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Silane-Induced Polymerization of Vinyl Ethers Catalyzed by a Triruthenium Carbonyl Cluster, (μ_3,η^2,η^3,η^5-Acenaphthylene)$Ru_3(CO)_7$

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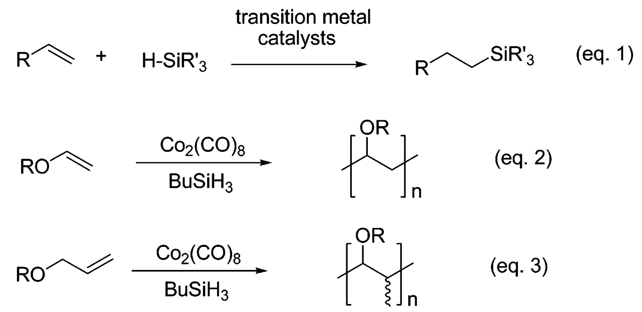
The polymerization of vinyl ethers ($CH_2{=}CHOR$, R = ^{n}Bu, ^{i}Bu, ^{t}Bu, ^{i}Pr) is catalyzed by a ruthenium cluster, (μ_3,η^2:η^3:η^5-acenaphthylene)$Ru_3(CO)_7$ (**1**), using several hydrosilanes as the initiator to give polyvinyl ethers with M_n = 2000−25 000 and M_w/M_n = 1.2−3.4. Spectroscopic analysis of the polymer reveals the existence of an organosilyl moiety at the end group, which is supported by UV and RI detection of GPC. The poly(*tert*-butyl vinyl ether) prepared by $PhMe_2SiD$ as the initiator contains a $-CDHO^tBu$ group at the other polymer end. These data suggest the polymer structure is $R_3Si-(CH_2CHOR)_n-H$. Dominant heterotacticity was observed for the polymer structure, which was independent of organosilanes or solvents.

1. Introduction

Transition metal-catalyzed hydrosilylation reactions of alkenes are useful for preparation of organosilicon compounds, in which an H−Si bond in hydrosilanes is activated by the transition metals and is added across a carbon−carbon double bond of alkenes and other unsaturated molecules.[1,2] In general hydrosilylation reactions, only one carbon−carbon double bond is inserted into an Si−H bond to give the 1:1 adduct as shown in eq 1 in Scheme 1. Although multiple insertion of alkenes to an Si−H bond makes it possible to produce polyalkenes bearing an organosilicon terminus, such polymerization has rarely been reported to our knowledge.[2] A closely related example is vinyl ether polymerization reported by Crivello and co-workers, who briefly noted that a vinyl ether is polymerized in the presence of $BuSiH_3$ and a catalytic amount of $Co_2(CO)_8$.[3,4] The authors extended similar catalyst systems to isomerization of a carbon−carbon double bond in 2-propenyl alkyl ethers, followed by polymerization of the resulting 1-propenyl alkyl ethers.[5] These reactions are proposed to involve multiple insertion of vinyl ether molecules between the Si−H bond via cationic intermediates,[6] though detailed studies including the role of the cobalt catalyst have not been undertaken. Reactions of vinyl ethers with hydrosilanes leading to vinyl polymerization are not common in transition metal-catalyzed hydrosilylation; it was reported that platinum and nickel catalysts afforded β-alkoxysilanes by insertion of one molecule of vinyl ether between an Si−H bond in hydrosilanes.[7]

Scheme 1



We reported previously that a ruthenium cluster, (μ_3,η^2,η^3,η^5-acenaphthylene)$Ru_3(CO)_7$ (**1**),[8] is a unique catalyst for the hydrosilylation of alkenes, alkynes, and carbonyl compounds;[8a] catalytic activity is extremely high and adequate enough to carry out the reduction of

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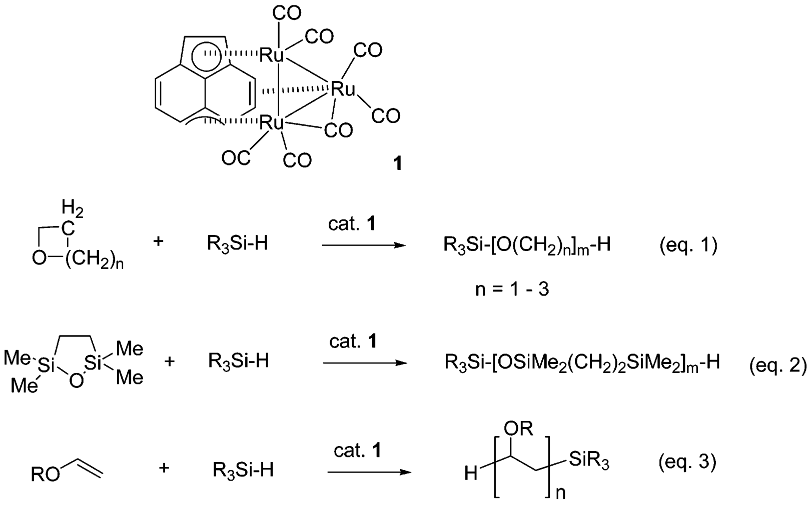
Scheme 2



esters, carboxylic acids, and amides.[8c,d] A unique feature of this catalyst, which is not seen in other commonly used hydrosilylation catalysts, is that **1** exhibits excellent catalytic activity for the ring-opening polymerization of cyclic ethers induced by trialkylsilanes besides the hydrosilylation described above (Scheme 2).[8a] Detailed research on the end groups of formed polyalkylene oxides revealed that the reaction involves multiple insertions of a "$-O(CH_2)_n-$" unit into an Si$-$H bond of trialkylsilanes.[8a] Similar multiple insertion of a "$-OSiMe_2(CH_2)_2SiMe_2-$" unit formed by a ring-opening reaction of 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane into an Si$-$H bond of trialkylsilanes results in the production of poly(tetramethylsilethylenesiloxane) by the catalysis of **1**.[8b] We were interested in the fact that the silane-induced polymerization of cyclic ethers was also catalyzed by $Co_2(CO)_8$,[9] though it was less reactive at lower catalyst concentration than **1**.[8a] This indicates that **1** may also catalyze the silane-induced polymerization of vinyl ethers shown in Scheme 1, eq 2. In this paper, we wish to report that **1** is an active catalyst for the polymerization of vinyl ethers under mild conditions, and in particular, the polymerization of *tert*-butyl vinyl ether gives polyvinyl ether with narrow molecular weight distributions. It is also noteworthy that two important findings not previously clarified in the $Co_2(CO)_8$-catalyzed reactions were obtained: (1) An organosilyl group and a hydrogen atom derived from the hydrosilane used were proved to exist at the polymer terminal, and (2) although alkoxysilanes cannot be used for hydrosilylation of unsaturated molecules or ring-opening polymerization of cyclic ethers in our earlier studies, the vinyl ether polymerization readily occurs by catalysis of **1**. These two discoveries provide a synthetic route to functional polymers,[10] vinyl ethers having an organosilyl end group including alkoxysilyl groups, which are known to be useful for further chemical transformation of polymers.[11] No significant isotacticity was observed.[12]

