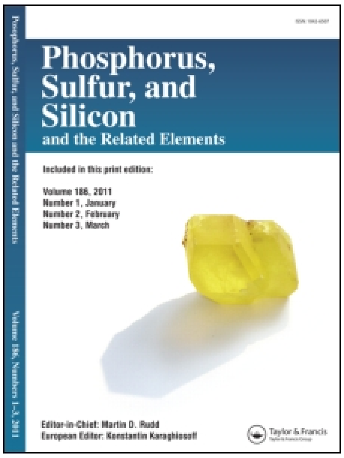
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Anionic Polymerization of Silicon-Containing Rings

Hideki Sakurai; Takanobu Sanji; Takahiro Sakai; Hiroyuki Hanao

To cite this Article Sakurai, Hideki , Sanji, Takanobu , Sakai, Takahiro and Hanao, Hiroyuki(1997) 'Anionic Polymerization of Silicon-Containing Rings', Phosphorus, Sulfur, and Silicon and the Related Elements, 124: 1, 173 — 182

To link to this Article: DOI: 10.1080/10426509708545622

URL: http://dx.doi.org/10.1080/10426509708545622

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1997, Vol. 124 & 125, pp. 173–182
Reprints available directly from the publisher
Photocopying permitted by license only

ANIONIC POLYMERIZATION OF SILICON-CONTAINING RINGS

HIDEKI SAKURAI, TAKANOBU SANJI, TAKAHIRO SAKAI, and HIROYUKI HANAO
Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278, Japan

Silole-containing polysilanes and polysilane heteropolymers are prepared by ring-opening anionic polymerization. Properties of novel polymers are discussed.

Keywords: polysilane; silole; ring-opening polymerization

INTRODUCTION

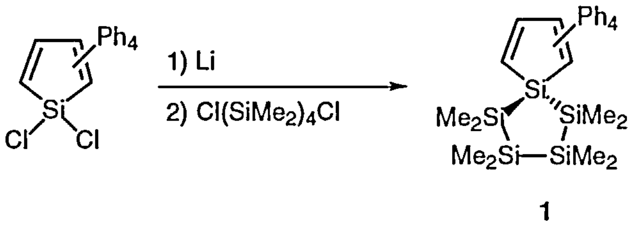
Polysilanes,[1] a relatively new class of polymers, have attracted considerable interest in the last two decades because of their potential applications in the field of materials science. Indeed polysilanes are very promising as advanced materials for high technology of the next generation. However, at the same time, applications of those materials require the ability to customize the structure and composition within the bulk and interfaces. In this paper, we present two new polysilanes prepared by ring opening anionic polymerization.

SILOLE-CONTAINING POLYSILANE

Siloles,[2] silacyclopentadienes, have long been known as interesting rings because of their very unique electronic structures. We have previously reported low reduction potentials for both diphenyl and tetraphenyldimethylsiloles by cyclic voltammetry.[3] More recently, Tamao and his co-workers have indicated by MO calculations that the silole has a relatively low LUMO energy level due to the σ^*-π^* conjugation, compared with a carbon analogue, cyclopentadiene.[4] Since polysilanes are characterized by their high-lying HOMO energy level, silole incorporated polysilanes should be an interesting polymer, in which the polysilane chain is expected to play as an electron donor while the silole ring acts as an acceptor.

Our synthetic strategy for the silole incorporated polymer is based on a ring opening polymerization of tetraphenylsilole-*spiro*-octamethylpentasilane (1) which can be prepared, as shown in SCHEME 1, by the reaction of the silole dianion and 1,4-dichlorooctamethyltetrasilane.

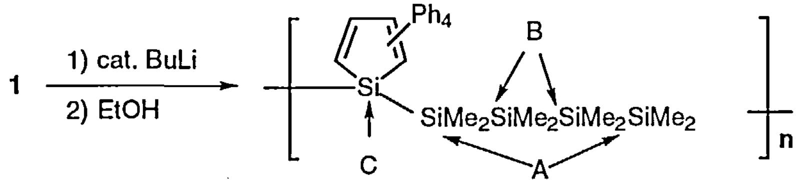
SCHEME 1



1

Anionic ring opening polymerization of **1** with a catalytic amount of butyllithium as an initiator in THF at -40 ℃ proceeded smoothly (SCHEME 2), the polymer **2** being obtained in 41 % yield (Mn = 17,000, Mw/Mn = 1.3). The structure of the polymer was highly ordered as estimated by NMR analyses. FIGURE 1 shows the ^{29}Si NMR spectra of the polymer where only three different kinds of signals exist. These signals are assigned to the silole silicon (c), the central silicon (B), and the terminal silicon adjacent to the silole ring (A), respectively. Thus the ^{29}Si NMR spectrum is consistent with the polymer chain of highly regulated structure. The ^{1}H and ^{13}C NMR spectra also supported the conclusion. These results indicate that the anionic ring opening polymerization process itself must be highly regioselective.

