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Thermal and Photochemical Conversion of Poly(methylsilane) to Polycarbosilane

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ABSTRACT: The use of some highly branched soluble copolymers, -$[(CH_3SiH)_x(CH_3Si)_y]_n-$, as pyrolytic precursors to silicon carbide (SiC) was examined. A progressive increase in the ceramic yield with increased branching was observed, parallel to a drastic decrease in the soluble polymer synthetic yield. Poly(methylsilane), PMS, was thermally and photochemically cross-linked before its conversion to SiC. The changes in the PMS structure were monitored by FTIR and ^{29}Si, ^{13}C, and ^{1}H NMR spectra. An increase in the ceramic yields for irradiated polymers was observed. This effect was stronger when the polymer irradiation was performed in the presence of AIBN. The PMS thermolysis was also studied using *n*-hexane or toluene as solvent, at 70 °C, in the presence of AIBN. Toluene showed an inhibiting effect on Kumada rearrangement, while *n*-hexane was a good solvent to obtain the conversion of PMS to polycarbosilane, at a relatively low temperature.

Introduction

Many of the devices employed in high technology require the use of materials with good chemical stability and a potential to operate at high temperatures. Silicon carbide is a non-oxide ceramic material which combines these characteristics with other physical and electronic properties that lead to several applications.[1−3]

SiC is obtained in large scale by the Acheson process, where SiO_2 and C are pyrolyzed at temperatures as high as 2500 °C, producing an intractable solid, which then limits its use.[4] In the mid 1970s, Yajima and coworkers[5] showed the preparation of this material by means of a set of chemical transformations starting from poly(dimethylsilane). The polymeric nature of the ceramic precursors makes the production of fibers, coatings, binders, etc. feasible. The polysilane conversion into polycarbosilane (PCS) is the critical step in this process and therefore considerable efforts have been made to optimize this or even to explore, with some success, the development of improved polymer precursors for high ceramic yield and also high phase purity.[1] West et al.[6] have also developed a series of soluble copolysilanes called "polysilastyrene", which have been used successfully as SiC fiber precursors. However, both precursors show high carbon contents in their structures, leading to a SiC rich in this element. Schilling[7] and Seyferth,[8] independently, used the poly(methylsilane) (PMS) as a SiC precursor. This polymer was prepared, via the dehalocoupling of chlorosilane monomers, using either K or Na, obtaining $-[(CH_3SiH)_x(CH_3Si)_{1-x}]_n-$, with variable *x*, depending on the reaction conditions. However, the corresponding ceramic yields were quite low, varying from 12 to 20%, and the ceramic products had a 25% excess of Si. In 1984, Harrod found that molecular organosilicon compounds, with more than one Si−H bond, react to form oligomers and hydrogen in the presence of dimethyltitanocene or dimethylzirconocene.[9] Recently, several groups[10−13] have explored the dehydrogenative polycondensation of the methylsilane catalyzed by transition metal organometallic compounds to obtain PMS as a SiC precursor.

The PMS was also modified by hydrosilylation with organic or organosilicon compounds, in the presence of H_2PtCl_6, leading to an increase in the ceramic yields (57−72%).[14] The cross-linking, promoted by metals, was also described as a means of improving the ceramic yield of PMS. For example, when an appropriate mixture of PMS and Nicalon PCS was irradiated in the presence of $Ru_3(CO)_{12}$, a ceramic yield of 68% and a chemical composition of 99% SiC and 1% C was obtained.[1] However, no detailed analyses were performed on the pyrolyzed samples to confirm the ceramic stoichiometry.

SiC was also prepared by pyrolysis of polycarbosilanes cured by electron beam radiation in a helium atmosphere.[15]

In this present work, PMS was thermally and photochemically converted to polycarbosilane. A series of highly branched copolymers, $[(CH_3SiH)_x(CH_3Si)_y]_n-$, were also obtained from a mixture of CH_3SiCl_3 and CH_3HSiCl_2. The yield and the composition of the produced ceramics were analyzed as a function of the polymer precursor. The possibility of producing polycarbosilanes at low temperatures was also explored.

Experimental Section

General Comments. All the reactions and processes were carried out in an argon atmosphere, by means of standard Schlenk manipulations or inside a glovebag. Solvents were dried and distilled before use. Chlorosilane derivatives were freshly distilled prior to their use in the presence of CaH_2. AIBN (azobis(isobutyronitrile)) was used after recrystallization from methanol.

