Poly(carbosilane) Precursors of Silicon Carbide: The Effect of Cross-Linking on Ceramic Residue

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Received December 3, 1990. Revised Manuscript Received January 30, 1991

Poly(carbosilanes) of general structure X[-Si(H)(Y)C_2H_4-]$_n$-SiH_2Z (I, X = Y = H, Z = vinyl; II, X = Y = Z = H; III, X = Z = vinyl, Y = H; IV, X = Z = vinyl, Y = vinyl and H) have been prepared by means of hydrosilylation polymerization, followed by chemical transformation of the resulting polymer including a final $LiAlH_4$ reduction step. Thus, I was prepared from dichlorovinylsilane (V), II from V together with trichlorosilane as a chain-terminating agent, and III from V together with dichlorodivinylsilane as a chain-terminating agent. IV was made by polymerization of anisylvinylsilane followed by anisyl group cleavage with $HCl/AlCl_3$ and then reaction with vinyl Grignard reagent. Ceramic yield from I–IV was found to increase with polymer vinyl group content, ranging from a low yield for I (12%) to a high yield for IV (60%). This is explained by cross-linking through hydrosilylation occurring during pyrolysis, as shown by the exotherm at ca. 200 °C, and also by changes in the IR spectrum.

Introduction

We have previously reported[1] an alternative route to the Yajima and Verbeek preparations of SiC and SiC/Si_3N_4 ceramics[2] from monomeric organosilanes. Our approach was to elaborate a poly(carbosilane) directly from a monomer using catalytic hydrosilylation[3] in order to avoid the polysilane step in the Yajima process (see Scheme I). Furthermore, catalytic hydrosilylation[3] offers the advantage of affording poly(carbosilanes) of precise structure. In contrast, the poly(carbosilane) obtained in the Yajima process has been found to have a structure much more complicated than that expected.[4]

We describe here the preparation of oligomers I–III having the structures shown in Scheme II with 10 < DP_n < 35. ^1H, ^{13}C, and ^{29}Si NMR spectroscopies indicate the presence of two different silicon atom triads, $CH_2CH_2SiCH_2CH_2$ and $CH_2CH_2SiCH(CH_3)$.[1]

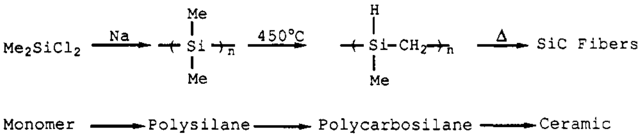
We also report here the results of a study of the pyrolysis of the oligomers ($DP_n \approx 15$). We observed that conversion to ceramic is possible in good yield when the oligomeric poly(carbosilane) contains at least some vinyl groups.

The great increase in ceramic yield arising from the presence of vinyl groups has been previously observed and studied by Schilling,[5] who suggested that densification occurred as a result of cross-linking of oligomeric chains brought about by hydrosilylation. In the present paper, we describe our results in support of this hypothesis.

