Precise Synthesis of Discrete Sequence-defined Oligosiloxanes

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Precise oligomeric materials that lie between the low-molecular-weight discrete molecules and high-molecular-weight disperse polymers constitute a growing research area not only in terms of fundamental studies but also for various applications. In the field of silicone (polysiloxane) materials, several research groups have reported various methods for the synthesis of discrete oligosiloxanes but improvement in the control of siloxane sequences is still desirable. This review highlights our recent contributions to the precise synthesis of discrete sequence-defined oligosiloxanes by controlled iteration of B(C₆F₅)₃-catalyzed reactions. As controlled iteration can be performed in one pot, various discrete sequence-defined oligosiloxanes can be more readily synthesized in comparison to the other reported methods.

Keywords
Silicone material, Oligosiloxane, Discrete oligomer, Sequence-defined oligomer, Precise synthesis, Sequence-controlled synthesis

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1. Introduction

Precise synthesis of discrete oligomers is an emerging area of materials science research because these molecules can exhibit unprecedented properties in crystalline forms and after self-assembly1). For both biologically relevant oligomers such as oligopeptides, oligonucleotides, and oligosaccharides as well as abiotic synthetic oligomers, the sequence and/or length (degree of polymerization) of the oligomers is important for modulating their physical properties. The development of efficient methods for the precise synthesis of discrete abiotic synthetic oligomers can allow a flexible molecular design to obtain tailored materials with desirable properties and provide insights into the structure-property relationships.

Silicone (polysiloxane) is an important class of polymeric materials with broad industrial applications such as adhesives, lubricants, sealants, and electrical insulators because of its high-temperature tolerance, oxidation stability, low-temperature flexibility, and high chemical resistance2)3). Representative methods for the synthesis of oligo- and polysiloxanes include a) hydrolysis/dehydration of chloro- or alkoxysilanes, b) base- or acid-catalyzed ring-opening polymerization of cyclic siloxanes, and c) redistribution of siloxane compounds4)5). However, considering the reaction mechanisms, these methods are not suitable for the precise synthesis of structurally well-defined oligo- and polysiloxanes. Therefore, the development of efficient synthetic methods for oligo- and polysiloxanes that can allow precise control of the sequence and/or length has attracted considerable attention. For example, Meijer et al. reported an iterative method for the synthesis of discrete dimethylsiloxane oligomers with up to 40 repeating -Me₂Si- units6)8). The authors utilized two reactions, the hydroxylation of hydrosilanes with H₂O in the presence of a palladium catalyst (typically Pd/C) and condensation of silanols with chlorosilanes, for the synthesis of discrete oligomers. The original concept was reported by Masamune and coworkers in 1990, who synthesized the first structurally defined siloxane dendrimers via the iteration of hydroxylation and condensation (Scheme 1)9). Recently, a similar method for the iterative synthesis of oligosiloxanes was reported by Arzunmyan and Muzafarov10). While the condensation of silanols with chlorosilanes was employed for siloxane bond formation, they developed a copper-catalyzed aerobic oxidation reaction to transform the hydroxysilanes into the corresponding silanols. A control of the sequence as well as the length of oligosiloxanes was partially achieved by Kung and coworkers11). A silanol substrate, tris(t-butoxy)silanol, reacted with dichlorodimethylsilane and diphenylsilanediol alternately to afford a pentasiloxane with an alternating Ph₂Si/Me₂Si sequence.

Although these iterative methods have facilitated oli-
gosiloxane synthesis in terms of the control of length and sequence, all methods employ the condensation of silanols with chlorosilanes for siloxane bond formation. Condensation is a highly reliable reaction, but the addition of a base (typically pyridine) to neutralize the co-produced hydrogen chloride and subsequent removal of the poorly soluble salts is necessary at each condensation step, rendering the modifications laborious, particularly during the preparation of long oligosiloxanes.

2. B(C6F5)3-catalyzed One-pot Controlled Iteration Method

2.1. Basic Concept

To overcome the issues encountered in the previously reported methods for the synthesis of discrete and/or sequence-defined oligosiloxanes, a one-pot controlled iteration method based on four B(C6F5)3-catalyzed reactions was developed by our research group (Scheme 2). All reactions are triggered by the activation of hydrosilanes by B(C6F5)3 catalyst, and oxygen nucleophiles (alkoxysilanes, carbonyl compounds, silanols, and H2O) attack the activated hydrosilane (Scheme 2(a)).

