Synthesis and Characterization
POLY([SILYLENE]ETHYNYLENE) AND POLY([SILYLENE]ETHYNYLENE): NEW PRECURSORS FOR THE EFFICIENT SYNTHESIS OF SILICON CARBIDE

Soichiro Kyushin,1 Hiroyuki Shiraiwa,1 Masafumi Kubota,1 Keisuke Negishi,1 and Kiyohito Okamura,2
and Kenji Suzuki3

a) Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma
University, Kiryu, Gunma 376-8515, Japan
b) Advanced Institute of Materials Science, Sendai, Miyagi 982-0252, Japan

ABSTRACT

Poly([silylene]ethylylene) and poly([silylene]ethylylene) were found to become new precursors for the efficient synthesis of Si–C–O ceramics. These precursors were synthesized by the reactions of dilithiocacetylene with trichlorosilane or dichlorosilane in one step. When these precursors were heated gradually up to 1000 °C, Si–C–O ceramics were formed in high yields. The weight loss is 5% in the case of poly([silylene]ethylylene) and 10% in the case of poly([silylene]ethylylene). The remarkably low weight losses enable the molding of the Si–C–O ceramics and the formation of thin films.

INTRODUCTION

Silicon carbide and related ceramics have been used as materials which are thermally stable and have high tensile strength. Silicon carbide fibers have been industrially produced by the thermal rearrangement of poly(dimethylsilane) into polycarbosilane and the thermolysis of polycarbosilane at more than 1000 °C according to Yajima’s method.1,2 This method was well established, and no other methods could not replace it for more than thirty years. However, in order to improve versatility and applicability of silicon carbide and related ceramics, development of other synthetic routes is required and has been studied.3,4

Our concept for designing a new synthetic route is based on the formation of a network structure during the thermolysis of the precursor. If a network structure was highly developed by the formation of silicon–carbon bonds, the precursor might be expected to form silicon carbide efficiently. As such silicon–carbon bond formation, we focused our attention on hydrosilylation of carbon–carbon triple bonds with hydrosilanes, and planned to use poly([silylene]ethylylene) and poly([silylene]ethylylene) as precursors. We report herein the synthesis of these precursors and their thermolysis leading to the formation of Si–C–O ceramics without significant weight losses.
SYNTHESIS OF POLY[(SILYLNE)ETHYNYLNE] AND POLY[(SILYLENE)ETHYNYLNE]

Poly[(silylene)ethynylene] (1) and poly[(silylene)ethynylene] (2) were synthesized by the reactions of dilithioacetylene, which was prepared from trichloroethylene and n-butyllithium, with trichlorosilane or dichlorosilane in 82 and 42% yields, respectively. Compound 1 was obtained as pale yellow powder. Compound 2 was obtained initially as pale yellow viscous oil, but after the oil was fully dried under reduced pressure, this compound was obtained as pale yellow powder. The IR spectra of these compounds show the Si–H stretching band at 2190–2260 cm⁻¹ and the C=C stretching band at 2050–2060 cm⁻¹. As the Si–O stretching band is also observed at 1070–1110 cm⁻¹, these compounds contain oxygen atoms.

THERMOLYSIS OF POLY[(SILYLNE)ETHYNYLNE] AND POLY[(SILYLENE)ETHYNYLNE]

When these precursors were gradually heated up to 1000 °C under a nitrogen atmosphere, black powder was obtained in 95% yield from 1 and in 90% yield from 2. The weight losses of 5 and 10% are remarkably low compared with Yajima’s method, where polycarbosilane loses about 40% of its weight on thermolysis to silicon carbide. The elemental analysis showed that the product from 1 contains silicon, carbon, and oxygen atoms in 39, 32, and 21%, respectively, and the product from 2...
contains silicon, carbon, and oxygen atoms in 47, 22, and 20\%, respectively. These data show the products are Si–C–O ceramics. The structures of the Si–C–O ceramics were analyzed by X-ray diffraction, but no reflections were observed, indicating that the Si–C–O ceramics are amorphous.

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\begin{align*}
1 & \overset{1000 \, ^\circ\text{C}}{\longrightarrow} \text{Si–C–O} \\
2 & \overset{1000 \, ^\circ\text{C}}{\longrightarrow} \text{Si–C–O}
\end{align*}
\]

96\% 96\%

In order to obtain more information about thermal behavior of 1 and 2, TG-DTA measurements were carried out (Figure 1). Exothermic peaks were observed at 266 °C in the case of 1 and at 222 °C in the case of 2. These exothermic peaks are ascribed to hydrosilylation of the precursors. The weight losses of 1 and 2 at 1500 °C are 4.2 and 6.7\%, respectively. Although these values are slightly smaller than the above values in the synthetic experiments, both data show very low weight losses. Thus thermal stability of the Si–C–O ceramics is unusual because silicon carbide containing oxygen atoms has been known to evolve SiO and CO and reduce the weight considerably on heating from 1000 °C to 1500 °C.\(^6\) This unusual thermal stability of the Si–C–O ceramics cannot be explained clearly, but the development of the rigid network structure by hydrosilylation might be responsible for this thermal stability.

![Figure 1. TG-DTA data of 1 (left) and 2 (right) measured under a nitrogen atmosphere.](image)

MOLDING AND FORMATION OF A THIN FILM OF THE Si–C–O CERAMICS

The low weight losses enable the molding of the Si–C–O ceramics. As mentioned above, the powder of 1 gave black powder of the Si–C–O ceramics without a significant weight loss (Figure 2 (top)). On the other hand, a disk-shaped ceramic pellet was obtained by pressing the powder of precursor 1 into a disk-shaped pellet and heating it up to 1000 °C (Figure 2 (bottom)). Also, a thin film was obtained by spreading the oil of 2 on a quartz plate by spin coating technique and heating it up to 1000 °C. These methods expand the versatility and applicability of silicon carbide and related ceramics.
CONCLUSION

In summary, we have found that poly[(silylene)ethynylene] and poly[(silylene)ethynylene] can be used as precursors for the efficient synthesis of Si–C–O ceramics. The weight losses on heating the precursors up to 1500 °C are remarkably low, probably due to the formation of a rigid network structure by hydrolysis. These precursors provide the Si–C–O ceramics as powder, molds, and thin films.

REFERENCES