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# Copolymers from a Single Monomer: Synthesis of Poly(methylidene-*co*-trimethylsilylmethylidene)

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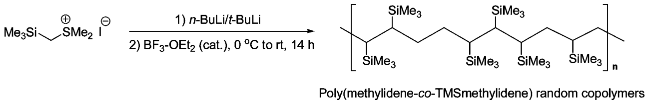
Trimethylsilyl (TMS)-modified polyethylenes have been prepared by the copolymerization of ethylene and vinyltrimethylsilane using the Ziegler−Natta catalyst.[1] The feed ratio of vinyltrimethylsilane to ethylene was varied from 5:95 to 95:5 in weight, and solid polymers with high molecular weight were synthesized. The ratio of incorporated $CHSiMe_3$ to $CH_2$ groups ranged from 0.71 to 0.008. Free radical copolymerization of those two monomers was also attempted, but the yield of polymerization was low (4.3%) and very few $CHSiMe_3$ groups were incorporated into the polymer backbone ($CHSiMe_3$:$CH_2$ = 0.004).[2] The polymer has also been prepared by the anionic homopolymerization of vinyltrimethylsilane, a traditional C2 olefin building block. The resultant homopolymer has one TMS group attached to the polymer backbone every two carbons.[3]

We are developing new polymerization reactions for the synthesis of polymers and copolymers with composition and topology that are not readily available by traditional olefin polymerization.[4] Current efforts have focused on carbon backbone polymers with TMS substituents. Recently, we reported a new polymerization reaction for the synthesis of TMS-modified polymethylenes. Oligomers were obtained by the trialkylborane-catalyzed copolymerization of trimethylsilyldiazomethane (TDM) and dimethylsulfoxonium methylide.[5] The resultant copolymer, poly(methylidene-*co*-trimethylsilylmethylidene), has a similar chemical composition as an ethylene−vinyltrimethylsilane random copolymer, but it arises from incorporation of C1 building blocks, trimethylsilylmethylidene ($CHSiMe_3$) and methylidene ($CH_2$) groups, into the growing polymer chain. Despite the novelty of this polymerization, the reaction was limited in the sense that $CHSiMe_3$:$CH_2$ ratios of no higher than 0.06 could be achieved.

Since important polymer properties such as gas permeability have been correlated to the molar ratio of $CHSiMe_3$ and $CH_2$ groups, we are continuing our investigation of TMS-substituted carbon backbone polymers. We believe that poly(methylidene-*co*-trimethylsilylmethylidene) copolymers with high $CHSiMe_3$:$CH_2$ ratio can lead to membranes with both high gas permeability and good gas selectivity. Generally, these two properties are inversely proportional to one another.[6] It is anticipated, however, that the bulky TMS substituents can lead to a stiff chain structure with high free volume, permeability, and diffusion coefficients; at the same time, more TMS functional groups can enhance the ability to selectively transport specific gases such as oxygen.

In this Communication, we report a new polymerization reaction for the synthesis of TMS-modified polymethylenes. The polymerization is capable of producing polymer with $CHSiMe_3$:$CH_2$ ratios higher than that obtained by vinyltrimethylsilane polymerization (Scheme 1). In addition, the polymer is built up *one carbon at a time* from $CH_2$ and $CHSiMe_3$ groups that are produced from a single monomer (trimethylsilylmethyldimethylsulfonium iodide).

**Scheme 1**



Dimethylsulfonium trimethylsilylmethylide was synthesized by the deprotonation reaction of trimethylsilylmethyldimethylsulfonium iodide using *n*-BuLi[7,8] or *t*-BuLi. The polymerization catalyzed by $BF_3$·etherate was then carried out. Results are summarized in Table 1.

Unexpectedly, the NMR of the isolated polymer exhibited features consistent with poly(methylidene-*co*-trimethylsilylmethylidene). Thus, the attempted homopolymerization of the ylide derived from trimethylsilylmethyldimethylsulfonium iodide gave a random copolymer product composed of both $CHSiMe_3$ and $CH_2$ groups. On the basis of the elemental analysis, the polymer of entry 3 has a [$CHSiMe_3$]:[$CH_2$] ratio of 1.75, indicating approximately two TMS groups attached to the polymer backbone for every three carbons. This ratio is higher than that can be achieved from the homopolymerization of vinyltrimethylsilane.

