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# Influence of the architecture of dendritic-like polycarbosilanes on the ceramic yield

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## Abstract

To investigate the influence of the architecture of preceramic polymers on the ceramic yield, two dendritic-like polycarbosilanes named as K3G3 and G3 were synthesized through different routes. The obvious difference in their molecular structures is related with the distribution of allyl groups. The decomposition and rearrangement reactions of the K3G3 occurred at lower temperatures compared with that of sample G3, due to the fact that the allyl groups in G3 are located in both inner and outer molecular layers while those in K3G3 are located in the outer layers, exclusively. As a result, the residual mass of the K3G3 at 1000 °C (18 wt%) is much lower than that of the G3 sample (35 wt%). The molecular weight of the dendritic-like polymers also has an important effect on their ceramic yield which increases from 34.6 to 67.6% with the increasing molecular weight of Gn ($3 \leq n \leq 5$).

*Keywords:* Polymer-derived ceramics; Dendritic polycarbosilanes; Silicon carbide; Polymeric architecture; Ceramic yield

## 1. Introduction

During the past decades, the design of new precursor systems suitable for the synthesis of high performance silicon-based ceramics has been a focus of considerable attention.[1–4] Si-based precursors have received much consideration because the chemical and physical properties of PDCs can be varied and adjusted to a great extent by the design of the molecular precursor.[5–8] A series of empirical rules for designing a proper ceramic precursor have been set forth.[9,10] The polymer should possess: (i) appropriate rheological properties and solubility for the shaping process, (ii) high molecular weight to avoid volatilization of low molecular components, (iii) presence of latent reactivity for subsequent curing and cross-linking steps and (iv) cage or ring structure for high ceramic yield. One important feature of the polymer-derived ceramic (PDC) route is related to the ceramic yield which ultimately determines the utility of the process as well as the bulk properties and shape retention of the resulting ceramics.[11] The ceramic yield of polymer precursors strongly depends on their chemistry including their backbone structure, their functional side groups (substituents), and their degree of cross-linking. E.g., cross-linked polysilazanes can give a ceramic yield of 80 wt% or higher while uncross-linked polymers of comparable composition gave only 20 wt% ceramic residue.[12] Lücke et al.,[13] systematically investigated the effect of branched and unbranched structure of polysilazanes on the ceramic yield. Hyperbranched polymers are different from linear ones in terms of the dimensionality of the molecular architecture, the former being three-dimensionally cross-linked forming a 3D-network structure while the latter is comprised of one-dimensional chains. As ceramic precursors, the hyperbranched polymers were found to be superior in terms of the ceramic yield.[14] Recently, hyperbranched polycarbosilanes (HBPCSs) have drawn great attention as precursors to form SiC.[15] In

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our previous work, we successfully synthesized a series of HBPCSs and studied their polymer-to-ceramic transformation systematically.[16–21] Our results indicate that the ceramic yield of the hyperbranched allylhydridopolycarbosilane was influenced by the structure factors such as branched structure, side chains, vinyl functionality, and molecular weight.[19] Meanwhile, many efforts have been undertaken to increase the ceramic yield of liquid HBPCSs.[22–27]

As mentioned above, the molecular structure (including backbone structure, functionalities, degree of cross-linking and molecular weight) of hyperbranched preceramic polymers significantly influence their ceramic yield.[12,13,19] However, little attention was paid on the influence of the distribution of functionalities such as vinyl groups of the hyperbranched polymers on the ceramic yield. As it is well-known, hyperbranched polymers are prepared in a random one-step synthesis from monomers having branching potential (e.g., $AB_2$ based) but with low control over structure and molar mass.[28,29] Therefore, it is difficult to control the distribution of the functionalities of hyperbranched polymers. In contrast dendrimers are perfectly branched molecules prepared in a stepwise manner with the potential to come close to the structural and molar mass uniformity.[29] However, the synthesizing process, either divergent or convergent approaches, is complex with multistep reaction to form high generation polymers.[30,31] To combine the merits of onestep synthesis for hyperbranched polymers and multistep reaction for dendrimers together, a new synthetic technique for dendritic-like polymers designated to the core-dilution/slow addition method was developed in a controlled manner.[32,33] In this paper, we synthesized a novel dendritic-like polycarbosilane with the slow addition method, namely pseudo-one-step method. In contrast, another dendritic-like polymer was synthesized by the stepwise approach, namely the iteration method. With the obtained two polymers as model compounds, the influence of the polymeric architecture on the ceramic yield of the dendritic-like preceramic polymers was investigated.

