2.1. Introduction

Polycarbosilanes (PCSs), in their broadest definition, are organosilicon polymers whose back bone is composed of appropriately substituted silicon atoms and difunctional organic groups which bridge the silicon atoms\textsuperscript{1,2}. Polycarbosilanes are organic-inorganic hybrid polymers which have both Si and C in their back bone structure; they have been of exacting significance as potential precursor to SiC\textsuperscript{3-10}, a ceramic material which is of considerable technological importance due to its high thermal, chemical and oxidative stability, as well as for its electrical (semiconductor) and mechanical (high hardness, shock resistance, strength etc.) properties\textsuperscript{11, 12}. It is not hard to envision variety of possible application that are opening up for these hybrid polymers in the areas such as nanotechnology, surface science, bio-medicine, catalysis, electrochemistry, liquid crystals, new ceramic materials, organic hybrid and nanocomposites etc\textsuperscript{14-22}. Many of these applications play dominant roles in the development of science in the twenty first century, and we have no doubt that silicon will occupy a prominent position in all of them as well.
Various routes\textsuperscript{7-10} to polycarbosilanes were put forward by different scientific groups. Several investigators\textsuperscript{20-22} have explored the use of alkali metals for the reductive-coupling of silanes. Appropriate route for the synthesis of partially cross-linked structure into the polycarbosilane have to be selected, to make the further functionalization easy.

The preparation of polycarbosilanes by reacting chlorosilanes with unsaturated compounds in the presence of metallic reducing agents has been adopted. This route proves to be moderately simple way to prepare cross-linked polycarbosilane.

The polycondensation of chlorosilanes and vinyl silanes to prepare polycarbosilanes have been carried out. The chlorosilane monomer on reaction in the presence of a metallic reducing agent such as sodium leads to the formation of polymer, by Wurtz type coupling\textsuperscript{28}. The polysilane on thermal rearrangement gives polycarbosilane. The transformation proceeds through Kumada rearrangement\textsuperscript{10,23}, which is an insertion of methylene group into a Si-Si bond. Wurtz coupling between chlorosilanes and unsaturated compounds leads to the formation of polycarbosilanes. Wurtz type coupling reaction, which makes use of alkali metals, can generally lead to appreciable Si-Si and C-C bonding, in addition to Si-C bonding, and extensive cross-linking.

The reactivity of Si-X (where X= Cl, OR or H) is very high\textsuperscript{24}, the nucleophilic reactions can direct to the formation of hyperbranched polycarbosilane back bone. This methodology has also been used widely to attach side chains and to modify the structure of the originally obtained polycarbosilane through reaction with Si-Cl or Si-OR groups on the polymer back bone. Consequently this methodology has been, and is expected to continue to be, an important component of the chemical tool kit that is available for the preparation and effective utilization of this important class of organosilicon polymers\textsuperscript{19,25,26}. 
In this chapter, preparation of polycarbosilanes is described. Polycarbosilanes were synthesized from corresponding monomers, trichloromethylsilane, chlorodimethylvinylsilane, diethoxymethylvinylsilane and trimethoxyvinylsilane. Homopolymers with trichloromethylsilane, diethoxymethylvinylsilane and copolymers with trichloromethylsilane in combination with chlorodimethylvinylsilane, diethoxymethylvinylsilane, trimethoxyvinylsilane were synthesized. In total five polymers were prepared. The preparation involves the Wurtz-type coupling reaction of monomer molecules in the presence of metallic sodium. The synthesized polymers were analysed using various spectral and chemical methods.

2.2. Results and Discussion

2.2.1. Preparation of polycarbosilanes

Trichloromethylsilane, chlorodimethylvinylsilane, diethoxymethylvinylsilane and trimethoxyvinylsilane were selected as the monomers to synthesise polycarbosilanes.

![Figure 1: Monomers](Image)

The monomers were selected with altered functionality, so as to compare the capability of the monomer to crosslink with varying functional groups.
2.2.2. Polycarbosilane from Trichloromethylsilane (PCS 1)

PCS 1 was prepared by two steps,

Former step is the synthesis of polysilane\textsuperscript{28}. Polysilanes are generally synthesized by the Wurtz-type reductive-coupling of the corresponding chlorosilane using sodium metal in a high boiling solvent such as toluene. Second step is the thermolysis of polysilane to polycarbosilane.

