# Synthesis of Chiral Poly(silyl ether)s via CuH-Catalyzed Asymmetric Hydrosilylation Polymerization of Diketones with Silanes

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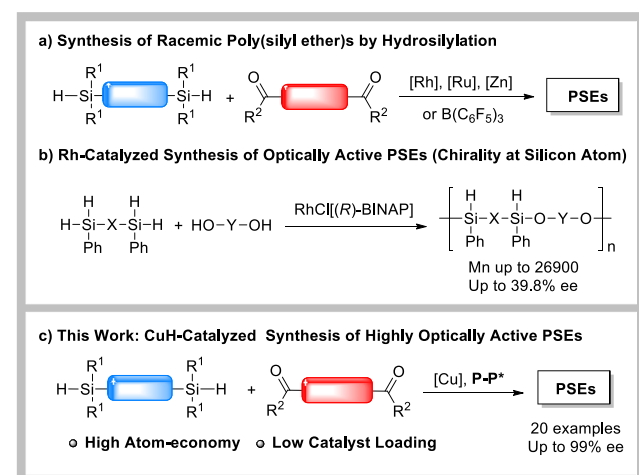
**ABSTRACT:** The precise synthesis of chiral poly(silyl ether)s remains a challenge, in contrast to the well-studied preparation of poly(silyl ether)s. Herein, an unprecedented approach for the synthesis of optically active poly(silyl ether)s with main-chain chirality has been developed via CuH-catalyzed hydrosilylation polymerization of diketones and silanes. The polymerization features low catalyst loading, mild condition, and broad substrate scope, including a wide range of aromatic diketones and heteroaromatic diketones with excellent yields and enantioselectivities (up to 98% yield and 99% ee). Thermal analysis indicated chiral poly(silyl ether)s exhibit good thermal properties. These enantiomerically enriched poly(silyl ether)s with good thermal stability have a promising application in chiral separation.



Chiral PSEs
20 Examples, Up to 99% ee

● High Atom-Economy ● Low Catalyst Loadings
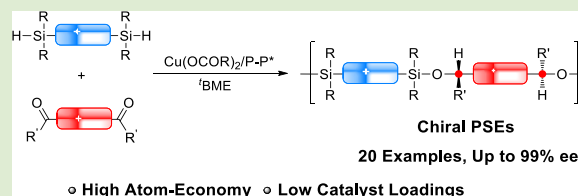
Polymers containing silicon—oxygen bonds in the main chain have emerged as one of the most important class of polymers and played a considerable role in high-temperature elastomers, degradable materials, and conductive polymeric materials.[1] Especially, they have a significant position in chiral column packing materials. The first chiral stationary phases based on polysiloxanes for GC (commercial name, Chiralsil-Val) which performed an efficient resolving power to separate $\alpha$-amino acid enantiomers was reported by Bayer in 1977.[2] Subsequently, a variety of chiral stationary phases based on polysiloxanes have been frequently used for analytical enantioseparations.[3] Poly(silyl ether)s have the structural propinquity to polysiloxanes and also have similar applications. Due to the remarkable significance of this framework, the past decade witnessed significant progress toward the synthesis of poly(silyl ether)s. The synthetic methods are focused on polyaddition,[4] polycondensation,[5] and hydrosilylation polymerization.[6] However, polyaddition[4] and polycondensation[5] are limited to availability of structurally diverse monomers or involve hazardous stoichiometric byproduct. In contrast, hydrosilylation polymerization is the most atom-economic way to synthesize poly(silyl ether)s (Scheme 1a).[6] In 1998, Weber and co-workers first disclosed the step-growth hydrosilylation copolymerization using ruthenium complexes as a catalyst precursor.[6a] In 2016, the Oro group developed the recyclable rhodium-NHC-catalyzed hydrosilylation polymerization to deliver poly(silyl ether)s.[6d] Subsequently, hydrosilylation polymerization of diphenylsilane with $\alpha,\omega$-dialdehydes was achieved using ZnH-based system.[6f] More recently, B(C₆F₅)₃ showed high reactivity to give the desired products containing a halogen group under the mild condition.[6h,6i]

Chiral polymers have received considerable attention in chiral separation, catalysis, biomaterials, and materials for nonlinear optics.[7] Nevertheless, the types of synthetic chiral

**Scheme 1. Approaches to Synthesis of Poly(silyl ether)s**



a) Synthesis of Racemic Poly(silyl ether)s by Hydrosilylation

b) Rh-Catalyzed Synthesis of Optically Active PSEs (Chirality at Silicon Atom)

