Highly Ordered High Molecular Weight Alternating Polysilylene Copolymer Prepared by Anionic Polymerization of Masked Disilene[1]

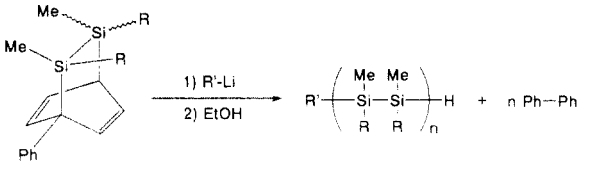
Recent findings of polysilylenes as SiC precursors by Yajima et al.[2] created new industrial applications of this class of polymers. More recently, potential applications of polysilylenes are indicated in microlithography,[3] in reprography,[4] as nonlinear optics,[5] and in other areas.[6,7] To date, polysilylenes are prepared mostly by the Wurtz-type coupling of dichlorodialkylsilanes with sodium in refluxing toluene.[7] However, the method has several difficulties such as the poor control of molecular weight and polydispersity. Yields of polymers are also generally low.

Very recently we have reported an entirely new method of preparing polysilylenes based on anionic polymerization of masked disilenes.[8] We have prepared polysilylene homopolymers $(SiMeR–SiMeR)_n$ and alternating copolymers $(SiMe_2–SiMeR)_n$ of highly ordered structure (Scheme I).

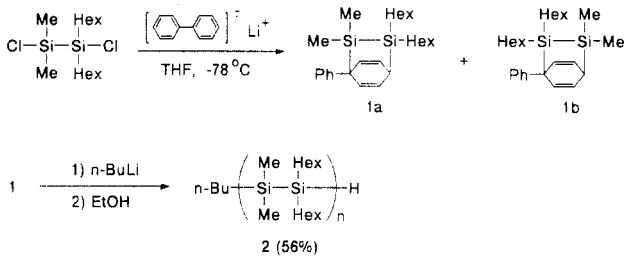
Herein we report the preparation of poly(1,1-dihexyl-2,2-dimethyldisilene) $(SiHex_2–SiMe_2)_n$ by the anionic polymerization method. The comparison of the polymer with those of the similar composition made by the conventional sodium coupling method revealed intriguing differences in structure and properties.

We have synthesized poly(dihexylsilylene-*co*-dimethylsilylene) by three different methods. A masked disilene monomer **1** was prepared by the process shown in Scheme II as described before.[8] Monomer **1b** was a major isomer over **1a** (**1b**/**1a** = 7.8/1). Separation of these two isomers may be possible but was not attempted at this time. Anionic polymerization of **1** with *n*-BuLi in THF followed by quenching with ethanol afforded polymer **2** in 56% yield.[9] The molecular weight distribution of the polymer was determined by gel permeation chromatography (GPC), calibrated by polystyrene standards, with chloroform as eluent; $\bar{M}_n = 6.1 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.3$.

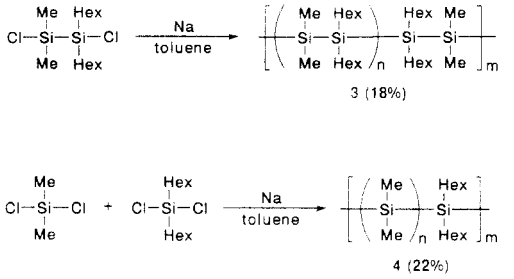
Scheme I



Scheme II



Scheme III



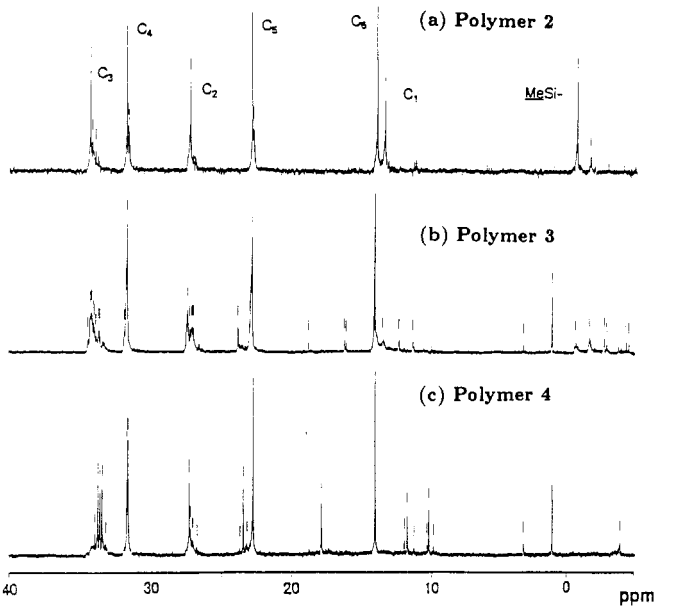


Figure 1. ^{13}C NMR spectra of (a) polymer **2**, (b) polymer **3**, and (c) polymer **4**.