The first is B(C6F5)3-catalyzed dehydrocarbonative condensation of an alkoxysilane with a hydrosilane to form a siloxane bond together with the coproduction of a hydrocarbon (Scheme 2(b)). This reaction is now recognized as the Piers-Rubinsztajn reaction and is widely applied for the synthesis of oligo- and polysiloxanes[15]. The second is B(C6F5)3-catalyzed hydrosilylation of a carbonyl compound (Scheme 2(c)). This reaction is typically used to reduce a carbonyl compound into the corresponding alcohol after deprotection of the silyl group, but from the viewpoint of organosilicon chemistry, it can be regarded as the conversion of a hydrosilane into an alkoxysilane. The third is B(C6F5)3-catalyzed dehydrogenative condensation of a silanol with a hydrosilane (Scheme 2(d)). In addition to alkoxysilanes, silanols also undergo siloxane bond formation with B(C6F5)3 catalysis. The fourth is B(C6F5)3-catalyzed dehydrogenative condensation of H2O with a hydrosilane to afford the corresponding silanol (Scheme 2(e)).

Among the four B(C6F5)3-catalyzed reactions, the most basic reaction for the one-pot synthesis of sequence-defined oligosiloxanes is the controlled iteration of the dehydrocarbonative condensation of an alkoxysilane with a hydrosilane and the hydrosilylation of a carbonyl compound (Scheme 3). In step 1, an alkoxysilane undergoes dehydrocarbonative condensation with a dihydrosilane in the presence of a catalytic amount of B(C6F5)3 to generate a disiloxane, in which one of the two Si-H groups of the dihydrosilane remains unreacted. Therefore, the successive addition of a carbonyl compound to the reaction media after the completion of the dehydrocarbonative condensation in step 1 induces B(C6F5)3-catalyzed hydrosilylation to transform the remaining Si-H group into an alkoxysilane (step 2). As the growing end of the disiloxane is the alkoxysilane, the second dehydrocarbonative condensation occurs by the addition of another dihydrosilane.
to produce a trisiloxane (step 3). The Si-H end of the produced trisiloxane can be converted into an alkoxy group by the hydrosilylation of the carbonyl compound (step 4). Consequently, the controlled iteration of the dehydrocarbonative condensation and hydrosilylation (i.e., iterative alternating addition of dihydrosilane and carbonyl compound) results in step-wise elongation of the siloxane bonds (step 5). Therefore, the one-pot iterative method permits the control of the length and sequence of oligosiloxanes in a highly selective manner.

Notably, to perform the controlled iteration in a single reaction container (Scheme 3), each reaction must proceed with an almost perfect yield and selectivity. Otherwise, the unreacted reagents, coproducts, and byproducts remaining in the reaction media can interfere with the subsequent reactions, leading to the accelerated formation of byproducts at each step and difficulty in purification. Therefore, the one-pot iterative method permits the control of the length and sequence of oligosiloxanes in a highly selective manner.

Another key to obtaining high yield and selectivity in a one-pot iteration is to kinetically control the B(C₆F₅)₃-catalyzed dehydrocarbonative condensation with dihydrosilane. Experimental and theoretical studies have revealed that B(C₆F₅)₃-catalyzed dehydrocarbonative condensation proceeds via a Sₙ₂-type mechanism (Scheme 4(a)). This is the reason that the siloxane product of dehydrocarbonative condensation, which still contains a Si-H group, is restricted to undergo further dehydrocarbonative condensation with the starting alkoxy silane to afford the undesirable double condensation product (Scheme 4(b)). Considering the balance between the steady progress of the first dehydrocarbonative condensation and effective suppression of the second dehydrocarbonative condensation, moderately bulky isopropoxysilane is usually employed as the alkoxy silane. In other words, acetone, which affords isopropoxysilane upon hydrosilylation, is used as the standard carbonyl compound.

Scheme 5 shows a representative example of the synthesis of discrete sequence-defined oligosiloxanes via the B(C₆F₅)₃-catalyzed, one-pot controlled iteration method. In the presence of 5 mol% B(C₆F₅)₃, seven continuous reactions including four dehydrocarbonative condensations and three hydrosilylations of acetone proceed smoothly in a single flask to produce pentasi-
loxane 1 with an alternating Ph2Si/Et2Si sequence in 70% yield. The four continuous siloxane bonds can be selectively formed within three hours. The average yield of each step is about 95%, demonstrating the high selectivity and efficiency of the B(C6F5)3-catalyzed one-pot controlled iteration method. Notably, in addition to pentasiloxane 1, all intermediates (di-, tri-, and tetrasiloxanes with Si_O−iPr and Si_H end groups) shown in the parentheses of Scheme 5 can be isolated because this is a controlled iteration method.