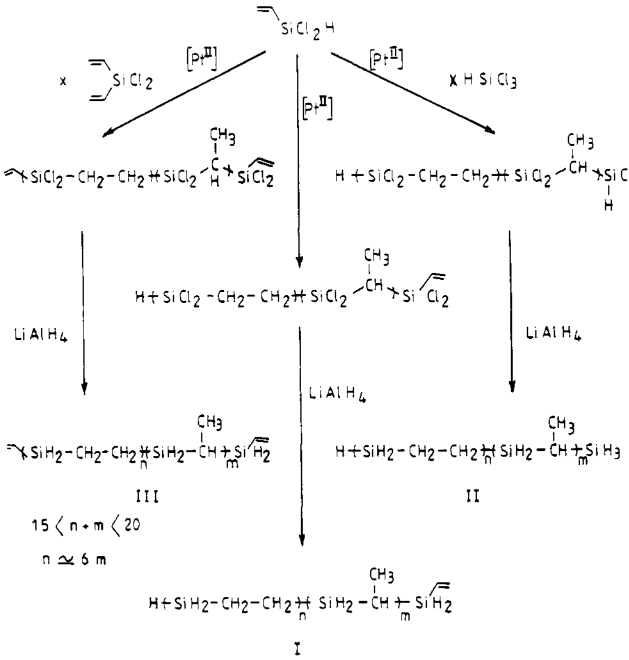
Experimental Section

The chlorosilanes were redistilled over Mg immediately before use. Solvents were purified and dried by standard procedures, and all manipulations were carried out under anaerobic conditions. Elemental analyses were performed by the Service Central d'Analyses du CNRS. ^1H NMR spectra were taken by using a Varian 360 or Bruker AW 60 spectrometer. IR spectra were recorded on a Perkin-Elmer 298 instrument. TG and DTA measurements were made using a Netzsch STA 409 thermobalance. Molecular weights were measured by gel permeation chromatography on a Waters 410 system equipped with 10^2-, 5 × 10^2-, 10^3-, and 10^4-Å μ-styragel columns, calibrated with polystyrene standards, the THF eluant flow rate being 1 mL min^{-1}. The Rhône-Poulenc catalyst 111 was used to promote hydrosilylation. This is made as described[6] from a solution of hexa-

Scheme I. The Yajima Process



Scheme II. Preparation of I–III



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chloroplatinic acid in 2-ethylhexanol and contains about 16 mmol L^{-1} of Pt. Dichlorovinylsilane[7] and dichlorodivinylsilane[8] were prepared as described.

Preparation of *p*-Anisylvinylsilane. To chlorovinylsilane (15 g, 160 mmol) in 250 mL of diethyl ether at 0 °C was added dropwise 110 mL (180 mmol) of 1.6 M *p*-anisylmagnesium bromide in diethyl ether. The mixture was heated under reflux for 1 h and then stirred at room temperature for a further 10 h. The salts were filtered from the resulting suspension, and the filtrate was hydrolyzed with 300 mL of H_2O. The aqueous phase was extracted with 3 × 100 mL of diethyl ether, and the combined organic fractions were dried over $MgSO_4$. Distillation gave *p*-anisylvinylsilane (102 °C/20 mmHg) in 87% yield: ^1H NMR (CCl_4) δ 6.7–7.3 m (4 H), 5.5–6.5 m (3 H), 4.5 s (2 H), 3.6 s (3 H).

Preparation of I. (a) Polymerization. In a typical reaction, dichlorovinylsilane (5 mL, 44.0 mmol) was polymerized in a 100-mL Schlenk tube equipped with a reflux condenser. Catalyst 111 (70 mL, 1.12×10^{-6} mol of Pt) in 5 mL of 1,2-dichloroethane (catalyst concentration in reaction mixture 10^{-4} mol L^{-1}) was added by syringe, resulting in reaction initiation after a short induction period. The very exothermic reaction led to self-maintained reflux for several minutes, after which the mixture was heated under reflux for a further 12 h. After removal of the solvent under reduced pressure, an off-white paste was obtained in ca. 94% yield: IR (CCl_4) 2970 2920 2870 1395 (CH_n), 2205 (SiH), 1140 ($SiCH_2CH_2Si$) cm^{-1}. Anal. Calcd for [$SiCl_2C_2H_4$]: C, 18.9; H, 3.2; Si, 22.1; Cl, 55.8. Found: C, 19.2; H, 3.7; Si, 22.4; Cl, 52.5.

(b) Reduction. To a suspension of 5.25 g (Cl, 82 mmol) of the polymer in 150 mL of Et_2O at 0 °C was added a suspension of 1.80 g (47.3 mmol) of $LiAlH_4$ in 50 mL of Et_2O. After warming to room temperature, the reaction mixture was heated under reflux for 2 h. Precipitation of the aluminum and lithium salts was achieved by treating the reaction mixture at 0 °C under N_2 with 1.80 g of 15% aqueous sodium hydroxide followed successively by three 1.80-g aliquots of water. After filtration, the precipitate was washed three times with 20 mL of Et_2O. The filtrate and washings were combined and dried over $MgSO_4$. After filtration, the solvent was removed under vacuum to give I as a colorless oil in 73% yield. M_n 590, M_w 1520. Anal. Calcd for I: C, 41.3; H, 10.4; Si, 48.3; Cl, 0.00. Found: C, 39.4; H, 9.6; Si, 43.2; Cl, 0.04.

