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Some Further Observations on Polymethylsilane as a Precursor for Silicon Carbide

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Poly(methylsilanes) produced by sodium coupling of methyldichlorosilane (2:1 molar ratio) contain residual chlorine which can be removed by reduction with $LiAlH_4$ at low temperature. Following this reduction, the polymers contain catalytically active centers (presumed to be silyl anions) which, in THF solution, further polymerize and crosslink the polymer at room temperature, while in toluene solution they are inactive. The reduced polymethylsilane gives high yields (*ca* 75%) of ceramic product on pyrolysis, but the composition is rich in silicon, compared with pure silicon carbide (SiC). Addition of catalytic amounts of dimethylzirconocene (DMZ) to this polymer gives a product which pyrolyzes to a product with stoichiometry close to that of SiC. It is concluded that the DMZ has an important influence in promoting Si–C bond formation, relative to Si–Si bond formation, during the pyrolysis.

Keywords: Poly(methylsilanes), catalysis, ceramic

INTRODUCTION

The fabrication of silicon carbide fibers by pyrolysis of organosilicon polymers has evoked considerable interest since Yajima and co-workers demonstrated the feasibility of spinning and processing poly(methylcarbosilane) to ceramic fibers.[1–6] Although the Yajima product, now commercialized in the form of Nicalon ceramic fibers, contains a large excess of carbon, it has so far led the way in stimulating research and development in the use of refractory fibers in composite materials. Despite the promising beginnings represented by these developments, there is still considerable room for improvement before the potential ultimate properties of silicon carbide (SiC) can be realized in this type of ceramic product.

Some years ago it was recognized by Seyferth *et al.* that polymethylsilane might be a better precursor for a stoichiometric SiC, in addition to offering the prospect of a higher ceramic yield.[7] However, early attempts at pyrolysis of polymethylsilanes, produced by sodium coupling of methyldichlorosilane, gave such poor ceramic yields (<20%) and such large excesses of silicon in the product that Seyferth was persuaded that such a route offered little promise of utility.[7]

We became interested in the possibility of producing SiC from polymethylsilane as a result of our investigations into the polymerization of primary organosilanes by Group 4 catalyzed dehydrocoupling.[8] Our efforts were rewarded when it was shown that polymethylsilane synthesized by this chemistry gave a SiC product not only in high ceramic yield (75–80%), but with a stoichiometry very close to that of SiC.[8–12]

More recently, Seyferth has made an important advance in this general area by demonstrating that prepolymers, prepared by sodium coupling of methyldichlorosilane under appropriate conditions, can be further polymerized by Group 4 metallocene catalyzed dehydrocoupling to give materials which pyrolyze to near-stoichiometric SiC in high ceramic yield.[11] The advantage of this approach is the relative availability and cheapness of methyldichlorosilane and its greater ease of handling, compared with methylsilane.

Independently, we have also studied the possibility of using prepolymers from sodium coupling of methyldichlorosilane. In addition to generally confirming the observations reported by Seyferth *et al.*, we also adventitiously discovered that, under certain conditions, $LiAlH_4$ can catalyze the further polymerization of the prepolymers to highly crosslinked polymethylsilylenes, which give high ceramic yields on pyrolysis. The ceramic

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products, however, contain large excesses of silicon. In the present paper, these experiments are described and their implications regarding the role of Group 4 catalyst residues in the pyrolyzate are discussed.

RESULTS AND DISCUSSION

Synthesis of poly(methylsilanes) by sodium condensation

The compositions of poly(methylsilanes) obtained from sodium coupling of methyldichlorosilane can be sensitive to slight variations in procedure.[11] We used two different methods which, apart from slight variations in molecular weights of the products, gave very similar results. In both cases, the same molar ratio of sodium to methyldichlorosilane (2:1) was used. This ratio was slightly lower than that used by Seyferth (2.5:1) and is probably responsible for the fact that our polymers contain residual Si—Cl, while those of Seyferth apparently did not.[11]