2. Results and Discussion

Polymerization of Vinyl Ethers. In our earlier studies on the silane-induced ring-opening polymerization of cyclic ethers and siloxanes catalyzed by **1**, the polymerization was performed in a vacuum-sealed glass tube.[8a] An improved process including preactivation of the catalyst with hydrosilylation, which is useful for reduction of carboxylic acid derivatives,[8d] offers a convenient method to carry out the experiment under an inert gas atmosphere. A series of vinyl ethers was subjected to the reaction with $PhMe_2SiH$ in the presence of a catalytic amount of **1**; in a typical example, **1** (3.3 μmol) dissolved in dioxane was treated with $PhMe_2SiH$ (0.33 mmol) for 30 min at room temperature. Addition of vinyl ether (3.3 mmol) to this solution resulted in formation of polyvinyl ether. As shown in Table 1, entries 1, 2, 3, and 9, four monomers, isopropyl, *n*-butyl, isobutyl, and *tert*-butyl vinyl ethers, were successfully converted to the polymer of M_n = ca. 10 000 at room temperature. The reaction time required for the completion of the polymerization and the molecular weight distributions of the formed polymer were dependent on the vinyl ether used. The polymerization of isopropyl, *n*-butyl, and isobutyl vinyl ethers required 60$-$180 min for the complete conversion of the monomer, and the formed polymer showed relatively wide molecular weight distribution ($M_w/M_n = 2.1-2.8$). In contrast, the reaction of *tert*-butyl vinyl ether was rapid (the conversion reached over 95% in a couple of minutes), giving the corresponding polyvinyl ether with much narrower molecular weight distribution ($M_w/M_n = 1.4$). As described later in detail, all of the polymeric materials

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[10] We have already reported treatment of $R_3Si[O(CH_2)_n]_mH$ with acyl halides resulted in formation of $RCO[O(CH_2)_n]_mH$. For example, reaction of $R_3Si[O(CH_4)_n]_mH$ with a half molar amount of $ClCO(CH_2)_4COCl$ gave $H[(CH_2)_4O]_mCO(CH_2)_4CO[O(CH_2)_4]_mH$, whereas that with $BrC(CH_3)_2COBr$ formed $BrC(CH_3)_2CO[O(CH_2)_4]_mH$, which is an initiator of living radical polymerization, see: Iura, T.; Matsubara, K.; Nagashima, H. *The Reports of Inst. Adv. Mater. Study, Kyushu University* **2000**, *14*, 119.

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Table 1. Polymerization of Vinyl Ethers with $PhMe_2SiH$ at Room Temperature[a]

entry	R of $ROCH{=}CH_2$	ratio cat./silane/monomer	time (min)	conv[b] (%)	yield[c] (%)	M_n	M_w	M_w/M_n
1	^iPr	1/100/1000	180	100	69	10 000	28 000	2.8
2	^nBu	1/100/1000	120	96	82	12 000	25 000	2.1
3	^iBu	1/100/1000	60	95	84	10 000	28 000	2.8
4		1/200/1000	60	90	60	12 000	25 000	2.1
5		1/1000/1000	180	91	70	2000	3700	1.8
6		1/100/10000	180	82	70	12 000	22 000	1.7
7	^tBu	1/5/1000	20	84	60	12 500	22 000	1.8
8		1/10/1000	10	95	85	8000	14 000	1.7
9		1/100/1000	5	96	92	9000	13 000	1.4
10		1/200/1000	10	96	80	6000	9000	1.5
11		1/1000/10000	240	84	70	7000	16 000	2.3
12		1/10000/1000	360	40	25	360	740	2.0

[a] All reactions except that reported in entry 11 were carried out with the catalyst (3.3 μmol) in dioxane (56 μL) under an argon atmosphere. The experiment of entry 11 was performed with 0.33 μmol of the catalyst in dioxane (5.6 μL). [b] Conversion of the monomer determined by ^{1}H NMR. [c] Isolated yield of the polymer after precipitation.

Table 2. Effect of Silanes in the Vinyl Ether Polymerization at Room Temperature[a]

entry	R	silane	time (min)	conv[b] (%)	yield[c] (%)	M_n	M_w/M_n
1	^iBu	$PhMe_2SiH$	60	95	84	10 000	2.8
2		$EtMe_2SiH$	1	98	82	22 000	3.4
3		Et_2MeSiH	5	95	85	13 000	2.8
4		$(HSiMe_2CH_2)_2$	120	90	57	4000	2.8
5	^tBu	$PhMe_2SiH$	5	96	92	9000	1.4
6		$EtMe_2SiH$	60	83	71	18 000	1.6
7		Et_2MeSiH	60	87	77	20 000	1.6
8		$(HSiMe_2CH_2)_2$	5	97	88	13 000	1.8
9		$(EtO)Me_2SiH$	10	89	87	10 000	1.7
10		$(EtO)_2MeSiH$	60	96	89	7000	2.2
11		$(EtO)_3SiH$	300	99	77	9000	2.4

[a] All reactions were carried out with the catalyst (3.3 μmol), the silane (0.33 mmol), and monomer (3.3 mmol) in dioxane (56 μL) under an argon atmosphere. [b] Conversion of the monomer determined by ^{1}H NMR. [c] Isolated yield of the polymer after precipitation.

obtained were subjected to ^{1}H and ^{13}C NMR analysis, from which the product was assignable as $PhMe_2Si-(CH_2CHOR)_n-H$. This suggests that the reaction involves multiple insertions of a carbon−carbon bond of vinyl ethers into an Si−H bond of $PhMe_2SiH$.

Results of the reactions changing the ratio of **1**, $PhMe_2SiH$, and the monomer (isobutyl or *tert*-butyl vinyl ether) are summarized in Table 1, entries 3−12. The polymerization of isobutyl vinyl ether tended to proceed slower than that of *tert*-butyl vinyl ether. The polymers of M_n = ca. 10 000 were formed in the experiments with the silane/monomer ratios of 1:5 to 1:100 for isobutyl vinyl ether and those of 1:5 to 1:200; this indicates that only a part of the charged hydrosilane was used for the polymerization.

The rate of the reaction was dependent on the combination of vinyl ether and silane as shown in Table 2 and was $EtMe_2SiH > Et_2MeSiH > PhMe_2SiH > (HSiMe_2CH_2)_2$ with isobutyl vinyl ether, whereas it was $PhMe_2SiH = (HSiMe_2CH_2)_2 > Et_2MeSiH = EtMe_2SiH$ with *tert*-butyl vinyl ether. When the charged ratio of **1**/silane/monomer is 1:100:1000, the polymerization is completed in a few minutes to 3 h to form the polymer of M_n = 10 000−20 000. Interestingly, alkoxysilanes can be used for polymerization as shown in entries 9−11, though the reaction is slower than $PhMe_2SiH$. This is in sharp contrast to the fact that alkoxysilanes exhibited no reactivity in our earlier studies on the polymerization of cyclic ethers.