Mn up to 26900
Up to 39.8% ee

c) This Work: CuH-Catalyzed Synthesis of Highly Optically Active PSEs

● High Atom-economy ● Low Catalyst Loading

20 examples
Up to 99% ee

polymers are very finite,[8,9] so developing structural diverse chiral polymers remained on the chemists' wish list. Although considerable efforts have been devoted to the preparation of poly(silyl ether)s, the asymmetric version is still rare and challenging. The major difficulty is the control of the molecular weight and the stereoselectivity of polymerization. In 2000, Kawakami's group reported the first asymmetric synthesis of

## Table 1. Optimization of Reaction Conditions[a]
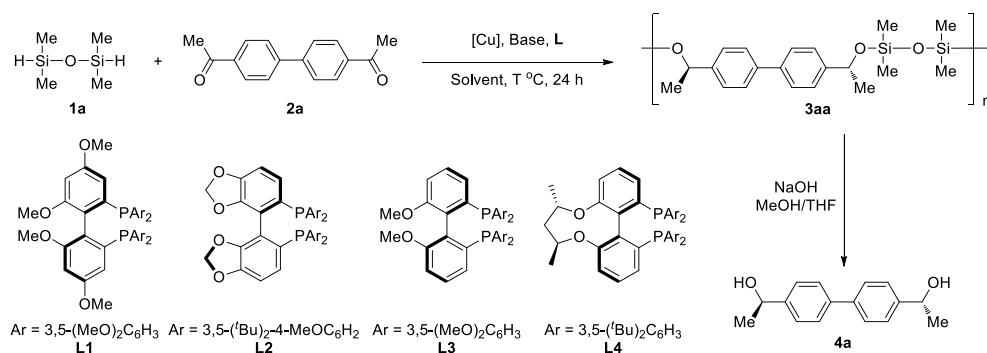


| entry | solvent | [Cu] | L | cat. ($x$ mol %) | $T$ (°C) | $M_n$[b] | PDI[b] | yield[c] (%) | ee[d] (%) | dl/meso[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | toluene | CuOtBu | L1 | 2.0 | 60 | 6600 | 1.99 | 87 | 99.2 | 90:10 |
| 2 | 1,4-dioxane | CuOtBu | L1 | 2.0 | 60 | 7700 | 1.66 | 69 | 99.2 | 90:10 |
| 3 | CPME | CuOtBu | L1 | 2.0 | 60 | 6300 | 1.50 | 47 | 99.0 | 90:10 |
| 4 | tBME | CuOtBu | L1 | 2.0 | 60 | 8200 | 1.74 | 81 | 99.6 | 92:08 |
| 5 | tBME | Cu(OAc)$_2$ | L1 | 2.0 | 60 | 7800 | 2.22 | 96 | 99.6 | 93:07 |
| 6[e] | tBME | CuR$_2$ | L1 | 2.0 | 60 | 9600 | 2.16 | 95 | 99.6 | 93:07 |
| 7 | tBME | CuR$_2$ | L1 | 0.5 | 60 | 11700 | 2.00 | 87 | 99.6 | 93:07 |
| 8 | tBME | CuR$_2$ | L1 | 1.0 | 60 | 10300 | 1.90 | 83 | 99.6 | 93:07 |
| 9 | tBME | CuR$_2$ | L1 | 0.5 | 0 | | | | | |
| 10 | tBME | CuR$_2$ | L1 | 0.5 | 30 | 14600 | 1.97 | 87 | 99.8 | 96:04 |
| 11 | tBME | CuR$_2$ | L2 | 0.5 | 30 | 9700 | 2.04 | 67 | 98.6 | 86:14 |
| 12 | tBME | CuR$_2$ | L3 | 0.5 | 30 | 13600 | 2.04 | 81 | 99.8 | 95:05 |
| 13 | tBME | CuR$_2$ | L4 | 0.5 | 30 | 10400 | 1.74 | 56 | 99.4 | 92:08 |
| 14[f] | tBME | CuR$_2$ | L1 | 0.5 | 30 | 11800 | 2.39 | 87 | 99.8 | 96:04 |

[a]Unless otherwise noted, reaction conditions are as follows: monomer (0.5 mmol), [Cu] ($x$ mol %), L ($x$ mol %), $T$ °C, 24 h, solvent (1.5 mL). [b]Determined by GPC with RI. [c]Isolated yield. [d]Measured by hydrolyzing the polymer and analyzing the resulting diol via HPLC. [e]CuR$_2$ = copper(II) cyclohexanebutyrate. [f]Reaction conditions: monomer (1.0 mmol), [Cu] (0.5 mol %), L1 (0.5 mol %), 30 °C, 24 h, solvent (3.0 mL).