Instrumental Methods and Procedures. Elemental analyses of the ceramic materials were performed in a Perkin Elmer 2400 elemental analyzer using the procedure suggested in ref 16. All ^{29}Si (59.6 MHz), ^{13}C (75.4 MHz), and ^{1}H (300 MHz) NMR spectra were recorded on a Bruker AC-300 spectrometer using C_6D_6 as the solvent at room temperature. The ^{29}Si NMR spectrum of PMS using the inverse gated sequence showed overlapping peaks. In order to assign these peaks, two spectra using the INEPT program were obtained. The values $^{1}J_{Si-H} = 200$ Hz and $^{2}J_{Si-H} = 6.7$ Hz were used to estimate the delay times. 2-D ($^{13}C-^{1}H$) experiments were also recorded using the HETCOR sequence. FTIR transmission spectra were obtained using a Perkin Elmer 1600 spectrometer operating at a 4 cm^{-1} resolution with neat film samples between salt plates or with KBr pellets. UV spectra were measured at room temperature, in 0.2 g L^{-1} *n*-hexane solutions, with an Intralab DMS 100 spectrophotometer. The number-average molecular weights ($\bar{M}_n$) were determined by vapor pressure osmometry on a Knauer instrument, using toluene solutions thermostatically controlled at 45 °C. Pho-

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Table 1. Composition and Synthetic and Ceramic Yields of the Copolymers Obtained from CH_3SiHCl_2/CH_3SiCl_3 Coupling

copolymer comp	synthetic yield, % (soluble products)	ceramic yield (TGA) %
$[CH_3HSi)_{0.6}(CH_3Si)_{0.4}]$	50.0	20.0
$[CH_3HSi)_{0.5}(CH_3Si)_{0.5}]$	28.4	37.0
$[CH_3HSi)_{0.4}(CH_3Si)_{0.6}]$	25.4	50.5
$[CH_3HSi)_{0.3}(CH_3Si)_{0.7}]$	3.1	67.0
$[CH_3HSi)_{0.2}(CH_3Si)_{0.8}]$	2.3	66.7

[a] Obtained by the integration of the ^1H NMR peaks.

tochemical studies were carried out using a Philips 125 W mercury lamp, operating in the range 200–600 nm, with main emissions at 310 (weak) and 366 nm (strong). The pyrolysis experiments were performed on a DuPont 1090B thermogravimetric analyzer on line with a DuPont 951 thermal analyzer, under an argon flux and a heating rate of 10 °C/min. The XRD pattern was recorded on a Shimadzu diffractometer, Model XD3A, using a Cu Kα radiation.

Preparation of Poly(methylsilane) (PMS).[17] A three-necked round-bottom flask, equipped with a Teflon-coated magnetic stir bar, oven-dried, and flushed with argon, was fitted with a pressure-equalizing addition funnel, a reflux condenser and an argon inlet and outlet. Then 350 mL of toluene and 23 g (1 mol) of sodium (in small pieces) were put in the flask, and this system was immersed in an oil bath at 110 °C. Vigorous stirring was maintained until a fine sodium dispersion formed. The oil bath was removed, and 52.5 mL (0.51 mol) of CH_3SiHCl_2 was added dropwise at a convenient rate to keep the gentle reflux of the solvent. After addition, the mixture was refluxed for 5h. Then, 3 mL (0.024 mol) of $(CH_3)_3SiCl$, used as a blocking-chain agent, was added dropwise and the reflux was maintained for another 2 h. The mixture was filtered under argon to remove the NaCl and the residual sodium traces. The resulting clear yellow solution was concentrated under vacuum, until it reached approximately 20 mL, and the PMS was precipitated, from methanol, as a viscous pale yellow oil. PMS was dried under vacuum at 50 °C for 4 h. $\bar{M}_n = 1000$. The found composition was $[CH_3SiH)_{0.6}(CH_3Si)_{0.4}]_n$, $n \sim 23$ with a 50% yield. FTIR (neat, cm^{-1} (assignment)):[18,19] 2956, 2893 (νCH, $SiCH_3$), 2104 (νSiH), 1408, 1247 (δC–H, $SiCH_3$), 1038 (νSiOSi), 931 (γSiH_2), 866 (ϱCH_3), 774, 685 (νSiC). ^{13}C NMR (ppm, assignment):[20] −9.76, 2.51 ($HSiCH_3$, $SiCH_3$). ^{29}Si NMR (ppm, assignment):[10, 20] −68.0 ($SiCH_3$), −63.0 ($HSiCH_3$), and the minor peaks at −34.9, 7.5, and 20.4 ppm resulting from $-Si(CH_3)H_2$, $(CH_3)_3Si$, and CH_3SiHCl end groups, respectively. ^1H NMR (ppm, assignment):[20] 0.50 ($HSiCH_3$, $SiCH_3$); 3.93, 4.10 (Si–H); 5.14 (SiH_2 end group, Si(H)Cl); 5.55 (SiOH traces).

