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Nonhydrolytic Synthesis of Branched Alkoxysiloxane Oligomers $Si[OSiH(OR)_2]_4$ (R = Me, Et)**

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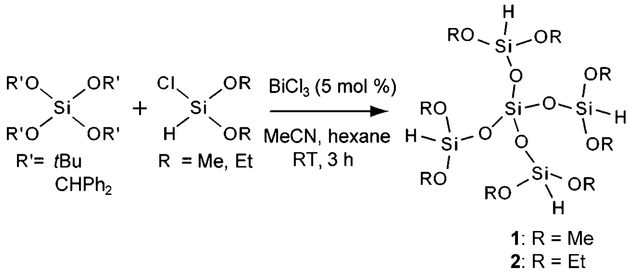
Silicon alkoxides are ideal starting materials for the preparation of silica-based materials.[1] The development of synthetic methods toward various alkoxysiloxane oligomers with finely controlled structures and reactivities is important for the synthesis of materials with defined compositions, structures, morphologies, and functionalities.[2,3] However, examples of the rational synthesis of alkoxysiloxane oligomers are limited.

The controlled formation of Si−O−Si bonds is a key step in the synthesis of alkoxysiloxane oligomers.[2–4] A conventional synthesis involves hydrolysis of silicon alkoxides or chlorosilanes to form silanol groups and a subsequent condensation reaction. Although the reaction of chloroalkoxysilanes with organosilanols have been reported,[3,4] the number of molecules synthesized by using this reaction are quite limited because the reaction is restricted to the cases where the resulting organosilanols are stable. The formation of silanol groups during the reaction causes unwanted side reactions, such as self-condensation of silanols and subsequent hydrolysis of terminal alkoxy groups. Therefore, the synthesis of siloxane oligomers that contain alkoxy groups with defined structures is a challenge in circumventing the problem of side reactions.

The formation of siloxane bonds without using silanols has attracted much interest.[5–16] Alkoxysiloxanes can be synthesized by the reaction between chlorosilane and sodium alkoxysilanolates.[5] On the other hand, the use of alkoxysilanes as a precursor with a Lewis acid catalyst is the most promising pathway.[8–15] The formation of siloxane bonds proceeds with the generation of RX (X = Cl,[8–10] Br,[10] I,[10] AcO,[11] or H[12–15]). No competing reagents, such as compounds containing silanol groups, H_2O, or HCl, are involved in the overall process. Oligosiloxanes with defined structures that contain more than one alkoxy group are difficult to synthesize,[14,15] as side reactions, such as ligand exchange, compete with the formation of siloxane bonds.[8,9,13,14]

Herein we report the nonhydrolytic synthesis, with suppressed side reactions, of branched alkoxysiloxanes $Si[OSiH(OR)_2]_4$ (R = Me (**1**), Et (**2**)), which possess both reactive SiOR and SiH groups. The reaction proceeds by direct alkoxysilylation of tetraalkoxysilanes with $ClSiH(OR)_2$ in the presence of $BiCl_3$ (Scheme 1). $BiCl_3$, a weak Lewis acid, was chosen as the SiOR groups would not be retained when conventional Lewis acids, such as $AlCl_3$ or $FeCl_3$, were used.[9,10] $Si(OtBu)_4$ and $Si(OCHPh_2)_4$ were chosen as precursors because the stable carbocations (tBu^+ and Ph_2HC^+, respectively) probably formed in the reaction should enhance siloxane formation while suppressing other competing side reactions. In addition, the bulky substituents should provide the benefit of higher stability toward hydrolysis than conventional SiOMe and SiOEt groups.[1a]



Scheme 1. Nonhydrolytic synthesis of branched alkoxysiloxane oligomers $Si[OSiH(OR)_2]_4$.

A conventional synthesis of **1** and **2** is by ambient hydrolysis of a tetraalkoxysilane and subsequent alkoxysilylation with a chloroalkoxysilane. However, unwanted hydrolysis of the terminal alkoxy groups and generation of other oligomers by condensation will inevitably occur. The isolation of an unstable tetrahydroxysilane intermediate (monosilicic acid, $Si(OH)_4$) is also impractical. With our method, $Si(OtBu)_4$ and $Si(OCHPh_2)_4$ can be used as precursors instead of $Si(OH)_4$.