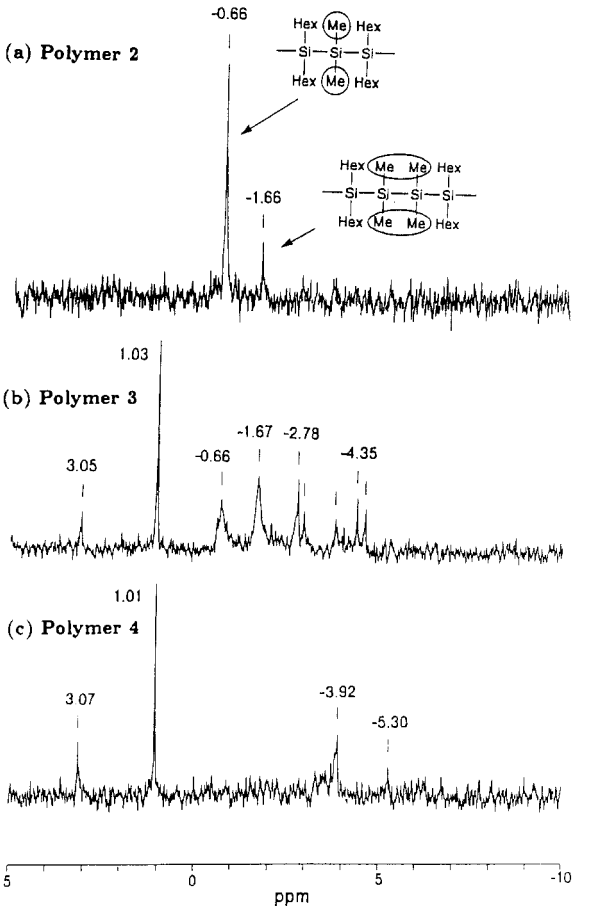


Figure 2. ^{13}C NMR spectra of methyl signals of (a) polymer **2**, (b) polymer **3**, and (c) polymer **4**.

Polymer **3** (Scheme III) was made by sodium coupling of the corresponding 1,2-dichlorodisilane.[10] Thus sodium coupling of 1,2-dichloro-1,1-dihexyl-2,2-dimethyldisilane in refluxing toluene gave **3** in 18% yield (**3**, $\bar{M}_n = 1.4 \times 10^4$, $\bar{M}_w/\bar{M}_n = 3.8$). Polymer **4** was also made by sodium coupling of a 1:1 mixture of dichlorodimethylsilane and dichlorodihexylsilane in 22% yield (**4**, $\bar{M}_n = 4.8 \times 10^4$, $\bar{M}_w/\bar{M}_n = 5.1$). It is clear that the anionic polymerization method is far superior to other methods in both polydis-

