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Silane-induced ring-opening polymerization of 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane catalyzed by a triruthenium cluster

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Abstract

The silane-induced ring-opening polymerization of a cyclic siloxane, 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane (**2**), is catalyzed by a ruthenium cluster, (μ_3,η^2:η^3:η^5-acenapthylene)$Ru_3(CO)_7$ (**1**), to give poly(tetramethylsilethylenesiloxane) with $M_n = 6300–780{,}000$ and $M_w/M_n = 1.5–3.0$. The molecular weight of the polymer can be controlled by changing the concentration of the monomer solution. Addition of acetone results in formation of the polymer with $M_n = 4400$, spectroscopic analysis of which reveals existence of a siloxy and an isopropoxy moieties at the end group.

Keywords: Ruthenium clusters; Hydrosilanes; Ring-opening polymerization; Cyclic siloxane; Poly(tetramethylsilethylenesiloxane)

1. Introduction

Activation of hydrosilanes by transition metal salts or complexes is known to lead to catalytic hydrosilylation of the unsaturated molecules, alkenes, alkynes, aldehydes, and ketones [1]. In our previous papers [2–4], we reported a triruthenium carbonyl cluster, (μ_3,η^2:η^3:η^5-acenaphthylene)$Ru_3(CO)_{12}$ (**1**), to be an efficient catalyst for hydrosilylation of ketones, aldehydes, esters, carboxylic acids, and amides. A striking feature of this catalyst different from that observed in other commonly used hydrosilylation catalysts such as Spier's catalyst and $RhCl(PPh_3)_3$ is that **1** is not only useful for addition of trialkylsilanes to carbon–oxygen double bonds but is also effective for the reduction of acetals and silane-induced ring-opening reduction of cyclic ethers [2]. The silane-induced ring opening polymerization catalyzed by **1** is a rare example of the transition metal-catalyzed production of polyalkylene oxides; a short paper appearing in 1970 reported that $Co_2(CO)_8$ catalyzed the ring-opening polymerization of THF in the presence of $HSiR_3$, and its extension to other monomers was investigated later [5]. The polymerization catalyzed by **1** is particularly of interest, because ring-opening polymerization of cyclic ethers can be accomplished by appropriate choice of reaction conditions to result in efficient production of polyalkylene oxide bearing siloxy and alkyl ends, $R_3SiO[(CH_2)_nO]_m(CH_2)_nCH_3$ [2], with relatively narrow molecular weight distribution. Since this ring-opening polymerization is a unique method for synthesis of polyalkylene oxides of which the end groups have been identified, we were interested in the possibility of catalytic ring-opening polymerization of other monomers.

A cyclic siloxane, 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (**2**), is a monomer which undergoes ring-opening polymerization to form polysilalkylene oxide [6]. The formed polysilalkylene oxide and its analogues have received attention from materials scientists as unique polymers with elastomeric, release, and electrical properties useful for encapsulants, rubber materials, and others [7]. The polymerization is usually conducted in the presence of anionic initiators [6]; however, there is no example of the transition-metal catalyzed polymerization of **2**. In this paper, we wish to report the first transition metal-catalyzed ring-opening polymerization

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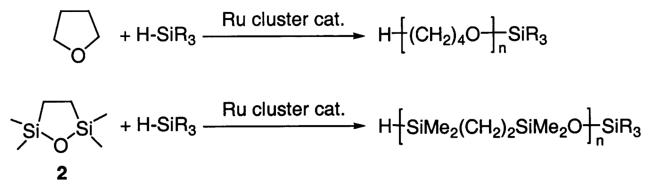


Scheme 1.

of **2**, in which the triruthenium carbonyl cluster **1** and its analogues catalyze the silane-induced ring-opening polymerization similar to the above described polymerization of cyclic ethers (Scheme 1). Of particular interest is that the ring-opening polymerization of cyclic ethers commonly proceeds with cationic initiators [8], whereas that of **2** does so by anionic initiators [6]. In sharp contrast, the trialkylsilanes activated by **1** polymerize both cyclic ethers and **2** in similar fashion. NMR analysis of the end group of the polymer revealed that the reaction proceeded through a similar mechanism to that operated in the silane-induced ring-opening polymerization of THF: the $-SiMe_2(CH_2)_2SiMe_2O-$ unit produced by ring opening of **2** is repeatedly inserted between the Si–H bond in the trialkylsilane.