Method 1

Polymers prepared by refluxing 2 equivalents of dispersed sodium with 1 equivalent of methyldichlorosilane in a mixture of hexane and tetrahydrofuran (THF) (6:1, v/v) for 4 h were obtained as nonvolatile liquids in about 80% yield. GPC measurements, using polystyrene calibration, indicated an M_n of *ca* 700 Da (M_w *ca* 1200 Da) for these materials. ^1H NMR spectra were essentially the same as that of the poly(methylsilane) obtained by dehydrocoupling of methylsilane,[8,10] except that resonances due to small amounts of Si(H)Cl were detected in both ^1H and ^{29}Si NMR spectra. The ^{29}Si NMR (INEPT pulse sequence) also revealed the presence of considerably larger amounts of $MeSiH_2$ groups than is observed with the methylsilane-derived polymer. These groups give two ^{29}Si resonances: one at 61.0 ppm, the same as observed with the $MeSiH_3$-derived polymer and attributed to end groups, and another at 64.0 ppm, which is tentatively assigned to pendant $MeSiH_2$ groups along the polymer backbone. Seyferth has suggested that this abundance of SiH_2 groups arises either by secondary reactions, involving electron transfer processes between sodium and the silicon reactants, or from intermediate formation of NaH, which is then consumed by reaction of Si—Cl to give Si—H.[11] In either case, the SiH_2 groups are a result of both the low molecular weight of the polymers (end groups) and of the attachment of $MeSiH_2$ groups to the backbone.

Method 2

Another synthesis, using the same reactants and solvents, was carried out under sonication at room temperature for 20 h.[12] This reaction yielded a white, hexane-soluble solid with the same NMR features as the polymer obtained by the thermal reaction. GPC measurements revealed a bimodal molecular weight distribution. The higher molecular weight fraction (46% of the chromatogram) has a styrene-equivalent M_n of 1270 Da ($M_w = 1490$ Da) and the lower fraction (54%) has an M_n of 460 Da ($M_w = 520$ Da).

Reactions of prepolymers with $LiAlH_4$

Treatment of the chlorine-containing prepolymers with $LiAlH_4$ in THF at −78 °C for 30 min resulted in the complete disappearance of the ^1H NMR resonance due to Si($\underline{H}$)Cl. the liquid polymer (method 1) was recovered as a colorless liquid after $LiAlH_4$ reduction and found to have an M_n of 730 Da ($M_w = 1200$ Da), not significantly different from the starting polymer.

When the solvent-free, reduced poly(methylsilane) was dissolved in THF at room temperature, it immediately evolved hydrogen and changes color from colorless to orange–red. After 4 h the mixture became a yellow, viscous gel which, following removal of THF under vacuum, could not be redissolved. If the THF was removed after only 20 min of reaction time, the polymer had become a solid which could be easily redissolved in THF. This polymer had a bimodal molecular weight distribution. The higher molecular weight fraction had an M_n of 2100 Da ($M_w = 3190$ Da); the lower fraction (39%) had an M_n of 580 Da ($M_w = 640$ Da). After standing under vacuum for two days, this polymer had become partly insoluble in THF. Both solid-state and solution NMR experiments showed the polymers to have essentially the same chemical composition as the starting materials.

Dehydrocoupling of poly(methylsilane) catalyzed by dimethylzirconocene (DMZ)

The reduced poly(methylsilanes), described in the previous section, did not react spontaneously with DMZ at room temperature, but reaction could be initiated by gentle heating. After initiation, the reaction continued slowly at room temperature. DMZ could also be activated by reaction with $MeSiH_3$ to give a more active catalyst. Pretreatment with $MeSiH_3$ also avoids the transfer of methyl groups from DMZ to the polymethylsilane (giving unreactive $SiMe_2H$ end groups), since they are consumed to produce Me_2SiH_2. This catalyst polymerized the liquid prepolymer ($M_n = 730$ Da) to an insoluble glass in four to five days at room temperature. A sample taken after 24 h of reaction at room temperature had $M_n = 2130$ Da. The polymerization of the reduced prepolymer was greatly accelerated by heating. At 80 °C, the liquid prepolymer became an insoluble, infusible solid after about 30 min.

