipitate poly(EHO-H-*co*-EHO-Bn). Yield 92% (431 mg; EHO-H/EHO-Bn = 53:47); $M_n = 2.1 \times 10^4$, $M_w/M_n = 2.2$; IR (film): ν_{OH} 3434 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.36–7.20 (br, 5H, Ph), 4.49–4.39 (m, 2H, CH₂Ph), 3.51 (brs, 2H, CH₂OH), 3.39–3.15 (m, 10H, CH₂-O of polymer chain and CH₂OBn), 1.44–1.24 (m, 4H, C-CH₂CH₃), 0.81 (brs, 6H, C-CH₂CH₃); ¹³C NMR (99.5 MHz, CDCl₃): δ 139.2–138.4 (m, *ipso*-Ph), 128.2 (*o*- or *m*-Ph), 127.7–126.8 (m, *o*- or *m*-Ph and *p*-Ph), 74.5–70.5 (m, CH₂-O of polymer chain, CH₂Ph and C-OBn), 67.6–64.5 (m, CH₂OH), 43.8–42.8 (m, C-Et), 23.7–22.7 (C-CH₂CH₃), 7.7 (brs, C-CH₂CH₃); $T_g = 2.2$ °C.

Organosilyl/Acyl Exchange; Terminal Silyl Group: The following is a typical example: poly(EHO-Bn) (294 mg) prepared by a procedure described above, of which M_n was estimated as 2.7×10^4 (GPC) and 9.7×10^3 (¹H NMR), contained 30.3 μ mol of PhMe₂SiO group. This was dissolved in benzene (5 mL), and treated with acetyl chloride (22 μ L, 0.30 mmol) at room temperature for 18 h. After removal of the volatiles, the residue was dissolved in ether (50 mL). The ether solution was washed with aqueous NaHCO₃. The aqueous layer was extracted five times with ether. The combined extracts were dried over MgSO₄ and the solvent was removed under reduced pressure. Then the residue was dissolved in a mixture of ether (3 mL) and MeOH (15 mL) and the solution was stored at -30 °C for 24 h to give the polymer as a precipitate. Yield 90% (265 mg); $M_n = 2.7 \times 10^4$, $M_w/M_n =$

2.2 (determined by GPC); $M_n = 7.0 \times 10^3$ (determined by ^1H NMR); IR (film): $\nu_{\text{C=O}}$ 1742 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3), signals due to the polymer chain: δ 7.31–7.16 (m, 5H, Ph), 4.40 (s, 2H, CH_2Ph), 3.30 (s, 2H, $\text{CH}_2\text{-OBn}$), 3.25–3.16 (m, 4H, $\text{CH}_2\text{-O}$ of polymer chain), 1.38 (q, $J = 7.3$ Hz, 2H, CH_2 of Et), 0.79 (t, $J = 7.3$ Hz, 3H, CH_3 of Et). Small peaks due to the terminal acetyl group were visible at δ 2.01–1.89 (m, CH_3 of Ac); ^{13}C NMR (99.5 MHz, CDCl_3), signals due to the polymer chain: δ 139.1 (*ipso*-Ph), 128.2 (*o*- or *m*-Ph), 127.3 (*o*- or *m*-Ph), 127.2 (*p*-Ph), 73.4 ($\text{O-CH}_2\text{Ph}$), 71.8 ($\text{CH}_2\text{-O}$ of the polymer chain), 71.5 (C-OBn), 43.6 (C-Et), 23.5 ($\text{C-CH}_2\text{CH}_3$), 7.9 ($\text{C-CH}_2\text{CH}_3$). Small peaks due to the terminal acetyl group were visible at δ 170.9 (C=O), 20.9 (CH_3 of Ac).