2. Results and discussion

As reported earlier, the silane-induced ring-opening polymerization of cyclic ethers is achieved by catalysis of **1** (0.01 mol% to the cyclic ether) and $HSiR_3$ (1–10 mol% to the cyclic ether) in a glass tube sealed *in vacuo*. We first carried out the polymerization of **2** with similar procedures, and the results are summarized in Table 1. Ring opening polymerization of THF induced by $PhMe_2SiH$ was accomplished by the catalysis of **1** in a glass tube sealed *in vacuo* at 40 °C as reported previously [2], and two representative examples are shown in Table 1, entries 1 and 2. The polymer, $PhMe_2Si-[O(CH_2)_4]_n-O(CH_2)_3CH_3$, was obtained in 60–70% yield, dispersity of which was 1.5–2.5. The molecular weight of the polymer was dependent on the ratio of the silane to THF. We carried out the polymerization of **2** under the same conditions as those used for the THF polymerization shown in entry 3. After an induction period of several hours, the monomer was quickly consumed to form the polysilethylene siloxane, $-[OMe_2Si(CH_2)_2SiMe_2]_n-$ with $M_n = 780{,}000$ and $M_w/M_n = 3.0$ [9]. Because of low solubility of the catalyst, it is likely that the active species is hardly generated and a small amount of the formed catalytic species promotes the polymerization to form the polymer with large molecular weight. By performing the polymerization in a benzene solution, homogeneous polymerization occurred and polymers with relatively small molecular weight were obtained as shown in entries 4–7. In entry 4, a benzene solution of **2** (0.53 mol l^{-1}) underwent the $PhMe_2SiH$-induced polymerization catalyzed by **1** to form the polymer with $M_n =$ 62,000 ($M_w/M_n = 2.4$). Other solvents, $CHCl_3$ and Et_2O were not effective, whereas the polymerization behavior in toluene, dioxane or tetrahydropyran was similar to that in benzene. Presence of amine cocatalysts sometimes affects the reaction rate in ruthenium-catalyzed reactions of hydrosilanes [10], however, the presence of Et_3N (10 equivalents to **1**) completely inhibited the reaction in benzene. Addition of relatively large amounts of $PhMe_2SiH$ (one equivalent to **2**) was necessary to initiate the polymerization, presumably because excess amounts of $PhMe_2SiH$ are required to generate the catalytically active species in dilute solutions. A series of experiments changing the catalysts as shown in Fig. 1 showed that triruthenium clusters **3** and **5** were active towards the polymerization (entries 5 and 7), whereas $Ru_3(CO)_{12}$ was inactive. Although a tetraruthenium hydride cluster **4** was active for polymerization (entry 6), the activity was lower than that with **1**. The triruthenium cluster **5** was rather more active than **1**, however, the polymer obtained was multimodal. Other mono-, di-, and tetranuclear ruthenium complexes, (η^5-pentahydroguaiazulene)$Ru(CO)_2H$, $[CpRu(CO)_2]_2$, ($\mu_2,\eta^3:\eta^5$-guaiazulene)$Ru_2(CO)_5$, and (μ_3,η-guaiazulene)$Ru_4(CO)_9$ showed no catalytic activity. Other catalysts which are known to be active towards the hydrosilylation of unsaturated molecules [1], $RhCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$, and $Co_2(CO)_8$, were also inactive. The lack of activity of $Co_2(CO)_8$ is interesting considering the fact that it catalyzes the THF polymerization [5]. A catalyst for dehydrogenative

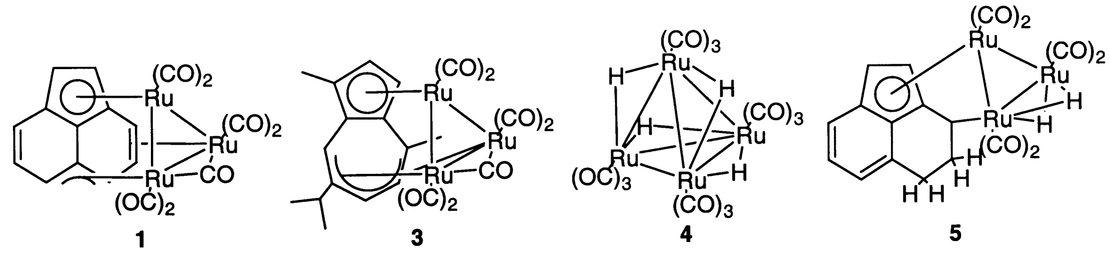


Fig. 1. Ruthenium clusters for the polymerization of **2**.

