

Carbon-rich SiCN ceramics derived from phenyl-containing poly(silylcarbodiimides)

Gabriela Mera^{a,*}, Ralf Riedel^a, Fabrizia Poli^b, Klaus Müller^{b,c,d}

^a Technische Universität Darmstadt, Institut für Materialwissenschaft, Petersenstrasse 23, D-64287 Darmstadt, Deutschland, Germany

^b Universität Stuttgart, Institut für Physikalische Chemie, Pfaffenwaldring 55, D-70569 Stuttgart, Deutschland, Germany

^c Dipartimento di Ingegneria dei Materiali e Tecnologie Industriali, Università degli Studi di Trento, via Mesiano 77, I-38100, Trento, Italy

^d INSTM, UdR Trento, Italy

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Abstract

Novel phenyl-containing polysilylcarbodiimides were synthesized and their thermolysis and crystallization behavior up to 2000 °C was investigated. The Si/C ratio of the preceramic polymer was varied in a defined way by starting from dichlorosilanes with different organic substituents, namely R and R' with R = phenyl and R' = H, phenyl, methyl or vinyl. Several techniques were employed to study the structural features of the polymers and their thermolysis products. The temperature of crystallization depends on the carbon content of the precursors. Thus, in the sample with the highest carbon content the separation of β -SiC from the amorphous SiCN matrix is observed at $T > 1500$ °C, resulting in the highest temperature of thermal stability against crystallization ever reported for a SiCN ceramic derived from polysilylcarbodiimides. Moreover, no crystallization of β -Si₃N₄ was observed.

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1. Introduction

Polymer-derived ternary SiCN ceramics are a new class of materials possessing oxidation and creep resistance up to exceptionally high temperatures,^{1,2} properties which are improved when the ceramics are fabricated with a high content of excess carbon, as published recently in the case of SiCO materials.^{3–5} The high-temperature stability was also traced back to the presence of nanodomains with 1–3 nm in size as shown recently by SAXS measurements of polymer-derived ceramics (PDC) with low carbon content.⁶

A main feature of polymer-derived ceramics is their possibility to incorporate free carbon into the microstructure. This issue has been addressed in several publications where primarily PDCs of low free carbon content were considered.^{1,7,8} Until recently it was assumed that an excess of carbon is detrimental to the mechanical and electrical properties as well as to the oxida-

tion resistance of such ceramics. This view has been completely revised, since studies on SiCO–carbon hybrids showed a much higher stability against crystallization and high-temperature resistance to oxidation than originally anticipated.^{9,10} It was also reported that carbon-rich PDCs retain their amorphous character to higher temperatures than the carbon-poor PDC analogues.¹¹ Based on these investigations, it was concluded that the presence of carbon is essential for the inhibition of crystallization and lowering the carbothermal reactivity.

Polysilylcarbodiimides represent an important class of precursors for SiCN ceramics which are thermally more stable than the analogous polysilazanes.^{1,2,12,13} They are known to form two amorphous phases, namely Si₃N₄ and free carbon, at about 1000 °C, as can be demonstrated, for instance, by solid-state NMR studies.¹⁴ However, until now there have been no reports about carbon-rich SiCN ceramics obtained from thermolysis of polysilylcarbodiimides.

For this reason, we synthesized several phenyl-substituted polysilylcarbodiimides, which after thermolysis are expected to yield SiCN ceramics containing a substantial amount of free carbon. Klebe and Murray reported the synthesis of

* Corresponding author. Tel.: +49 6151 166340; fax: +49 6151 166346.
E-mail address: mera@materials.tu-darmstadt.de (G. Mera).

diphenyl-substituted polysilylcarbodiimide for the first time in 1967¹⁵ followed by Kumar and Shankar in 2002 who obtain a mixture of cyclic silylcarbodiimides and cyclosilazanes.¹⁶

In the current work, the novel phenyl-substituted polysilylcarbodiimides have an identical substituent $R^1 = \text{phenyl}$. The carbon content in these materials is varied by the second substituent, R^2 , which is either a phenyl ring (sample S1), a methyl group (S2), a hydrogen atom (S3) or a vinyl group (S4). Thus, from a comparative study of samples S1–S4 it is possible to examine the effect of the carbon content on both the structural evolution during thermolysis and the properties of the resulting SiCN ceramics. In this context, the precursor polymers, the intermediates during thermolytic conversion and the resulting SiCN ceramics are thoroughly characterized by means of several spectroscopic methods, X-ray diffraction and related techniques.

