

SYNTHESIS AND CHARACTERIZATION OF NOVEL SILAZANE PRECURSORS

Haifeng Hu, Zhaohui Chen, Wenwei Zheng, and Jiayu Xiao

Department of Material Engineering & Applied Chemistry, National University of Defense Technology, Changsha 410073, P.R.China

SUMMARY: Two silazane precursors, PHAASZ (cyclo-[MeHSiNCH₂CH=CH₂]₄) and PMAASZ (cyclo-[Me₂SiNCH₂CH=CH₂]₄), were obtained by reacting allylamine with MeHSiCl₂ and Me₂SiCl₂, respectively. PHAASZ crosslinked readily under catalyst H₂PtCl₆ or initiator dicumyl peroxide (DCP), while PMAASZ under DCP and heat treatment. Upon pyrolysis in N₂ crosslinked PHAASZ (H₂PtCl₆) led to a black solid with 71.0wt% yield (1273K), and PMAASZ (DCP) with 65.4wt% yield.

KEYWORDS: polysilazane, pyrolysis, ceramic yield

INTRODUCTION

Ceramic preparation (ceramic fiber, ceramic matrix composite) via precursor pyrolysis has been an active field in recent two decades [1, 2, 3]. This route is especially attractive in that complicated structures of ceramic matrix composites can be easily processed by combining woven technology of fibers with plastic forming of precursors. The precursors for CMCs, however, must have two basic characteristics: low viscosity (in the form of either solution or melt) to benefit infiltration, and molecular structure with latent active functionalities to render further crosslinking. Chong and his coworkers [4] synthesized [(CH₂=CH)HSiNH]_n, which had a low viscosity and upon pyrolysis led to a high ceramic yield (>80wt%). Hu [5, 6] also reported a series of precursors with latent active groups and high ceramic yields upon pyrolysis, in which active groups (Si-H, C=C) were attached to silicon atoms.

In this paper novel precursors with latent active groups attached to nitrogen instead of Si atoms were synthesized, and crosslinking conditions and ceramic yields were also investigated.

EXPERIMENTAL PROCEDURE

In a 500ml three-necked round bottom flask equipped with a dropping funnel, a stirrer and a gas inlet, 250ml fresh-distilled benzene, quantitative chlorosilane (MeHSiCl₂ or Me₂SiCl₂) and triethylamine were charged by syringe after the air in the flask was replaced by over-NaOH dried N₂. Then quantitative allylamine/benzene was transferred by syringe into the

dropping funnel. Allylamine was added dropwise in 30 minutes while stirring, then the temperature was raised to reflux for over 12 hours. A light yellow liquid was obtained after gravity filtration and reduced pressure distillation (667Pa/333K) to remove solid, solvent and excess triethylamine.

Crosslinking was carried out in an autoclave under the conditions of 393K, 0.1MPa N₂, 6 hours unless otherwise noted. Crosslinked polymers were pyrolyzed in a programmable temperature-controlled tube furnace under N₂ stream, and held for 30 minutes at maximum temperature.

Following instruments were employed to characterize the structures of the synthesized products: Hitachi 270-30 infrared spectrometer (Japan), AC-80 Brucker nuclear magnetic resonance spectrometer (Swiss), KYKY-QP1000A GC-MS analyzer (P.R.China), Rigaku Thermoflex analyzer (Japan), KNAuER freezing-point determinator (German), and PE2400CHN elemental analyzer (USA).

RESULTS AND DISCUSSION

Structural Characterization

According to the structures of the reagents, following equations can be assumed reasonable if the reactions proceed under the usual principles:



The properties of as-synthesized products, PHAASZ (in Eq.1) and PMAASZ (in Eq.2) with molar ratio of chlorosilane/allylamine=1/1, are listed in Table 1.

Table 1: Properties of as-synthesized products

Sample	Appearance	Mn	Viscosity (cp, 298K)	Composition (wt%)
PHAASZ	oil	396.1	12.40	Si29.50C47.25H9.22N14.03
PMAASZ	oil	448.2	17.52	Si26.02C52.44H9.69N11.85

Both products are oils with low viscosity. IR spectrum of PHAASZ indicates that following characteristic absorption peaks exist: a strong peak of Si-H at 2160cm⁻¹, a peak of C=C (stretching vibration) at 1600cm⁻¹, a strong peak at 1260cm⁻¹ ascribed to Si-Me, a broad peak of Si-N-Si at 940cm⁻¹, and a peak of Si-C at 830cm⁻¹. It is noticeable that the spectrum does not show any sign of N-H bending vibration at 1180cm⁻¹, indicating both H atoms attached to N atom might have been substituted.

Chemical shifts of absorption peaks of PHAASZ in ¹HNMR spectra are ascribed as follows: δ=0ppm (Si-Me, area=92.29), 3.4ppm (-CH₂-, area=40.82), 4.67ppm (Si-H, area=21.08), 4.98ppm (=CH₂, area=39.65), 5.7ppm (=CH, area=21.05), 7.2ppm (C₆H₆, area=8.45). The integrated intensity ratio of S_{Si-H}/S_{C=CH}=1.00 suggests that PHAASZ contains equal moles of SiMeH and CH₂=CH-CH₂- unit in the molecular structure.

PMAASZ shows almost the same pattern as PHAASZ except without Si-H absorption peak

seated at 4.7ppm.