Preparation of Copolymers $[CH_3SiH)_x(CH_3Si)_y]_n$. A series of PMS copolymers were synthesized from a mixture of CH_3SiCl_3 and CH_3HSiCl_2 monomers, at different ratios. The characterization of the copolymers was performed by ^1H and ^{13}C NMR and FTIR measurements like those of the PMS. These copolymers showed no qualitative changes in the characterization data. In the FTIR spectra, changes in relative intensities were observed, as expected. The composition of the copolymers can be seen in Table 1.

Cross-linking of PMS by UV Irradiation. PMS (2 g, 2 mmol) was dissolved in dry hexane inside a quartz Schlenk-type tube, and the system was purged by three freeze–pump–thaw degassing cycles. Then, the solution was irradiated by UV light for 1.5 h and also 3 h, in the presence or not of AIBN (30 mg, 0.34 mmol), under constant magnetic stirring. The obtained polymers were dried under vacuum, at 50 °C for 4 h. The products were coded: PMS 1.5 h UV (from 1.5 h exposure), $\bar{M}_n = 300$; PMS 3 h UV (from 3 h exposure), $\bar{M}_n = 400$; PMS 1.5 h UV AIBN (from 1.5 h exposure in AIBN presence), $\bar{M}_n = 1400$; and PMS 3 h UV AIBN (from 3 h exposure in AIBN presence), $\bar{M}_n = 900$.

Cross-linking of PMS by Thermolysis in the Presence of AIBN. Solvent Effect. A Schlenk-type system was charged with PMS (2 g, 2 mmol), AIBN (30 mg, 0.34 mmol) and dry toluene (or dry *n*-hexane (8 mL)). This system was filled with argon and immersed in an oil bath at 80 °C for 3 h. Afterward, the solution was concentrated under vacuum and the polymer was precipitated and washed in methanol. The product was dried under vacuum at 50 °C for 4 h and coded: PMS 3 h Tol (from 3 h of cross-linking in toluene) and PMS 3 h Hex (from 3 h of cross-linking in *n*-hexane).

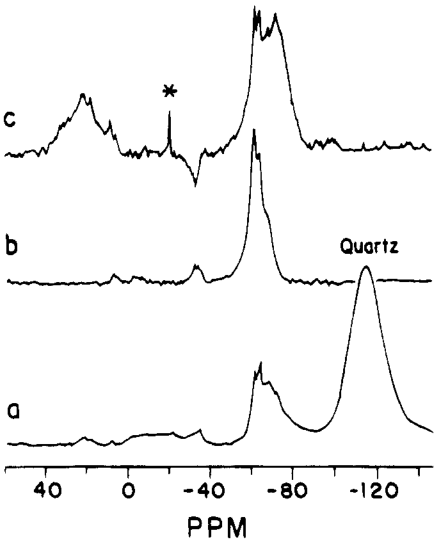

Figure 1. ^{29}Si NMR spectra of PMS using (a) inverse gated sequence, (b) INEPT sequence (delay time from $^1J_{SiH} = 200$ Hz), and (c) INEPT sequence (delay time from $^2J_{SiH} = 6.7$ Hz). *Silicone wax.

Results and Discussion

PMS was prepared by dehalocoupling of CH_3SiHCl_2 with Na dispersion in toluene and a partially branched polymer was obtained, with di- and trifunctional units, and the $[(CH_3SiH)_{0.6}(CH_3Si)_{0.4}]_n$ composition was determined by the integration of the ^1H NMR spectrum.