2.2.2.1. Preparation of polysilane (PMS)

Polysilane was prepared by the Wurtz type coupling of trichloromethylsilane in the presence of metallic sodium in toluene at 100\(^\circ\)C. The monomer to sodium metal ratio was 1:1. The reaction was done under N\(_2\) atmosphere.

\[
\begin{align*}
\text{CH}_3 & \quad \text{Si} \quad \text{Cl} \\
\text{Cl} & \quad \text{Si} \quad \text{Cl} \\
\text{Na/Toluene} & \quad \rightarrow \\
\text{Cl} & \quad \text{Si} \\
\text{Si} & \quad \text{Cl} \\
\end{align*}
\]

Scheme 1: Preparation of polysilane

The polysilane obtained was a gelatinous liquid which was soluble in toluene and a white solid which was insoluble in all solvents. The molecular weight was determined for liquid fraction by GPC technique. A pale yellow liquid oligomer of molecular weight \(M_n = 544, M_w = 865\) from GPC using polystyrene as standard was obtained. The liquid fraction was discarded.

The insoluble polysilane was analysed with UV-DRS, FT-IR spectroscopy, \(^{13}\)C NMR spectroscopy and \(^{29}\)Si NMR spectroscopy.

UV absorption spectra are very important for the analysis of \(\sigma\) conjugation systems along the Si-Si backbones. The relationship between these spectra and linear polysilane and oligosilane structures have been investigated both theoretically and experimentally. It was found that the UV absorption band
of the $\sigma-\sigma^*$ transition shows a red-shift, which increases with the length of the linear permethylated Si-Si chains both in polysilanes and in their shorter oligomers. This shift, however, has a limit at about 296 nm, which corresponds to that of the octadecasilane, Si$_{18}$Me$_{36}$, unit and if the number of silicon atom is increased above 18, no significant further red shift is observed.

Silicon polymers show UV absorption above 200 nm. This result is totally unexpected for a species containing no double bonds. PMS shows an absorbance maximum at 273 nm. This is due to the $\sigma$- conjugation of the Si back bone.

The FT-IR spectrum of the polymer has the corresponding peaks of the polysilane. The spectrum shows a peak at 2952 cm$^{-1}$ which is corresponding to the C-H stretching, peak at 2089 cm$^{-1}$ is due to the Si-H stretching, peak at 1447 cm$^{-1}$ is due to Si-CH$_3$ stretching, peak at 1252 cm$^{-1}$ corresponds to Si-CH$_3$ deformation, and 777 cm$^{-1}$ is due to Si-CH$_3$ wagging. 1045 cm$^{-1}$ due to the Si-O stretching.

**Figure 2:** $^{29}$Si NMR spectrum of PMS
$^{29}$Si NMR spectrum of PMS is shown in Figure 2. Chemical shifts are based on tetramethylsilane as the internal standard. In the spectrum, the peak around -66.01 ppm was assigned to be due to the resonance of Silicon in $(\text{CH}_3)_2\text{SiSi}$ unit (branching unit). A small peak in close proximity to it around -60 ppm is corresponding to the $(\text{CH}_3)_2\text{ClSiSi}_2$ unit (linear unit). The branching unit was formed by the elimination of Cl atom from the Si-Cl groups during Wurtz coupling.

Figure 3: $^{13}$C NMR spectrum of PMS
The solid state $^{13}$C NMR spectrum of PMS (shown in figure 3) exhibits only one resonance signal centered at -2.93 ppm, which can be assigned to SiSiCH$_3$. The $^{13}$C NMR spectrum of PMS indicates that it has only single sort of carbon atom and also that it is attached to the Si atom.

### 2.2.2.2. Thermolysis of polysilane

The polysilane was heated upto 400°C in a muffle furnace for 4h. The polysilane has undergone Kumada rearrangement and gave crosslinked polycarbosilane.

The polycarbosilane was characterised with TG-DTA, X-ray Diffraction analysis, Surface area analysis, FT-IR spectroscopy, $^{13}$C NMR spectroscopy and $^{29}$Si NMR spectroscopy.