Fig.1 shows ^{13}C NMR spectrum of PHAASZ. It is obvious that there are only four kinds of C atoms with different chemical environment, suggesting PHAASZ is highly symmetrical when considering the reagents involved. Furthermore GC analysis gives there is only one single evolution peak. All the results (elemental analysis, molecular weight, IR, and ^1H NMR) combined, we can conclude that PHAASZ has a cyclotetrasilazane structure: cyclo-[MeHSiN(CH₂CH=CH₂)]₄. This structure agrees with the predictions in Eqn.1.

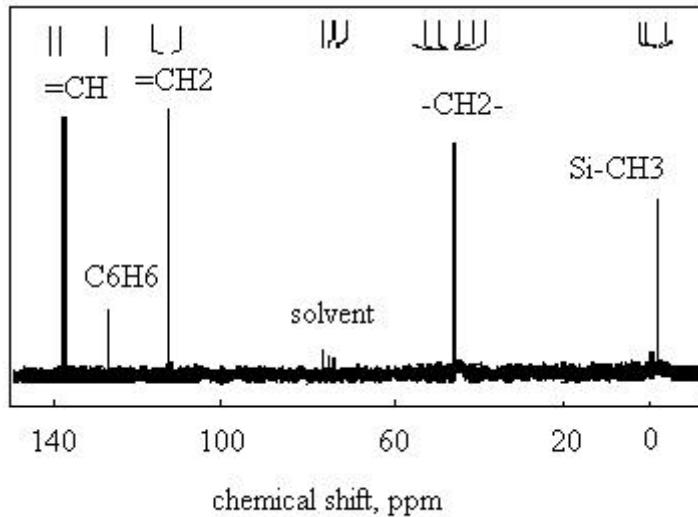


Fig.1: ^{13}C -NMR pattern of PHAASZ

Similarly PMAASZ is determined to be cyclo-[Me₂Si-N(CH₂-CH=CH₂)]₄.

Crosslinking Treatment

Crosslinking treatment plays a rather important role in precursor processing. Firstly crosslinking treatment helps enhance ceramic yields, and secondly it can prevent softening and keep form during pyrolysis. These are two key points in precursor processing. In our study, PHAASZ and PMAASZ with Si-H and C=C functionalities, might be crosslinked through hydrosilylation, chain reactions, and dehydrocoupling reaction as well:



Chloroplatinic acid (H_2PtCl_6) as catalyst, dicumyl peroxide (DCP) and 2,2'-Azobisisobutyronitrile (AIBN) as initiator, and heat treatment were adopted to study the crosslinkability of PHAASZ and PMAASZ. Table 2 lists the results.

From Table 2 H_2PtCl_6 can catalyze PHAASZ's crosslinking readily. By analyzing the relative absorption peak intensity prior to and after crosslinking, we can deduce that PHAASZ in the presence of H_2PtCl_6 crosslinked via hydrosilylation reaction, and perhaps involved chain reaction. PMAASZ, on the other hand, crosslinked mainly via chain reaction.

Table 2: Crosslinking results under different conditions

Sample	H ₂ PtCl ₆	DCP	AIBN	Heat
PHAASZ	Yellow solid	Yellow solid	No	Foamed solid
PMAASZ	—	Yellow solid	No	Waxy solid

Ceramic Yield upon Pyrolysis

Ceramic yield is another key point to evaluate a precursor. The higher the ceramic yields, the better. The ceramic yields of PHAASZ and PMAASZ were investigated under different pyrolysis conditions, and the results are listed in Table 3.

Table 3: Ceramic yields under different pyrolysis conditions

Sample	Ceramic yield (wt%)		
	10K/min	5K/min	2K/min
PHAASZ	51.3	—	—
PHAASZ (H ₂ PtCl ₆)	65.2	68.2	71.0
PMAASZ	22.2	—	—
PMAASZ (DCP)	62.8	63.4	65.4

Note: Pyrolysis at ramping rates of 10 and 5K/min was conducted in TG, while at ramping rate of 2K/min in tube furnace.

From the above table it is obvious to find that crosslinking and ramping rate exert great influences upon ceramic yields. Ceramic yields of PHAASZ increase from 51.3% without crosslinking to 65.2% after crosslinking, while ramping rates decrease from 10K/min to 2K/min, ceramic yields increase from 65.2% to 71.0%.

Upon pyrolysis ceramic yields of PMAASZ show great improvement after crosslinking treatment (from 22.2% to 62.8%, 10K/min). PMAASZ without crosslinking treatment might lose structural unit step by step, leading to a rather low ceramic yield, while crosslinked PMAASZ with a three dimensional net structure maintains its backbone and leads to a much higher ceramic yield.

CONCLUSIONS

1. By reacting allylamine with MeHSiCl₂ and Me₂SiCl₂ respectively (molar ratio 1:1), in refluxing benzene for over 12 hours, two oligomers PMAASZ and PHAASZ were obtained. Characterization by means of infrared analysis, GPC, ¹H and ¹³C nuclear magnetic resonance spectra, and elemental analysis shows both are cyclotetrasilazanes: PMAASZ (cyclo-[Me₂Si-N(CH₂-CH=CH₂)]₄) and PHAASZ (cyclo-[MeHSiN(CH₂-CH=CH₂)]₄).
2. Both PHAASZ and PMAASZ crosslinked readily under initiator dicumyl peroxide and heat treatment via chain reaction, while PHAASZ also crosslinked under catalyst chloroplatinic acid via hydrosilylation reaction.
3. Upon pyrolysis in N₂ crosslinked PHAASZ (H₂PtCl₆) led to a black solid with 71.0wt% yield (1273K), and PMAASZ (DCP) with 65.4wt% yield.

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