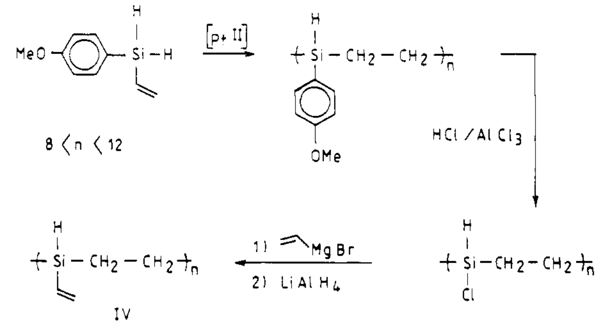
Preparation of II. Dichlorovinylsilane (8.90 g, 70 mmol) and trichlorosilane (1.90 g, 14 mmol) were copolymerized following addition, by use of a syringe, of 3.1 mg (7.5×10^{-6} mol) of hexachloroplatinic acid in 10 mL of 1,2-dichloroethane. After 20–30 min at room temperature vigorous reflux began and was maintained for a further 10 min. To a suspension of the resulting waxy solid in 300 mL of Et_2O at 0 °C was added a suspension of 4.00 g (105 mmol) of $LiAlH_4$ in 100 mL of Et_2O. After hydrolysis and extraction a colorless oil was obtained in 78% yield. M_n 890, M_w 1470. ^1H NMR (CCl_4) δ 3.8–3.4 (2.2 H, SiH_2), 1.3–0.2 (4 H, CH_n).

Preparation of III. Dichlorovinylsilane (12.0 g, 94 mmol) and dichlorodivinylsilane (2.9 mL, 21 mmol) were copolymerized following addition, by use of a syringe, of 60 mL (0.96×10^{-6} mol of Pt) of catalyst 111 in 13 mL of 1,2-dichloroethane. After a few minutes vigorous reflux began, and the reaction mixture was then held at 60–70 °C for 10 h. To a suspension of the resulting waxy solid in 400 mL of Et_2O at 0 °C was added 5.06 (133 mmol) of $LiAlH_4$ in 140 mL of Et_2O. After hydrolysis and extraction a colorless oil was obtained in 82% yield. M_n 500, M_w 740. ^1H NMR (CCl_4) δ 6.2–5.8 (0.55 H, vinyl protons), 3.9–3.7 (2 H, SiH_2), 1.4–0.2 (4 H, CH_n).

Preparation of IV. Anisylvinylsilane (20.00 g, 121 mmol) was polymerized in the presence of 150 mL (2.4×10^{-6} mol of Pt) of catalyst 111 by stirring for 48 h at 120 °C, thus affording a sticky solid: M_n 1320, M_w 3040; IR ν(Si–H) 2120 cm^{-1}.

The resulting polymer was dissolved in 100 mL of dichloromethane containing 0.053 g (0.4 mmol) of $AlCl_3$. The mixture was cooled to 0 °C, and a stream of HCl (dried by passing through sulfuric acid) was bubbled through the solution, which became slightly orange. The reaction was monitored by ^1H NMR, and after 3 h the crude mixture was filtered to remove part of the aluminum salts. Elimination of the solvent and anisole under vacuum gave a very viscous paste in 76% yield. Anal. Calcd for [$SiHClC_2H_4$]: C, 25.9; H, 5.4; Si, 30.3; Cl, 38.3. Found: C, 29.5; H, 5.5; Si, 30.5; Cl, 30.2.