Figure 1a shows the ^{29}Si NMR spectrum of PMS obtained by the inverse gated sequence technique, with overlapped signals at ∼−63.0 and ∼−68.0 ppm. These peaks could be separated by altering the time between the pulses in the INEPT sequence.[21] Figure 1b shows the run using the $^1J_{Si-H}$ value (200 Hz) to estimate the delay time, where only groups containing SiH were detected. The signal at −68.0 ppm disappeared, thus, it can be assigned as a characteristic of $SiCH_3$ in trifunctional units. In Figure 1c, the run using the $^2J_{Si-H}$ value (6.7 Hz) detected all $SiCH_3$ units. In the Figure 1a spectrum, there are also low-intensity signals at −34.0, +7.5, and +20.4 ppm due to $-CH_3\mathit{Si}HSi(CH_3)_3$, $-Si(CH_3)_3$, and CH_3SiHCl end groups, respectively.[20]

The INEPT sequence is not a quantitative method due to the NOE.[21] Therefore, the medium-intensity signal at 20.4 ppm (Figure 1c) must represent only a small amount of the $-CH_3SiHCl$ groups. This fact was confirmed by the spectrum in Figure 1a.

The PMS polymer is easily oxidized in contact with air, so extreme care is necessary with this material during its manipulation and measurements. Freshly prepared PMS showed a low amount of SiOSi moieties, evidenced by the broad absorption in the 1000–1100 cm^{-1} region, corresponding to νSiOSi,[18] as can be seen in the FTIR spectrum (Figure 2a). Three TGA runs with PMS in the following conditions were carried out: (a) recently prepared and exposed to air for (b) 10 and (c) 20 min. The ceramic yields obtained were 20, 40, and 60% respectively. This increase in the ceramic yield was generated due to the cross-linking promoted by the

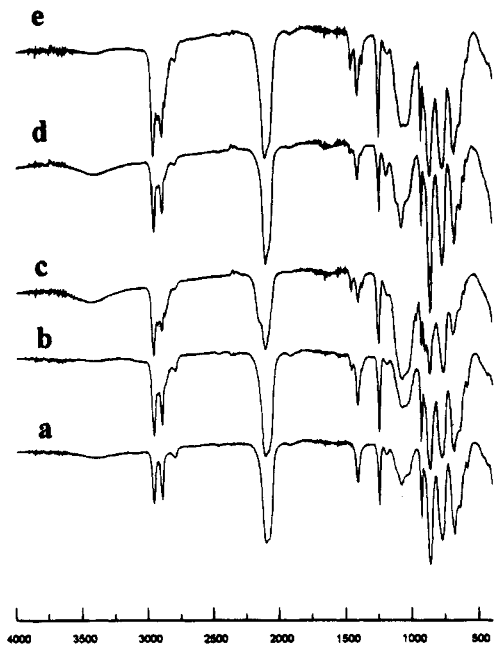

Figure 2. FTIR spectra of (a) PMS, (b) PMS 1.5 h UV, (c) PMS 3 h UV, (d) PMS 1.5 h AIBN UV, and (e) PMS 3 h AIBN UV.

PMS oxidation. Considering this fact, all PMS manipulations were performed in a glovebag. Thermal analyses were run under an argon flux of 50 mL/min after the samples were purged for 10 min at room temperature.

It is well-known that low ceramic yields are a consequence of the thermal degradation leading to formation of oligomers, including volatile cycles. If the preceramic polymer is cross-linked, the formation of oligomers and cycles is more difficult, due to restrictions imposed on the polymeric chain, which then promotes an increase in the ceramic yield.[1] However, the branching level must be well controlled to avoid polymer insolubility.

In order to maximize the ceramic yield conversion, a series of copolymers, taken from the mixture of CH_3SiHCl_2 and a trifunctional monomer (CH_3HSiCl_3) in variable proportions, was prepared. The last monomer was chosen to keep the preceramic polymer stoichiometry equivalent to that of the SiC. A progressive increase in the ceramic yield, with the branching increase, was observed, as can be seen in Table 1. However, the soluble polymer synthetic yield showed a drastic decrease, which rendered it an impracticable synthetic pathway.

Actually, it would be interesting to cross-link the PMS without altering its synthetic yield. One alternative, would be to branch the PMS after its synthesis by means of ultraviolet radiation. Seyferth et al.[14] explored, with success, the photochemical cross-linking of PMS in the presence of catalytic amounts of transition metal carbonyls, as a means of improving the ceramic yields of this polymer. It is well-known,[22,23] from polysilane studies, that Si–Si bonds undergo photoscission in UV light and that secondary reactions with Si–H bonds can occur, which are also susceptible to radical reactions. These properties could be used to degrade or to branch the PMS chain through photochemical processes, without affecting its synthetic yield.

Exposure of PMS to UV Light. Table 2 shows the changes in the molecular weight of PMS, in its ceramic yield, and also in its residue composition, as a function of the exposure conditions upon UV irradiation. As expected, an increase in the ceramic yields for all exposed polymers was obtained, suggesting that there was some branching in the polymer chain by means of this treatment. In spite of this, a decrease in its molecular weight was observed.

