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The data supporting this article have been included as part of the Supplementary Information.

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PAPER

Building-Block Approach to Discrete and Sequence-Specific Oligosiloxanes

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Discrete and sequence-speciic oligomers that combine molecular-level structural precision with macroscopic properties have attracted increasing attention in polymer and materials science. This study reports a facile method to selectively synthesize discrete and sequence-specific oligosiloxanes of up to 26-mer in a single flask on a gram scale by incorporating a siloxane building block into a $B(C_6F_5)_3$-catalyzed one-pot controlled iteration. The building blocks enable the incorporation of a well-defined oligosiloxane unit into an intermediate of controlled iteration in a single step, thereby significantly reducing the number of iterations. The four obtained 26-mers with molecular weights higher than 3,400 bearing different Me_2SiO/Ph_2SiO sequences exhibit distinct thermal, structural, and mechanical properties, even though the substituents on the silicon atoms are simple methyl and phenyl groups. These results indicate that controlling the monomer ratio and sequence are both crucial in determining the physical properties of copolymerized polysiloxane (silicone) materials.

Introduction

Precise synthesis of discrete and sequence-specific synthetic polymers is one of the major challenges in polymer and materials science.[1] Because discrete and sequence-specific polymers combine the structural precision, at the molecular level of organic chemistry, with the macroscopic properties and functions of polymeric materials, this emerging research area is termed “macro-organic chemistry.” Moreover, it is expected to provide transformative opportunities in materials science.[2] Biopolymers, such as peptides and oligonucleotides, found in nature are inherently discrete and sequence-specific and are of significant biological and pharmaceutical importance. Therefore, tremendous research efforts have been devoted toward the development of synthetic methods for discrete and sequence-specific biopolymers. Consequently, researchers have gained access to a wide variety of discrete and sequence-specific biopolymers. However, the discrete and sequence-specific syntheses of synthetic polymers remain challenging. Because both the molecular weight distribution and the sequence structure of polymers affect their macroscopic properties and behavior, discrete and sequence-specific oligomeric analogs are expected to provide a fundamental and unprecedented understanding of structure–property relationships as ideal synthetic models. Additionally, they are expected to exhibit different or superior properties compared to conventional dispersed polymers.[3] Furthermore, its application in molecular-level information storage is underway,[4-7] accompanied by the concurrent development of techniques for reading information stored in molecules.[8,9]

Methods for obtaining discrete oligomeric molecules are broadly classified into two categories: 1) synthesis of polymers with a molecular weight distribution followed by separation, and 2) selective synthesis of discrete oligomers. The typical approach to separate dispersed polymers into discrete oligomers is chromatographic separation. Recent remarkable developments in separation technology, such as automated flash chromatography systems, have enabled the isolation of discrete oligomers on a preparative scale.[10-13] The major advantage of chromatographic separation is the ability to separate a series of discrete oligomers with different degrees of polymerization simultaneously and system scalability. However, this approach is less economical atomically when only one or a few discrete oligomers are required. Although it is possible to separate discrete oligomers from polymers comprising a single monomer unit or copolymerized polymers with regular periodic sequences, separating discrete and sequence-specific oligomers from random copolymers comprising multiple monomer units is difficult. Therefore, the development of selective synthesis methods is essential to obtain discrete and sequence-specific oligomers. Controlled iteration is a promising approach for selectively synthesizing discrete and sequence-specific oligomers.[14,15] Solid- and liquid-phase methods are the two main methods generally used. Solid-phase methods are operationally simple but require excess amounts of reagents and solvents and are difficult to scale up. Although linear monodirectional iterations are used in solid-phase methods, liquid-phase methods can synthesize a wider variety of discrete oligomers by adopting linear monodirectional, linear bidirectional, and multidirectional iteration strategies. However, in most cases, liquid-phase methods require a purification process at each step of the controlled iterations, which complicates the synthetic operation, particularly while synthesizing oligomers with high degrees of polymerization. Iterative exponential growth (IEG) is an excellent method for the scalable synthesis of discrete oligomers with high degrees of polymerization.[16] The number of synthetic steps required can be dramatically reduced compared to the conventional controlled iteration in which the monomer units react repeatedly. For example, Meijer et al. achieved