In Table 1, the polymer of entry 2 has a number-average molecular weight of 7840, corresponding to a DP (degree of polymerization) of 231, $(CHSiMe_3)_{64}$ and $(CH_2)_{167}$ groups. Polydispersities (PDI) are high, indicating this is not a controlled/“living” polymerization. A possible side reaction, chain transfer, is shown in Scheme 3. The reaction regenerates the initiating species and a polymer chain with a terminal vinyl group. This has been observed in the $^1H$ and $^{13}C$ NMR spectra of polymers in entries 3 and 4 of Table 1.

Possible explanations for the incorporation of methylene ($CH_2$) groups are proposed in Scheme 2. One prospect is by formation of a methylide, i.e., trimethylsilylmethylmethylsulfonium methylide (**B**). This ylide can be generated either from a kinetically controlled deprotonation reaction of the iodide salt precursor or by the equilibration of dimethylsulfonium trimethylsilylmethylide (**A**) under the polymerization conditions. A second possibility is by the generation of dimethylsulfonium methylide (**C**) under the reaction conditions for ylide synthesis or during the polymerization reaction. Contribution of this ylide was confirmed by the isolation of $[Me_3S]^+[I]^-$ salt during workup, i.e., redissolving the resultant polymer in cyclohexane followed by filtration. This desilylated methylide (**C**) can be generated by three pathways. One is the reaction of iodide salt with dimethyl sulfide. An additional pathway could involve attack of bases (*n*-BuLi/*t*-BuLi) on the electropositive silicon atom of the iodide salt. Considering the steric difference between those two bases, *t*-BuLi would be expected to be less nucleophilic. This could explain why entries 3 and 4 in Table 1 have higher $CHSiMe_3$:$CH_2$ ratios than entries 1 and 2. A third possible pathway to generate dimethylsulfonium methylide (**C**) is the reaction of iodide salt with dimethylsulfonium trimethylsilylmethylide (**A**). This reaction was also confirmed by the control experiment 1 shown in Scheme 2. In a word, the polymerization reaction mixture could contain dimethylsulfonium trimethylsilylmethylide (**A**) as well as two other ylides, methyltrimethylsilylmethyl sulfonium methylide (**B**) and dimethylsulfonium methylide (**C**). This point was further supported through control

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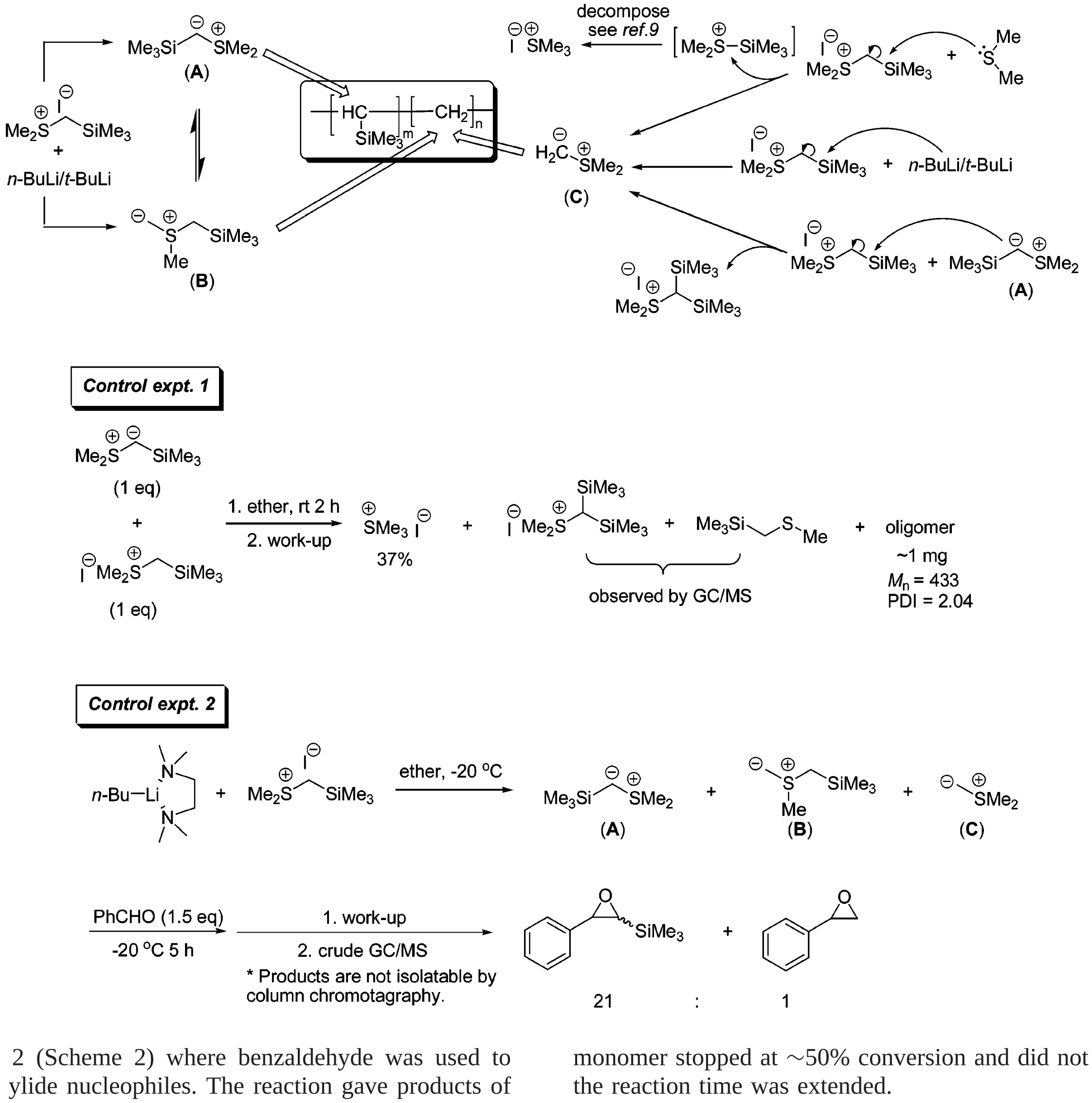
**Table 1. Results of the *in situ* Polymerization of Dimethylsulfonium Trimethylsilylmethylide Catalyzed by $BF_3$·Etherate**