## 2. Experimental procedure

### 2.1. General

All synthesis and sample manipulations were carried out by using standard high vacuum or inert atmosphere techniques as described by Shriver and Drezdzon.[34] Dichloromethylvinylsilane ($CH_3Si(CH{=}CH_2)Cl_2$), dichloromethylsilane ($CH_3SiHCl_2$) and allyl chloride ($CH_2{=}CHCH_2Cl$) are industrial grade and distilled before use. Karstedt catalyst ($H_2PtCl_6$, divinyltetramethyldisiloxane solution) was purchased from J&K and stored in a glove box until use. THF was distilled from a sodium benzophenone ketyl prior to use. All other reagents are analytical grade and used as received.

Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet Avator 360 apparatus (Nicolet, Madison, WI) in the range of 4000–500 $cm^{-1}$ with KBr plates for liquid samples and KBr disks for solid samples. Nuclear magnetic resonance (NMR) experiments were carried out on a Bruker AV300 MHz spectrometer operating at 300.13 MHz for hydrogen-1, 75.46 MHz for carbon-13 ($^1H$ decoupling) and 59.63 MHz for silicon-29 ($^1H$ decoupling). The specimens used for NMR were dissolved in $CDCl_3$. The $^1H$, $^{13}C$ and $^{29}Si$ chemical shifts were all referred to tetramethylsilane. The polymer-to-ceramic transformation studies of the cured polymers were performed by thermal gravimetric analysis (TGA, DTG-60H, Japan) in argon gas with a heating rate of 10 °C/min ranging from room temperature to 1000 °C.

### 2.2. Synthesis of dendritic polycarbosilanes

#### 2.2.1. Synthesis of K3G3

*2.2.1.1. Synthesis of KG0 core.* All reactions were carried out in purified argon atmosphere using standard Schlenk techniques. Synthesis of KG0 was described as the following procedure, according to Ref. 35. $CH_3Si(CH{=}CH_2)Cl_2$ (56.40 g, 0.4 mol), $CH_3SiHCl_2$ (55.20 g, 0.48 mol, 20% excess) and Karstedt catalyst in THF solution (the weight ratio of Pt to two chlorosilanes is 0.01%) were mixed in a 250 mL flask in an ice-water bath. Under magnetic stirring for 24 h, the completed reaction was checked by FT-IR spectroscopy, excessive $CH_3SiHCl_2$ was removed under vaccum to give 97.21 g (a yield of about 95.0%) of liquid product KG0-4Cl. Subsequently, KG0 was synthesized by Grignard coupling of KG0-4Cl and $CH_2{=}CHCH_2Cl$ as follows: Dry THF (400 mL) and 37.4 g of magnesium powder (1.56 mol) were added to a 2 L, four-neck flask equipped with an argon inlet, mechanical stirrer, a constant pressure drop funnel, and a reflux condenser with an argon outlet. The mixture of KG0-4Cl (76.80 g, 0.30 mol), $CH_2{=}CHCH_2Cl$ (119.41 g, 1.56 mol, 30% excess) and dry THF (400 mL) in the drop funnel was added to the flask over about 2 h. After the addition was complete, the reaction mixture was heated in a 60 °C oil bath for 12 h to obtain a reaction slurry as large amounts of $MgCl_2$ precipitated. Then, the reaction mixture was cooled to ambient temperature and washed with $NH_4Cl$ solution (0.50 mol/L). After the obtained mixture was extracted with hexane, the organic phase was then separated and dried over powdered sodium sulfate under argon atmosphere for 2 h. Finally, after being filtered, the resultant solvent was stripped off at 60 °C and under vacuum to give a transparent liquid with a yield of 55.0 wt% (45.80 g). The obtained KG0 was characterized by FT-IR and NMR spectroscopy (see Supplementary Information).

*2.2.1.2. Synthesis of K3G3.* The hydrosilylation reaction between KG0 (20.00 g, 0.07 mol) and $CH_3HSiCl_2$ (38.61 g, 0.336 mol, 20% excess) was performed in a 60 °C oil bath with Karstedt catalyst (the weight ratio of Pt to mixture of KG0 and $CH_3HSiCl_2$ is 0.01%) and dry THF as a solvent. The completed reaction was checked by FT-IR. After the C=C absorption peak (1629 $cm^{-1}$) of KG0 disappeared completely, the excessive $CH_3HSiCl_2$ was removed under vacuum to give a liquid KG0-8Cl (41.31 g) with a yield of 80 wt%. The first generation (K1G1) was synthetized by Grignard coupling of KG0-8Cl and $CH_2{=}CHCH_2Cl$. With this iteration method, the second generation (K2G2) and the third generation (K3G3) were synthesized. The obtained compounds K1G1, K2G2 and K3G3