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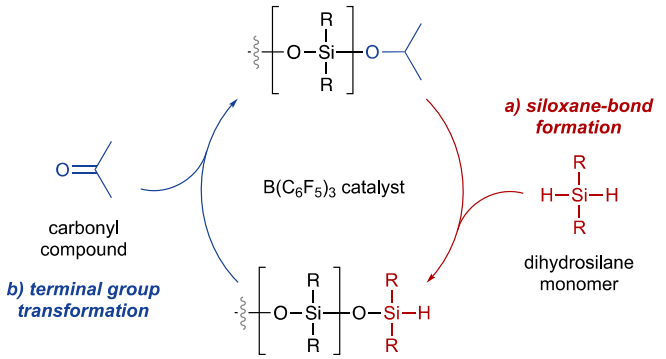
the synthesis of oligodimethylsiloxanes up to 40-mer on a multigram scale using IEG.[17-20] However, IEG has limitations in terms of precisely controlling both the degree of polymerization and sequence structure. Therefore, to synthesize discrete and sequence-specific oligomers with the desired control over both the degrees of polymerization and sequence structure, linear monodirectional iterations would be an ideal choice. However, it is essential to resolve the synthetic inefficiencies to make the resulting oligomers available for further study as materials.

Recently, we reported a one-pot controlled iteration for the synthesis of discrete and sequence-specific oligosiloxanes (Scheme 1).[21-23] This method consists of two reaction steps: a) Siloxane bond formation via the $B(C_6F_5)_3$-catalyzed dehydrocarbonative condensation of an alkoxysilane and a hydrosilane (Piers–Rubinsztajn reaction),[24-26] and b) transformation of a hydrosilane terminal into an alkoxysilane terminal via the $B(C_6F_5)_3$-catalyzed hydrosilylation of a carbonyl compound,[27,28] which can be carried out alternately in a single flask. Depending on the number of times the two reactions are repeated and the type of dihydrosilane monomer used, oligosiloxanes with any degree of polymerization and sequence structure can be synthesized in a highly selective manner. A range of discrete and sequence-specific oligosiloxanes can be synthesized using a simple one-pot procedure because each step results in high yields, is highly selective (typically > 95%), does not require excess reagents, and does not produce coproducts that interfere with downstream reactions. Our method is both efficient and streamlined, enabling the synthesis of diverse range of oligosiloxanes without the need for purification in each step. However, because one Si1 monomer unit is elongated in the two reaction steps, synthesizing oligomers with high degrees of polymerization remains cumbersome because many reaction steps are required. For example, using alkoxysilane as a starting material, 15 reaction steps were required to synthesize a 9-mer by elongating eight monomer units, and the total yield of the desired 9-mer was reasonably high, but less than 50%.[21]



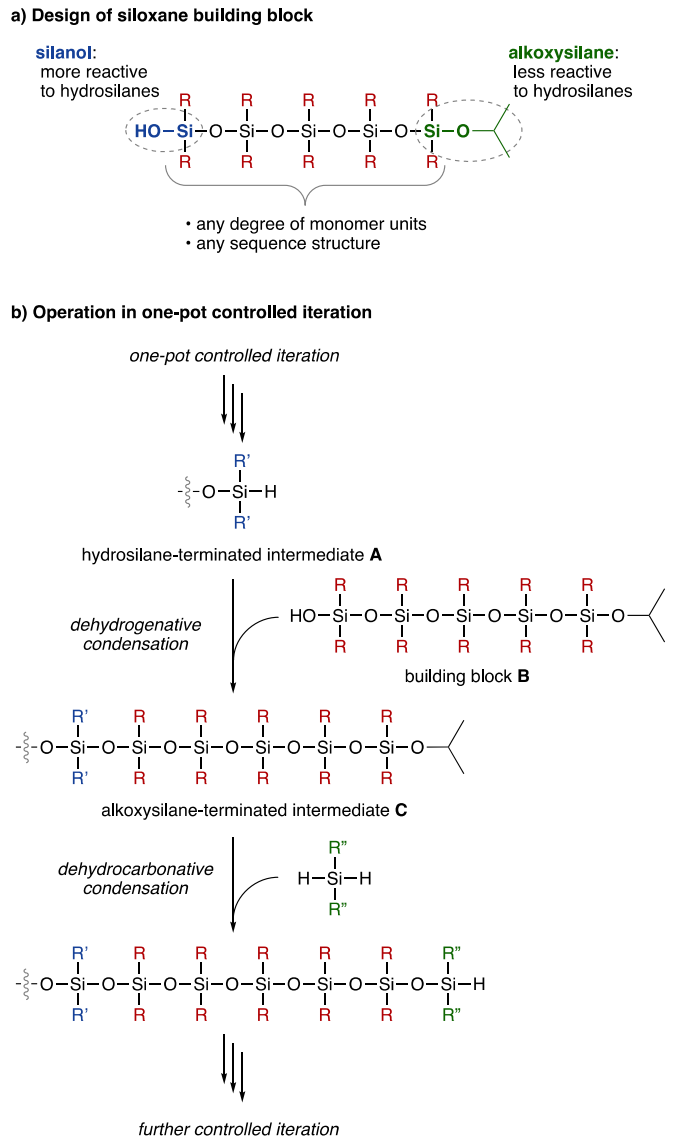
Scheme 1. One-pot controlled iteration for the synthesis of discrete and sequence-specific oligosiloxanes.

