

STRATEGY TO CHARACTERIZE PRECURSORS FOR SiC CERAMICS BY LIQUID AND SOLID-STATE NMR.

Corine GERARDIN, Francis TAULELLE, Jacques LIVAGE.

Laboratoire de Spectrochimie du Solide.

Université P. et M. Curie. Tour 54 E5

4 Place Jussieu.

75252 PARIS Cedex 05 FRANCE.

and

Marc BIROT and Jacques DUNOGUES

Laboratoire de Chimie Organique et Organometallique

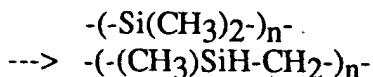
Université de Bordeaux I

33405 TALENCE Cedex FRANCE.

I. INTRODUCTION

The purpose of this paper is to indicate some types of structural information that liquid and solid-state NMR experiments can provide in case where the systems lack order and homogeneity. The compounds we examined are organometallic polymers that are related to the preparation of ceramic fibers such as silicon carbide systems.

In the Yajima's process (1) for the obtention of SiC ceramics, the polydimethylsilane (PDMS) polymer is thermolysed at 470°C and leads to a precursor for SiC called polycarbosilane (PC). The thermal decomposition of PDMS leads to insertion of CH₂ groups between the silicon atoms of the polysilane chain according to Kumada's arrangement (2):



In fact, the actual structure of the PCs cannot be described by the simple linear chain $\text{---}(-(\text{CH}_3)\text{SiH}-\text{CH}_2\text{---})_n\text{---}$. Yajima has reported (3) that PCs possess a certain degree of crosslinking. In the literature, three types of silicon sites in PC skeleton have been mentioned:

SiC_4 units correspond to silicon atoms bonded with four carbon atoms

SiC_3H units correspond to silicon atoms bonded with three carbon atoms and one hydrogen atom

$\text{SiC}_x\text{Si}_{4-x}$ units correspond to silicon atoms bonded with x carbon atoms and 4-x silicon atoms.

Thanks to specific liquid NMR experiments, we prove the existence of different sites in our polycarbosilanes. Our strategy is to study hexane-soluble fractions of PCs by one-dimensional and two-dimensional ¹H-, ¹³C- and ²⁹Si- liquid NMR experiments and to use the PDMS polymer as a solid reference for solid-state NMR spectra. After having identified some proton, carbon and silicon environments in liquid fractions, we try to assign the different signals in solid-state NMR spectra of insoluble PC fractions.

II. EXPERIMENTAL:

Synthesis of Polycarbosilanes:

PCs were prepared by thermal decomposition of PDMS in an autoclave. PC-350 was obtained by thermolysis of PDMS at 350°C with 3wt% of polyborodiphenylsiloxane and PC-470 by thermolysis of PDMS at 470°C for 8 hours without polyborodiphenylsiloxane. The autoclaving gave hexane-soluble (PC350S and PC470S) and insoluble (PC350I AND PC470I) fractions.

Characterization:

The different samples were investigated by NMR spectral measurements as follows:

¹H and ¹³C liquid NMR spectra were measured with a Bruker AM250 NMR spectrometer at 250.13 MHz for ¹H

and 62.8 MHz for ^{13}C , in CDCl_3 solution. ^1H and ^{13}C NMR spectra were recorded with pulsewidths of 11 ms for ^1H and 4 ms for ^{13}C and delays between pulses of 1 s for ^1H and 2 s for ^{13}C . ^{29}Si liquid NMR spectra and ^1H , ^{13}C and ^{29}Si solid-state NMR spectra were measured with a Bruker MSL400 NMR spectrometer at 400.13 MHz for ^1H , 100.62 MHz for ^{13}C and 79.5 MHz for ^{29}Si .

^{29}Si liquid NMR spectra were recorded with a pulsewidth of 5 ms and a relaxation time of 10 s.

A refocused INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) experiment with polarization transfer from ^1H to ^{29}Si nuclei and ^1H -decoupling was carried out on the PC470S polymer in solution. This technique is very advantageous for ^{29}Si nuclei which suffer from both deficiencies: long T1 and negative gyromagnetic ratio g .

The theoretical enhancement from Polarisation Transfer is $\gamma(^1\text{H})/\gamma(^{29}\text{Si}) = 5.03$. Our aim is to select the multiplicities of silicon atoms in the structure. The variable delays in the INEPT pulse scheme were chosen in order to give doublets and quartets positive and triplets negative.

A DEPT (Distortionless Enhancement by Polarization Transfer) experiment with polarisation transfer from ^1H to ^{13}C nuclei was also carried out on the PC470S polymer in CDCl_3 solution. The delays were chosen in the same way: $\underline{\text{C}}\text{H}$ and $\underline{\text{C}}\text{H}_3$ peaks appear positive and $\underline{\text{C}}\text{H}_2$ ones negative.