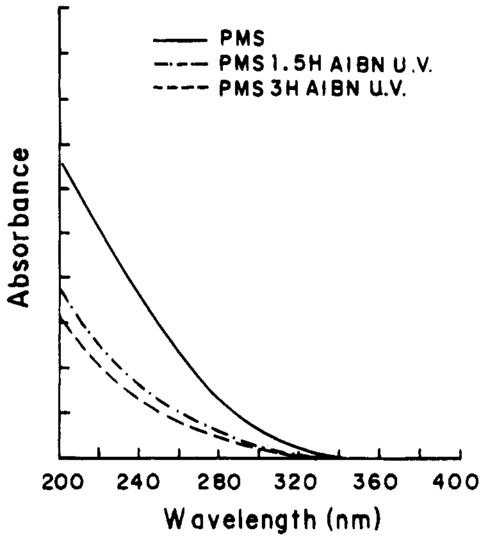

Figure 3. Electronic spectra of PMS, PMS 1.5 h AIBN UV, and PMS 3 h AIBN UV.

Table 2. Ceramic Yield, Molecular Weight, and Residue Composition of the Irradiated Polymers

polymer	$\bar{M}_n$	ceramic yield (TGA, 10 °C/min, %)	residue comp, %
PMS	1000	20	62.4 SiC + 37.6 Si
PMS 1.5 h UV	300	32	58.8 SiC + 41.2 Si
PMS 3 h UV	400	33	56.5 SiC + 43.5 Si
PMS 1.5 h AIBN UV	1400	49	71.8 SiC + 28.2 Si
PMS 3 h AIBN UV	900	57	70.8 SiC + 29.2 Si

The UV irradiation promotes other effects on the polymer chain, in addition to the branching. Actually, simultaneously to cross-linking, photodegradation of the main chain can occur, contributing to the decrease in the polymer molecular weight and to the maintenance of the solubility of the material. This behavior is in accordance with the previously proposed mechanism for the photodegradation process in polysilanes.[22,24]

PMS was also irradiated in the presence of AIBN (azobis(isobutyronitrile)), a common radical initiator, in order to verify its effect on the structure of the polymer. The ceramic yields were highest when the AIBN was present, which suggests the predominance of the photo-cross-linking process, under the conditions described above.

PMS shows an absorption UV spectrum characteristic of branched polysilanes,[25] with strong absorption in the shorter-wavelength region (λ < 250 nm), which decreases monotonically to 350 nm. After exposure, a photobleaching in the UV spectra was observed, as can be seen in Figure 3, which is associated with a decrease in the delocalization of the σ Si–Si electrons, due to the inclusion of $-CH_2-$ groups in the PMS polymeric chain, from Kumada rearrangement.[26]

The changes in the PMS structure produced by UV exposure were also monitored by FTIR spectroscopy, as can be seen in Figure 2. The bands centered at 1460, 1377, and 1082 cm^{-1} could be assigned to the $-CH_2-$ groups,[19] which were practically absent in the freshly prepared polymer (Figure 2a). Another evidence of the