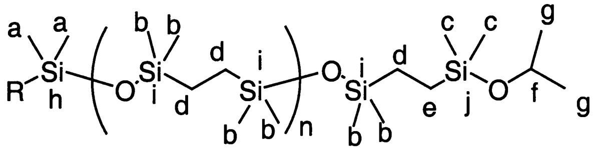
Table 1
Representative examples of the silane-induced polymerization of **2**

Entry	Method [a]	Silane	Solvent (concentration of monomer M (mol l^{-1}))	Monomer [monomer/silane ratio	cat. [mol%/**2** *r*]	Temperature (°C)	Time (h)	conv. of the monomer (%)	M_n (× 10^3)	M_w/M_n
1	A	$PhMe_2SiH$	Neat	THF [10]	**1** [0.01]	40	64	58	3.7	1.7
2	A	$PhMe_2SiH$	Neat	THF [100]	**1** [0.01]	40	20	72	27	2.5
3	A	$PhMe_2SiH$	Neat	**2** [100]	**1** [0.01]	40	12	100	780	(3.0) [b]
4	A	$PhMe_2SiH$	Benzene [0.53]	**2** [1]	**1** [0.1]	40	8	100	62	2.4
5	A	$PhMe_2SiH$	Benzene [0.53]	**2** [1]	**3** [0.1]	40	26	100	39	2.1
6	A	$PhMe_2SiH$	Benzene [0.53]	**2** [1]	**4** [0.1]	40	18	100	56	2.1
7	A	$PhMe_2SiH$	Benzene [0.53]	**2** [1]	**5** [0.1]	40	3.5	100	73	(3.3) [b]
8	A	$[HMe_2SiCH_2]_2$	Benzene [0.53]	**2** [1]	**1** [0.1]	40	4	100	130	2.3
9	A	$[HMe_2SiCH_2]_2$	Benzene [0.53]	**2** [10]	**1** [0.1]	40	13.5	100	124	3
10	A	$[HMe_2SiCH_2]_2$	Benzene [0.53]	**2** [100]	**1** [0.1]	40	17	100	157	1.8
11	A	$[HMe_2SiCH_2]_2$	Benzene [0.27]	**2** [1]	**1** [0.1]	40	10.5	100	62	2.7
12	A	$[HMe_2SiCH_2]_2$	Benzene [0.053]	**2** [1]	**1** [0.1]	40	34	80	7.6	1.5
13	A	$[HMe_2SiCH_2]_2$	Benzene [0.053]	**2** [10]	**1** [0.1]	40	40	82	33	1.8
14	B	$PhMe_2SiH$	Dioxane [neat]	THF [100]	**1** [0.01]	r.t.	7	15	109	2.5
15	B	$PhMe_2SiH$	Dioxane [2.36]	**2** [1]	**1** [0.1]	r.t.	6	100	6.3	(4.3) [b]
16	B	$[HMe_2SiCH_2]_2$	Dioxane [2.16]	**2** [1]	**1** [0.1]	r.t.	0.5	100	68	1.5
17	B	$[HMe_2SiCH_2]_2$	Dioxane [3.50]	**2** [10]	**1** [0.1]	r.t.	0.5	100	139	2.1
18	B	$[HMe_2SiCH_2]_2$	Dioxane [0.81]	**2** [1]	**1** [0.1]	r.t.	0.5	100	44	2.7
19	B	$EtMe_2SiH$	Dioxane [2.52]	**2** [1]	**1** [0.1]	r.t.	0.5	100	12	2.2
20	B	$[HMe_2SiCH_2]_2$	THP [2.16]	**2** [1]	**1** [0.1]	r.t.	0.5	100	55	1.6
21	B	$[HMe_2SiCH_2]_2$	THP [2.16]	**2** [1]	**1** [0.1]	−30	10	100	16	(2.8) [b]

[a] Method A; the reaction was done in a glass tube sealed *in vacuo*. Method B; the catalyst preactivated by the silane in the solvent was used for the polymerization.