For solid-state NMR experiments, powder samples in the cavity were spinning at the magic angle ($54^\circ 44'$). A pulsewidth of 6 ms and a relaxation time of 4 s were used for the ^1H MAS NMR spectra.

^{13}C and ^{29}Si Cross Polarization-Magic Angle Spinning NMR experiments were carried out to study solid fractions. A pulsewidth of 5 ms and a relaxation time of 10 s were used for both ^{13}C and ^{29}Si CPMAS spectra. An optimum cross-polarization

contact time of 1,5 ms was measured and used. The ^1H , ^{13}C and ^{29}Si chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane.

III. RESULTS-DISCUSSION

III. 1. Characterization of soluble PC fractions in CDCl_3 solution:

First, we characterized the soluble fraction PC470S by one-dimensional and two-dimensional liquid NMR experiments. The ^{13}C NMR spectrum of PC470S in solution (figure 1b) shows a large distribution of carbon sites: the chemical shifts lie from about -7 to +7 ppm. The resolution is quite good and so, we carried out a DEPT experiment to reveal the different multiplicities of carbon atoms in the polymer and so to assign the signals to primary or secondary sites. The ^{13}C DEPT spectrum of PC470S (figure 2a) shows a large distribution of positive peaks characteristic of primary carbon atoms $\underline{\text{C}}\text{H}_3$ and a large distribution of negative signals due to secondary carbon atoms $\underline{\text{C}}\text{H}_2$.

A ^1H - ^{13}C heteronuclear shift-correlation experiment was carried out on the PC470S polymer: the two-dimensional diagram is shown in figure 3a. Thanks to this correlation, we again distinguish the two distributions of carbon atoms and we can assign in the ^1H liquid NMR spectrum (figure 1a) the signals of protons directly bonded with primary or secondary carbon atoms. The peaks at about 0,2 ppm are due to hydrogen atoms in $\text{Si}-\underline{\text{C}}\text{H}_3$ units and the peaks at -0.1 ppm to $\text{Si}-\underline{\text{C}}\text{H}_2$ units. The assignments of signals in the ^1H NMR spectrum are in agreement with those of literature (4).

A lot of information relating to environments of silicon atoms is obtained from liquid ^{29}Si NMR spectra of polycarbosilanes. The single pulse ^{29}Si NMR spectrum of PC470S in solution (figure 1c) reveals three groups of signals at about -1, -18 and -40 ppm.

In the ^{29}Si spectrum of PC470S via INEPT from ^1H and with ^1H -decoupling (figure 2b), the broad peak at -1 ppm is very weak : it is due to silicon atoms bonded with no hydrogen atom. So, the signal at -1 ppm corresponds to SiC_4 sites where the four carbon atoms may be either two CH_3 groups with two CH_2 ones or one CH_3 unit with three CH_2 ones. The second region of the spectrum shows two broad doublets in the single pulse ^{29}Si NMR spectrum : they are characteristic of silicon atoms bonded with one hydrogen atom, so SiC_3H sites. These units may be : $\text{Si}(\text{CH}_3)(\text{CH}_2)_2\text{H}$ or $\text{Si}(\text{CH}_2)_3\text{H}$. The value of the spin-spin coupling constant $1J(^{29}\text{Si}-^1\text{H})$ is 175 Hz. In the spectrum via INEPT and with ^1H -decoupling, the corresponding signals are positive and give two single peaks, at and ppm, what is in agreement with the previous assignments. We show the presence of two types of SiC_3H sites. The single pulse ^{29}Si spectrum of PC470S also shows two triplets centred at -16 et -16.7 ppm: the value of the spin-spin coupling constant $1J(^{29}\text{Si}-^1\text{H})$ is 182.5 Hz. We note that the values of the coupling constants are in agreement with those of literature (5,6). The triplets correspond to silicon atoms bonded with two hydrogen atoms. In the INEPT spectrum, the signals appear negative and give two single peaks : we show the presence of two types of SiC_2H_2 sites in the structure of PC470S.

We also carried out a $^{29}\text{Si}-^1\text{H}$ heteronuclear shift correlation experiment on the PC70S : the two-dimensional diagram is shown in figure 3b. Thanks to the correlation, we clearly see the two types of sites : SiC_3H and SiC_2H_2 and we can assign, in the ^1H liquid spectrum, the sites of the protons directly bonded with silicon atoms. We show that peaks at 4.1 ppm are due to Si-H and peaks at 3.9 ppm to SiH_2 .

The integration of the peaks, in the ^1H NMR spectrum, gives a value of 8,5 for the ratio C-H/Si-H , this value reveals the degree of transformation of the PDMS in PC.

So, a combination of one-dimensional and two-dimensional NMR techniques was used to unambiguously assign all the ^1H , ^{13}C and ^{29}Si signals.