The ^{1}H NMR spectrum of **1** (Figure 1), which was synthesized from $Si(OtBu)_4$, shows signals at $\delta = 4.27$ and

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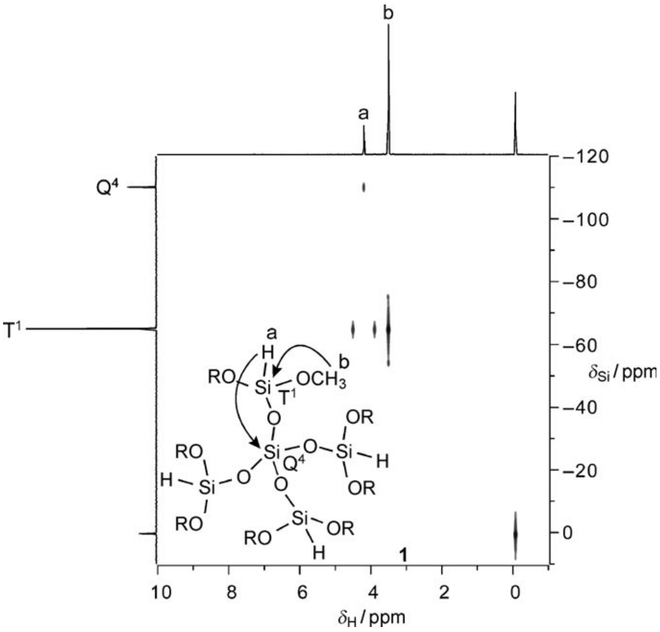


Figure 1. ^{29}Si–^{1}H HMBC spectrum of **1** synthesized from Si(O*t*Bu)$_4$.

3.58 ppm (intensity ratio 1.0:6.2), which can be assigned to H^a and H^b,[17] respectively. The ^{13}C NMR spectrum of **1** (Figure S1 in the Supporting Information) shows a signal at $\delta = 49.9$ ppm, which is assigned to C^b. The ^{29}Si NMR spectrum (Figure 1) shows signals at $\delta = -110.5$ and -65.4 ppm (intensity ratio 1.0:4.3), which correspond to Q^4(*Si*(OSi)$_4$) and T^1(*Si*H(OSi)(OMe)$_2$), respectively. Further evidence for the structure of **1** is obtained from the ^{29}Si–^{1}H HMBC spectrum (Figure 1).[18] The signals of Q^4 and H^a show a correlation, which indicates the *Si*–O–Si–*H* connectivity. The signals for T^1 and H^b also show a correlation that arises from the *Si*–O–C–*H* connectivity. The direct bonding of H^a to the Si atom T^1 was confirmed by the presence of doublet correlation signals. The high-resolution EI-MS spectrum shows a peak at *m*/*z* 425.0242, which corresponds to [M−MeO$^-$]$^+$ (calcd for $C_7H_{25}O_{11}Si_5^+$: 425.0243), thus confirming the selective formation of **1**.[19]

A gas-phase product that was obtained during purification of **1** by solvent evaporation shows a signal at $\delta = 1.61$ ppm in the ^{1}H NMR spectrum (Figure S3 in the Supporting Information) and signals at $\delta = 68.0$ and 34.6 ppm in the ^{13}C NMR spectrum (Figure S4 in the Supporting Information), which can be assigned to the formation of *t*BuCl.[20] This result also confirms that the reaction shown in Scheme 1 took place.

When Si(OCHPh$_2$)$_4$ was used as a precursor instead of Si(O*t*Bu)$_4$, all the NMR spectra (Figure S5–7 in the Supporting Information) and HRMS data (*m*/*z* 425.0244) of a crude sample before distillation (in this case, **1** could not be isolated because of the similar boiling points of Ph$_2$CHCl and **1**) confirmed the formation of **1**, thus indicating that Si(OCHPh$_2$)$_4$ can also be used in the synthesis. The ^{1}H NMR spectrum of the crude sample (Figure S6 in the Supporting Information) shows a multiplet signal at $\delta = 7.19$–7.35 ppm (10H), and a singlet at $\delta = 6.10$ ppm (1H); the ^{13}C NMR spectrum (Figure S7 in the Supporting Information) shows signals at $\delta = 64.3$, 127.8, 128.0, 128.6, and 141.3 ppm, which correspond to chlorodiphenylmethane (Ph$_2$CHCl).[20] The formation of an alkyl chloride is consistent with the behavior of the reaction with Si(O*t*Bu)$_4$.