To address these inefficiencies and provide a more efficient method for the precise synthesis of discrete and sequence-specific oligosiloxanes with higher degrees of polymerization, we report a siloxane building block approach that can be directly applied to the above-mentioned $B(C_6F_5)_3$-catalyzed one-pot controlled iteration and can introduce a structurally well-defined oligosiloxane unit in a single reaction step. By combining the building blocks in a one-pot controlled iteration, we successfully synthesized four 26-mer sequence isomers on a gram scale. Furthermore, we found that the monomer sequences affected the physical properties, even when the substituents on the silicon atoms were simple methyl and phenyl groups ubiquitously found in commercial polysiloxane (silicone) materials.

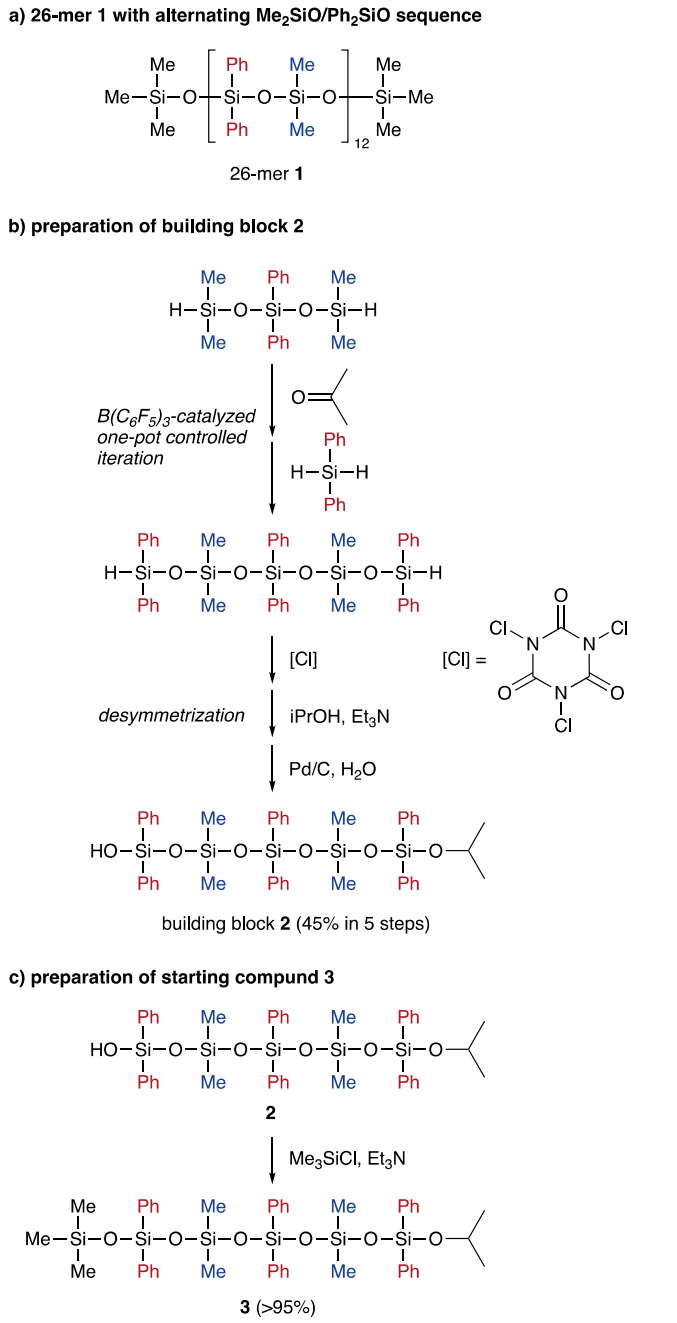
Results and Discussion

The requirements for the building blocks to be directly applicable to the $B(C_6F_5)_3$-catalyzed one-pot controlled iteration are: 1) They react with a hydrosilane-terminated intermediate to form a siloxane bond, yielding an alkoxysilane-terminated intermediate, or with an alkoxysilane-terminated intermediate to form a siloxane bond, yielding a hydrosilane-terminated intermediate; 2) the siloxane bond formation reaction must proceed in high yield and with high selectivity in the presence of $B(C_6F_5)_3$ as the catalyst without the need for excess amounts of building blocks; and 3) byproducts of the siloxane bond formation do not affect downstream reactions.

In view of these requirements, we designed oligosiloxane compounds with a silanol functional group on one terminal and an alkoxysilane functional group on the other as the building blocks (Scheme 2a). Although pentasiloxane is shown in this scheme, any degree of monomer units and sequence structures can be used as building blocks for this purpose. Scheme 2b shows how the building blocks react in the $B(C_6F_5)_3$-catalyzed one-pot controlled iteration. The silanol terminal of building block **B** undergoes $B(C_6F_5)_3$-catalyzed dehydrogenative condensation with a hydrosilane-terminated intermediate **A** formed under one-pot controlled iteration conditions to yield the corresponding alkoxysilane-terminated intermediate **C**, along with the coproduction of dihydrogen, which does not affect downstream reactions.[29] The resulting alkoxysilane-terminated intermediate **C** can maintain the one-pot controlled iteration and undergo further dehydrocarbonative condensation with a hydrosilane monomer. Although both silanols and alkoxysilanes can react with hydrosilanes in the presence of $B(C_6F_5)_3$ as the catalyst, we expected that less sterically demanding silanols would react much faster than alkoxysilanes. In the $B(C_6F_5)_3$-catalyzed one-pot controlled iteration, an alkoxysilane terminal can react with a less sterically demanding dihydrosilane monomer. However, the reaction of the resulting hydrosilane-terminated intermediate with the alkoxysilane-terminated starting material is sufficiently slow, practically negligible, because of steric hindrance. This finding was attributed to the fact that the reactions based on the activation of a hydrosilane by the $B(C_6F_5)_3$ catalyst proceed via an S_N2-type reaction mechanism, which was susceptible to steric hindrance.[30-32]



Scheme 2. Siloxane building blocks: a) design and b) operation in one-pot controlled iteration.