optically active poly(silyl ether)s by rhodium-catalyzed stereo-selective cross-dehydrocoupling polymerization of bis(silane)s and diols with moderate enantioselectivities (up to 40% a.v. ee; Scheme 1b).[10] However, the products with unstable Si–H groups would react with water in air, prohibiting their application. To the best of our knowledge, the enantioselective synthesis of highly optically active poly(silyl ether)s is still unknown. Thus, the development of an atom economic asymmetric hydrosilylation polymerization to obtain highly optically active poly(silyl ether)s with high stability is highly desirable. Conscious of great success in asymmetric hydro-silylation of ketones via CuH-based system,[11] we speculated this approach could be extended to catalytic asymmetric hydrosilylation polymerization of prochiral diketones, which would enable the enantioselective synthesis of poly(silyl ether)s. Herein, we report unprecedented CuH-catalyzed asymmetric hydrosilylation polymerization, delivering highly optically active poly(silyl ether)s. This approach features atom economy, low catalyst loading, broad substrate scope, mild condition, high activity, and stereoselectivity (Scheme 1c). These enantiomerically enriched poly(silyl ether)s, which are easy to prepare, would expand the application in chiral separation.

At the outset of the investigation, 1,1,3,3-tetramethyl-disiloxane 1a and diketone 2a were chosen as model substrates in the presence of CuH catalyst prepared in situ. To our delight, the asymmetric hydrosilylation polymerization per-formed smoothly in toluene, delivering the chiral poly(silyl ether) in 87% yield with 99% ee and 90:10 dl/meso (Table 1, entry 1). Solvents played an important role in reactivity and

diastereoselectivity (entries 1−4). *tert*-Butyl methyl ether proved to be the most suitable solvent in view of reactivity, enantioselectivity, and diastereoselectivity (entry 4). The reason would be the good solubility of 3aa in tBME. Subsequently, copper precursors were evaluated. The reactions catalyzed by CuOtBu, Cu(OAc)$_2$, and copper cyclohexanebu-tyrate gave similar stereoselectivity, copper cyclohexanebuty-rate delivered 3aa with the highest molecular weight (entries 4−6). We proposed the steric hindrance properties of copper precursor would advance the polymerizations. Decreasing the catalyst loading to 0.5 mol %, the higher molecular weight of product was obtained (entry 7). Then the effect of temperature was examined. When the temperature was decreased to 30 °C, the better enantioselectivity and diastereoselectivity were achieved (entries 10). Finally, the influence of chiral bisphosphine ligands was explored, electron-donating ligand L1 was the best in overall terms (entry 10). L2, which played a potent role in hydrosilylation of simple ketones, showed moderate diastereoselectivity (entry 11). L3 exhibited comparable stereoselectivity with L1 albeit with lower reactivity (entry 12). Therefore, the optimal reaction conditions were established: using copper cyclohexanebuty-rate/L1 as catalyst (0.5 mol % catalyst loading), *tert*-butyl methyl ether (3.0 mL) as solvent to perform the reaction at 30 °C, delivering the desired optically active poly(silyl ether) with a molecular weight of 11800, good reactivity, and stereo-selectivity (87% yield, 99% ee, and 96:4 dl/meso).

With the optimal reaction conditions in hand, we first investigated the substrate scope by reaction of various dihydrosilanes 1 with diketone 2a. Pleasingly, good yields,