| | | | | elemental analysis | | |
|---|---|---|---|---|---|---|
| entry | reaction conditions | yield[c](%) | $M_n$ (PDI) | found (%) | calcd Si% [100% − $(C + H)_{found}$] | $CHSiMe_3:CH_2$ |
| 1[a] | cat. = 12.5 mol %<br>solvent: hexanes[a] | 40 | 604<br>(1.56) | C 63.42,<br>H 12.09 | 24.49 | 0.48[d]<br>(0.31) |
| 2 | cat. = 12.5 mol %<br>solvent: ether | 38 | 7847<br>(1.63) | C 63.61,<br>H 12.03 | 24.36 | 0.45<br>(0.38) |
| 3[b] | cat. = 12.5 mol %<br>solvent: ether | 30 | 690<br>(2.00) | C 58.35,<br>H 11.24 | 30.41 | 1.75<br>(1.11) |
| 4 | cat. = 5 mol %<br>solvent: ether | 10 | 475<br>(1.39) | C 59.81,<br>H 11.01 | 29.18 | 1.05<br>(0.42) |

[a] Dimethylsulfonium trimethylsilylmethylide of entries 1 and 2 was synthesized by the deprotonation reaction using *n*-BuLi. [b] In entries 3 and 4, the deprotonation reaction was conducted by *t*-BuLi. [c] Yields are based on the consumption of ylide (~50%) and does not include oligomers. [d] The ratio was calculated from results of elemental analysis; the ratio in parentheses was obtained from integration of $SiMe_3$ and $CH_2$ groups in the $^1H$ NMR spectra.

**Scheme 2. Proposed Sources of Methylene ($CH_2$) Groups**



experiment 2 (Scheme 2) where benzaldehyde was used to quench the ylide nucleophiles. The reaction gave products of trimethyl(3-phenyloxiran-2-yl)silane by trapping ylide (**A**) and 2-phenyloxirane by trapping ylides (**B**) and/or (**C**).