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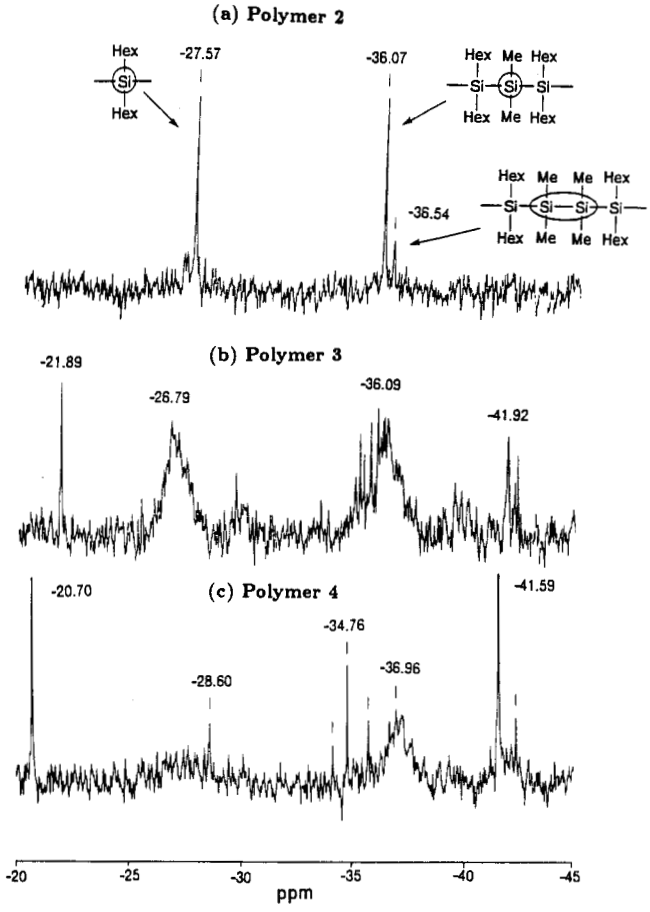

Figure 3. ^{29}Si NMR spectra of (a) polymer **2**, (b) polymer **3**, and (c) polymer **4**.

persity and yield of the polymer.

Figure 1 shows the ^{13}C NMR spectra for these three polymers. Six well-defined peaks are observed for the hexyl part of **2**. The methyl region of the spectra is expanded in Figure 2. The signal at −0.66 ppm of **2** is assigned to the methyl group of $SiHex_2$–$SiMe_2$–$SiHex_2$ (the unit A), while the minor signal at slightly higher field (−1.66 ppm) can be assigned to that of $SiHex_2$–$SiMe_2$–$SiMe_2$–$SiHex_2$ (the unit B). The latter arose from the concomitant minor monomer **1a**.[11] Judging from these results, the polymerization process itself is indicated to be strictly in a head-to-tail fashion. This conclusion is further supported by ^{29}Si NMR spectra shown in Figure 3. Thus the ^{29}Si NMR spectrum of **2** shows only two sharp signals assignable to those of $SiMe_2$–$SiHex_2$–$SiMe_2$ (−27.57 ppm) and $SiHex_2$–$SiMe_2$–$SiHex_2$ (−36.07 ppm). These signals are surprisingly sharp as for polymer signals, indicating a highly ordered structure for **2**. A minor peak at −36.54 ppm can be ascribed to the silicon signal of the minor unit B ($SiHex_2$–$SiMe_2$–$SiMe_2$–$SiHex_2$).

The ^{13}C spectral features of **3** are much more complicated. It might be expected that the Wurtz-type condensation of 1,2-dichloro-1,1-dihexyl-2,2-dimethyldisilane should give only two kinds of methyl signals corresponding to the head-to-head (the unit B) and the head-to-tail (the unit A) structures. However, at least four methyl peaks at −0.66, −1.67, −2.78, and −4.35 ppm were observed in the ^{13}C NMR spectrum (Figure 2b). The former two can be easily assigned to the expected peaks of units A and B as similarly observed for **2**. The other high-field methyl peaks should arise from the poly(dimethylsilylene) part $SiHex_2$–$(SiMe_2)_n$–$SiHex_2$ (the unit C). A sharp peak at 1.03 ppm is assigned to $SiHex_2$–$SiMe_2$–O–$SiHex_2$ because partial oxidation of **2** with *m*-chloroperbenzoic acid to disiloxane[12,13] produced the same peak. The ^{29}Si NMR spectrum of **3** shows two broad peaks corresponding to the units A and B in addition to that corresponding to the unit C. A sharp signal at −21.89 ppm arose from disiloxane.[14]