## Table 2. Substrates Scope with Respect to Diketones and Silanes[a]
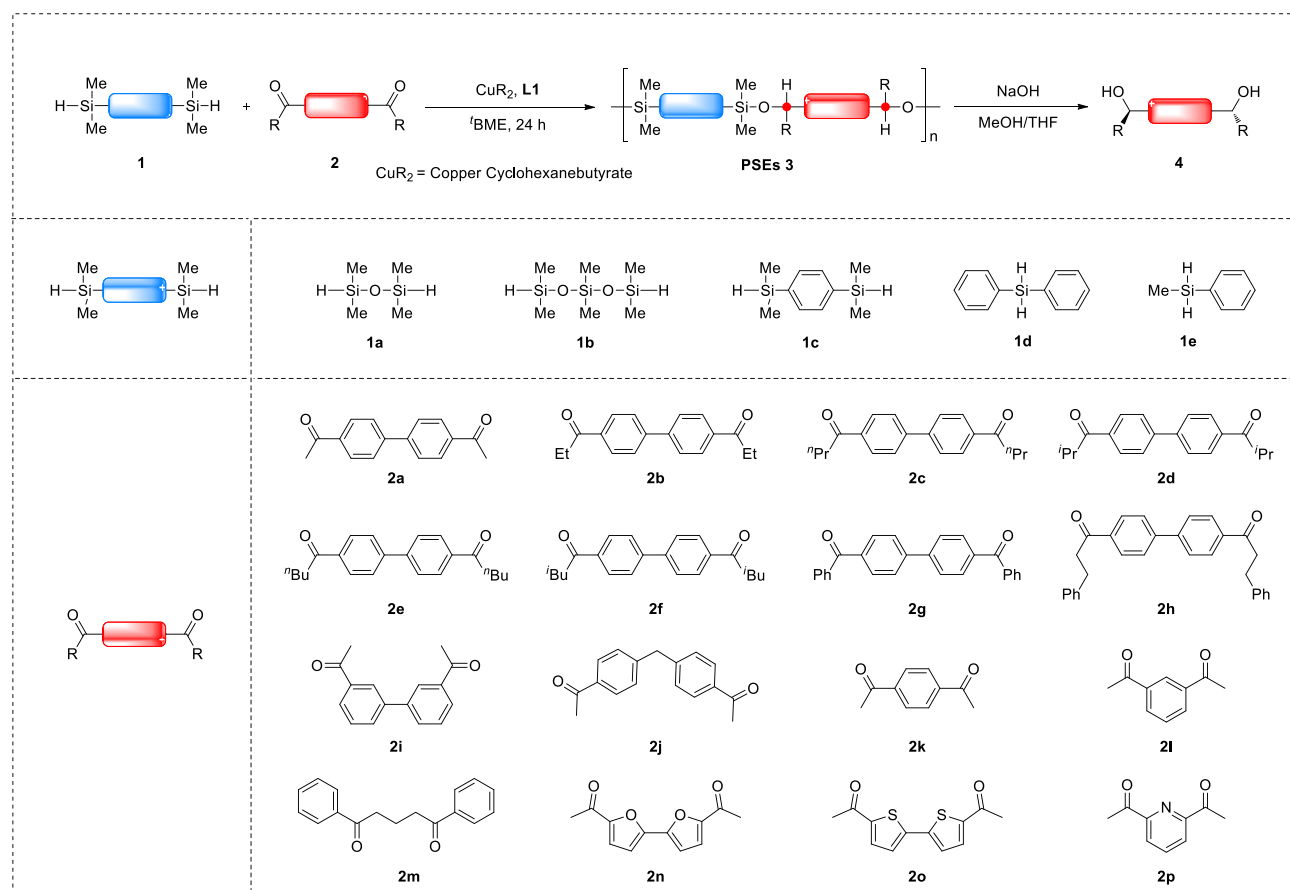


| entry | dihydrosilanes | diketones | $M_n$[b] | PDI[b] | yield[c] (%) | ee[d] (%) | dl/meso[d] |
|---|---|---|---|---|---|---|---|
| 1 | 1a | 2a | 11800 | 2.39 | 87 | 99 | 96:04 |
| 2 | 1b | 2a | 17600 | 1.98 | 84 | 99 | 96:04 |
| 3 | 1c | 2a | 27400 | 2.55 | 96 | 99 | 96:04 |
| 4 | 1d | 2a | 17900 | 2.59 | 99 | 99 | 95:05 |
| 5 | 1e | 2a | 10600 | 2.05 | 92 | 99 | 95:05 |
| 6 | 1c | 2b | 12700 | 1.96 | 84 | 99 | 96:04 |
| 7 | 1c | 2c | 16000 | 1.70 | 97 | 99 | 95:05 |
| 8 | 1c | 2d | 11400 | 2.05 | 98 | 99 | 96:04 |
| 9 | 1c | 2e | 8400 | 1.92 | 96 | 99 | 95:05 |
| 10 | 1c | 2f | 17800 | 2.22 | 95 | 99 | 93:07 |
| 11 | 1c | 2g | 30800 | 2.31 | 98 | 81 | 63:37 |
| 12 | 1c | 2h | 20900 | 2.20 | 98 | 99 | 95:05 |
| 13 | 1c | 2i | 15800 | 2.20 | 91 | 99 | 95:05 |
| 14[e] | 1c | 2j | 10300 | 1.99 | 67 | 99 | 90:10 |
| 15[e] | 1c | 2k | 7600 | 1.71 | 70 | 99 | 94:06 |
| 16 | 1c | 2l | 8100 | 1.62 | 66 | 98 | 90:10 |
| 17[e] | 1c | 2m | 8300 | 1.87 | 83 | 98 | 83:17 |
| 18 | 1c | 2n | 18000 | 2.07 | 85 | f | f |
| 19[g] | 1c | 2o | 21500 | 2.08 | 96 | 99 | 94:06 |
| 20[e] | 1c | 2p | 5900 | 1.56 | 49 | 98 | 90:10 |