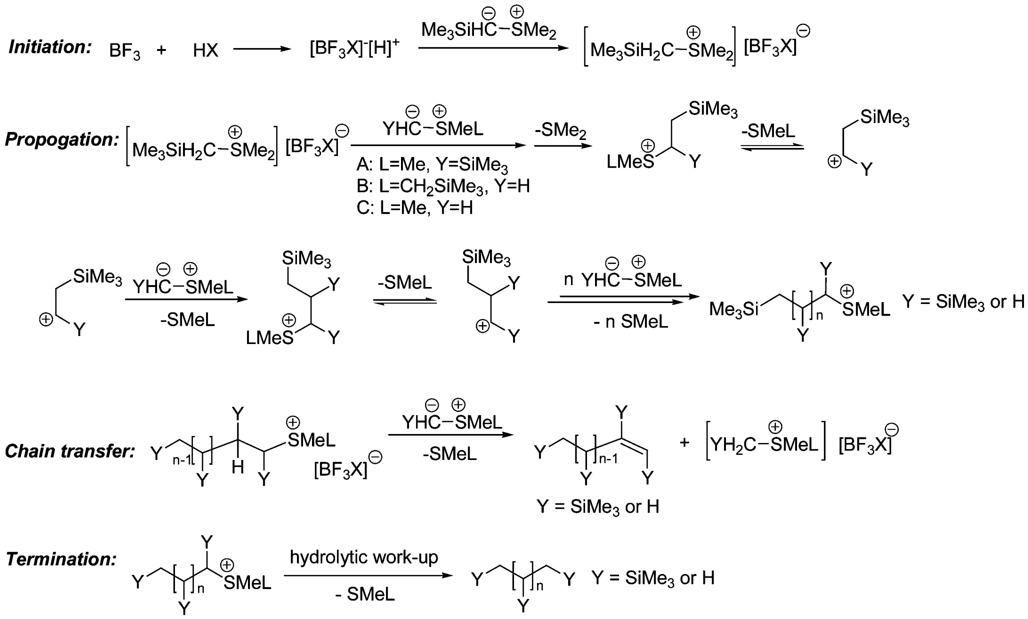
We suggest that this polymerization reaction is similar to the reported $BF_3$-catalyzed polymerization of diazomethane.[10] In this case a cationic polymerization initiated by trialkylsulfonium salt, $[Me_2SCH_2SiMe_3]^+[BF_3X]^-$, is proposed (Scheme 3). The cationic nature of this polymerization is consistent with the observed broad PDI of the resultant polymers.

A byproduct of the polymerization is dimethyl sulfide. Its accumulation can inhibit or slow the reaction as it progresses, consistent with the observation that consumption of ylide monomer stopped at ~50% conversion and did not change as the reaction time was extended.

Instead of conducting the polymerization reaction in situ, we distilled the dimethylsulfonium trimethylsilylmethylide. An air-stable zwitterionic complex was prepared when this ylide was treated with $BF_3$·etherate according to literature procedures.[7] The $^{11}B$ NMR spectrum of the complex gave a quartet at 2.82 ppm with a $^1J_{BF}$ value of 50.72 Hz. We did not observe the complex of ylide **B** or **C** (see Scheme 2) with $BF_3$. This suggests that those two ylides are generated under polymerization conditions.

With dimethylsulfonium trimethylsilylmethylide in hand, its bulk polymerization was catalyzed by 1.6 mol % of $BF_3$·

**Scheme 3. Proposed Mechanism of $BF_3$-Catalyzed Cationic Polymerization of Sulfonium Ylides**



etherate. The resulting crude polymer, a light yellow rubbery solid, was purified by dissolving in hot toluene and then precipitating in methanol to give the product in low yield as a white translucent rubbery solid. Its number-average molecular weight and PDI were 31 540 and 2.35, respectively. Oligomers with low molecular weight were lost upon workup, which accounts for the low isolated yield of the polymer.

A broad methylene ($CH_2$) absorption was observed in the NMR spectrum of the resultant polymer, indicating the product was also a poly(methylidene-*co*-trimethylsilylmethylidene) random copolymer. The $CHSiMe_3$:$CH_2$ ratio obtained from integration of the $SiMe_3$ and $CH_2$ peaks of the $^1H$ NMR spectrum turned out to be 0.12. This result supports one of the proposed pathways of the methylene group formation (see Scheme 2); i.e., there is a fast equilibration of dimethylsulfonium trimethylsilylmethylide (**A**) under polymerization conditions to generate methylide (**B**). More rapid incorporation of ylide **B** into the growing polymer chain could account for the high $CH_2$/$CHSiMe_3$ ratio.

In conclusion, we have developed a synthesis of poly(methylidene-*co*-trimethylsilylmethylidene) random copolymers. The polymer has a similar chemical composition as an ethylene−vinyltrimethylsilane copolymer. However, in this case, the copolymer backbone is constructed one carbon at a time. Polymers were obtained with a [$CHSiMe_3$]:[$CH_2$] ratio of 1.75, a composition that cannot be achieved by the homopolymerization of vinyltrimethylsilane.

Interestingly, the polymerization employs a single starting material (trimethylsilylmethyldimethylsulfonium iodide). This method, therefore, allows one to rethink the synthetic methodology of copolymers. This novel synthesis of substituted polymer chains marks an important step in diversifying the methods for polymer synthesis.

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**Supporting Information Available:** Detailed experimental procedures and representative polymer characterizations and data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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