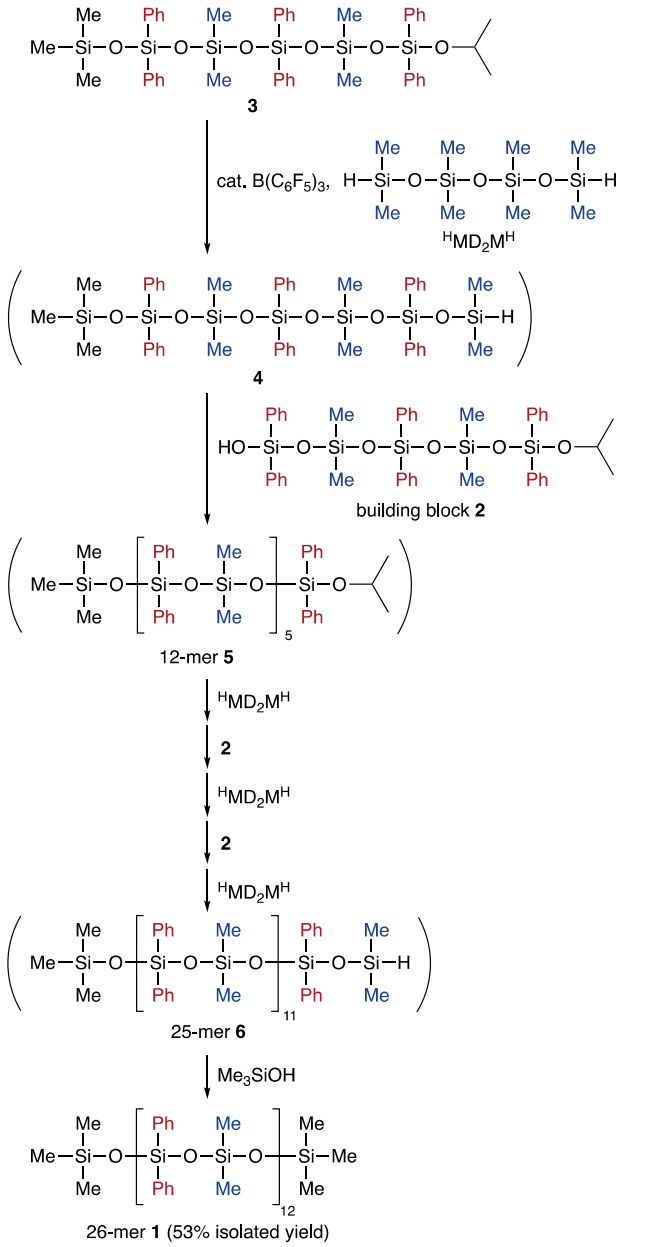


Scheme 3. Structure of 26-mer **1** and preparation of building block **2**.

First, we synthesized 26-mer **1** with an alternating Me_2SiO/Ph_2SiO sequence (AB sequence) bearing Me_3SiO groups at both ends (Scheme 3). Considering that the $B(C_6F_5)_3$-catalyzed reactions are susceptible to steric hindrance, we designed pentasiloxane building block **2** to prepare 26-mer **1**, whose silanol terminal reacts with the sterically less hindered dimethylhydrosilane-terminated intermediate. The building block **2** was synthesized via a three-step desymmetrization including a key chlorination[33] of 3,3,7,7-tetramethyl-1,1,5,5,9,9-hexaphenylpentasiloxane, which could be prepared by a linear bidirectional iteration of commercially available 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane under $B(C_6F_5)_3$-catalyzed one-pot controlled iteration conditions. The starting compound, hexasiloxane **3**, with an isopropoxysilane terminal can be prepared by the standard siloxane bond formation reaction of **2** with Me_3SiCl.