[a]Unless otherwise noted, reaction conditions are as follows: monomer (1.0 mmol), Cu cat. (0.5 mol %), 30 °C, 24 h, *tert*-butyl methyl ether (3.0 mL). [b]Determined by GPC with RI. [c]Isolated yields. [d]Measured by hydrolyzing the polymer and analyzing the resulting diosl via HPLC. [e]40 °C. [f]Not detected. [g]36 h.

high molecular weight, and excellent stereoselectivity (up to 99% ee and 96:4 dl/meso) were achieved under the standard conditions. The results indicated that this protocol was suitable with commercial inexpensive dihydrosilanes 1a−1e (Table 2, entries 1−5).

To further demonstrate the versatility of this method, we valued a plethora of diketones (Table 2, entries 6−20). For diketones 2a−2f containing different substituents, the steric properties had only marginal influence on the enantioselectivities and diastereoselectivities, furnishing the desired products

in high yields and stereoselectivities with high molecular weight (entries 3 and 6−10). Moreover, the monomer **2h** with steric hindrance also performed smoothly to give the desired product in 98% yield and 99% ee with an $M_n$ value of 20900 and PDI value of 2.20 (entry 12). For aryl-substituted diketone **2g**, high yield and molecular weight albeit with moderate enantioselectivity were obtained under the standard conditions (entry 11). Unfortunately, benzyl-substituted diketone did not afford the product, which might be attributed to the isomerization from ketone to enol. To extend the substrate scope, we also assessed *meta*-substituted biphenyl **2i**, which showed similar results as **2a** (entry 13). Additionally, other skeletons of diketones also gave the desired poly(silyl ether)s **3ci−3cm** with high stereoselectivity (up to 99% ee and 94:6 dl/meso) (entries 14−17). To our surprise, the catalytic system exhibited good reactivity and enantioselectivity for the polymerization of aromatic heterocyclic diketones **2n−2p** (entries 18−20). For example, the asymmetric polymerization produced the enantiopure product **3co** in 96% yield and 99% ee (entry 19). It is a pity for failing to characterize stereoselectivity of **3cn** due to the unstability of diol containing active furan-based functional group, which was sensitive to acids or bases (entry 18). These enantiopure poly(silyl ether)s with heteroatom in main chain may expand the application in field of heterogeneous asymmetric catalysis.[9b,9d]

Thermal properties of some representative polymers were investigated under nitrogen atmosphere using TGA and DSC (as shown in SI, S112−S120). All of tested chiral poly(silyl ether)s exhibited good thermal stability, $T_5$ values ranged from 281 to 408 °C, and $T_{50}$ values varied from 434 to 568 °C. Due to the more regular structure of polymer **3ca**, it had the highest $T_5$ value (entry 1). Owing to the alkyl link in polymer **3 cm**, it had a relatively lower $T_5$ value (entry 3). Polymers **3ca** and **3ci** exhibited indiscernible glass transition temperatures via DSC (entries 1 and 2). For polymers **3cm** and **3co**, glass transition temperatures could be detected at 121 and 80 °C, respectively (entries 3 and 4).

On the basis of the previously proposed mechanism for the CuH-catalyzed hydrosilylation of ketones, a plausible catalytic cycle for hydrosilylation polymerization is proposed (as shown in SI, S13).[11] First, the silane is presumably responsible for an initial reduction from Cu(II) to Cu(I) to give active Cu−H species. Diastereoselective and enantioselective hydrocupration of **2k** generates the intermediate **B**, which is an irreversible and enantiodetermining step. Then, it would interact with the hydrosilane **1c** and facilitate the σ-bond metathesis to regenerate Cu−H species **A** and complete the catalytic cycle.

In conclusion, we have successfully synthesized highly optically active poly(silyl ether)s via CuH-catalyzed asymmetric hydrosilylation polymerization. An array of poly(silyl ether)s with structural diversity were obtained with excellent yields, high molecular weight, and excellent enantioselectivities (up to 98% yield and 99% ee) under convenient-to-perform conditions. The enantiopure poly(silyl ether)s with good thermal properties may have a potential application in chiral separation. Polymers containing heteroaromatic rings in main chain may play a promising role in heterogeneous asymmetric catalysis. Further studies are currently underway toward the expanding of this strategy to aliphatic diketones and the application of these enantiopure poly(silyl ether)s in enantioseparation as chiral stationary phases or asymmetric catalysis.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00225.

Experimental procedures and characterization data for the compounds (PDF)

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### Notes

The authors declare no competing financial interest.

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