Table 3. $PhMe_2SiH$-Induced Polymerization of *tert*-Butyl Vinyl Ether Dependent on the Solvent Used for Preactivation of the Catalyst[a]

entry	solvent	time (min)	conv[b] (%)	yield[c] (%)	M_n	M_w/M_n
1	none	60	86	70	25 000	1.6
2	dioxane	5	96	92	9000	1.4
3	benzene	60	91	83	15 000	1.5
4	toluene	120	90	78	14 000	1.5
5	ether	120	89	79	14 000	1.7
6	THP	1	95	85	9000	1.2
7	dichloromethane	15	95	80	14 000	2.0

[a] All reactions were carried out with *tert*-butyl vinyl ether (3.3 mmol) in minimum amounts of the solvent (56−140 μL) under an argon atmosphere at room temperature. The charged ratio of *tert*-butyl vinyl ether/silane/catalyst was 1000:100:1. [b] Conversion of the monomer determined by ^{1}H NMR. [c] Isolated yield of the polymer after precipitation.

Interestingly, the reaction rate and the molecular weight distribution of the formed polymer are sensitive to the solvent, which is used to dissolve the catalyst for its preactivation with hydrosilane, as shown in Table 3. In the absence of the solvent, the reaction mixture is heterogeneous at the initial stage due to poor solubility of the catalyst to the silane and the vinyl ether, which gradually became homogeneous. After 60 min, the conversion reached 86%. When the catalyst was dissolved in minimum amounts of the solvent shown in the table, the reaction was homogeneous from the initial stage to the end. Polar aprotic solvents such as dioxane, tetrahydropyrane (THP), and dichloromethane were effective for rapid polymerization, whereas slower reaction occurred in benzene, toluene, and ether. We could not use THF, because its polymerization took place concomitantly.

It is noteworthy that the polymerization of *tert*-butyl vinyl ether in THP afforded poly(*tert*-butyl vinyl ether) with narrow molecular weight distribution (M_w/M_n = 1.2), which may indicate the living nature of this polymerization; however, the following results support that hydrosilanes act as a chain transfer reagent in the polymerization. First, the molecular weights of the formed polymer determined by GPC (M_n = 9000 and M_w = 11 000) and estimated from the integral ratio of the peaks due to the organosilyl group to those due to the polymer chain in the ^{1}H NMR of the polymer (M_n = 3900) are apparently larger than the molecular weight of the polymer formed by the catalyst-induced living polymerization (the charged ratio of **1**/$PhMe_2SiH$/

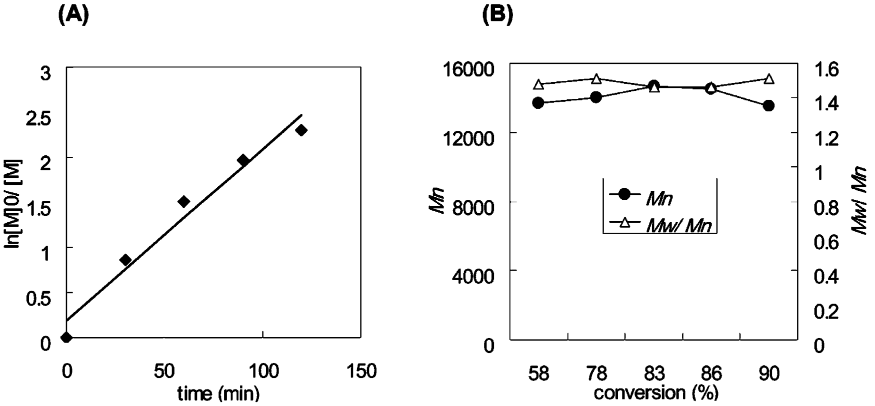

Figure 1. (A) Plot of ln$[M]_0$/[M] vs time, where $[M]_0$ and [M] are the concentration of *tert*-butyl vinyl ether at time = 0 and *t*. (B) Dependence of the molecular weight and polydispersity of poly(*t*-BVE) on the monomer conversion. All reactions were carried out with *tert*-butyl vinyl ether (3.3 mmol) in toluene (140 μL) under an argon atmosphere at room temperature. The charged ratio of *tert*-butyl vinyl ether/silane/catalyst was 1000:100:1.

^{t}BuOCH=CH$_2$ = 1:100:1000; the estimated M_n should be 100 000). Second, the M_n of the polymer is independent of the conversion of the monomer. Since the polymerization of *tert*-butyl vinyl ether in THP is too rapid to measure the conversion/M_n relationship, the relatively slow reaction in toluene was monitored as shown in Figure 1 (A and B). The conversion of the monomer reached 100% after 2 h, but the M_n (ca. 14 000) and M_w/M_n (ca. 1.4) were similar at the conversion = 58, 78, 83, 86, and 90%. The reason that small M_w/M_n are achieved may be attributed to the very high rate of the polymerization of *tert*-butyl vinyl ether, but details are not clear at present. Involvement of chain transfer reactions is suggested in the polymerization induced by other hydrosilanes; for example, the number of inserted vinyl ethers was decreased when larger amounts of PhMe$_2$SiH were added as shown in entries 5 (silane/monomer = 1:1) and 12 (silane/monomer = 10:1) in Table 1.

Several other factors, which may affect the feature of polymerization, were also studied with the charged ratio of **1**/PhMe$_2$SiH/monomer = 1:100:1000 in dioxane. First, the temperature effect is not easy to understand: in the polymerization of isobutyl vinyl ether, the reaction at 60 °C somewhat contributed to decreasing the reaction time (40 min; 99% conv) to form the polymer with smaller molecular weight (M_n = 6500) and wider molecular weight distribution (M_w/M_n = 3.4). In the polymerization of *tert*-butyl vinyl ether in THP, the polymerization at 0 °C, rt, and 40 °C proceeded within 5 min to give the polymer of M_n = 7000, 9000, and 8300, respectively, but the narrowest molecular weight distribution was observed at room temperature (M_w/M_n = 1.2 at rt; 1.7 at 0 and 40 °C). Other ruthenium cluster catalysts, which are active toward hydrosilylation of carbonyl compounds and ring-opening polymerization of cyclic ethers,[8] also catalyzed the slow polymerization of *tert*-butyl vinyl ether at room temperature. With (μ_3,η-4,6,8-trimethylazulene)Ru$_3$(CO)$_7$ (**2**), the conversion reached 92% after 2.5 h to give the polymer of M_n = 13 000 and M_w/M_n = 1.8 in 80% yield. With (μ_3,η-guaiazulene)Ru$_3$(CO)$_7$ (**3**), the conversion after 36 h was 77% to afford the polymer of M_n = 10 000 and M_w/M_n = 1.8 in 68% yield. As noted in the Introduction, Co$_2$(CO)$_8$ and H$_2$PtCl$_6$·6H$_2$O were reported to catalyze the polymerization of vinyl ethers.[7] Polymerization of *tert*-butyl vinyl ether with Co$_2$(CO)$_8$ is complete in 5 min at room temperature to form the polymer with M_n = 7000 having large molecular weight distribution (M_w/M_n = 2.8), whereas no reaction took place with H$_2$PtCl$_6$·6H$_2$O. As seen in the polymerization of THF, **1** was active at lower catalyst concentration. For example, when a dioxane solution of **1** (2.1 mg in 20 μL of dioxane) was treated with PhMe$_2$SiH (100 equiv to **1**) and *tert*-butyl vinyl ether (10 000 equiv to **1**), conversion reached 84% after 10 min to give the polymer with M_n = 10 000, M_w/M_n = 1.8 (73% isolated yield), while Co$_2$(CO)$_8$ was inactive under the same conditions.