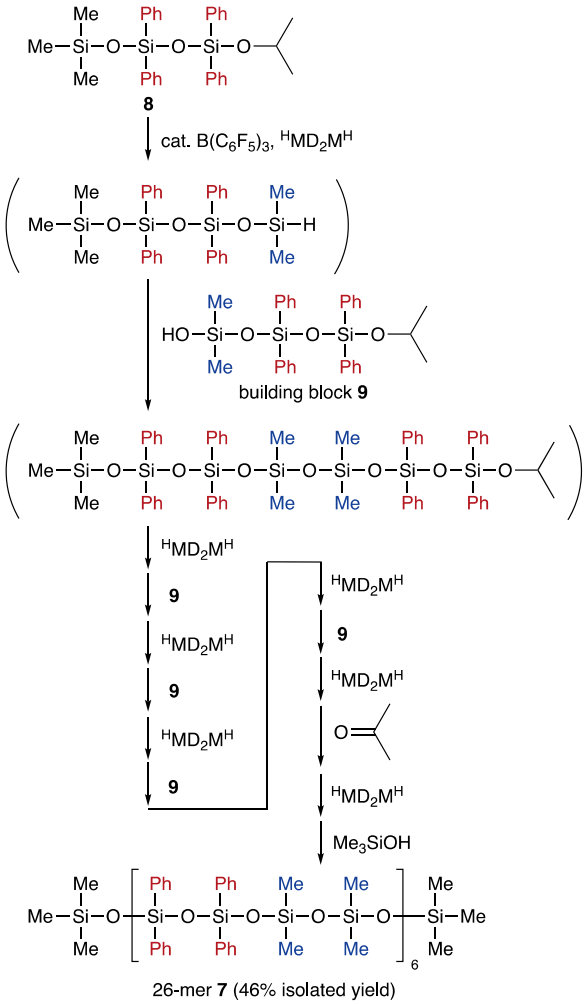
Scheme 4 shows the one-pot synthesis of 26-mer **1** using the building-block approach. Compound **3** first reacts with 1,1,3,3,5,5,7,7-octamethyltetrasiloxane ($^HMD_2M^H$), which generates Me_2SiH_2 in situ in the presence of $B(C_6F_5)_3$,[23] to yield heptasiloxane intermediate **4** with an $SiMe_2H$ terminal. Subsequently, **4** undergoes dehydrogenative condensation with building block **2**, yielding 12-mer intermediate **5** with an isopropoxysilane terminal. Controlled iterative additions of $^HMD_2M^H$ and building block **2** to the reaction medium yielded 25-mer intermediate **6**. Finally, the-$SiMe_2H$ terminus of **6** was capped with a Me_3SiO group via dehydrogenative condensation with Me_3SiOH. The desired 26-mer **1** with a molecular weight of 3431.78 was obtained in 53% isolated yield on a gram scale after a one-pot 8 step reactions. All reactions were catalyzed by the