[b] The polymer is multimodal.

Table 2
NMR data of the polymer formed in the presence of acetone



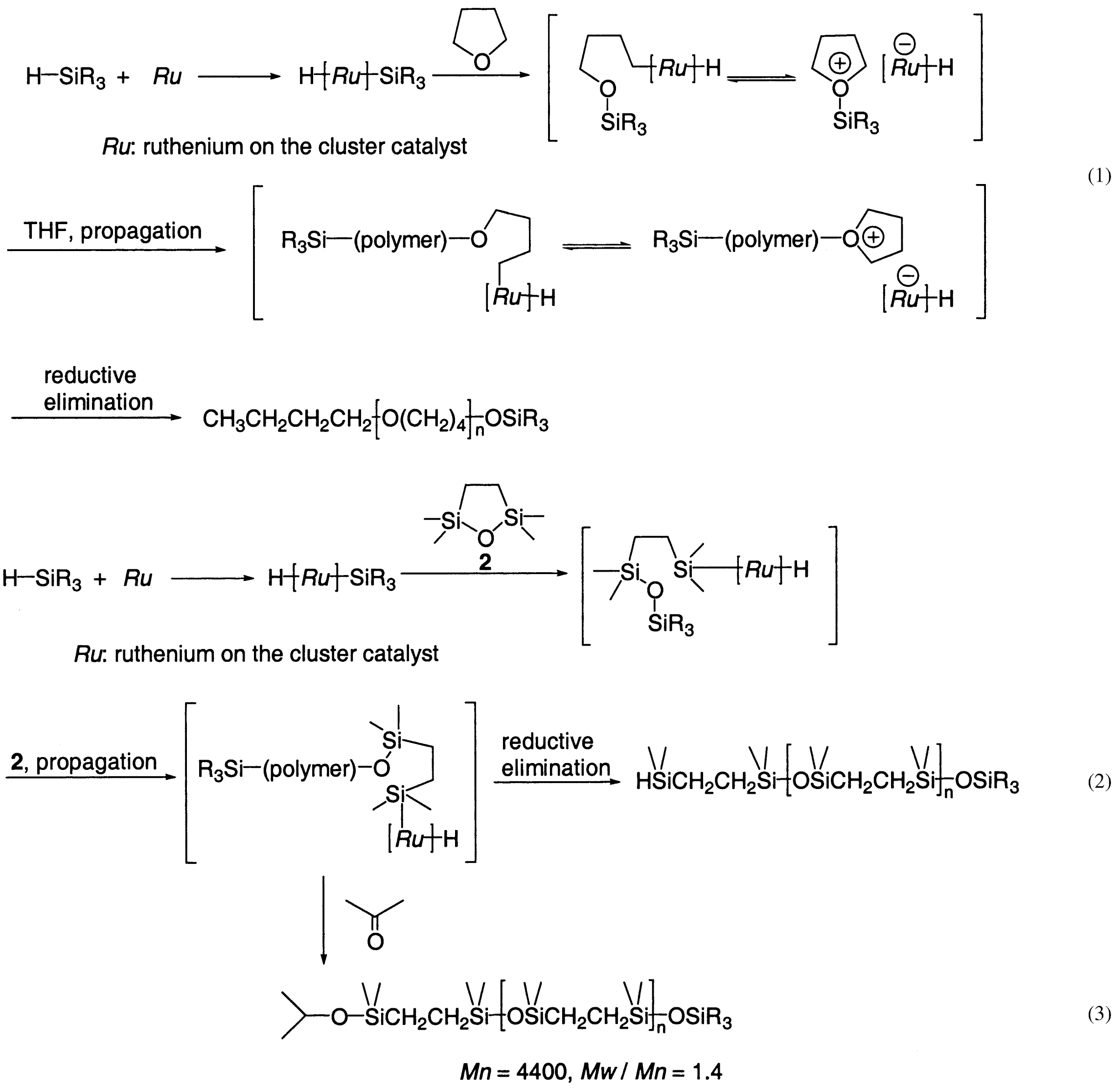
		R=Ph	R=Et			R=Ph	R=Et
^{1}H NMR	Me of a	0.36(br)	0.30(br)	^{13}C NMR	Me of a	1.02	1.17
	Me of b	0.20(br)	0.18(br)		Me of b	-0.03	-0.03
	Me of c	0.15(br)	0.14(br)		Me of c	-0.23	-0.23
	CH_2 of d	0.64(br)	0.62(br)		CH_2 of d	10.29	10.24
	CH_2 of e	0.59(br)	0.58(br)		CH_2 of e	-0.17	-0.17
	CH of f	3.90(sep)	3.90(sep)		R	129.58,	8.76(CH_3)
	CH_3 of g	1.13(d, br)	1.13(d, br)			133.33,	7.01(CH_2)
	R	7.24(m)(Ph) 7.59(m)(Ph)	1.00(t)(CH_3) 0.71(q, br)(CH_2)			128.06, 128.30	
^{29}Si NMR	Si of h	-2.53	-2.75	IR (KBr, cm^{-1})		3052 – 2907, 1256, 1049	
	Si of i	8.19	8.19				
	Si of j	9.61	9.94				