End Group Analysis of the Polymer. As described in the Introduction, it was reported that Co$_2$(CO)$_8$ catalyzed polymerization of vinyl ethers or isomerization/vinyl polymerization of diallyl ethers by the catalysis of Co$_2$(CO)$_8$ in the presence of hydrosilanes.[3-5] In these reports, formation of polyvinyl ether bearing an organosilyl group at the polymer end, R$_3$Si$-$(CH$_2$CHOR)$_n-$H, was postulated without clear evidence. In our earlier studies on the silane-induced ring-opening polymerization of cyclic ethers and a cyclic siloxane catalyzed by **1**, we proved formation of H$-$[(CH$_2$)$_m$O]$_n-$SiR$_3$ (m = 2$-$4) and H$-$[Me$_2$Si(CH$_2$)$_2$-Me$_2$SiO]$_n-$SiR$_3$ by isolation of low molecular weight polymers and careful analysis of their NMR spectra. Although the end group analysis of poly(*tert*-butyl vinyl ether) obtained by the method described above was hampered due to overlapping of ^{13}C resonances, that of poly(isobutyl vinyl ether) provided evidence for the polymer structure of R$_3$Si$-$(CH$_2$CHOR)$_n-$H. Low molecular weight polyvinyl ether, PhMe$_2$Si$-$(CH$_2$CHO^{i}Bu)$_n-$H, suitable for the NMR analysis was prepared from **1**, PhMe$_2$SiH, and isobutyl vinyl ether (1:1000:1000) at room temperature, of which M_n = 2000, M_w/M_n = 1.8. ^{1}H and ^{13}C NMR spectra of the polymer in CD$_2$Cl$_2$ revealed the existence of a peak due to Ph and Me groups attached to the silicon atom at δ_H 7.46$-$7.64, 7.21$-$7.41 (m) and δ_C 128.15, 129.20, 134.01, and 140.04, and δ_H 0.31 (s), δ_C $-$2.73, respectively, as expected (Figure 2). A ^{29}Si signal appeared around δ_{Si} $-$4.5. For comparison, a 1:1 adduct of PhMe$_2$SiH and isobutyl vinyl ether, PhMe$_2$SiCH$_2$CH$_2$O^{i}Bu, was prepared by treatment of a large excess amount of PhMe$_2$SiH with isobutyl vinyl ether, and ^{1}H and ^{13}C resonances are completely assigned by two-dimensional

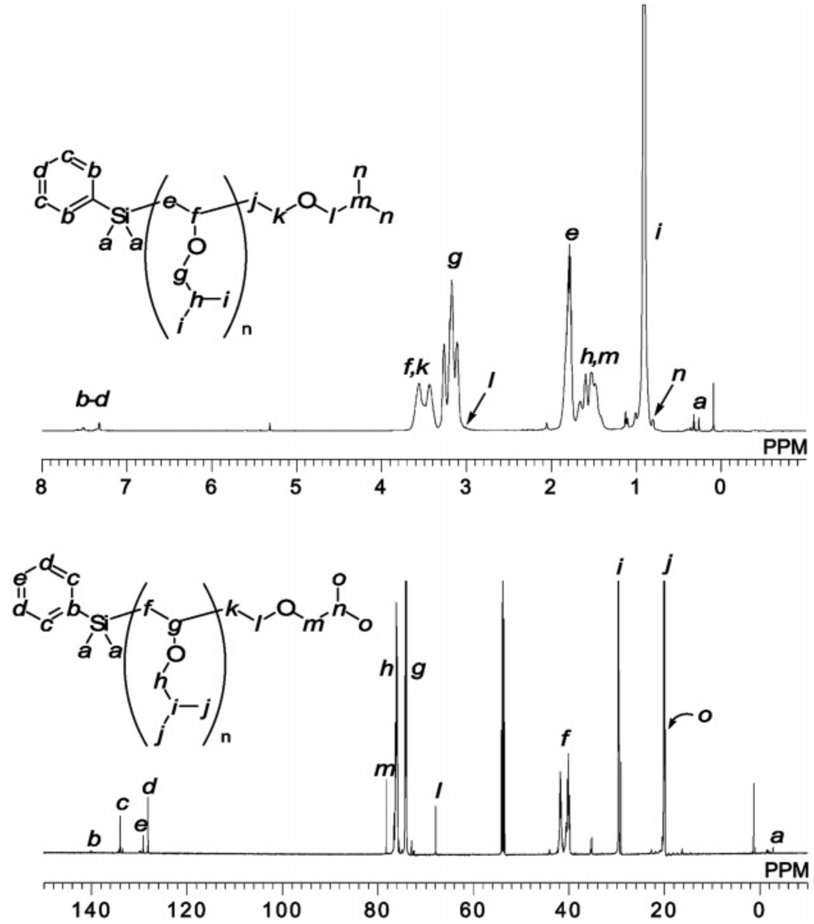

Figure 2. NMR spectra of $PhMe_2Si(CH_2CHO^iBu)_nH$ ($M_n = 2000$) in CD_2Cl_2.

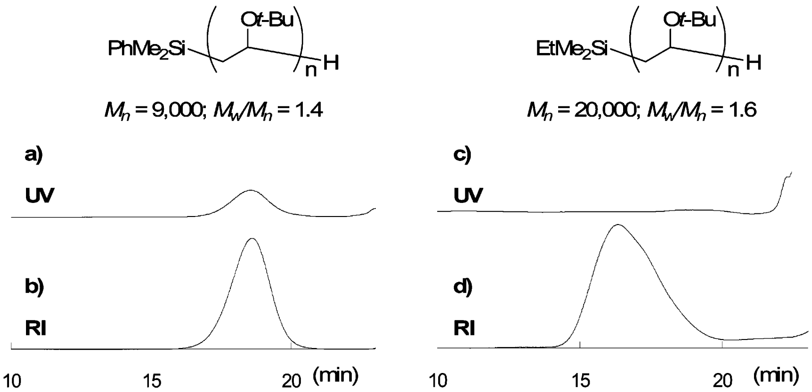

Figure 3. End group analyses by GPC (R = ^{t}Bu).

NMR; the details are shown in the Experimental Section. The spectral features of the polymers described above due to the $PhMe_2Si$ group are in accord with those seen in the NMR spectra of the 1:1 adduct, where $\delta_H = 7.50-7.53$, $7.31-7.35$ (m), and 0.29 (s); $\delta_C = 128.01$, 129.15, 133.89, 139.56, and −2.59; δ_{Si} −4.3. NMR signals due to the other part of the polymers were also reasonably assigned in comparison with the spectra of the 1:1 adduct.