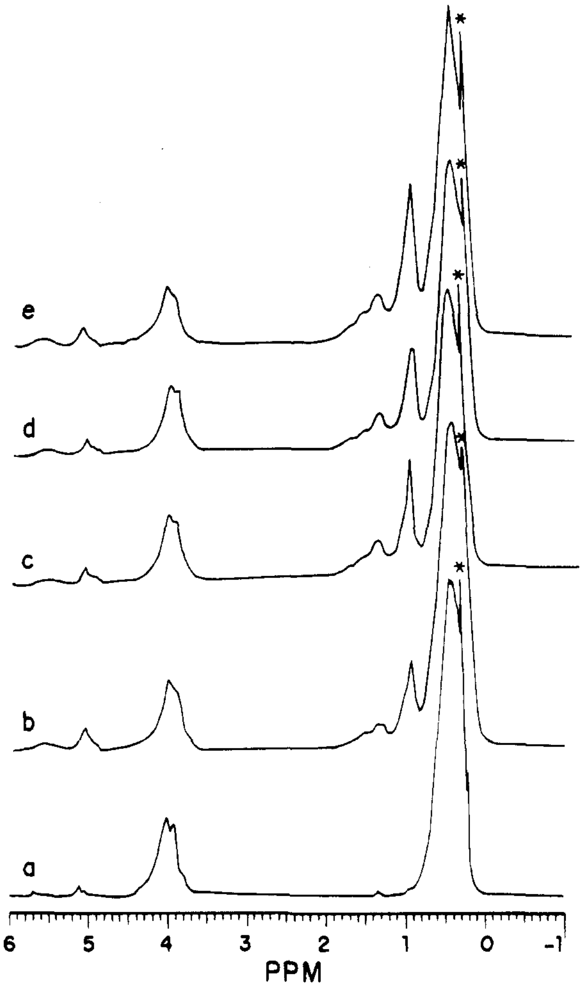

Figure 4. ^{1}H NMR spectra of (a) PMS, (b) PMS 1.5 h UV, (c) PMS 3 h UV, (d) PMS 1.5 h AIBN UV, and (e) PMS 3 h AIBN UV. *Silicone wax.

presence of these groups was the change in the shape and in the relative intensities of the bands in the 2960–2870 cm^{-1} region, assigned to C–H stretching.[18,19] In the ^{1}H NMR spectra (Figure 4) peaks at 0.93, 1.35, and 1.55 ppm appeared in the characteristic region of the CH_2 groups, while others at 5.05 and 5.55 were intensified. In the ^{13}C NMR spectra several signals appeared in the 5–45 ppm range, also confirming PMS conversion to polycarbosilane (Figure 5). These signals were correlated by 2-D NMR experiments using a HETCOR sequence (Figure 6). The peaks from -13.0 to $+5.0$ ppm (^{13}C) corresponded to the relatively broad peak centered at 0.5 ppm (^{1}H) assigned to $SiCH_3$ groups; several signals from 10 to 25 ppm (^{13}C) corresponded to the peak centered at 0.95 ppm (^{1}H) (methylene groups), others that appeared in the region from 20 to 45 ppm were also related to methylene groups at 1.35 and 1.55 ppm.[20] This complex profile suggests that the $-CH_2-$ groups are found in several different environments in the polymer chain, generated by the combination of different radical fragments. This photodegradation process also generated more SiH_2 end group species, confirmed by the increase in the relative intensity of the signal at 5.05 ppm, assigned to these groups.[20] Meanwhile the signal at 5.55 ppm, attributed to SiOH species,[20] was slightly intensified due to the high sensibility, of the Si–H bond, to traces of humidity.

The ceramic powders obtained from thermal treatments of irradiated PMS samples still showed a composition rich in silicon (Table 2). This result suggested

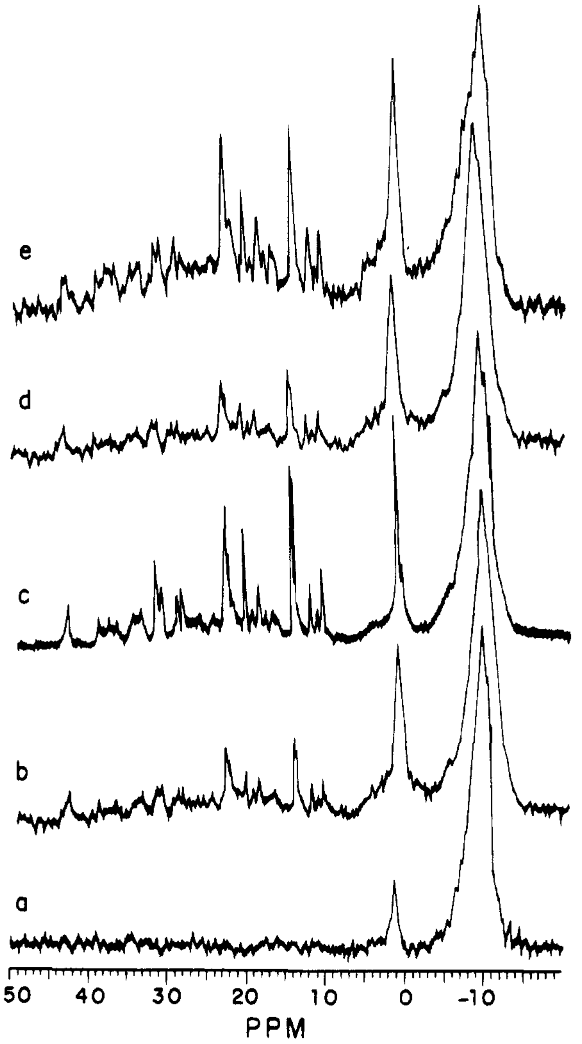

Figure 5. ^{13}C NMR spectra of (a) PMS, (b) PMS 1.5 h UV, (c) PMS 3 h UV, (d) PMS 1.5 h AIBN UV, and (e) PMS 3 h AIBN UV.