All of the spectra were measured in C_6D_6 at 25 °C (δ, ppm).

silylation of alcohols, Pd/C, was also ineffective. Controlled experiments revealed that the polymerization of **2** did not take place in the absence of either the catalyst or $PhMe_2SiH$ similar to the THF polymerization.

Addition of large amounts of $PhMe_2SiH$ to the reaction medium apparently facilitates the generation of active species leading to the polymerization of **2**, although it is not enough to shorten the induction period (2–4 h); this causes difficulty in controlling the amount of active species which results in no reproducible molecular weight of the polymer obtained ($M_n =$ 5,000–150,000). We have overcome this problem by using $HMe_2Si(CH_2)_2SiMe_2H$ (**6**) as the silane (**2**:**6**:**1** = 1:1:0.001). As shown in entry 8, polymerization of **2** induced by **6** was catalyzed by **1**, in which the reaction smoothly took place with a short induction period (< 30 min) and the molecular weight of the polymer ($M_n =$ 7000–130,000) obtained was reproducible (over three times). Furthermore, the polymerization was successfully initiated by smaller amounts of **6** (**2**:**6**:**1** = 1:0.1:0.001 and 1:0.01:0.001) as shown in entries 9 and 10 to give the polymer with $M_n =$ 120,000–150,000, though the reactions were slower than the experiment shown in entry 8. The control factor of the molecular weight is not the monomer/silane ratio seen in the THF polymerization but the concentration of the monomer in benzene. As shown in entries 8, 11, and 12 with **2**:**6**:**1** = 1:1:0.001, decrease of the monomer concentration from 0.53 mol l^{-1} to 0.27 and 0.053 mol l^{-1} resulted in lower molecular weight of the polymer (from $M_n =$ 130,000 to 60,000 and 7000, respectively). The experiment with low monomer concentration (0.053 mol l^{-1}) and a smaller amount of **6** (**2**:**6**:**1** = 1:0.1:0.001) gave a polymer with $M_n =$ 33,000. In all cases using **6** as the silane, the polymer was monomodal ($M_w/M_n =$ 1.5–3.0). Thus, the reaction initiated by **6** is a good method for polymerization of **2** to form the polysilethylene siloxane of $M_n =$ 7000–150,000.

All of the experiments shown above were carried out in a glass tube sealed *in vacuo*. It is important to keep the reaction medium *in vacuo*, presumably because it triggers to generate the net catalyst species from **1**. Use of bifunctional organosilane **6** helps to generate the active species as reported previously [2], and use of **6** gave reproducible polymerization behavior as described above. Very recently, we have found that prior activation of **1** by $HSiR_3$ in dioxane effectively produced an active catalyst species, which promoted reduction of esters, carboxylic acids, and amides under an inert gas atmosphere [3]. Application of this prior activation method of **1** to the polymerization of THF and **2** was effective as shown in entries 14–19. Addition of **2** to the activated catalyst species by $PhMe_2SiH$ (**2**:$PhMe_2SiH$:**1** = 1:1:0.001) in a small amount of dioxane led to the polymerization at room temperature with relatively shorter induction period (0.5–1 h). The reaction can be performed under an argon atmosphere, and it is not necessary to keep the reaction medium *in vacuo*. As shown in entry 15, the reaction with $PhMe_2SiH$ proceeded smoothly to give the corresponding polymer in good yield. Use of **6** instead of $HSiMe_2Ph$ resulted in rapid polymerization of **2**; in fact, the reaction was over almost instantly as shown in entry 16. The polymerization in the presence of a smaller amount of **6** (**2**:**6**:**1** = 1:0.1:0.001) also proceeded smoothly (entry 17). In these two experiments, polymer