The synthesis of Si[OSiH(OEt)$_2$]$_4$ (**2**) from Si(O*t*Bu)$_4$ was also investigated because the SiOEt group exhibits a different hydrolysis behavior and is frequently used in sol–gel processes. The ^{1}H NMR spectrum of **2** (Figure 2) shows signals at $\delta = 4.33$, 3.86 and 1.24 ppm (intensity ratio 0.9:4.0:6), which can be assigned to H^a, H^b, and H^c,[21] respectively. The ^{13}C NMR spectrum (Figure S8 in the Supporting Information) also shows signals at $\delta = 58.3$ and 18.2 ppm, which can be assigned to C^b and C^c, respectively. These results show that the SiH and SiOEt groups are retained in the product. The ^{29}Si NMR spectrum of **2** (Figure 2) shows signals at $\delta = -111.0$ and -68.3 ppm (intensity ratio of 1:4.1), which can be assigned to Q^4 and T^1, respectively. Further evidence for **2** is obtained from the ^{29}Si–^{1}H HMBC spectrum (Figure 2). The signals of T^1 and H^b show a correlation that arises from *Si*–O–C–*H*, in addition to an *Si*–O–Si–*H* correlation. The high-resolution EI-MS spectrum shows a peak at *m*/*z* 523.1335, which corresponds to [M−EtO$^-$]$^+$ (calcd for $C_{14}H_{39}O_{11}Si_5^+$: *m*/*z* 523.1339), which confirms the selective formation of **2**.

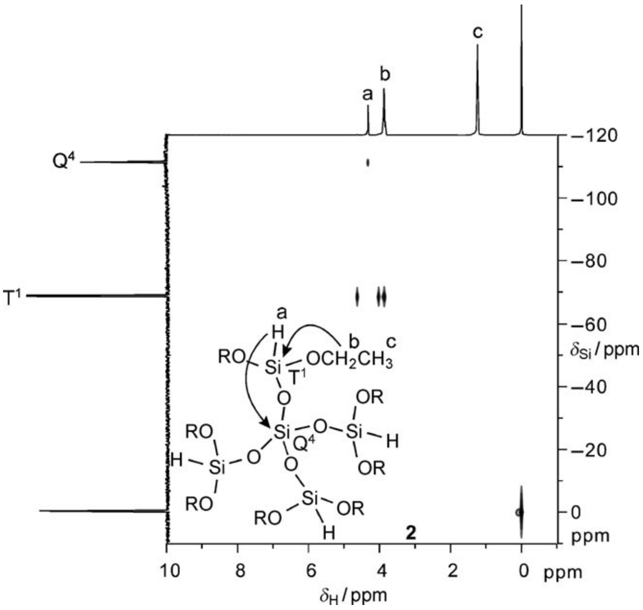


Figure 2. ^{29}Si–^{1}H HMBC spectrum of **2** synthesized from Si(O*t*Bu)$_4$.