The preactivated catalyst initially showed some activity towards polymerization of the unreduced polymethylsilane, but with the passage of time the catalyst slowly deactivated due to the formation of dichlorozirconocene (detectable by its characteristic sharp cyclopentadienyl (Cp) resonance in the ^1H NMR spectrum). This was accompanied by disappearance of the characteristic orange–red color of the silylzirconocene intermediates and a gradual cessation of the hydrogen evolution. Heating to 100 °C resulted in darkening of the reaction mixture and a rapid hydrogen evolution since the zorconocene dichloride is reactive with Si—H groups at this temperature. After about 30 min the initially liquid prepolymer had set to an infusible, insoluble solid.

Pyrolysis of poly(methylsilanes)

A number of polymethylsilanes produced in the present study were pyrolyzed under argon. The results are summarized in Table 1. The liquid prepolymer that had not been reduced with $LiAlH_4$ gave a poor ceramic yield, and an elemental analysis corresponding to a mixture of SiC and silicon in the molar proportion of *ca* 70:30. The solid, unreduced prepolymer gave a slightly higher ceramic yield, but otherwise behaved in the same way as the lower-molecular-weight liquid prepolymer.

The ceramic yields from polymethylsilanes that had been crosslinked by the $LiAlH_4$-catalyzed reaction were notably higher, in line with the well-established correlation between crosslinking and ceramic yield. However, the products of these pyrolyses were still rich in elemental silicon.

All of the samples that were crosslinked with a dimethylzirconocene-derived catalyst gave high ceramic yields (75–80%). Those for which analyses were carried out gave analytical results corresponding closely to stoichiometric SiC, in conformity with previous observations.[9] This clearly shows that the residues of the catalyst have an important effect on the outcome of the pyrolysis reactions.

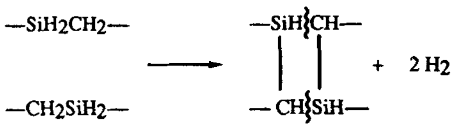
Table 1 Pyrolysis results for some poly(methylsilanes)

Sample	Ceramic yield (%)	Analysis (%)[a]	
		C	Si
1	45	22.93	72.96
2	54	23.45	72.49
3	72	—	—
4	75	23.63	72.55
5	75	—	—
6	77	29.39	67.84
7[b]	81	28.55	67.06

[a] It is estimated that the error ranges for analyses are ±1.5% for C and ±3.0% for Si. Hence, for the most part the total analyses are not statistically different from 100%. However, due to the air sensitivity of the polymethylsilanes and the presence of catalysts in samples 4, 6 and 7, there must be traces of oxygen and catalyst residues in the products.
[b] Sample same as 6, but held for 1 h at 150 °C before pyrolysis.

Mass-spectrometric analysis of the gaseous products of pyrolysis of polymethylsilanes (800 °C in a static system) in the presence and absence of DMZ showed that they are mostly composed of hydrogen (H_2) and methane (CH_4). Only traces of CH_4 are obtained in the presence of DMZ, but the polymers without DMZ gave ratios up to 4:1 (mol H_2/mol CH_4). This suggests that the DMZ residues catalyze a reaction which shortcircuits the demethanation reaction. A good candidate would be the intervention of hetero-dehydrocoupling between Si–H and C–H bonds. There is a precedent for this kind of catalytic process in the presence of later transition-metal catalysts.[14] Given that the activation energy for this process is expected to be higher than that for Si—H/Si—H coupling, it is reasonable that it would become more important at higher temperature, and if it is faster than the demethanation reaction, it will give higher selectivity towards the formation of Si–C bonds, relative to the formation of Si–Si bonds. It has been shown by vibrational spectroscopy that the pyrolysis of polymethylsilane in the presence of titanocene or zirconocene catalyst residues proceeds by initial formation of poly(carbosilane) at 350–400 °C, followed by hydrogen loss to give a hydrogenated SiC between 500 and

900 °C, and finally near-stoichiometric SiC at *ca* 1000 °C (Ref. 9, and M. Scarlete, J. F. Harrod and I. S. Butler, unpublished results). Since pyrolyses carried out in the absence of metallocene residues result in ceramic products containing large excesses of silicon, it may be concluded that the early transition-metal residues promote a selective crosslinking of the poly(carbosilane) through Si—H/C—H reactions, as shown schematically in Eqn [1].