Then, we used the previous results to analyse the PC350S fraction. We note that the PC350S polymer essentially possesses CH_3 groups : the ^1H and ^{13}C solution spectra (figures 1a and 1b) show that CH_2 units are almost inexistant in the skeleton of the molecule. The value of the ratio C-H/Si-H is 87. The ^{29}Si spectrum (figure 1c) shows broad and weak signals of SiC_4 and SiC_3H , characteristic of some intermediate units that appear during the thermal decomposition of PDMS. A sharp peak exists at -35.7 ppm, it's due to $(\text{Si}(\text{CH}_3)_2)_n$ ($n>2$) sequences that weren't transformed during the autoclaving. We show that in this fraction, Kumada's transposition was not complete.

III. 2. Characterization of insoluble samples:

The PDMS, PC350I and PC470I polymers were investigated by ^1H MAS, ^{13}C CPMAS and ^{29}Si CPMAS NMR measurements. The assignments that we give for the different nuclei are a consequence of the previous study. We also used the PDMS polymer as a reference for the different sites in solid-state fractions : the ^1H , ^{13}C and ^{29}Si chemical shifts in the sites $(\text{Si}(\text{CH}_3)_2)_n$ are respectively : 0.1 ppm, -3.3 ppm and -35.7 ppm.

First, we note that the ^1H MAS, ^{13}C CPMAS and ^{29}Si CPMAS NMR spectra of PC350I and PDMS are all similar, showing that there has been no Kumada's transposition in the PC350I fraction.

Then, we analysed the PC470I fraction. The ^1H MAS spectrum (figure 4a) shows a large peak centred

at 0.1 ppm and a small peak at about 4 ppm. The former is due to hydrogen atoms in SiCH_3 and SiCH_2 (C-H protons) and the latter to hydrogen atoms bonded with a silicon atom (Si-H protons). In the ^{13}C MAS NMR spectrum of PC470I (figure 4b), a broad signal centred at about 2 ppm corresponds to a large distribution of CH_3 and CH_2 groups, according to ^{13}C spectra in solution. No sharp and large peak appears at -3.3 ppm: Si-Si bonds, if they exist, are very few in number. By comparison with the ^{29}Si NMR spectrum of PC470S, we assign the signals in the ^{29}Si spectrum of PC470I at -1.6, -18.6 and -40 ppm to respectively SiC_4 and SiC_3H and SiC_2H_2 sites (figure 4c). The structures of the liquid and the solid fractions of PC470 are very similar.

IV. CONCLUSION

The purpose of this paper was to define our strategy to characterize organometallic precursors for SiC ceramics. The aim was to determine the structures of liquid and solid polysilacarbosilanes. First, we studied a soluble polymer by one-dimensional (1D) and two-dimensional (2D) liquid NMR experiments to define the main sites of protons, carbon and silicon atoms. The DEPT ^{13}C NMR spectrum and the ^{29}Si INEPT NMR spectrum of polymer PC470S gave the multiplicities of carbon and silicon atoms and so the assignments of the main ^1H and ^{13}C signals.

The chemical shifts of CH_2 , CH_3 sites in ^{13}C spectra and SiC_4 , SiC_3H and SiC_2H_2 sites in ^{29}Si spectra were determined (table A). Then, with ^1H - ^{13}C and ^1H - ^{29}Si heteronuclear shift correlations of PC470S, the assignments of signals in ^1H spectra were possible (table A).

So, a combination of 1D and 2D liquid NMR experiments gave unambiguous assignments of ^1H , ^{13}C and ^{29}Si signals in a soluble PC fraction.

Then the structures of PC350S and insoluble fractions were investigated by liquid and solid-state NMR experiments. According to the liquid assignments and the PDMS solid-state assignments (in ^1H , ^{13}C and ^{29}Si), all the sites observed were assigned.

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Table and figures

Table A : PC470S

	^{29}Si INEPT				^{29}Si NMR simple				^1H NMR			^{13}C NMR simple			DEPT- ^{13}C
	Sites	$\delta(\text{ppm})$	% sites	$^1J(\text{Si-H})$	Sites	$\delta(\text{ppm})$	% sites	Sites	$\delta(\text{ppm})$	$^1J(\text{S-H})$	Sites	$\delta(\text{ppm})$	$^1J(\text{S-H})$		
multiplicities					CH_2	-0.1	89.5	CH_2	-7 → +4	118 Hz	CH_2	-7 → +4	multiplicities		
					CH_3	+0.1		CH_3	-7 → +4						
					SiC_2H_2	-37.7	9.5	182 Hz	SiH_2	3.9	10.5				
					SiC_3H	-38.5			47.6	175 Hz		SiH	4.1		
					SiC_4	-16.7									
					-16										
					+0.7	42.9									