The reaction of chlorotrimethoxysilane (ClSi(OMe)$_3$) with Si(OCHPh$_2$)$_4$ was also investigated. The ^{13}C NMR spectrum (Figure S9 in the Supporting Information) of the crude sample shows several signals around $\delta = 51.1$–51.4 ppm, which correspond to the SiOCH$_3$ groups. Signals for these groups also appear around 3.57 ppm in the ^{1}H NMR spectrum (Figure S10 in the Supporting Information). The ^{13}C NMR spectrum shows signals at $\delta = 64.4$, 127.9, 128.1, 128.8, and 141.5 ppm, and the ^{1}H NMR spectrum shows signals at $\delta = 6.28$ and 7.05–7.44 ppm. These signals indicate the generation of chlorodiphenylmethane by siloxane bond formation and thus suggest that the same reaction scheme can successfully be applied to $ClSi(OMe)_3$. However, the branched alkoxysiloxane like **1** or **2** was not obtained in this case. The ^{29}Si NMR spectrum of the product (Figure 3) shows multiple signals at $\delta = -78.2$, -85.6 to -85.8, and -93.6 ppm, which can be assigned to $Si(OMe)_4$,[22] the silicon atom in **3**, and a mixture of linear alkoxysiloxanes, such as octamethoxytrisiloxane (**4**; Scheme 2a).[17] These various alkoxysilanes were formed by transesterification and ligand exchange in addition to the formation of siloxane bonds (Scheme 2b). The difference between $-Si(OMe)_3$ and $-SiH(OMe)_2$ groups is presumably due to the larger steric hindrance of $-Si(OMe)_3$ and the weaker electron-withdrawing effect of the hydrogen atom attached to the silicon atom.

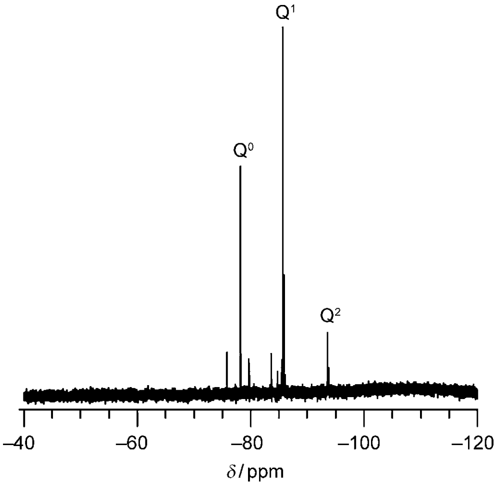
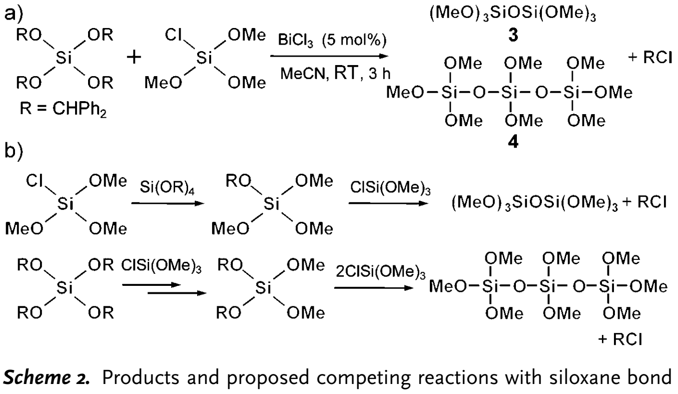


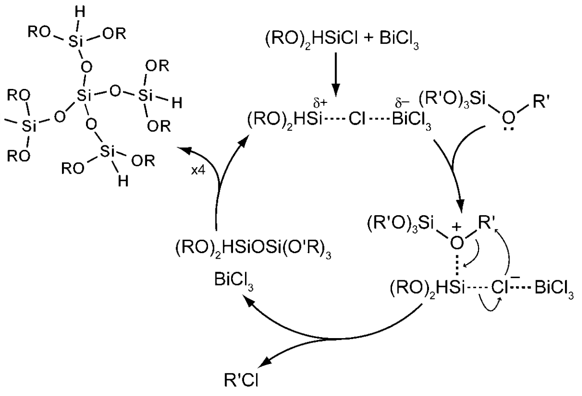
Figure 3. ^{29}Si NMR spectrum of the sample obtained from the $Si(OCHPh_2)_4/ClSi(OMe)_3/BiCl_3$ system.