Scheme 2.

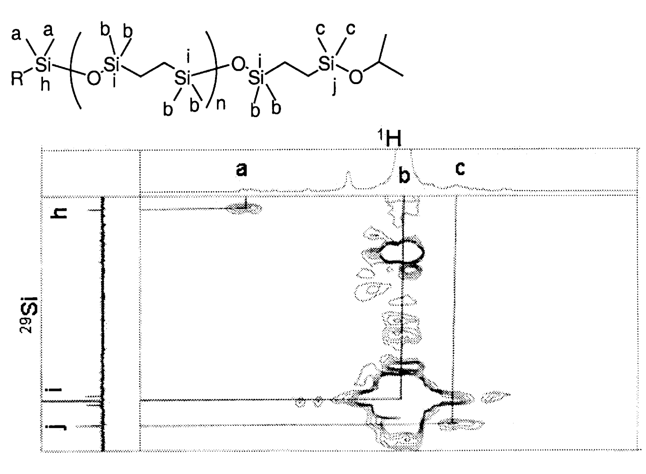


Fig. 2. ^{29}Si–^{1}H COSY NMR of the polymer with $PhMe_2SiO$ and O^iPr end groups measured in C_6D_6 at room temperature.

with $M_n = 70{,}000$–$140{,}000$ was formed. When the polymerization of **2** similar to that shown in entry 18 was carried out in a benzene solution (0.81 mol l^{-1}), polymer with smaller molecular weight ($M_n = 44{,}000$) was obtained. As shown in entry 19, the reaction with $EtMe_2SiH$ also took place instantly to give a polymer with $M_n = 12{,}000$. In these reactions, preactivation of the catalyst in dioxane resulted in rapid polymerization of **2**. Similar smooth polymerization also took place in tetrahydropyran as shown in entry 20, in this solvent, the reaction at −30 °C was possible as shown in entry 21.

The end groups of the polysilethylene siloxane are an interesting point in comparison with that of the silane-induced ring opening polymerization of THF, in which the poly-THF formed has a siloxy and a butyl terminal. A possible mechanism of THF polymerization is shown in Scheme 2, Eq. (1) [2]. If similar mechanisms operate in the silane-induced ring opening polymerization of **2** (Scheme 2, Eq. (2)), an R_3SiO group should be at one end of the polymer, and a Si–H moiety should exist at the other end. Direct observation of these end groups of polysilethylene siloxane obtained in the above experiments by NMR was hampered because of the high molecular weight of the polymer. A breakthrough was made, when we carried out the polymerization induced by $PhMe_2SiH$ in the presence of acetone. As shown in Scheme 2, Eq. (3), a relatively low molecular weight polymer ($M_n = 4400$, $M_w/M_n = 1.4$) was formed accompanied by a hydrosilylation product of acetone $PhMe_2SiO^iPr$, which was removed by heating the crude product *in vacuo*. In the ^1H-, ^{13}C-, and ^{29}Si-NMR spectra of the purified polymer, resonances due to the $PhMe_2Si$ (δ_H 0.36(CH_3), 7.24, 7.59(Ph). δ_C 1.02(CH_3), 129.58, 133.33(Ph). δ_{Si} −2.53) and the ^iPrO (δ_H 1.13(CH_3), 3.90(CH)) groups were observed (Table 2). Two-dimensional NMR technique (^{29}Si–^1H COSY) clearly supports existence of the $PhMe_2SiO$ group in the polymer as shown in Fig. 2. Formation of the ^iPrO moiety demonstrates that the primary product of the polymerization of **2** includes a Si–H terminus, which reacts with acetone by catalysis of **1** to form the ^iPrO species. In other words, existence of the $PhMe_2SiO$ and the ^iPrO moiety in the polysilethylene siloxane supports the mechanism shown in Scheme 2, Eq. (2), which is comparable to the polymerization mechanism of THF shown in Scheme 2, Eq. (1) [11].