Scheme III. Preparation of IV



A solution of 5.00 g (0.054 mol of SiCl) of this polymer in 20 mL of THF was reacted at room temperature with 67.5 mL (67.5 mmol) of 1 M vinylmagnesium bromide in THF. The rate of addition was adjusted to keep the temperature between 40 and 50 °C. The resulting red solution was stirred for 12 h at 50 °C then cooled to 0 °C, and treated with a suspension of 1.00 g (26.2 mmol) of $LiAlH_4$ in 50 mL of Et_2O. The reaction mixture was then heated under reflux for 1 h, and the solvent subsequently removed under vacuum to give a grey paste, which was partly dissolved in 200 mL of Et_2O. The resulting suspension was hydrolyzed with 200 mL of 4 M HCl and 100 g of ice. Normal workup gave IV as a yellow oil in 72% yield: IR (CCl_4) 3050, 3004, 1910, 1592, ($SiCH{=}CH_2$), 2115 (SiH) cm^{-1}. ^1H NMR (CCl_4) δ 5.9 m (2.3 H, vinyl protons), 3.6–4.1 (1 H, SiH), 0.5–0.8 (3.8 H, CH_n). Anal. Calcd for [$Si(H)(CH{=}CH_2)C_2H_4$]: C, 57.1; H, 9.6; Si, 33.4. Found: C, 57.7; H, 8.9; Si, 24.1. M_n 1100, M_w 12800.

Polymer Pyrolyses. These was performed in a furnace in an Al_2O_3 boat under N_2 at a heating rate of 5 °C min^{-1} from 25 to 1400 °C followed by 2 h at 1400 °C.

Thermolysis of IV. This was carried out on 2.00 g of IV under N_2 by slowly heating to 180–200 °C. After 3–4 min the polymer started to solidify and was held at this temperature for a further 15 min before being allowed to cool to room temperature.

Results and Discussion

The poly(carbosilanes) were prepared by means of hydrosilylation polymerization, followed by chemical transformation of the resulting polymer including a final $LiAlH_4$ reduction step, as illustrated in Scheme II. The polymers are slightly air sensitive, but under N_2 at −15 °C they may be kept unchanged for at least several months.

We prepared oligomer IV, which contains Si–H and Si–vinyl groups, in order to increase the potential extent of cross-linking by hydrosilylation. The preparation is depicted in Scheme III. By hydrosilylation of anisylvinylsilane in the presence of H_2PtCl_6, we obtained an oligomeric materials ($10 < DP_n < 15$). This was transformed into [$-Si(H)(Cl)CH_2CH_2-$]$_n$– by cleavage of the Si–anisyl bond with hydrogen chloride in the presence of a catalytic amount of $AlCl_3$. The *p*-methoxy substituent is known to increase the rate of cleavage of silicon–aryl bonds by electrophilic reagents.[9] The introduction of vinyl groups was achieved by reaction with vinyl Grignard reagent in the ratio vinylmagnesium bromide/SiCl = 1.25. The remaining Si–Cl bonds were reduced in situ by $LiAlH_4$ followed by hydrolysis. The resulting oligomer IV contains Si–H/Si–vinyl in the ratio of about 0.8 as determined by ^1H NMR.

Thermolysis studies of the polymers indicate that hydrosilylation of the oligomeric chains occurs at ca. 200 °C.

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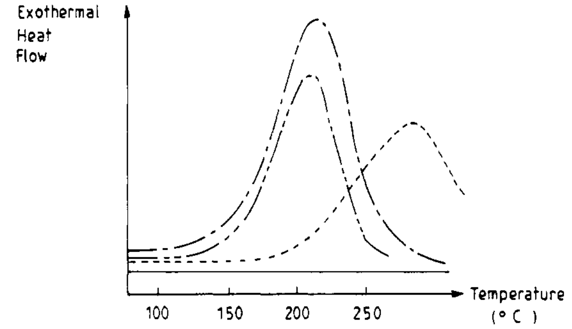


Figure 1. DSC results: (—) II; (- - - -) III; (— — —) IV; (- - -) 0.5(II) + 0.5(IV).