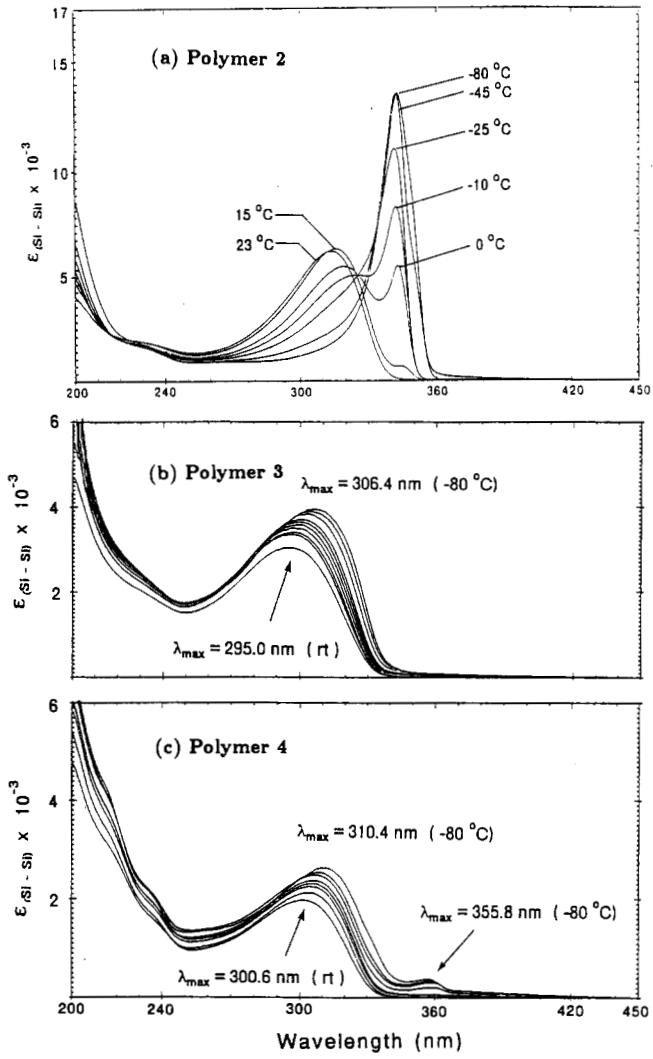

Figure 4. Temperature-dependent UV spectra of (a) polymer **2**, (b) polymer **3**, and (c) polymer **4**.

The Wurtz-type condensation of chlorosilanes with sodium metal involves silylsodium and/or silyl radicals in the mechanism.[7,15] Under rather vigorous reaction conditions, polysilylene chains may be cleaved to create new reactive ends, which may undergo further condensation. Some years ago, we had demonstrated that trimethylsilylsodium can cause facile redistribution of the Si–Si bonds to create a new silylsodium end in a polar solvent.[16] Similar redistribution of the polymer end may occur under these conditions, and this may be the reason for rather poor control of polydispersity as well as of molecular weight of polysilylenes made by the Wurtz-type coupling method with sodium.

The ^{13}C NMR spectra of polymer **4** is shown in Figure 1. The presence of peaks in the methyl and hexyl regions indicates that it is definitely a copolymer. However, rather simple peaks of methyl groups appear at high field (Figure 2). This means that **4** is composed of blocklike components, $(SiMe_2)_n$ and $(SiHex_2)_m$.

The differences in the structures of these polymers are quite remarkable and are demonstrated most dramatically in the UV spectra. Figure 4 shows temperature-dependent

UV spectra of **2**–**4**. Polymer **2** shows well-defined thermochromic behavior. Thus **2** shows absorption at λ_{max} 314.0 nm at 23 °C, but below 0 °C a new band at λ_{max} 342.4 nm starts to grow. Below −40 °C, the peak at λ_{max} 314.0 nm disappears completely.

The thermochromic behavior of polysilylenes has attracted much interest and has been studied extensively.[17] Thermochromic shifts have been observed for symmetrically and unsymmetrically[18] substituted polysilylene homopolymers but have never been observed for copolymers. As shown in Figure 4, no such bathochromic thermochromism was observed for either **3** or **4**. Only a small peak growing at λ_{max} 355.8 nm at low temperature may be recognized for **4**. We believe this is due to blocks of poly(dihexylsilylene). The bathochromic shift observed for **2** is comparable and similar to that observed for poly(dihexylsilylene).

The fact that a thermochromic shift is observed only for the high molecular weight polysilylene alternating copolymer of *highly ordered structure* creates a new interesting challenge in the structural chemistry of polysilylenes. The present results also demonstrate additional values and usefulness of the new method of preparing polysilylene high polymers based on anionic polymerization of masked disilenes.

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Kenkichi Sakamoto, Masaru Yoshida, and Hideki Sakurai*

Department of Chemistry, Faculty of Science Tohoku University, Aoba-ku, Sendai 980, Japan

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