Using the preactivation method in dioxane, polymerization of **2** with $EtMe_2SiH$ was followed by the addition of acetone. The resulting low molecular weight polymer ($M_n = 9500$, $M_w/M_n = 5.6$) was subjected to NMR studies similar to those described above, which revealed the existence of $EtMe_2Si$– and isopropoxy groups at the polymer end.

3. Conclusion

A triruthenium cluster **1** effectively catalyzes the silane-induced ring-opening polymerization of a cyclic siloxane **2** to form poly(tetramethylsilethylenesiloxane) with $M_n = 6300–780{,}000$ and $M_w/M_n = 1.5–3.0$, which are varied with the reaction conditions. Two procedures can be used for the polymerization: one is polymerization *in vacuo* and the other is preactivation of the catalyst by silane in dioxane followed by polymerization under an inert gas atmosphere. The reaction can be explained by insertion of $–OSiMe_2(CH_2)_2SiMe_2–$ moiety derived from **2** between the Si–H bond in the hydrosilane. In fact, the polymerization of **2** with R_3SiH in the presence of acetone gave the polymer with end groups of R_3SiO and SiO^iPr, since the SiO^iPr group is formed by the reaction of the Si–H terminus of the polymer with acetone. Poly(tetramethylsilethylenesiloxane) is reportedly a silicone with interesting physical properties [6,7]. The present method has thus been proved to be useful as the first transition metal-catalyzed polymerization of **2**, which proceeds under neutral conditions.

4. Experimental

4.1. General

All manipulations were carried out under an Ar atmosphere using standard Schlenk techniques. Ether, THF, C_6H_6, $C_6H_5CH_3$, hexane and C_6H_6-d_6 were distilled from benzophenone ketyl and stored under an Ar atmosphere, and all 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 (^1H, ^{13}C: solvent) or the external standard (^{29}Si: Me_4Si). Assignments of the NMR signals were performed with the aid of DEPT and 2D [^1H–^1H, ^1H–^{13}C, ^1H–^{29}Si COSY] techniques. IR spectra were recorded in cm^{-1} on a JASCO FT/IR-550 spectrometer. Size exclusion chromatography analysis of the polymer was carried out using a JASCO HPLC system in THF using a standard sample of polystyrene.

4.2. General procedure for the silane-induced polymerization of 2

Typical experimental examples are shown below.

4.2.1. Method A (bulk polymerization)

In a 5Φ NMR tube was placed **1** (0.1 mg, 0.1 μmol), **2** (0.21 ml, 1.12 mmol), and $PhMe_2SiH$ (1.7 μl, 0.011 mmol). For the NMR measurement, a small amount (7 μl) of C_6H_6-d_6 was also added. The solution was degassed and the tube was sealed *in vacuo* ($< 10^{-3}$ Torr), which was warmed at 40 °C for 12 h. The polymer was obtained quantitatively (180 mg, 100% yield).

4.2.2. Method A (solution polymerization)

In a 5Φ NMR tube was placed **1** (0.18 mg, 0.27 μmol), **2** (50 μl, 0.27 mmol), $PhMe_2SiH$ (41 μl, 0.27 mmol), and C_6H_6-d_6 (0.5 ml). The solution was degassed and the tube was sealed *in vacuo* ($< 10^{-3}$ Torr), which was then warmed at 40 °C for several hours, during which conversion of **2** was monitored periodically by ^1H-NMR. After the reaction was complete, removal of the solvent from the reaction mixture gave the polymer quantitatively (42 mg, 98% yield). Alternatively, $HMe_2Si(CH_2)_2SiMe_2H$ was used as the silane instead of $PhMe_2SiH$, and the reaction was carried out in a manner similar to that described above.