SCHEME 2



2

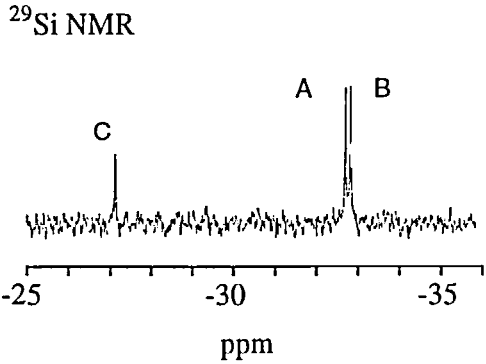
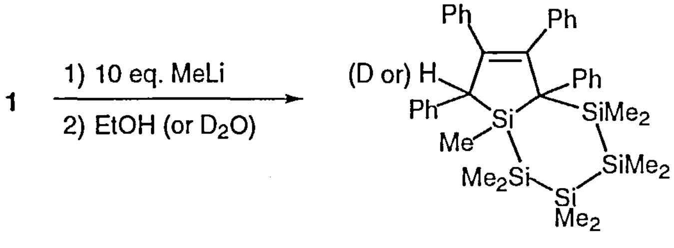


FIGURE 1 ^{29}Si NMR spectra of the polymer **2** in $CDCl_3$.

For the elucidation of the polymerization mechanism, the reaction of **1** with large excess of methyllithium at -40 °C, followed by addition of ethanol, was examined. The reaction gave **3** exclusively as shown in SCHEME 3.

SCHEME 4 shows the possible reaction mechanism for the formation of **3**. In the initial step of the reaction, methyllithium attacks the silole silicon atom of **1** to form a pentacoordinate silicate intermediate. Then the silicon-silicon bond is cleaved to form a silyl anion which should be quite reactive to counter attack the silole carbon to form allyl anionic species. The resulting allyl anionic species is resonance stabilized by the two phenyl groups. These two species must be in an equilibrium but in favor of the allyl anionic species. Then quenching by ethanol gave the ring compound **3**. The polymerization itself must proceed by the attack of the silyl anions to the silole silicon of **1** and similar reactions take place to form the polymer. Therefore, the reactive end should always be in an equilibrium between the silyl anion ends and ring allyl anions. This is an interesting new kind of degenerate living anionic polymerization.