Conversion of Organosilyl Groups at the Polymer Side Chain to an Acetoxy Moiety: In a similar manner to the terminal acetylation, poly(EHO-SiPhMe_2) ($M_n = 3.3 \times 10^4$, $M_w/M_n = 3.2$; 370 mg containing 1.48 mmol of Me_2PhSi groups) was dissolved in benzene (3 mL). To this solution, acetyl chloride (0.32 mL, 4.44 mmol) was added and the mixture was stirred at room temperature for 24 h. After removal of the volatiles, the residue was dissolved in ether (25 mL). The ether solution was washed with aqueous NaHCO_3 . The aqueous layer was extracted five times with ether. The combined extracts were dried over MgSO_4 and the solvent was removed under reduced pressure. The residue was dissolved in a mixture of ether (3 mL) and hexane (7 mL) and the solution was kept at -30°C for 24 h. The desired copolymer was precipitated. Yield 82% (192 mg); $M_n = 2.6 \times 10^4$, $M_w/M_n = 2.6$; IR (film): $\nu_{\text{C=O}}$ 1735 cm^{-1} ; ^1H NMR (396 MHz, CDCl_3): δ 3.95 (s, 2H, $\text{CH}_2\text{-OAc}$), 3.20 (s, 4H, $\text{CH}_2\text{-O}$ of polymer chain), 2.03 (s, 3H, CH_3 of Ac), 1.39 (q, $J = 7.2$ Hz, 2H, $\text{C-CH}_2\text{CH}_3$), 0.82 (t, $J = 7.2$ Hz, 3H, $\text{C-CH}_2\text{CH}_3$); ^{13}C NMR (67.8 MHz, CDCl_3): δ 170.8 (C=O), 71.3 ($\text{CH}_2\text{-O}$ of polymer chain), 65.1 (C-OAc), 42.3 (C-Et), 23.1 ($\text{C-CH}_2\text{CH}_3$), 20.8 (CH_3 of Ac), 7.5 ($\text{C-CH}_2\text{CH}_3$); $T_m = 66.7^\circ\text{C}$.

One-Pot Synthesis of Poly(EHO-Ac-co-EHO-Bn) from EHO-H and EHO-Bn. In a 20 mL Schlenk tube, **1** (4.3 mg, 6.6 μmol) was dissolved in dioxane (120 μL). To this solution, PhMe_2SiH (540 mg, 3.96 mmol) was added and the mixture was stirred at ambient temperature for 30 min. The mixture of EHO-H (192 mg, 1.65 mmol) and EHO-Bn (340 mg, 1.65 mmol) was placed in another 20 mL Schlenk tube. A half amount of the catalyst solution described above was added dropwise at 0°C . The mixture was stirred at 0°C for 30 min, and then, gradually warmed to room temperature. Evolution of H_2 was observed, and the reaction was exothermic. Viscosity of the reaction mixture was gradually increased. After 1 h, the reaction mixture was dissolved in toluene (4 mL). To this solution, acetyl chloride (389 mg, 4.95 mmol) was added and the mixture was stirred at room temperature for 10 h. After removal of volatiles, the residue was dissolved in a mixture of toluene (7 mL) and methanol (50 mL) and the solution was kept at -30°C for 24 h. The desired copolymer was precipitated. Poly(EHO-Ac-co-EHO-Bn). Yield 88% (528 mg; EHO-Ac/EHO-Bn = 51:49); $M_n = 3.1 \times 10^4$, $M_w/M_n = 2.2$; IR (film): ν_{CO} 1735 cm^{-1} ; ^1H NMR (396 MHz, CDCl_3): δ 7.34–7.20 (m, 5H, Ph), 4.42 (brs, 2H, $\text{O-CH}_2\text{Ph}$), 3.96 (brs, 2H, $\text{CH}_2\text{-OAc}$), 3.30 (brs, 2H, $\text{CH}_2\text{-OBn}$), 3.26–3.15 (m, 8H, $\text{CH}_2\text{-O}$ of