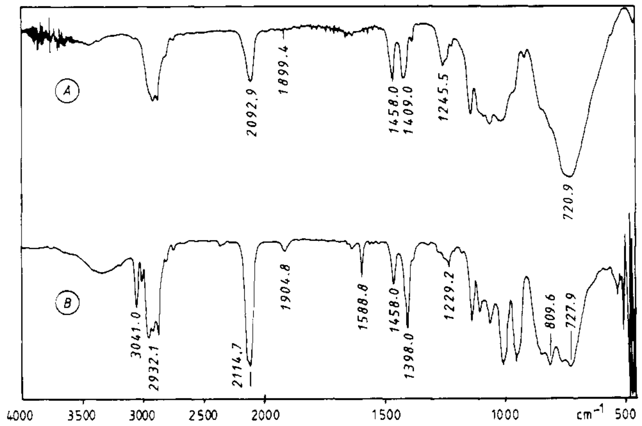


Figure 2. IR spectrum of IV (a) after and (b) before being heated at 200 °C for 20 min under N_2.

This is suggested by the presence of an exothermic peak, exhibited by both DTA[1] and DSC (see Figure 1), which occurs only for those polymers containing vinyl groups, e.g., for III but not for II since the latter has no vinyl groups. Furthermore, the IR spectrum of the product resulting from thermolysis of IV at 200 °C shows a decrease in intensity of ν(Si–H) (ca. 2100 cm^{-1}), accompanied by disappearance of the vinyl absorbances (3040 and 1590 cm^{-1}) together with increased intensity of the C–H absorbance (1458 cm^{-1}, see Figure 2). This suggests that hydrosilylation takes place during the exothermic transformation. The same exotherm was observed in the case of oligomer III terminated by a vinyl group at each end, but there was no exotherm for oligomer II, which is without vinyl groups.

We have compared the ceramic yields obtained from IV with those observed from I–III. The results are shown in Table I, which demonstrates the very great effect of hydrosilylation on ceramic yield. Oligomer II, which contains no vinyl groups, gives a very poor ceramic yield (12%). Analysis by TG-MS shows that depolymerization giving $H_3SiCH{=}CH_2$ occurs to a large extent; the results of this study will be published separately. The ceramic yield increases with one terminal vinyl group (30%) in the case of I and even more so for III with two terminal vinyl groups (56%).

Table I. Effect of Vinyl Groups on Ceramic Yield

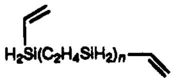
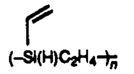
polymer	SiH/ Si(vinyl)	DP_n	ceram yield, %	theor yield of SiC, %
$H_3Si(C_2H_4SiH_2)_nH$ II	∞	12	12	69
 I	21	10	30	69
 III	10	10	56	69
 IV	1	13	60	48
2.5(II) + 1.0(IV)	4.5		62	59

Table II. Ceramic Elemental Analysis and Stoichiometry

poly(carbosilane)	ceram elem anal., % Si	C	O	ceram stoichiometry
I	66.2	33.4	0.6	SiC, 0.19C, 0.01(SiO_2)
IV	41.9	55.9	1.5	SiC, 2.21C, 0.03(SiO_2)
2.5(II) + 1.0(IV)	48.2	46.6	3.5	SiC, 1.41C, 0.07(SiO_2)

Oligomer IV affords a high yield of ceramic (60%) which contains much carbon (see Table II). Interestingly, the mixture of II and IV provides a high ceramic yield with respect to the number of silicon atoms involved. In this case too, the residue contains excess C. Thus, II, which on its own is a poor ceramic precursor, becomes a good one when it is mixed with IV before conversion to ceramic. Because of its ability to hydrosilylate the vinyl groups of IV by means of its SiH_2 and SiH_3 functionalities, it gives a cross-linked network and thus a high ceramic yield. This illustrates the efficiency of the hydrosilylation cross-linking process in increasing the ceramic yield. The effectiveness of cross-linking in increasing ceramic residue has been previously pointed out in other cases.[10]

In conclusion, we have shown that the transformation of oligomeric poly(carbosilanes) into ceramic SiC is facilitated when cross-linking of the oligomeric chains is made possible by hydrosilylation. This cross-linking process avoids the release of volatile components and permits densification of the material, thus favoring formation of SiC.

Acknowledgment. We thank the CNRS and Rhône-Poulenc for financial support and Rhône-Poulenc for a generous gift of catalyst 111.

Registry No. Silicon carbide, 409-21-2.

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