We also examined the use of $Si(OiPr)_4$ in order to investigate the reactivity of the alkoxy groups. The ^{13}C NMR spectrum (Figure S11 in the Supporting Information) of the crude sample from the $Si(OiPr)_4/ClSiH(OMe)_2/BiCl_3$ reaction system shows many signals between $\delta = 25.2$–25.7, 66.1–68.4, and 50.2–52.1 ppm, which can be assigned to $OCH(CH_3)_2$ and OCH_3 groups, respectively. The ^{29}Si NMR spectrum of the product (Figure S12 in the Supporting Information) shows several signals down to $\delta = -80.2$ ppm, which can be assigned to $Cl_aSiH_b(OMe)_c(OiPr)_d$ ($a+b+c+d=4$), thus showing that ligand exchange and transesterification occur prior to siloxane bond formation.[9] In this case, the ^{13}C and ^1H NMR spectra of the crude product (Figures S11 and S13 in the Supporting Information) did not show the signals that correspond to 2-chloro-2-methylpropane, thus indicating that siloxane bond formation did not occur. Although alkoxy groups that can generate stable carbocations are known to enhance siloxane bond formation in nonhydrolytic sol–gel processes and related reactions,[7,9,10] iPr^+ is less stable than tBu^+ and Ph_2HC^+,[24] and therefore the expected reaction did not occur.



Scheme 2. Products and proposed competing reactions with siloxane bond formation in the $Si(OCHPh_2)_4/ClSi(OMe)_3/BiCl_3$ system.

A plausible reaction mechanism (Scheme 3) is proposed on the basis of previous studies on the reaction mechanisms between SiX (X = Cl, Br, I, or H) and a Lewis acid,[7–10,13,23] and consists of the following steps: 1) The Si–Cl bond is activated by the $BiCl_3$ catalyst; 2) the silyloxonium cation is formed by nucleophilic attack of the alkoxysilane; 3) the cation rearrangement reaction is driven by the stability of tBu^+ or Ph_2HC^+ and subsequent attack of Cl^- on the carbocation; 4) the siloxane bond is formed by elimination of R′Cl; 5) compounds **1** and **2** are formed by repeating steps (1) to (4).



Scheme 3. Proposed reaction mechanism for the siloxane formation. See main text for descriptions of each step.

As observed for the reaction systems of $Si(OCHPh_2)_4/ClSi(OMe)_3/BiCl_3$ and $Si(OiPr)_4/ClSiH(OMe)_2/BiCl_3$, siloxane formation competes with unwanted transesterification and/or ligand-exchange reactions (Scheme S1 in the Supporting Information). Thus, the most important criterion for the success of direct alkoxysilylation to obtain **1** and **2** is preferential siloxane formation. For this purpose, the following factors are crucial: 1) the stability of carbocations obtained from starting alkoxysilanes, 2) molecular structures of the silylating agents, and 3) the use of appropriate Lewis acid catalysts. A previously proposed reaction mechanism for nonhydrolytic formation of amorphous gels[7–9] involves competition between siloxane formation and ligand exchange. In this study, we achieved selective siloxane formation and obtained **1** and **2**. We believe that our findings may also contribute to the understanding of nonhydrolytic sol–gel processes for silica and metal oxides.

In order to clarify the essential role of $BiCl_3$ in the reaction, we carried out the reaction without the use of the Lewis acid catalyst. When $Si(OCHPh_2)_4$ was allowed to react with $ClSiH(OMe)_2$ without the addition of $BiCl_3$, **1** was not formed, even after a longer reaction time (12 h).[25] This result indicates that $BiCl_3$ accelerates the siloxane formation. Previous reports show that the presence of $BiCl_3$ does not lead the primary alkoxy groups (SiOMe, SiOEt) in the products to form siloxane bonds.[10] On the other hand, siloxane bond formation prior to the occurrence of side reactions was reported to occur for the SiO*i*Pr group when $B(C_6F_5)_3$ was used as catalyst.[13] However, the selective synthesis of alkoxysiloxane oligomers such as **1** and **2** is impossible with $B(C_6F_5)_3$ because primary alkoxy groups in the products have a strong tendency to form extended siloxane networks.[14]