Further evidence to support the existence of a $PhMe_2Si$ group in the polymer was obtained from UV and RI detection of GPC. A sample of poly(*tert*-butyl vinyl ether) ($M_n = 10\,000$, $M_w/M_n = 1.4$) was prepared by $PhMe_2SiH$ as the initiator, of which GPC charts detected by UV and RI are shown in parts a and b in Figure 3. In both these chromatograms, the same shape of the signal was observed. In contrast, GPC charts of the poly(*tert*-butyl vinyl ether) prepared by the $EtMe_2SiH$-induced polymerization of *tert*-butyl vinyl ether [$M_n = 20\,000$, $M_w/M_n = 1.6$; (c) = UV detection, (d) = RI detection] were different from the charts (a) and (b) in the points that no peak was seen in (c), whereas a signal appeared in (d). These apparently showed that the polymer prepared by the $PhMe_2SiH$-induced polymerization contained phenyl groups homogeneously.

The above results strongly suggest the existence of an organosilyl group in the polymer chain and support the proposed polymer structure $R_3Si-(CH_2CHOR)-H$. Other support for this structure was obtained from the

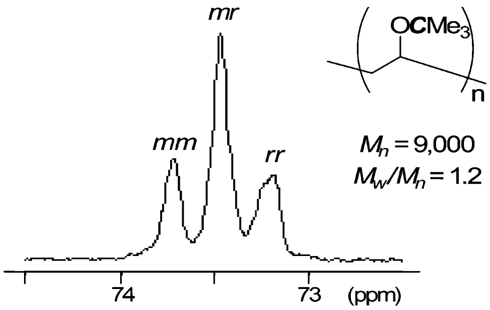

Figure 4. ^{13}C NMR (150 MHz, toluene-d_8) spectrum of poly(*t*-BVE) at 95 °C.

polymerization of *tert*-butyl vinyl ether induced by PhMe$_2$Si−D. A ^{13}C signal due to the methylene group, −*C*H$_2$O^{t}Bu, at the polymer end is visible at δ 67.77−68.02. In contrast, the signal due to the −*C*HDO^{t}Bu showed higher field shift by 0.5 ppm (δ 67.27−67.76), appearing as a broad triplet with J_{HD} = 18.43 Hz. This clearly demonstrates the ^{13}C signal due to −*C*DHO^{t}Bu, providing evidence for the polymer structure, R$_3$Si−(CH$_2$CHOR)−*D*.

Stereoregularity. Tacticity of polyvinyl ethers has received considerable attention from polymer chemists, because the stereoregularity of polyvinyl ethers seriously affects their physical properties.[11] Attempted control of the streoregularity by design of the catalyst and the selection of the monomer has been made by Brönstead acids,[11a,b] Lewis acids including “designed” titanium phenoxides,[12] and metallocene/methylaluminoxane catalysts;[13] some of them give isotactic-rich polymers effectively.[13] Stereoregularity of the polymers formed by the method presented in this paper was determined by ^{13}C NMR, in which assignment of the peaks was carried out in comparison with the literature data.[12,13] As a representative example, a ^{13}C NMR spectrum of poly(*tert*-butyl vinyl ether) of M_n = 9000 and M_w/M_n = 1.2 is shown in Figure 4. The diad *m* sequence is 40%, whereas triad *mm*, *mr*, and *rr* are 24, 51, and 25, respectively. Treatment of the formed poly(*tert*-butyl vinyl ether) (M_n = 9000, M_w = 11 000, M_w/M_n = 1.2) with iodotrimethylsilane instantly resulted in deprotection of the alcohol function,[11b] and poly(vinyl alcohol) was obtained quantitatively. ^{1}H NMR of the formed poly(vinyl alcohol) in dry DMSO-d_6 provided further information on the stereoregularity from the ^{1}H resonances due to the O−H groups, which appeared at δ 4.16−4.26 (*rr*), 4.39−4.52 (*mr*, br), and 4.61−4.72 (*rr*) in an integral ratio of 21:55:24, which is almost identical with that obtained from the ^{13}C NMR data of poly(*tert*-butyl vinyl ether). Stereoregularity of the other polymers is compared with representative reported data catalyzed by titanium-based Lewis acid as summarized in Table 4. In all cases, the ruthenium-catalyzed process did not give the polymer with high isotacticity (meson dyad = 48−61%). The experiments changing the organosilanes provided little difference in stereoregularity of the formed poly(*tert*-butyl vinyl ether). The solvent effect was also not significant as long as THP, ether, toluene, or dichloromethane was used instead of dioxane, though it should be noted that the amount of these solvents was small.

Mechanistic Consideration. We previously proposed the mechanism involving a [Ru$_3$−H]$^-$···(SiR$_3$)$^+$ ion pair in the silane-induced ring-opening polymerization of cyclic ethers or a cyclic siloxane.[8] Activation of the oxygen atom of the monomer by the R$_3$Si$^+$ species initiated the polymerization, which was terminated by hydride transfer from the ruthenium hydride. A similar mechanism can be adopted for the explanation of the silane-induced polymerization of vinyl ethers as shown in Scheme 3, which is supported by spectral evidence for the existence of an R$_3$Si group in the polymer as well as incorporation of a deuterium atom at the polymer end in the experiment with R$_3$Si−D. The process involves chain transfer reaction to R$_3$SiH, and hence the molecular weight distribution observed is, in many cases, around 2.0. Of particular interest is M_w/M_n = 1.2−1.4 of the poly(*tert*-butyl vinyl ether) obtained by this ruthenium-catalyzed reaction, though the polymerization involves a chain transfer process. Such a narrow molecular weight distribution was not achieved with Co$_2$(CO)$_8$, and further investigation is awaited to explain this phenomenon. There is a problem whether the polymer end active in propagation may interact with the ruthenium species. Although this could be seen in the stereoregularity, the present results did not suggest any clear evidence and more detailed experiments changing the structures of the ruthenium catalysts are necessary.