[1]

The mechanism of LiAlH$_4$-catalyzed polymerization of poly(methylsilane)

There is little doubt that the coupling of polymethylsilanes in the presence of LiAlH$_4$ involves anionic processes. The appearance of a red color, and the triggering of enhanced catalytic activity, when the colorless toluene solutions of reduced polysilanes are exposed to tetrahydrofuran, strongly suggest the formation of a solvated silyl anion from unsolvated silyl clusters. The activity of potassium hydride (KH) for the catalytic coupling of phenylsilane has been reported by Corriu.[15] In that case, only low-molecular-weight oligomers were produced and there was some migration of phenyl groups. In the present study, LiAlH$_4$ was not found to have any polymerization activity towards phenylsilane, or polyphenylsilanes, but color changes indicative of the formation of silyl-lithiums were observed. If we assume the reaction goes by the sequence shown in Eqns [2] and [3], the difference in behavior between PhSiH$_3$ and MeSiH$_3$ may be explained by the greater stabilization of the PhSiH$_2^-$ anion, relative to MeSiH$_2^-$ and the consequent failure of equilibrium [3] to proceed to the right.

$$\mathrm{Li^+H^- + P{-}SiR'H_2 \rightarrow Li^+[P{-}SiR'H]^- + H_2} \quad [2]$$

$$\mathrm{Li^+[P{-}SiR'H]^- + P{-}SiR'H_2 \rightarrow Li^+H^- + P{-}SiR'HSiR'H{-}P} \quad [3]$$

EXPERIMENTAL

Preparation of polymethylsilane

Method 1

Sodium sand (18.4 g) in paraffin (9.2 g Na; 0.4 mol) was dispersed in hexane (80 ml), filtered and washed with 4 × 30 ml aliquots of hexane. The cleaned sand was then dispersed in a mixture of hexane (110 ml) and THF (18 ml). The suspension was brought to reflux by external heating and, after removing the external heat, freshly distilled methyldichlorosilane (22 ml; 0.2 mol) was added dropwise at a rate just sufficient to maintain steady reflux. On the completion of addition, the mixture was further refluxed for a period of 4 h, cooled to room temperature and filtered. The precipitate was washed with 4 × 20 ml of hexane and the combined filtrates were evaporated to dryness and redissolved in hexane (60 ml). Following a second filtration, the solvent was again removed under vacuum to give 7.1 g of an oily liquid (sample 1 in Table 1) (yield 80% based on MeCl$_2$SiH). ^{1}H NMR: δ 4.1 [(Si, Si, Me)Si$\underline{\mathrm{H}}$ and (Si, Me, H)Si$\underline{\mathrm{H}}$] *ca* 95%; 5.05 ppm [(Cl, Me, Si)Si$\underline{\mathrm{H}}$] *ca* 5%. ^{29}Si NMR: δ 67.0 [very broad; (Si, Si, Me)$\underline{\mathrm{Si}}$H)] *ca* 60%, 64.0 and 61.0 [(Si,Me)$\underline{\mathrm{Si}}$H$_2$, branch and terminal] *ca* 35%, 35.0 ppm (Si, Me, H)$\underline{\mathrm{Si}}$Cl] *ca* 5%. The percentage abundances are estimated from integrals and are not accurate to better than ±10%.