It can be easily envisioned that control over the siloxane sequences can be achieved by simply varying the addition order of the silane monomers (dihydrosilanes). As shown in Fig. 1, pentasiloxanes 1-3, which are the sequence isomers of each other, are easily synthesized in a highly selective manner by changing the addition order of diphenylsilane and diethylsilane. The 1H, 13C, and 29Si nuclear magnetic resonance (NMR) data of these sequence isomers confirmed their selective syntheses.

As shown in Scheme 2(d), silanols also undergo siloxane bond formation with hydrosilanes. When an oligosiloxane intermediate with a Si-H end group prepared via one-pot controlled iteration is treated with a silanol, B(C6F5)3-catalyzed dehydrogenative condensation occurs to form a siloxane bond (Scheme 6(a)). Therefore, this reaction can be used for end-capping (termination of one-pot controlled iteration). Scheme 6(b) exhibits the dehydrogenative condensation of a Si-H oligosiloxane intermediate with H2O to convert the Si-H group into a Si-OH group. As silanols are typically smaller than the alkoxysilanes and exhibit higher nucleophilicity, the generated silanol undergoes the second dehydrogenative condensation with the Si-H intermediate, as shown in Scheme 6(a). Thus, the two-fold dehydrogenative condensation with half an equivalent of H2O can be applied to the one-pot...
dimerization of oligosiloxanes with Si-H end groups.

Using a sophisticated combination of B(C6F5)3-catalyzed reactions including (1) dehydrocarbonative condensation of alkoxysilanes with hydrosilane, (2) hydro-silylation of carbonyl compounds, (3) dehydrogenative condensation of silanols with hydrosilanes, and (4) dehydrogenative condensation of hydrosilanes with H2O, a wide variety of discrete sequence-defined oligosiloxanes can be synthesized in a single reaction container.

2.2. Installation of Dimethylsilyl (Me2Si) Units

The B(C6F5)3-catalyzed one-pot iteration employs dihydrosilanes as silane monomers. As dimethylsilane (Me2SiH2) is a gas under ambient conditions, the addition of an exact amount of dimethylsilane into the reaction media is operationally difficult. Thus, sequence-defined oligosiloxanes including Me2Si units could not be synthesized under the above-mentioned standard conditions. However, the Me2Si unit is a fundamental component of the polysiloxane materials that are widely used in industry. Therefore, Me2SiH2 precursors that can be easily handled under ambient conditions and produce dimethylsilane in-situ under one-pot iteration conditions were explored. After several experiments, 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (HMD2MH), which has been reported to undergo redistribution in the presence of a catalytic amount of B(C6F5)3 to produce dimethylsilane and hexamethylcyclotrisiloxane (D3) (Scheme 7(a)) was mainly focused upon. Although the redistribution was reversible and HMD2MH itself was possibly involved in dehydrocarbonative condensation leading to byproduct formation, the resulting dimethylsilane was expected to react more rapidly with an alkoxysilane than HMD2MH because of the low steric hindrance around the silicon atom. Therefore, B(C6F5)3-catalyzed dehydrocarbonative condensation of isopropoxymethylsilane with HMD2MH was investigated (Scheme 7(b)). As a result, the desired pentamethyldisiloxane was obtained in a high yield of 93%, which clearly showed that isopropoxymethylsilane reacted with the dimethylsilane produced in-situ in a highly selective manner. The reversibility of the redistribution reaction indicates that D3 with a six-membered ring can also react with the hydrosilanes, but the observed high yield clearly demonstrates that such a side reaction is sufficiently suppressed under the reaction conditions.

HMD2MH was successfully used as a Me2SiH2 precursor to B(C6F5)3-catalyzed one-pot controlled iteration. Scheme 8 shows an example of the one-pot synthesis of oligo(dimethylsiloxane-co-diphenylsiloxane) 4 with a Me2Si/Ph2Si alternating sequence, in
which the two Me₂Si units are introduced by the reaction with HMD₂M₄. The final step of the one-pot synthesis is an end-capping reaction by dehydrogenative condensation with trimethylsilanol, as shown in Scheme 6(a).