3. Conclusion

As described above, **1** is a good catalyst for the silane-induced polymerization of vinyl ethers. In particular, polymerization of *tert*-butyl vinyl ether takes place in a few minutes, and the polymers, of which $M_n = 10^3$ and $M_w/M_n < 1.4$, are obtained in high yields. Significant isotacticity is not observed regardless of the monomer used, and heterotacticity is predominant. Of importance is the end group of the polymer; detailed spectroscopic analyses and the results using PhMe$_2$SiD reveal that the structure of the polymer is R_3Si−(CH$_2$CHOR)$_n$−H, indicating that the reaction involves multiple insertion of vinyl ethers between an Si−H bond activated by the ruthenium cluster. This actually brings about possible extension of this chemistry by way of further chemical transformation of the organosilyl group at the polymer end;[14,15] in particular, possible usage of alkoxysilanes actually opens the way to functional polymers.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere. Solvents were distilled in the presence of standard drying reagents (1,4-dioxane, ether, THP, benzene, toluene, hexane, and benzene-d_6; benzophenone ketyl: CDCl$_3$, CD$_2$Cl$_2$; CaH$_2$) and stored under an argon atmosphere. Vinyl ethers and other reagents were distilled just before use. NMR spectra were taken with a JEOL Lambda 400 or 600 spectrometer. Chemical shifts were recorded in ppm from the internal standard (^{1}H, ^{13}C: solvent) or the external standard (^{29}Si: tetramethylsilane). Assignments of the NMR signals were performed with the aid of DEPT and

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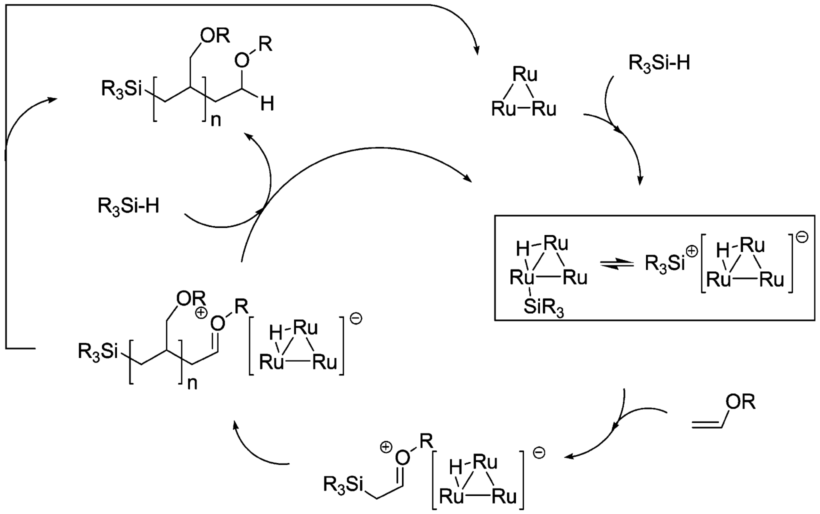
Table 4. Comparison in Tacticity

	monomer	catalyst	M_n	M_w/M_n	triad *mm*:*mr*:*rr*	dyad *m*:*r*
1	^{t}BuVE	$(ACE)Ru_3(CO)_7/PhMe_2SiH$	9000	1.2	24:51:25	50:50
2		$CpTiCl_3/MAO^a$	6300	2.03	28:48:24	52:48
3		$TiCl_2\text{-}\{OC_6H_4(^iPr)_2(2,6\text{-})\}_2{}^b$	57 600	2.19	49:41:10	69:31
4	^{i}BuVE	$(ACE)Ru_3(CO)_7/PhMe_2SiH$	2000	1.8	50:43:7	61:39
5		$CpTiCl_3/MAO^a$	44 100	3.50		65:35
6		$TiCl_2\text{-}\{OC_6H_4(^iPr)_2(2,6\text{-})\}_2{}^b$	36 500	2.01	83:10:7	90:10
7	^{n}BuVE	$(ACE)Ru_3(CO)_7/PhMe_2SiH$	12 000	2.1	32:50:18	57:43
8		$TiCl_2\text{-}\{OC_6H_4(^iPr)_2(2,6\text{-})\}_2{}^b$	25 800	2.72	56:35:9	76:24
9	^{i}PrVE	$(ACE)Ru_3(CO)_7/PhMe_2SiH$	10 000	2.8	21:54:25	48:52
10		$TiCl_2\text{-}\{OC_6H_4(^iPr)_2(2,6\text{-})\}_2{}^b$	110 000	3.96	83:11:6	88:12

[a] Ref 12. [b] Ref 13. [c] All of the tacticity data were determined by ^{13}C NMR.

Scheme 3. Proposed Catalytic Cycle of the Silane-Induced Vinyl Ether Polymerization



2D [^{1}H−^{1}H, ^{1}H−^{13}C COSY] techniques. IR spectra were recorded in cm^{-1} on a JASCO FT/IR-550 spectrometer. GPC analyses of the polymers were performed with a JASCO 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 a Shodex GPC-KF-804L connected with a GPC KF-805L in THF. Calibration was carried out on the basis of retention time of a standard sample of polystyrene (8 samples ($M_w/M_n = 1.07$), of which the M_n range is 1.31×10^3 to 3.85×10^6). The ruthenium clusters **1**, **2**, and **3** were prepared by the methods reported previously. $Co_2(CO)_8$ and $H_2PtCl_6 \cdot 6H_2O$ were purchased from commercial sources.

General Procedures for the Polymerization of Vinyl Ethers. The general procedure for the polymerization and two typical examples are as follows: In a 30 mL two-necked flask fitted with a three way stopcock, **1** (2.1 mg, 3.3 μmol) was dissolved in a solvent (56 μL). To this solution, $PhMe_2SiH$ was added via a syringe and the solution was stirred for 30 min at room temperature. Initial dark orange color of the solution gradually faded to light orange. Then, vinyl ether was added and the solution was stirred at room temperature. After the reaction was completed, volatiles were removed in vacuo. Hexane solution of the residue was poured into methanol to precipitate the polymer. *Example 1.* The reaction was carried out with $PhMe_2SiH$ (50 μL, 0.33 mmol) and $^tBuOCH{=}CH_2$ (0.43 mL, 3.3 mmol) in dioxane (56 μL). The reaction was completed almost instantly to yield the corresponding polymer (conv. 96%, yield 92%, $M_n = 9000$, $M_w = 13\,000$, $M_w/M_n = 1.4$). *Example 2.* The reaction was carried out with $(EtO)Me_2SiH$ (45 μL, 0.33 mmol) and $^tBuOCH{=}CH_2$ (0.43 mL, 3.3 mmol). The solution was stirred at room temperature for 10 min to yield the corresponding polymer (conv 88%, yield 87%, $M_n = 10\,000$, $M_w = 17\,000$, $M_w/M_n = 1.7$).

Representative NMR Data of the Polymer (all measurements were carried out in C_6D_6 at room temperature). $PhMe_2Si(CH_2CHOiPr)_nH$ ($M_n = 10\,000$, $M_w = 28\,000$, $M_w/M_n = 2.8$). ^{1}H NMR (395 MHz, C_6D_6, rt), signals due to the polymer chain: δ 0.94−1.40 (br, 6H, CH_3 of ^{i}Pr), 1.56−2.19 (br, 2H, CH_2), 3.35−4.07 (br, 2H, CH−O−CH). Small peaks due to the terminal silyl group were visible at δ 0.25 (s, 6H, SiMe), 7.21−7.37 (m, 3H, SiPh), 7.49−7.62 (m, 2H, SiPh). ^{13}C NMR (99 MHz, C_6D_6, rt), only the signals due to the polymer chain were observed: δ 22.64−24.03 (CH$_3$ of ^{i}Pr), 41.29−43.20 (CH$_2$), 70.93−72.59 and 67.86−69.54 (CH−O−CH).