SCHEME 3

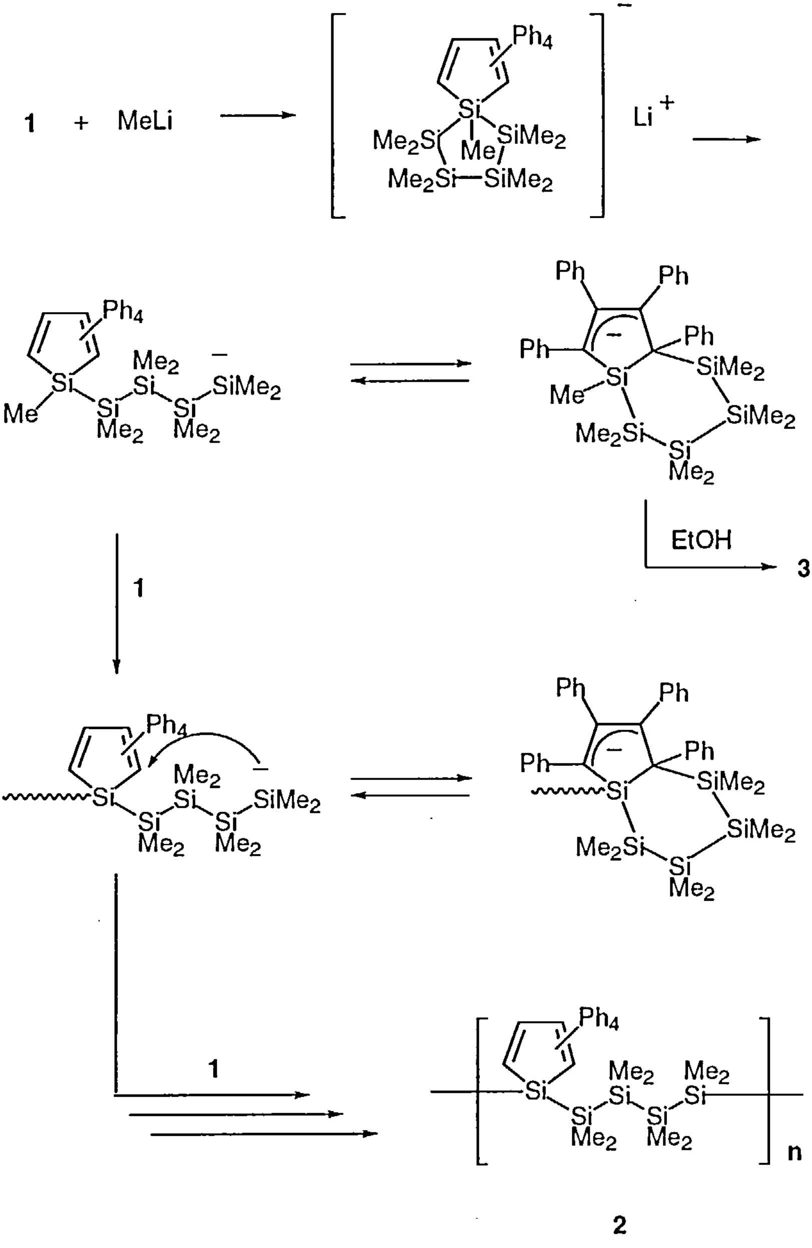


3

Absorption spectrum of the polymer **2** shows two maxima around 320 and 360 nm, assignable to those of the polysilane skeleton and the silole ring, respectively. It is quite interesting that the excited spectrum, monitored at 520 nm, reproduced the absorption spectrum almost completely, indicating the extensive energy transfer between the silole ring and the polysilane chain. It should also be noted that fluorescence quantum yield of the polymer (4.1×10^{-2}) increased about 10 times more than that of the parent hexaphenylsilole (4.5×10^{-3}).[5]

The polymer must be a quite interesting material, application of which is currently under way including the use in EL devises.

SCHEME 4



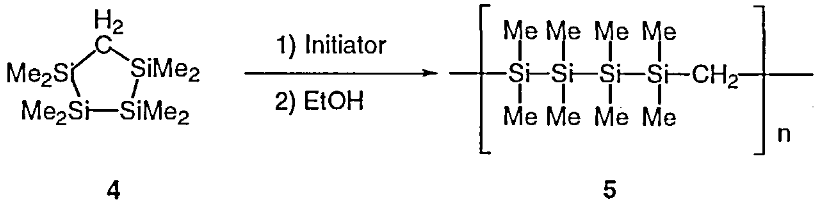
POLYSILANE HETEROPOLYMER

Although the main chain of the polysilanes comprises saturated σ-bonds, electrons delocalizes highly though the silicon backbone, which is now known as σ-conjigation. As a result of the σ-conjugation, the polysilanes exhibit an intense absorption in an ultraviolet region, while the polyalkanes exhibit no absorption in such a region. The unique photophysical and photochemical properties of the polysilanes have been explained in terms of a simplified segment model;[6] the polysilane chain is a collection of certain short length segments of 10-20 silicon atoms with different length and photoexcitation energies. Then the characteristic nature of the polysilanes must be explained in terms of the interaction among the segments. It is therefore of interest to investigate the conjugation among the segments of the polysilanes. Especially, studies are highly desired on heterocatenates with polysilane chains at least longer than tetrasilane chains separated by a methylene, since the tetrasilane is a minimum unit as the polysilane with every possible conformations around the central silicon-silicon bond.

Herein an anionic ring opening polymerization of octamethyltetrasilacyclopentane (4) to structurally highly regulated poly(1,1,2,2,3,3,4,4-octamethyltetrasilanylenemethylene) (5) is presented.[7] The polymer consists of tetrasilanylene units linked with methylene units and should be a good model for the segment model proposed for polysilanes.

Octamethyltetrasilacyclopentane (4) was prepared in 68% yield by coupling of bis(2-chloro-1,1,2,2-tetramethyldisilanyl)methane with lithium. The ring compound 4 was readily polymerized with anionic initiators (SCHEME 5). The polymerization in THF with a catalytic amount of HMPA at -78 ℃ proceeded smoothly, the polymer 5 being obtained in 64 % yield.