initially added $B(C_6F_5)_3$, and the crude final product was purified using a commercial recycling gel permeation chromatography system. The conventional one-pot iteration utilizes Si1 monomers (Me_2SiH_2 and Ph_2SiH_2) to synthesize 12-mer **5** from 7-mer **4**, which requires 11 steps, whereas the building-block approach can drastically reduce the number of long and tedious iterations, enabling the synthesis to occur in a single step. This approach is much more advantageous, even when considering the effort required to prepare the building blocks. Diphenylsilanol terminal of **2** undergoes dehydrogenative condensation with sterically less hindered dimethylhydrosilane-terminated ($–SiMe_2H$) intermediates smoothly. However, the dehydrogenative condensation of the opposite combination, a dimethylsilanol terminal and a sterically more demanding diphenylhydrosilane-terminal ($–SiPh_2H$) does not proceed well under these conditions.



Scheme 4. One-pot synthesis of AB sequence 26-mer **1** by controlled iteration using building block **2**.

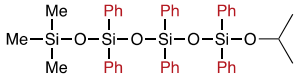
$B(C_6F_5)_3$-catalyzed one-pot controlled iteration combined with the building-block approach is highly effective and applicable for the precise synthesis of a wide range of discrete and sequence-specific oligosiloxanes by appropriately designing the building blocks used. We synthesized 26-mer **7** with an AABB sequence, which is a sequence isomer of 26-mer **1**, isolated in 46% yield via a one-pot controlled iteration (14 steps) using the starting compound **8** and building block **9** (Scheme 5). Other sequence isomers, 26-mer **10** with the AAABBB sequence and 26-mer **13** with AAAABBBB sequence, are also synthesized on a gram scale in 48% and 58% isolated yields from starting compounds **11** and **14** and building blocks **12** and **15**, respectively (Figure 1; for synthetic details, see Schemes S1 and S2).



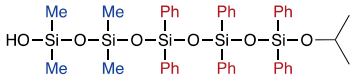
Scheme 5. One-pot synthesis of AABB sequence 26-mer **7** by controlled iteration using building block **9**.

AAABBB-sequence

26-mer **10** (48% isolated yield)



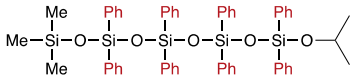
starting compound **11**



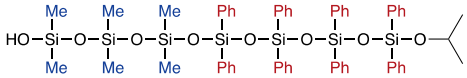
building block **12**

AAAABBBB-sequence

26-mer **13** (58% isolated yield)



starting compound **14**



building block **15**

Figure 1. Structures of 26-mers **10** and **11**, starting compounds **11** and **14**, and building blocks **12** and **15**.

The discrete and sequence-specific nature of the 26-mers (**1**, **7**, **10**, and **13**) is confirmed by $^{29}Si\{^{1}H\}$ NMR (Figure 2) and MALDI-TOF MS (Figure 3). Although the 26-mers exhibited different NMR spectra owing to sequence differences,[34,35] they showed the same *m*/*z* value for the $[M+Na]^+$ ions. No other peaks were detected in the MALDI-TOF MS spectra, confirming the high purity of the obtained 26-mers.

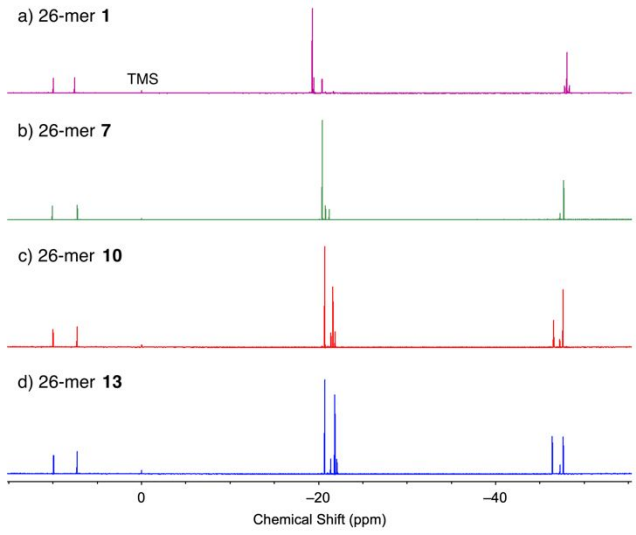


Figure 2. $^{29}Si\{^{1}H\}$ NMR spectra of 26-mers **1**, **7**, **10**, and **13** (TMS = tetramethylsilane; internal standard).