Method 2

The technique used was based on that reported by Kim and Matyjaszewki.[13] Sonicated reactions were carried out with essentially the same recipe as described above. No heat was applied. The reactor was subjected to ultrasonication for 20 h at room temperature in a Cole Parmer Model 8845-4 ultrasonic cleaner. Following the same workup as above, a white, solid polymer was isolated in 60% yield (sample 2 in Table 1). The NMR spectral details were indistinguishable from those of the liquid polymer prepared by the thermal route.

Reduction of poly(methylsilane)

Polymethylsilane (5 g, prepared by the thermal method above) was dissolved in THF (15 ml). The solution was cooled to −78 °C and a cold solution of LiAlH$_4$ in ether (5.7 ml of 1 M) was added slowly with stirring. After 30 min the THF was pumped off at low temperature and the residue was extracted with hexane (4 × 15 ml). The extracts were combined and filtered. Removal of the hexane at room temperature left a pale yellow oil (4.45 g; 90%). The NMR spectra of this polymer showed no resonances attributable to the presence of Si—Cl. A broad weak resonance at 3.6 ppm in the ^{1}H NMR spectrum (barely discernible in the unreduced polymer) is attributed to a higher concentration of SiH_2 end groups arising from the reduction of SiHCl groups.

Anionic polymerization of reduced poly(methylsilane)

A sample of reduced poly(methylsilane) (1.25 g) was dissolved in THF (3.0 ml) at room temperature. Polymerization began immediately with a visible gas evolution and a change of color from colorless to orange. After 20 min of reaction, the THF was removed under vacuum and the polymer was completely redissolved on addition of more THF (sample 3 in Table 1). A similar reaction, allowed to proceed for 4 h, produced a viscous gel. When the THF was removed under vacuum, the resulting solid could not be redissolved in THF (sample 4 in the Table). The soluble fractions of these polymers had ^{1}H NMR spectra essentially identical to those of the starting materials. Although there may have been a decrease in the intensity of the 3.6 ppm peak, low intensity and the extreme broadness of this resonance resulted in large limits of error on the integrals.

DMZ-catalyzed polymerization of unreduced poly(methylsilane)

A sample of liquid poly(methylsilane), prepared by method 1 (1.5 g) was added to a solution of DMZ (50 mg) in toluene. After stirring for several hours, no visible reaction had occurred. When a similar reaction was carried out, but with the DMZ solution activated by addition of a small dose of $MeSiH_3$, the active catalyst solution was orange in colour; after addition of the polymethylsilane sample hydrogen evolution was initially observed, but after 24 h there was no gas evolution and the orange color had been completely discharged. The recovered polymer was still an oil, indicating that very little dehydrocoupling had occurred.

The same recipe, except for omission of the solvent, gave no evidence of reaction over extended periods at room temperature, but when the mixture was heated to 100 °C the color changed to dark brown and there was an observable evolution of gas. After about 20 min under these conditions the mixture became a solid (sample in Table 1).

DMZ-catalyzed polymerization of reduced poly(methylsilane)

A sample of DMZ (29 mg) was dissolved in a solution of reduced poly(methylsilane) (2.0 g) in toluene (4.0 ml) at room temperature. No reaction was observed after one hour but, on gentle heating to *ca* 60 °C, the color changed to orange and a smooth evolution of gas commenced. After 6 h the recovered polymer was a brittle glass, still soluble in toluene. When the solid polymer, still containing catalyst, was left for seven days it was no longer soluble.

If the catalyst was pre-activated by treatment with a small amount of $MeSiH_3$, it was not necessary to warm the mixture to initiate the reaction and the polymer became completely insoluble after four to five days (sample 6 in Table 1).

Pyrolysis of polymethylsilanes

All pyrolyses were carried out under argon (UHP) in a Lindberg single-zone furnace equipped with a Eurotherm temperature controller. All samples were heated at 8 °C min^{-1} from 25 °C to 1000 °C and held for 1 h at the highest temperature. Solid-state ^{29}Si NMR spectra were recorded on a Chemagnetics CMS-300 spectrometer. Elemental analyses were carried out by Galbraith Laboratories.

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