4.2.3. Method B (preactivation method in dioxane)

The catalyst **1** (0.5 mg, 0.8 μmol) dissolved in dioxane (66 μl) was treated with $PhMe_2SiH$ (0.12 ml, 0.77 mmol) at room temperature (r.t.) for 30 min under an Ar atmosphere. Exothermic reaction occurred, and some gas evolution, presumably H_2 formed by reaction of $PhMe_2SiH$ and moisture, was observed. Then, **2** (0.14 ml, 0.77 mmol) was added at r.t. The polymerization was completed almost instantly, and the polymer (119 mg/100 yield) was obtained. Alternatively, $EtMe_2SiH$ or $HMe_2Si(CH_2)_2SiMe_2H$ was used as the silane instead of $PhMe_2SiH$. Tetrahydropyran was useful as a substitute of dioxane. The reaction was carried out in a similar manner to that described above.

4.2.4. NMR and IR data of the polymer

^{1}H-NMR (C_6D_6): δ 0.20 (CH_3), 0.64 (CH_2); ^{13}C -NMR(C_6D_6): δ −0.03 (CH_3), 10.29 (CH_2); ^{29}Si-NMR (C_6D_6): δ 8.19; IR (KBr): 3052, 2907, 1256, 1049 (SiOSi).

4.3. Polymerization in the presence of acetone as the chain transfer reagent

4.3.1. The reaction in vacuo

A mixture of **1** (0.18 mg, 0.27 μmol), **2** (50 μl, 0.27 mmol), $PhMe_2SiH$ (41 μl, 0.27 mmol), acetone (19 μl, 0.27 mmol), and C_6H_6-d_6 (0.5 ml) was sealed in a 5Φ NMR tube *in vacuo*. The solution was heated at 40 °C, during which the reaction was monitored by ^{1}H-NMR periodically. After the reaction was over (18.5 h), the reaction mixture was concentrated. The polymer with $PhMe_2SiO$ and O^iPr end groups was obtained (45 mg, 100% yield, $M_n = 4{,}200$, $M_w/M_n = 1.3$).

4.3.2. Application of the preactivation method

The catalyst **1** (0.75 mg, 1 μmol) dissolved in dioxane (100 μl) was treated with $EtMe_2SiH$ (0.15 ml, 1.1 mmol) at r.t. under an Ar atmosphere. After 30 min, **2** (0.21 ml, 1.1 mmol) was added. The polymerization was complete within 1 min. Acetone (0.16 ml, 2.2 mmol) was then added, and the mixture was stirred at r.t. for 1 h. After all of the volatiles were removed *in vacuo*, the polymer with $EtMe_2SiO$ and O^iPr end groups was obtained (45 mg, 100% yield, $M_n = 9{,}500$, $M_w/M_n = 5.6$). After stirring for several minutes, the purified polymer was obtained as white precipitate (40 mg, 90% yield). Low molecular weight polymers including $PhMe_2SiO^iPr$ were completely removed by this purification method. Furthermore, the NMR signals due to the isopropyl group at the polymer ends (δ 3.90; CH of ^{i}Pr) were apparently different from those of $PhMe_2SiO^iPr$ (δ 3.87; CH of ^{i}Pr).

4.3.3. NMR characterization of the end group

The polymer, which was purified by addition of the hexane solution of the crude sample to methanol, was used for the NMR analysis. For example, the crude polymer (45 mg) formed by **2**, $PhMe_2SiH$, and acetone was dissolved in hexane (8 ml), and MeOH (2 ml) was added to the solution.

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[9] Ring strain of the siloxane **2** is driving force of ring-opening polymerization of **2**. Other siloxanes, hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4) did not polymerize under the conditions of Method A and B.

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[11] The integral ratios of the peaks due to the $PhMe_2SiO$ group to those of the ^{i}PrO group were in the range of 5:1–3:1. We believe that the polymer is a mixture of $PhMe_2Si–[OMe_2Si(CH_2)_2SiMe_2]_n–O^iPr$ and $PhMe_2Si–[OMe_2Si(CH_2)_2SiMe_2]_n–OH$. The results can be explained by competitive hydrolysis of the Si–H terminus of the $PhMe_2Si–[OMe_2Si(CH_2)_2SiMe_2]_n–H$ intermediate by moisture exist in the reaction medium with the hydrosilylation of the same intermediate with acetone.