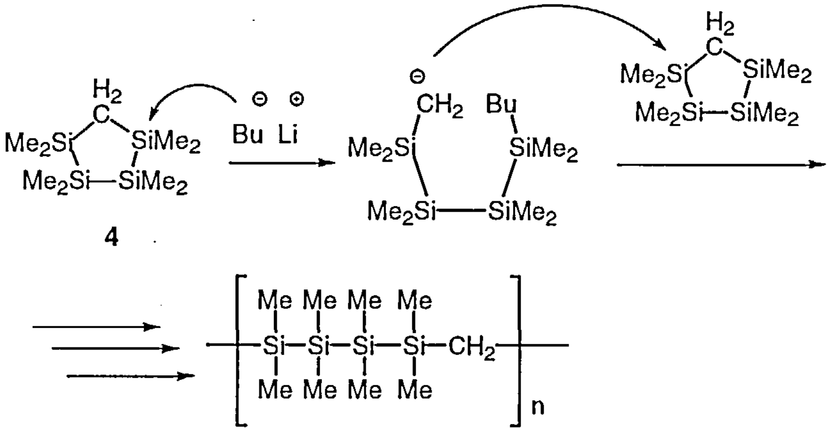
SCHEME 5



4

5

SCHEME 6



4

5

The sequence structure of the polymer was highly ordered as indicated by NMR analyses. FIGURE 2 shows the ^1H, ^{13}C, and ^{29}Si NMR spectra of the polymer. In the ^1H and ^{13}C NMR spectra, there are only three signals. These signals are assigned to the methylene, the methyl groups of the $-CH_2-\underline{SiMe_2}-SiMe_2-$ unit adjacent to the methylene (unit A), and the $-CH_2-SiMe_2-\underline{SiMe_2}-$ unit (unit B), respectively. Thus the ^1H and ^{13}C NMR spectra are consistent with those for **5** in the heterocatenated structure with highly regulated structure. This conclusion is further supported by ^{29}Si NMR spectrum; the ^{29}Si NMR spectrum of **5** shows only two sharp signals assignable to those of the unit A and B. These results indicate that the anionic ring opening polymerization process itself must be highly regioselective.

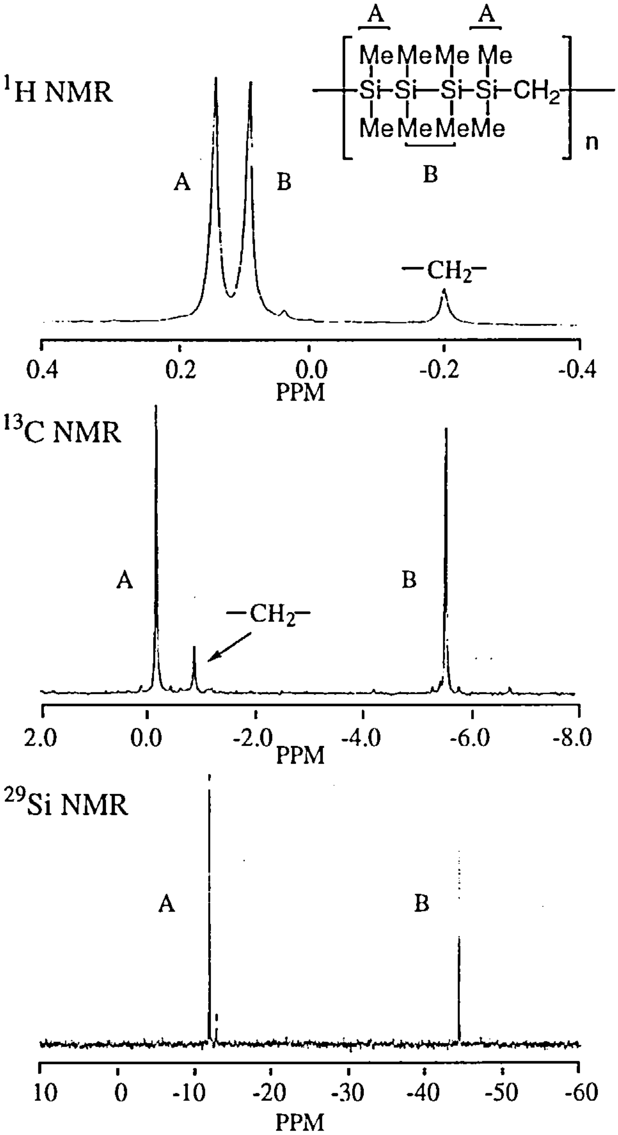


FIGURE 2 ^1H, ^{13}C, and ^{29}Si NMR spectra of **5** in $CDCl_3$

SCHEME 6 shows the possible reaction mechanism of **4**. The anionic polymerization of **4** proceeds at first by nucleophilic attack at the silicon atom adjacent to the methylene. The ring opening results in relief of the ring strain and the formation of a primary carbanion adjacent to the silyl groups. Next, the carbanion attacks the silicon atom adjacent to the methylene of another monomer. It is well documented that such α-silyl carbanions are stabilized by σ*-π conjugation.[8] The polymerization proceeds further in this manner.