Figure 2 clearly shows the high efficiency of the B(C₆F₅)₃-catalyzed one-pot controlled iteration method for the preparation of discrete sequence-defined oligosiloxanes. Six decasiloxanes 5-10 bearing Me₃Si endcaps and different Me₂Si/Ph₂Si sequences were selectively synthesized by the one-pot iterative method. While the isolated yields varied depending on the Me₂Si/Ph₂Si sequence, the decamers with alternating sequence (5), block sequence (6), triblock sequence (7) with four continuous Ph₂Si units in the center of the molecule, and others (8-10) were obtained on a gram scale. Although the decamers are sequence isomers and have identical molecular weights, these afforded similar but clearly distinct NMR spectra, confirming that these were isolated as single molecules (Fig. 3).

As decamers 9 and 10 have symmetrical sequences and the central sequence in each is -Me₂Si-O-Me₂Si-, these can be synthesized by the dimerization strategy using dehydrogenative condensation with H₂O (Scheme 9).

2.3. Product Scope
A wide variety of discrete sequence-defined oligosiloxanes were selectively synthesized in a single flask by applying the basic concept of B(C₆F₅)₃-catalyzed one-pot controlled iteration. When a starting compound with multiple Si-H or Si-OR groups is used, multi-directional siloxane-bond elongation is possible. For example, Scheme 10(a) shows a bidirectional siloxane-bond elongation starting from a trisiloxane bearing a Si-H functional group at both ends of the molecule, affording undecasiloxane 11 in 44 % isolated yield via nine continuous reactions. The key to obtaining a high yield is the use of pentan-3-yl oxide that is bulkier than the isopropanoxy group via B(C₆F₅)₃-catalyzed hydrosilylation, preventing undesired cyclization (formation of cyclic trisi-
loxane) in the first step. Not only linear oligosiloxanes but also branched oligosiloxanes were synthesized by B(C₆F₅)₃-catalyzed one-pot controlled iteration (Scheme 10(b)). When one-half equivalent of trihydrosilane is used instead of dihydrosilane in the B(C₆F₅)₃-catalyzed dehydrocarbonative condensation step, a two-fold dehydrocarbonative condensation occurs to combine one trihydrosilane and two alkoxy-silanes in one molecule. As the obtained pentasiloxane intermediate still contains a Si-H group, the addition of a carbonyl compound, benzaldehyde, and diethylsilane further induces siloxane bond formation to afford branched oligosiloxane 12 in 44% isolated yield.

Owing to the crowding around the Si-H functionality of the combined pentasiloxane, sterically less-demanding benzaldehyde (benzyloxysilane) is more effective than the standard acetone (isopropoxysilane) for hydrosilylation (dehydrocarbonative condensation). Therefore, an appropriate choice of carbonyl compounds in terms of steric hindrance is important in some cases for obtaining the desired oligosiloxanes in high yields, while acetone is effective in most cases.

In the B(C₆F₅)₃-catalyzed dehydrogenative condensation step, not only simple silanols such as trimethylsilanol but also complicated silanol compounds can be used, allowing the construction of sophisticated oligosiloxane compounds. For example, incompletely condensed silsesquioxane (POSS-triol; POSS = polyhedral oligomeric silsesquioxane) 13, which bears three silanol groups, undergoes a three-fold dehydrogenative condensation with a pentasiloxane intermediate containing a Si-H group, which is prepared in-situ by one-pot iteration, affording a shuttlecock-shaped siloxane compound 14 in 41% isolated yield (Scheme 11).

Functional group tolerance is an important parameter in B(C₆F₅)₃-catalyzed reactions. Oxygen-containing functional groups such as alcohols, ethers, and esters and nitrogen-containing functional groups such as primary and secondary amines, amides, and nitriles are usually reactive under B(C₆F₅)₃-catalyzed conditions employing hydrosilanes, rendering the synthesis of oxygen- and nitrogen-functional oligosiloxanes difficult. As these functionalities are inherently more nucleophilic than alkoxy silanes, it is impractical to completely inhibit side reactions under one-pot iterative conditions. In contrast, vinyl and chloro functional groups are well-tolerated. Therefore, bifunctional oligosiloxanes (vinyl/Si-H (15) and chloro/Si-H (16)) are selectively obtained in high yields (Fig. 4). Hydrometallation of the vinyl groups and cross-coupling reactions using chloro functionalities allow the post-functionalization of the obtained oligosiloxanes. Such post-functionalization can afford new applications of discrete sequence-defined oligosiloxanes as high-performance, highly functional materials.