$PhMe_2Si(CH_2CHO^nBu)_nH$ ($M_n = 12\,000$, $M_w = 25\,000$, $M_w/M_n = 2.1$). ^{1}H NMR (395 MHz, C_6D_6, rt), signals due to the polymer chain: δ 0.77−1.02 (br, 3H, CH_3 of ^{n}Bu), 1.32−1.50 (br, 2H, CH_2CH$_3$ of ^{n}Bu), 1.50−1.66 (br, 2H, CH_2CH$_2$CH$_3$ of ^{n}Bu), 1.66−2.15 (br, 2H, CH_2 of the polymer chain), 3.23−3.95 (br, 3H, CH-O−CH_2). Small peaks due to the terminal silyl group were visible at δ 0.34 (s, 6H, SiMe), 7.57−7.62 (m, 2H, SiPh), 7.29−7.40 (m, 3H, SiPh). ^{13}C NMR (99 MHz, C_6D_6, rt), only the signals due to the polymer chain were observed: δ 14.25 (CH_3 of ^{n}Bu), 20.10 (CH$_3$$CH_2$ of ^{n}Bu), 32.99 (CH$_3$CH$_2$$CH_2$ of ^{n}Bu), 39.16−41.10 and 41.10−42.63 (CH_2 of the polymer chain), 67.96−69.46 (CH of the polymer chain), 73.74−74.57 (OCH$_2$ of ^{n}Bu).

$PhMe_2Si(CH_2CHO^iBu)_nH$ ($M_n = 2000$, $M_w = 3600$, $M_w/M_n = 1.8$). ^{1}H NMR (600 MHz, CD_2Cl_2, rt), signals due to the polymer chain: δ 0.80−0.98 (br, 6H, CH_3 of ^{i}Bu), 1.25−1.49 (br, 2H, CH_2 of the polymer chain), 1.34−1.72 and 1.70−1.92 (br, 2H, CH of ^{i}Bu and CH_2 of the polymer chain), 3.00−3.33 (br, 2H, OCH_2), 3.33−3.68 (br, 1H, OCH of the polymer chain). Small peaks due to the terminal silyl group were visible at δ 0.31 (s, 6H, SiMe), 7.45−7.64 (m, 2H, SiPh), 7.23−7.44 (m, 3H, SiPh). ^{13}C NMR (150 MHz, CD_2Cl_2, rt), signals due to the polymer chain: δ 19.65−20.57 (CH_3 of ^{i}Bu), 29.21−30.05 (CH of ^{i}Bu), 39.65−41.11 and 41.11−42.34 (CH_2 of the polymer chain), 67.86−68.10 (CH$_2$O^{i}Bu at the polymer terminal), 73.89−74.51 (CH of the polymer chain), 75.78−76.80 (OCH_2 of ^{i}Bu), 78.27 ($CH_2OCH_2{}^iPr$ at the polymer terminal). Peaks due to the terminal silyl group were visible at δ −2.87−2.68 (SiMe), 128.17, 129.23, 133.81−134.21, 140.04 (SiPh).

$PhMe_2Si(CH_2CHO^tBu)_nH$ (M_n = 9000, M_w = 13 000, M_w/M_n = 1.4). ^{1}H NMR (600 MHz, CD_2Cl_2, rt), signals due to the polymer chain: δ 1.11−1.34 (br, 9H, CH_3 of ^{t}Bu), 1.38−1.88 (br, 2H, CH_2 of the polymer chain), 3.42−3.80 (br, 1H, CH of the polymer chain). Small peaks due to the terminal silyl group were visible at δ 0.32 (s, 6H, SiMe), 7.27−7.41 (m, 3H, SiPh), 7.46−7.65 (m, 2H, SiPh). ^{13}C NMR (150 MHz, CD_2Cl_2, rt), signals due to the polymer chain: δ 28.68−30.60 (CH_3 of ^{t}Bu), 44.79−48.08 (CH_2 of the polymer chain), 66.44−68.73 (CH of the polymer chain), 72.81−74.30 (*C* of ^{t}Bu). Peaks due to the terminal silyl group were visible at δ −2.34(Ca), 127.79−128.40, 129.29−130.11, 133.02−134.30, 140.0 (SiPh).

$EtMe_2Si(CH_2CHO^tBu)_nH$ (M_n = 18 000, M_w = 29 000, M_w/M_n = 1.6). Peaks due to the terminal silyl group were not visible. ^{1}H NMR (600 MHz, C_6D_6, rt), signals due to the polymer chain: δ 1.12−1.54 (br, 9H, CH_3 of ^{t}Bu), 1.76−2.22 (br, 2H, CH_2 of the polymer chain), 3.77−4.00 (br, 1H, CH of the polymer chain). ^{13}C NMR (150 MHz, C_6D_6, rt), signals due to the polymer chain: δ 29.60−30.37 (CH_3 of ^{t}Bu), 45.46−47.15 (CH_2 of the polymer chain), 66.91−68.64 (*C*H of the polymer chain), 72.90−73.80 (*C* of ^{t}Bu).

$Et_2MeSi(CH_2CHO^tBu)_nH$ (M_n = 20 000, M_w = 32 000, M_w/M_n = 1.6). Peaks due to the terminal silyl group were not visible. ^{1}H NMR (600 MHz, C_6D_6, rt), signals due to the polymer chain: δ 1.18−1.53 (br, 9H, CH_3 of ^{t}Bu), 1.76−2.25 (br, 2H, CH_2 of the polymer chain), 3.72−4.15 (br, 1H, CH of the polymer chain). ^{13}C NMR (150 MHz, C_6D_6, rt), signals due to the polymer chain: δ 28.92−30.75 (CH_3 of ^{t}Bu), 45.37−47.12 (CH_2 of the polymer chain), 66.83−68.84 (*C*H of the polymer chain), 72.82−74.02 (*C* of ^{t}Bu).

$EtOMe_2Si(CH_2CHO^tBu)_nH$ (M_n = 10 000, M_w = 17 000, M_w/M_n = 1.7). ^{1}H NMR (600 MHz, C_6D_6, rt), signals due to the polymer chain: δ 1.19−1.46 (br, 9H, CH_3 of ^{t}Bu), 1.68−2.25 (br, 2H, CH_2 of the polymer chain), 3.70−4.09 (br, 1H, CH of the polymer chain). Peaks due to the terminal silyl group were visible at δ 0.25 (s, 3H, SiMe), 1.13 (t, *J* = 7.14 Hz, 3H, CH_3CH_2O), 3.65 (q, *J* = 7.14 Hz, 2H, CH_3CH_2O). ^{13}C NMR (150 MHz, C_6D_6, rt), signals due to the polymer chain: δ 28.61−30.47 (CH_3 of ^{t}Bu), 45.14−47.29 (CH_2 of the polymer chain), 66.71−68.73 (*C*H of the polymer chain), 72.69−73.95 (*C* of ^{t}Bu). Peaks due to the terminal silyl group were visible at δ −2.94 (SiMe), 18.64 (OCH_2CH_3), 57.76−58.11 (OCH_2CH_3).