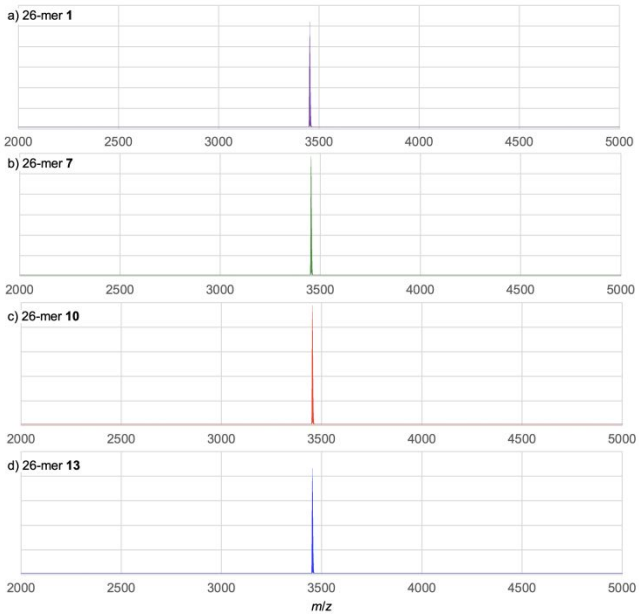


Figure 3. MALDI-TOF MS spectra of 26-mers **1**, **7**, **10**, and **13**.

Sequential isomers (**1**, **7**, **10**, and **13**) were characterized using differential scanning calorimetry (DSC), X-ray diffraction, and shear viscosity measurements. The 26-mer **1** with alternating Me_2SiO/Ph_2SiO sequence was obtained as a white wax at room temperature and melted to an isotropic liquid around 38–40 °C (Figure 4), while Nguyen et al. reported that strictly alternating poly(dimethylsiloxane-diphenylsiloxane) (M_n = 61763, M_w = 87817 and polydispersity) is a viscous oil showing a glass transition at –21 °C.[36] Its heating thermogram exhibited an endothermic peak at 37.7 °C (ΔH = 81.9 kJ/mol). In contrast, 26-mers **7**, **10**, and **13** were isotropic liquids and showed a glass transition at –37.3, –38.7, and –39.1 °C respectively, in the DSC runs from –50 °C to 100 °C. The X-ray diffractograms of the liquid isomers **7**, **10**, and **13** (27 °C) exhibit two broad peaks, whose tops are located at approximately 2θ of 9°–10° and 19°–20° (CuK_α line) (Figure 5). The peaks at approximately 9°–10° shifted toward smaller angles in the sequence from **7** via **10** to **13**. The shear viscosities at a shear rate of 10/s are evaluated as a function of temperature, and the viscosity monotonically decreases with increasing temperature (Figure 6). Between 50 and 150 °C, the highest viscosity curve was observed for **13**, and the second and third curves were observed for **10** and **7**, respectively. The lowest curve was obtained for **1** in liquid state (50 °C to 150 °C). The shear viscosity of **13** with AAAABBBB sequence at 50°C (2.31 Pa s) is about 1.5 times than that of **1** with AB sequence (1.49 Pa s).

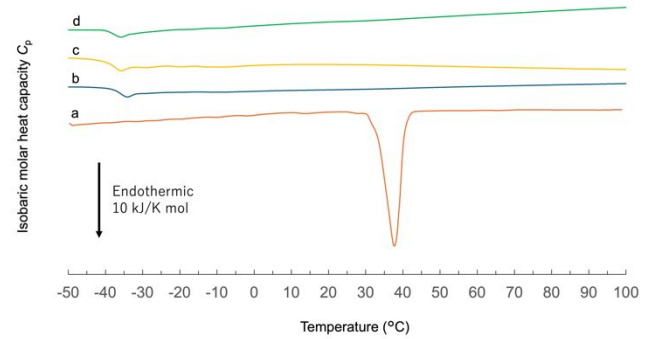


Figure 4. Differential scanning calorimetry heating thermograms of 26-mers at 5 K/min. a) Isomer **1** (orange), b) isomer **7** (blue), c) isomer **10** (yellow), and d) isomer **13** (green).