In conclusion, we have demonstrated the direct alkoxysilylation of alkoxysilanes catalyzed by $BiCl_3$ occurs without the formation of silanols. Alkoxysiloxanes **1** and **2** were synthesized nonhydrolytically by the reaction of stable tetraalkoxysilanes that possess bulky alkoxy groups ($Si(OR')_4$ $R' = t$Bu, $CHPh_2$) with silylating agents ($ClSiH(OR)_2$). Stable carbocations ($t\mathrm{Bu}^+$, Ph_2HC^+) and molecular structures of silylating agents are important in the $BiCl_3$-catalyzed siloxane formation prior to the occurrence of other competing reactions. The conventional methods that involve hydrolysis are impractical for the synthesis of branched alkoxysilanes **1** and **2**; our approach represents a new strategy for the synthesis of various oligomeric silicon alkoxides that can be applied to a wide variety of sol–gel reactions and hybrid materials. Further investigations into the versatility of direct alkoxysilylation together with applications of this synthetic methodology to alkoxysiloxane oligomers toward hybrid silica materials are in progress.

Experimental Section

Compound **1** was synthesized in a one-pot procedure. Solutions of $BiCl_3$ (0.29 g, 0.92 mmol) in acetonitrile (15 mL) and $Si(OtBu)_4$ (5.9 g, 18.4 mmol) in hexane (20 mL) were added to a solution of $ClSiH(OMe)_2$ in a 200 mL Schlenk flask. $ClSiH(OMe)_2$ was prepared from $HSiCl_3$ (25 g, 185 mmol) and MeOH (15 mL) at 0 °C (see the Supporting Information for details). Although a certain amount of $HSi(OMe)_3$ was present in the silylating agent, the reaction was not affected because the compound does not contain SiCl groups. The overall molar ratio was $Si(OtBu)_4/HSiCl_3/MeOH/BiCl_3 =$ 1:10:20:0.05. The mixture was stirred for 3 h at RT. The solvents, excess $ClSiH(OMe)_2$, $HSi(OMe)_3$, and *t*BuCl were removed under reduced pressure. Compound **1** (2.2 g, 4.8 mmol) was isolated by vacuum distillation. NMR spectra were recorded before and after the distillation.

Compound **2** was also synthesized in a one-pot procedure. Solutions of $BiCl_3$ (0.29 g, 0.92 mmol) in acetonitrile (15 mL) and $Si(OtBu)_4$ (5.9 g, 18.4 mmol) in hexane (20 mL) were added to a solution of $ClSiH(OEt)_2$ in a 200 mL Schlenk flask. $ClSiH(OEt)_2$ was prepared from $HSiCl_3$ (25 g, 185 mmol) and EtOH (21.6 mL) at 0 °C (see the Supporting Information for details). Although a certain amount of $HSi(OEt)_3$ was present in the silylating agent, the reaction was not affected. The molar ratio was $Si(OtBu)_4/HSiCl_3/EtOH/BiCl_3 = 1:10:20:0.05$. The mixture was stirred for 3 h at RT, after which time pyridine (29.8 mL) and EtOH (10.8 mL) were added and the mixture was stirred for 1 h for ethoxylation of the SiCl groups formed by ligand exchange. After the reaction, volatile components were removed under reduced pressure and extracted with hexane. Compound **2** (0.68 g, 1.2 mmol) was isolated by vacuum distillation.

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Keywords: Lewis acids · nonhydrolytic synthesis · oligomerization · silanes

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[19] The yield decreased during purification by vacuum distillation. The crude sample was also analyzed by NMR spectroscopy. The ^{29}Si NMR spectrum of the crude sample (Figure S2 in the Supporting Information) shows several small signals that arise from incomplete silylation or formation of $(MeO)_2HSiOSiH(OMe)_2$, in addition to two major signals that correspond to Q^4 and T^1.[17] The data indicate the highly selective formation of **1**.

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[25] The ^{29}Si NMR spectrum (see Figure S14 in the Supporting Information) showed several signals, which arose from siloxane formation, down to −103.5 ppm (Q^3). The ^{13}C and ^{1}H NMR spectra (Figures S15 and S16 in the Supporting Information) showed the generation of chlorodiphenylmethane. On the other hand, the presence of the $Ph_2HCO{-}Si$ bond was confirmed by ^{13}C NMR spectroscopy (Figure S15 in the Supporting Information). All the data imply that a partial condensation occurred.