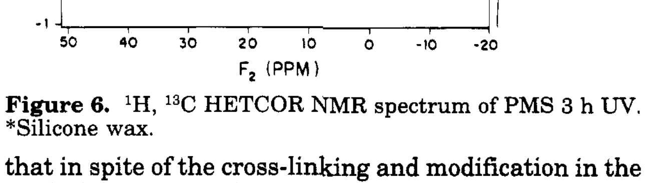

Figure 6. ^{1}H, ^{13}C HETCOR NMR spectrum of PMS 3 h UV. *Silicone wax.

that in spite of the cross-linking and modification in the PMS chain, its pyrolysis still produced a large quantity of $CH_4(g)$[27] and a ceramic residue with an undesirable stoichiometry. However, the X-ray diffraction measurement performed in this residue, showed characteristic reflections of β-SiC,[28] in an amorphous matrix, confirming its obtention, as can be seen in the Figure 7.

Solvent Effect Study on the Thermal Cross-Linking Promoted by AIBN. AIBN can undergo radical scission of its $-N{=}N-$ group either thermally, up to 70 °C, or photolytically, with a similar mechanism.[29] As expected, the PMS thermolysis carried out

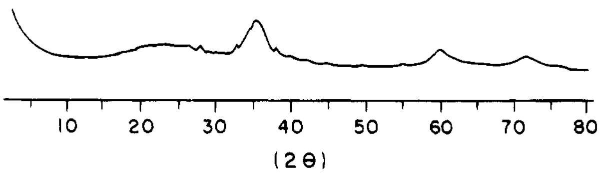

Figure 7. PMS-derived SiC XRD pattern.

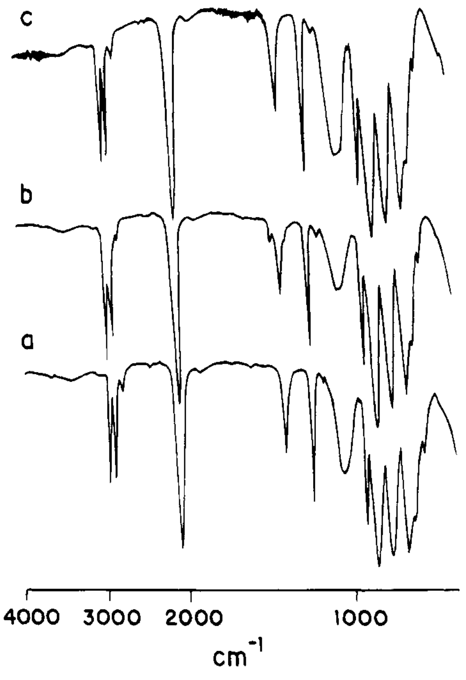

Figure 8. FTIR spectra of (a) PMS, (b) PMS 3 h Hex, and (c) PMS 3 h Tol.

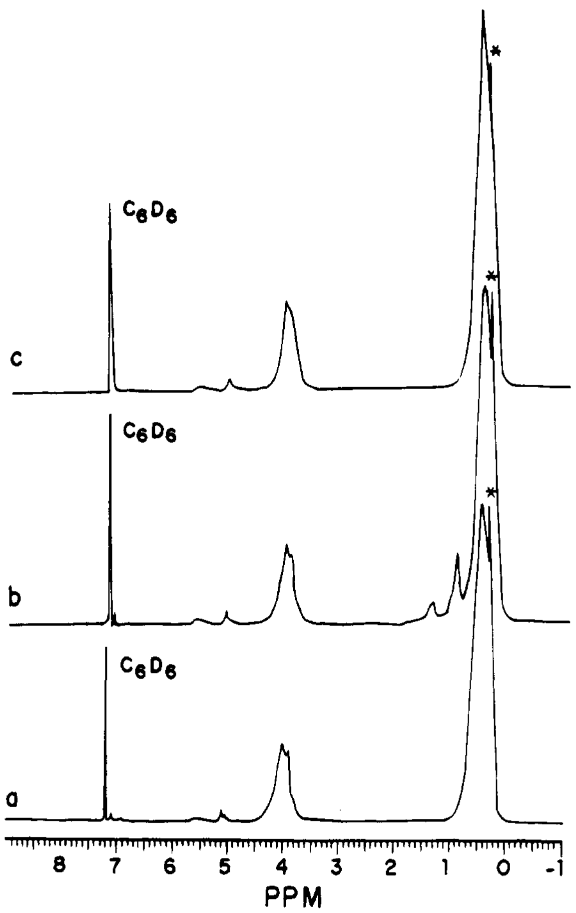

Figure 9. ^1H NMR spectra of (a) PMS, (b) PMS 3 h Hex, and (c) PMS 3 h Tol. *Silicone wax.