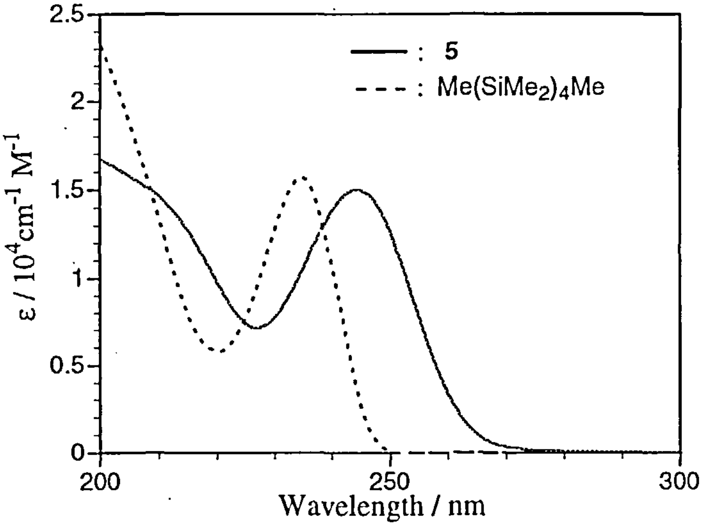


FIGURE 3 UV absorption spectra of 5 and decamthyltetrasilane in hexane.

FIGURE 3 shows the UV absorption spectra of 5 compared with decamethyltetrasilane in hexane at room temperature. While the absorption intensity of 5 was almost equal to that of the tetrasilane, the absorption maximum of 5 (245 nm) exhibited a 10 nm bathochromic shift in contrast with that of decamethyltetrasilane (235 nm). This bathochromic shift must be originated in the σ-conjugation between the tetrasilanylene units *via* the methylene units. It is interesting to note that the fluorescence spectra of the polymer in 3-methylpentane at 77 K is almost identical to that of the decamethyltetrasilane assignable to the self-trapped state.[9] These results indicate that the stabilization by σ-conjugation in the excited state is rather small. Thus the delocalization in the ground state is much important in the σ-conjugation between the tetrasilanylene units *via* the methylene units in this polymer.

Acknowledgments

We are grateful to the New Energy and Industrial Technology Development Organization (NEDO), the Japan High Polymer Center (JHPC) and the Japan Society for Promotion of Sciences (JSPS) for financial supports.

References

[1.] For reviews of polysilanes, see: (a) R. West, *J. Organomet. Chem.*, **300**, 327 (1986); (b) R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989); (c) H. Sakurai, *Advanced Technology of Organosilicon Polymers*, CMC Co., Ltd., Tokyo (1996).

[2.] K. Tamao and S. Yamaguchi, *Pure Appl. Chem.*, **68**, 139 (1996).

[3.] N. Tanaka, T.Ogata, Y. Uratani, Y. Nakadaira, and H. Sakurai, *Inorg. Nucl. Chem. Lett.*, **8**, 1041 (1972).

[4.] K. Tamao, S. Yamaguchi, Y. Ito, Y. Matsuzaki, T. Yamabe, and M. Fukushima, *Macromolecules*, **28**, 8668 (1995).

[5.] H. Hennig, K. H. Heckner, A. A. Pavlov, and M. G. Kuzmin, *Ber. Bunsenges Phys. Chem.*, 84, 1122 (1980).

[6.] (a) Y. -P. Sun, Y. Hamada, L.-M. Huang, J. Maxka, J.-S. Hsiao, R. West, and J. Michl, *J. Am. Chem. Soc.*, **114**, 6301 (1992); (b) Y.-P. Sun and J. Michl, *J. Am. Chem. Soc.*, **114**, 8186 (1992).

[7.] H. Isaka, *Macromolecules*, **30**, 344 (1997).

[8.] (a) L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952); (b) A. R. Bassindale and P. G. Taylor, in *Chemistry of Organic Silicon Compounds*, ed. by S. Patai and Z. Rappoport, John Willey & Sons, Chichester, England (1989), Chap. 14.

[9.] (a) H. S. Plitt and J. Michl, *Chem. Phys. Lett.*, **400**, 198 (1992); (b) H. S. Plitt, V. Balaji, and J. Michl, *Chem. Phys. Lett.*, **158**, 213 (1993); (c) B. Albinsson, H. Teramae, J. W. Downing, and J. Michl, *Chem. Eur. J.*, **2**, 529 (1996).