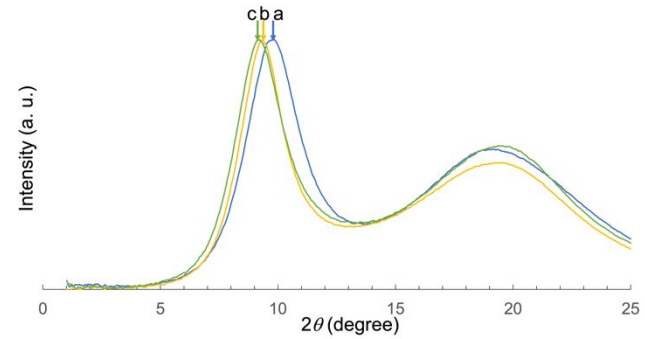


Figure 5. X-ray diffractograms of liquid 26mers at 27 °C (CuK$_\alpha$ line, λ=0.1542 nm). a) Isomer **7** (blue), b) isomer **10** (yellow), and c) isomer **13** (green). The arrows point the peak tops.

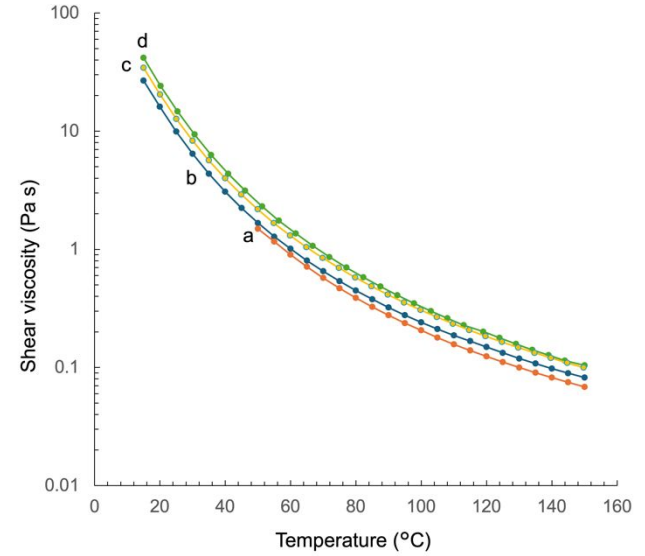


Figure 6. Shear viscosity of liquid 26-mers in a function of temperature (shear rate = 10 /s). a) Isomer **1** (orange), b) isomer **7** (blue), c) isomer **10** (yellow), and d) isomer **13** (green).

Sequence isomers **1**, **7**, **10**, and **13** were compared by several physicochemical measurements. Although the observed difference was not large, it was distinct, and the values shifted in accordance with the isomer sequences. These results demonstrate that discrete sequence control can have a measurable and evident impact on material properties, such as thermal, structural, and mechanical properties. To obtain a sufficient explanation for these observed differences, we will further develop the preparation and characterization of an array of sequence-controlled siloxanes.

Conclusions

This study developed a facile method to precisely synthesize discrete and sequence-specific oligosiloxanes up to 26-mer with molecular weights higher than 3,400; this was achieved by combining the siloxane building block approach with a $B(C_6F_5)_3$-catalyzed one-pot controlled iteration. Four 26-mers with different Me_2SiO/Ph_2SiO sequences (AB, AABB, AAABBB, and AAAABBBB) were successfully synthesized on the gram scale, demonstrating the high synthetic efficiency and versatility of this method. While the synthesis of linear oligosiloxanes with regular periodic sequences was presented in this study as a proof of concept, a wider variety of discrete and sequence-specific oligosiloxanes, for example, oligosiloxanes with irregular but specific sequences, non-linear oligosiloxanes, and oligosiloxanes longer than 26-mer, can be synthesized by appropriately designing the siloxane building blocks. A detailed and comprehensive structure–property relationship study of discrete and sequence-specific oligosiloxanes is ongoing in our laboratory to provide transformative opportunities in the field of polysiloxane materials.

Author Contributions

K. M. and K. S. conceived and directed the project. T. K. conducted the design, synthesis and structural analysis. H. M. carried out DSC, X-ray diffraction, and shear viscosity analysis. K. M. wrote the manuscript with assistance from all authors. All authors participated in the discussion of the results.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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