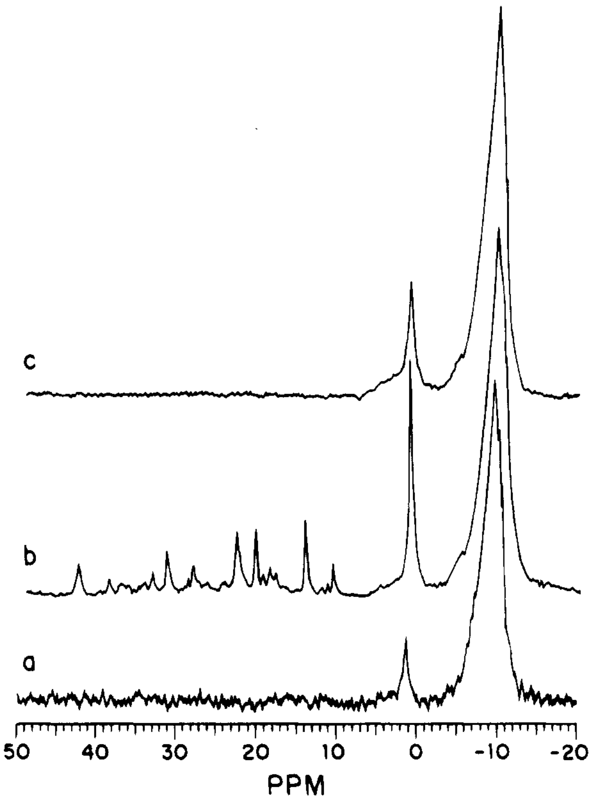

Figure 10. ^{13}C NMR spectra of (a) PMS, (b) PMS 3 h Hex, and (c) PMS 3 h Tol.

in a hexane solution, in the presence of AIBN, gave products similar to that generated from photo-irradiated PMS. However, when toluene was used as solvent, only cross-linked polymers produced by Si−H bond consumption were observed. In this case, $-CH_2-$ groups were not generated, as can be confirmed by FTIR and ^1H and ^{13}C NMR spectra, as seen in Figures 8−10, respectively, and also by the increase in the $\bar{M}_n$ value to 2000.

Considering that neither n-hexane or toluene has any effect on the AIBN scission efficiency,[30] these solvents must be acting on the PMS scission process. These results suggest that toluene inhibited the Kumada rearrangement. As already known,[31] toluene can solvate the radical silyl or can react with it at a very fast rate ($k = 1.2 \times 10^6$ M^{-1} s^{-1}). This feature plays an important role in stabilizing this radical, interfering in the rate of its conversion into the silene species, the formation constant of which is only 1 order of magnitude ($k = 7.5 \times 10^7$ M^{-1} s^{-1})[32] greater than that the former, but which can be diminished in the presence of toluene. It is important to note that no aromatic carbons appeared in the PMS 3h Tol ^1H NMR spectrum (besides C_6D_6 signal) (Figure 9c), indicating that there was no toluene incorporation in the polymer bulk. The silene formation step, responsible for the $-CH_2-$ formation in the Kumada rearrangement, quite probably did not occur and the final polymer did not show any $-CH_2-$ groups in its structure. When the hexane was used as solvent, the stabilization effect on the silyl radicals was absent, and so, the resulting polymer showed $-SiCH_2-Si-$ segments.

Thus, the PMS thermolysis with n-hexane as solvent, in the presence of AIBN, at 70 °C, revealed a way of obtaining polycarbosilanes at a relatively low temperature.

Conclusion

The conversion of PMS to polycarbosilane, as SiC precursor was carried out photochemically, by UV light, in the presence of AIBN. This procedure revealed an alternative route to obtain polycarbosilane at room temperature. The PMS thermolysis, at 70°C, using *n*-hexane as solvent, in the presence of AIBN, also promoted this PMS conversion. The same thermolysis, performed in toluene, increased the PMS branching, however, without promoting its conversion to polycarbosilane.

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