2. Experimental procedure

2.1. Chemicals

Dichlorodiphenylsilane, dichlorophenylsilane, dichloromethylphenylsilane, dichlorovinylphenylsilane, dichlorodimethylsilane and pyridine were purchased from Sigma–Aldrich Chemie GmbH, Germany. All chemicals were used as received without further purification. Bis(trimethylsilyl)carbodiimide was synthesized according to the literature.¹⁷

2.2. Synthesis and thermolysis

All reactions were carried out in purified argon atmosphere using standard Schlenk techniques.¹⁸ Bis(trimethylsilyl)carbodiimide (0.047 mol) was mixed under stirring with a catalytic amount of pyridine (0.024 mol). Afterwards, the substituted dichlorosilane (0.047 mol) was added and the reaction mixture was kept under reflux at 66 °C for 6 h (respectively 44 °C for S3, b.p. (PhHSiCl₂) = 65–66 °C) and then at 120 °C for another 12 h. The formation of the substituted polysilylcarbodiimide was monitored by means of high-resolution ²⁹Si NMR spectroscopy. After completion of the reaction, the by-product trimethylchlorosilane was removed by distillation.

For the thermolysis of the samples up to 1100 °C, 1–2 g of the polymeric precursor was filled in a quartz crucible. The crucible was then put in a quartz tube, and heated under a steady flow of purified argon (50 mL/min) in a programmable horizontal tube furnace. For the thermolysis below 1600 °C, the samples were first heated to the desired thermolysis temperature with a heating ramp of 100 °C/h. Afterwards, the samples (~0.5 g) were placed in BN crucibles and were heated in an Astro furnace with a heating ramp of 5 °C/min to the required thermolysis temperature, at which they were kept for 2 h. The thermolysis was completed by cooling the samples to room temperature with a cooling ramp of 10 °C/min. For the thermolysis at higher temperatures (up to 2000 °C), the samples were in a first step thermolyzed at 1100 °C following the procedure described above.

2.3. Characterization techniques

X-ray diffractograms of our samples were measured by a STOE X-ray diffractometer using Ni-filtered Cu K α radiation at a scan speed of 1° min⁻¹.

FT-IR spectra were recorded on a Nicolet Nexus 470 FTIR spectrometer with a nitrogen-purged optical bench (Nicolet, Madison, WI) equipped with a DTGS detector.

Chemical analysis of the polymers was carried out at Mikroanalytisches Labor Pascher (Remagen/Germany). For the ceramics, the determination of carbon in the ceramic product was measured by a carbon analyzer (CS 800, Eltra GmbH, Neuss). The oxygen and nitrogen content of the powdered ceramic sample was determined by an N/O analyzer (Leco, Type TC-436).

Thermal gravimetric analysis of the polymers was performed on a Netzsch STA 429 apparatus (Selb, Germany). The samples were heated to 1400 °C at a rate of 5 °C/min in argon atmosphere, while simultaneously measuring the mass loss and the gaseous decomposition products via mass spectrometry (Quadrupole Mass Spectrometer).

Raman spectra were recorded on a confocal Horiba HR800 micro-Raman spectrometer by using an excitation laser wavelength of 514.5 nm. For the evaluation of free carbon cluster size in ceramics, Gaussian–Lorentzian curve fitting of the Raman bands (LabSpec 5.21.08 Software) was applied.

Solid-state ²⁹Si NMR experiments were performed on a Varian InfinityPlus 400 NMR spectrometer operating at a static magnetic field of 9.39 T (²⁹Si frequency: 79.46 MHz), while solid-state ¹³C NMR measurements were carried out on a Bruker CXP 300 spectrometer operating at 7.05 T (¹³C frequency: 75.47 MHz). All measurements were done by using 4 mm magic angle spinning (MAS) probes. ²⁹Si and ¹³C NMR spectra were recorded using single pulse, cross-polarization (CP) and ramped cross-polarization (RAMP-CP) excitation.¹⁹ For the ²⁹Si single pulse experiments a pulse angle of 45° (1.75 μ s) and a recycle delay of 45 s was used. ²⁹Si RAMP-CP experiments were acquired with a contact time of 5 ms and a recycle delay of 5 s. ¹³C single pulse experiments were performed using a $\pi/2$ pulse length of 4 μ s and a recycle delay of 15 s, while for the CP experiments a contact time of 5 ms and a recycle delay of 5 s were used. ²⁹Si and ¹³C chemical shifts were determined relative to the external standards Q₈M₈ and adamantane, respectively and are given with respect to the standard TMS ($\delta = 0$ ppm).

3. Results and discussion

In the following, we report on the synthesis and characterization of a series of new preceramic polymers based on phenyl-substituted silylcarbodiimides and their thermal transformation to carbon-rich SiCN ceramics. The thermal stability of the resulting SiCN materials in terms of decomposition and crystallization is a further topic addressed here.

Four different preceramic polymers S1–S4 (see Table 1) were synthesized according to Scheme 1.

The polymers appeared as rubber-like (S1), solid (S3) or viscous liquids (S2 and S4). As shown by the elemental analysis data, the polymers still contain residual chlorine due to Si–Cl

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