Scheme 10 (a) Bidirectional Siloxane-bond Elongation and (b) Branched Oligosiloxane Formation

Scheme 11 Three-fold Dehydrogenative Condensation with POSS-triol 13
2.4. Polysiloxanes with Regularly Arranged Si–H Functional Groups

A B(C₆F₅)₃-catalyzed polycondensation reaction was developed to afford structurally well-defined polysiloxanes (not discrete polymers) with regularly arranged Si–H functional groups. As shown in Scheme 10(b), the trihydrosilanes undergo two-fold dehydrocarbonative condensation with the alkoxysilanes to generate a siloxane product with a Si–H functional group. This system can be applied to polycondensation, affording polysiloxanes with regularly arranged Si–H functional groups, that is, polycondensation via B(C₆F₅)₃-catalyzed dehydrocarbo-native condensation of a siloxane building block bearing two alkoxysilane moieties with a trihydrosilane (Scheme 12).

Polycondensation was performed using several siloxane building blocks with linear siloxane backbones, but degradation of the siloxane structure by backbiting was observed in some cases. Moreover, 1 : 1 and 2 : 2 macrocyclic oligosiloxanes were generated as major products. To prevent the degradation and formation of small macrocycles, spirosiloxane 17 was designed as a siloxane building block, which could be readily prepared from commercial tetrakis(dimethylsilyloxy)silane by double ring closure under B(C₆F₅)₃-catalyzed one-pot iteration conditions (Scheme 13). It was speculated that the restricted conformation induced by the spiro structure could retard the progress of backbiting and small macrocyclization.

As expected, spirosiloxane 17 underwent smooth polycondensation with phenylsilane to afford polysiloxane 18 (Scheme 14). The 1H, 13C, and 29Si NMR spectra of 18 confirmed that the spiro structure was preserved in the polymer structure. The MALDI-TOF mass spectrum of 18 clearly showed that macrocyclic polysiloxanes (n ≥ 3) were obtained solely, and no additional byproducts such as linear polysiloxanes and degraded byproducts were observed within the measured mass range. As polysiloxane 18 has Si–H groups, it can be post-functionalized by the hydrosilylation of functionalized olefins including hydroxyl, epoxy, and chloro functional groups under standard platinum-catalyzed conditions without degrading the spiro and macrocyclic structures.
3. Summary

A B(C₆F₅)₃-catalyzed one-pot controlled iteration method is developed for the synthesis of discrete sequence-defined oligosiloxanes based on four B(C₆F₅)₃-catalyzed reactions including the (1) dehydrocarbonative condensation of an alkoxysilane with a hydrosilane, (2) hydrosilylation of a carbonyl compound, (3) dehydrogenative condensation of a silanol with a hydrosilane, and (4) dehydrogenative condensation of a hydrosilane with H₂O. Compared to the previous methods, the one-pot controlled iteration method can allow easy synthesis of a larger number of well-defined oligosiloxanes. As shown in Fig. 2, control of the siloxane sequences is achieved, and an array of discrete sequence-defined oligosiloxanes are synthesized for various applications. Especially, post-functionalization of thus-obtained discrete sequence-defined oligosiloxanes with vinyl groups by hydrosilylation will be an effective way to create high-performance materials. An additional challenge in this research area is the development of the precise synthesis of discrete sequence-defined oligosiloxanes with significantly long siloxane chains, that is, polysiloxanes.

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配列制御オリゴシロキサンの精密合成

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分子量が一のオリゴマー材料は、基礎研究の観点からだけではなく、さまざまな応用の観点からも近年注目を集めている。シリコーン（ポリシロキサン）材料の分野では、いくつかの研究グループが単一分子量のオリゴシロキサンを合成する手法を報告しているが、シロキサン配列構造の制御には依然として改善の余地が残されていた。本総合論文では、我々の最近の成果である、B(C_6F_5)_3触媒を用いた複数の反応を逐次的に行うことにより、単一分子量かつ配列構造が制御されたオリゴシロキサンを選択的に合成する手法の開発について紹介する。我々が開発した逐次制御反応は、ワンポットで実施できることから、多種多様な配列制御オリゴシロキサンを既存の手法に比べて格段に容易に合成することが可能である。

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