polymer chain), 2.05–1.92 (m, 3H, CH_3 of Ac), 1.38 (brs, 4H, $\text{C-CH}_2\text{CH}_3$), 0.80 (brs, 6H, $\text{C-CH}_2\text{CH}_3$); ^{13}C NMR (99.5 MHz, CDCl_3): δ 171.0–170.8 (C=O), 139.2–139.0 (*ipso*-Ph), 128.3–128.2 (m, Ph), 127.4–127.2 (m, Ph), 73.4 ($\text{O-CH}_2\text{Ph}$), 71.9–71.2 (m, $\text{CH}_2\text{-O}$ of polymer chain), 65.6–65.1 ($\text{CH}_2\text{-OAc}$), 43.6–43.5 and 42.5 (m, $\text{CH}_2\text{-O}$ of polymer chain and C-Et), 23.5–23.2 ($\text{C-CH}_2\text{CH}_3$), 20.9 (CH_3 of Ac), 7.92–7.62 (m, $\text{C-CH}_2\text{CH}_3$); DSC ($10^\circ\text{C min}^{-1}$, $-100^\circ\text{C} < T < 100^\circ\text{C}$): -19.4°C (T_g).

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Supporting Information

Detailed experimental procedures, characterization data of both the substrates and the products. This material is available free of charge on the web at <http://www.csj.jp/journals/bcsj/>.

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7 One of the reviewers suggested that we should check the number of repeating units before and after the acetylation. Two samples, $\text{PhMe}_2\text{Si}(\text{EHO-Bn})_{47}\text{H}$ [M_n (GPC) = 2.7×10^4 , $M_w/M_n = 2.3$] and $\text{PhMe}_2\text{Si}(\text{EHO-Bn})_{18}\text{H}$ [M_n (GPC) = 1.4×10^4 , $M_w/M_n = 1.8$], were subjected to the acetylation. Comparison of ^1H resonances due to the Ac group and those due to the polymer units suggested that the number of the repeating units were calculated to be 40 and 11, respectively. They are relatively smaller than those of the samples bearing a terminal PhMe_2Si group. This is due to the contamination of a small amount of acetic acid or its derivatives derived from acetyl chloride, which was hardly removable from the polar polyoxetane. The impurities contribute to increase the integral value of the Ac peak to result in decrease of M_n .

8 In the ^1H NMR spectra of the polymer formed by the reaction of EHO-H with PhMe_2SiH described in the text, the signals are exactly the same as those observed for poly(EHO-SiPhMe₂) formed by polymerization of EHO-SiPhMe₂. The integral ratio of the signal due to $\text{CH}_2\text{OSiMe}_2$ vs. that due to CH_2 groups in the polymer chain are good indication; it is 1:2 in

the linear polymer, whereas no signal due to the $\text{CH}_2\text{OSiMe}_2$ moiety was seen in the hyperbranched polymer. Similarly, the integral ratio of the signal due to methylene protons of the ethyl group vs. CH_2 groups in the polymer chain are also good proof; an ideal ratio is 1:2 in the linear polymer, whereas that is 1:3 in the hyperbranched polymer. This clearly showed that hyperbranched structure was not included in poly(EHO-SiMe₂Ph) formed from EHO-H by the ruthenium-catalyzed dehydrogenative silylation and subsequent ring-opening polymerization.

9 In general, NMR spectra of random copolymers are not the precise sum of those of homopolymers. This results from magnetic interaction between the comonomer units. In the copolymers presented in this paper, two units derived from the comonomers, $-\text{CH}_2\text{C}(\text{R}^1)(\text{CH}_2\text{OR}^2)\text{CH}_2-$ and $-\text{CH}_2\text{C}(\text{R}^3)(\text{CH}_2\text{OR}^4)\text{CH}_2-$, were separated by oxygen atoms; this reduce the magnetic interaction.

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15 Polymers obtained by the present method are brownish solids due to the ruthenium residues, which are not completely removable by precipitation. Further treatment of the polymers with activated carbon or activated clay makes them colorless.

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