$(EtO)_2MeSi(CH_2CHO^tBu)_nH$ (M_n = 7000, M_w = 15 000, M_w/M_n = 2.2). ^{1}H NMR (600 MHz, C_6D_6, rt), signals due to the polymer chain: δ 1.03−1.48 (br, 9H, CH_3 of ^{t}Bu), 1.65−2.17 (br, 2H, CH_2 of the polymer chain), 3.64−3.99 (br, 1H, CH of the polymer chain). Peaks due to the terminal silyl group were visible at δ 0.20 (s, 3H, SiMe), 1.12 (t, *J* = 7.14 Hz,3H, OCH_2CH_3), 3.72 (q, *J* = 7.14 Hz, 2H, OCH_2CH_3). ^{13}C NMR (150 MHz, C_6D_6, rt), signals due to the polymer chain: δ 30.00 (CH_3 of ^{t}Bu), 45.37−47.18 (CH_2 of the polymer chain), 66.61.−68.72 (CH of the polymer chain), 72.67−74.17 (*C* of ^{t}Bu). Peaks due to the terminal silyl group were visible at δ −4.29 (SiMe), 18.54 (OCH_2CH_3), 57.83−58.57 (OCH_2CH_3).

$(EtO)_3Si(CH_2CHO^tBu)_nH$ (M_n = 9000, M_w = 22 000, M_w/M_n = 2.4). ^{1}H NMR (600 MHz, C_6D_6, rt), signals due to the polymer chain: δ 1.04−1.50 (br, 9H, He), 1.64−2.23 (br, 2H, Hc), 3.68−4.07(br, 1H, Hd). Peaks due to the terminal silyl group were visible at δ 1.16 (t, *J* = 7.14 Hz, 3H, Ha), 3.87 (t, *J* = 6.59 Hz, 2H, Hb). ^{13}C NMR (150 MHz, C_6D_6, rt), signals due to the polymer chain: δ 28.38−30.59 (CH_3 of ^{t}Bu), 44.46−48.24 (CH_2 of the polymer chain), 66.63−68.63 (CH of the polymer chain), 72.74−73.88 (*C* of ^{t}Bu). Peaks due to the terminal silyl group were visible at δ 23.00 (OCH_2CH_3), 59.24 (OCH_2CH_3).

Hydrolysis of Poly(*tert*-butyl vinyl ether). In a 5 cm ∅ NMR tube, $PhMe_2Si(CH_2CHO^tBu)_nH$ (37 mg, M_n = 9000, M_w = 11 000, M_w/M_n = 1.2) was dissolved in benzene-d_6 (0.5 mL). To this solution was added Me_3SiI (64 μL, 0.48 mmol). Deprotection of the *tert*-butyl group was complete within 30 min, which was confirmed by the disappearance of the *tert*-butyl group in the polymer in ^{1}H NMR. Addition of methanol (0.25 mL) resulted in the formation of a white precipitate, which was isolated by filtration. The polymer was rinsed with methanol and dried in a vacuum overnight. The obtained poly vinyl alcohol was subjected to NMR analysis in dry dmso-d_6 at room temperature. ^{1}H NMR (600 MHz, DMSO-d_6, rt, 25 mg/mL), signals due to the polymer chain: δ 1.18−1.66 (br, 2H, CH_2 of the polymer chain), 3.73−3.98 (br, 1H, CH of the polymer chain), 4.16−4.26 (tacticity = *rr*, br, OH), 4.39−4.52 (tacticity = *mr*, br, OH), 4.61−4.72 (tacticity = *rr*, br, OH). ^{13}C NMR (150 MHz, DMSO-d_6, rt, 25 mg/mL): δ 44.46−46.32 (CH_2 of the polymer chain), 63.49−64.06 (tacticity= *rr*, *C*H of the polymer chain), 65.37−66.25 (tacticity = *mr*, *C*H of the polymer chain), 67.32−68.20 (tacticity = *mm*, *C*H of the polymer chain).

Hydrosilylation of ^{i}BuOCH═CH₂ to Give the 1:1 Adduct, ^{i}BuOCH₂CH₂SiMe₂Ph. In a 30 mL two-necked flask fitted with a three-way stopcock, **1** (2.1 mg, 3.3 μmol) was dissolved in dioxane (56 μL). To this solution was added $PhMe_2SiH$ (2.5 mL, 16.5 mmol) via a syringe, and the solution was stirred for 30 min at room temperature. The initial dark orange color of the solution gradually faded to light orange; then, ^{i}BuOCH═CH₂ (0.43 mL, 0.33 mmol) was added and the solution was stirred at room temperature. After 24 h, the conversion reached 30%. The reaction mixture was concentrated, and the residue was purified by column chromatography (2.0 cm ∅ × 6.0 cm silica gel, Merck 7734). Fractions obtained by eluting with a 4:1 mixture of hexane/dichloromethane were concentrated to afford $PhMe_2SiCH_2CH_2(O^iBu)$ (156 mg, 20%) as a colorless oil. TLC: R_f = 0.32 (a 4:1 mixture of hexane/dichloromethane). IR (neat): 2955, 1427, 1249, 1174, 1112, 836, 821 cm^{-1}. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 0.29 (s, 6H, SiMe), 0.89 (d, *J* = 6.59 Hz, 6H, CH_3 of ^{i}Bu), 1.12 (m, 2H, $SiCH_2$), 1.78 (sept, *J* = 6.59 Hz, 1H, *CH* of ^{i}Bu), 3.09 (d, *J* = 6.59 Hz, 2H, OCH_2 of ^{i}Bu), 3.45 (m, 2H, $SiCH_2CH_2O$), 7.50−7.53 (m, 2H, SiPh), δ7.31−7.35 (m, 3H,SiPh). ^{13}C NMR (150 MHz,CD_2Cl_2): δ −2.59 (SiMe), 17.59 ($SiCH_2$), 19.59 (CH_3 of ^{i}Bu), 28.91 (*C*H of ^{i}Bu), 68.02 ($SiCH_2CH_2O$), 77.66 (OCH_2 of ^{i}Bu), 129.15 (SiPh), 128.01 (SiPh), 133.89 (SiPh), 139.56 (SiPh). ^{29}Si NMR (119 MHz, CD_2Cl_2): δ −4.3. Copies of ^{1}H and ^{13}C NMR spectra are shown in the Supporting Information. The assignment of these NMR data was carried out with the aid of H−H and C−H COSY experiments. Mass: 221 (M − CH_3), 222, 223 (intensity ratio = 100:20:5). HRMS: calcd for $^{12}C_{13}{}^1H_{21}{}^{16}O^{28}Si$ (M − 15), 221.1362; found, 221.1365. ESI-MS for $(M + Na)^+$: 259, 260, 261, 262 (intensity ratio = 100:25:25:3). Anal. Calcd for $^{12}C_{14}{}^1H_{24}{}^{16}O^{28}Si^{23}Na$: 259.1494. Found: 259.1492.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of poly(vinyl ether) and poly(vinyl alcohol), GPC charts of poly(*tert*-butyl vinyl ether), and EI and ESI mass spectra of ^{i}BuO(CH₂)₂SiMe₂Ph. This material is available free of charge via the Internet at http://pubs.acs.org.

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