![Scheme 2: Preparation of PCS 1](image)

The FT-IR spectrum of PCS 1 has the corresponding peaks of the polycarbosilane. Peaks at 1441, 1253, 772 cm$^{-1}$ are clearly seen in the spectrum which corresponds to the CHSiCH$_3$ and SiC. The spectrum shows peaks at 2948 and 2899 cm$^{-1}$ which corresponds to the C-H stretching and 1038 cm$^{-1}$ is due to CH$_2$ wagging in Si-CH$_2$-Si bond.
Figure 4: $^{29}$Si NMR spectrum of PCS 1

$^{29}$Si CP-MAS NMR spectrum of the PCS 1 is shown in figure 4. Spectrum gives a clear idea about the structure of the polycarbosilane. The spectrum shows a single peak. Peak around -15ppm corresponds to CH$_3$Si(CH$_2$)$_2$ linkage. The broad signal centered at -15.9 ppm is attributed to the overlapped signals of (CH$_2$)$_2$Si(CH$_2$)$_2$ units also which have a resonance around -5.1 ppm.

Figure 5: $^{13}$C NMR spectrum of PCS 1
The $^{13}$C NMR spectrum of PCS 1 shows a broad single peak around 1.70 ppm. The peak around -2.93 ppm of PMS has been shifted to 1.70 which points towards the conversion of polysilane to polycarbosilane. The peak indicates the resonance of carbon atom in Si-CH$_2$-Si linkage and the absence of carbon atom attached to Si-Si bond.

2.2.3. Preparation of polycarbosilane from trichloromethylsilane and chlorodimethylvinylsilane (PCS 2)

Polycarbosilane was prepared by the sodium metal mediated copolymerization of chlorodimethylvinylsilane with trichloromethylsilane in a ratio of 1:1. The reactions were done in toluene, as solvent and nitrogen atmosphere. The solid polycarbosilane, which was not soluble in any solvents, was characterised by TG-DTA, XRD analysis, FT-IR spectroscopy, $^{13}$C NMR spectroscopy and $^{29}$Si NMR spectroscopy.

![Scheme 3: Preparation of PCS 2](image)

A pale yellow liquid oligomer of molecular weight $M_n = 544$, $M_w = 865$ from GPC using polystyrene as standard and a white solid polymer was obtained. The liquid fraction was discarded.

The FT-IR spectrum of PCS 2 has the corresponding peaks of the polycarbosilane. Peaks at 1514, 1231, 800 cm$^{-1}$ are clearly seen in the spectrum which correspond to the CHSiCH$_3$ and SiC. The spectrum shows a peak at 2828 cm$^{-1}$ which corresponds to the C-H stretching, peak at 1514 cm$^{-1}$ which is due to Si-CH$_3$ stretching, 1231 cm$^{-1}$ corresponding to Si-CH$_3$ deformation, 1038 cm$^{-1}$ due to CH$_2$ wagging in Si-CH$_2$-Si bond and 800 cm$^{-1}$ due to Si-CH$_3$ wagging.
The peaks assigned to Si-O-Si bonds (around 1040 cm$^{-1}$) are observed in all polymers, since this peak intensified with prolonged air exposure, polymers may have oxidised during the handling and recording processes.

![Figure 6: $^{29}$Si CP-MAS NMR spectrum of PCS 2](image)

$^{29}$Si CP-MAS NMR spectrum of PCS 2 is given in figure 6. Peak around 19.47 ppm corresponds to Si-O-Si linkage, which might have resulted due to the oxidation of the pendant group. A peak at -9.79 ppm which corresponds to (CH$_3$)$_2$Si(CH$_2$)$_2$ may be observed due to the side chain polymerization, peaks around -28.34 ppm corresponds to (CH$_2$)$_3$Si and -56.793 ppm is because of the resonance of Si-Si which might be formed by the head to head polymerization of the monomers.
Figure 7: $^{13}$C NMR spectrum of PCS 2

The solid state $^{13}$C NMR spectrum of PCS2 (shown in figure 7) exhibits only one resonance signal centered at -2.59 ppm, which is a broad signal ranging from +10 ppm to -10 ppm. There is no signal in the vicinity of 120 ppm, which is a sign of the absence of unreacted vinyl group. The signal centered at -2.59 ppm is attributed to the overlapped signals of SiSiCH$_3$ units and Si-CH$_2$ units, which have the resonance signal around -4.3 ppm and 10.0 ppm respectively.
2.2.4. Preparation of polycarbosilane from trichloromethylsilane and diethoxymethylvinylsilane (PCS 3)

Polycarbosilane was prepared by the sodium metal mediated copolymerization of diethoxymethylvinylsilane with trichloromethylsilane in a proportion of 1:1. The monomer to sodium metal ratio was maintained as 1:1. The reactions were done in toluene, as solvent under nitrogen atmosphere.

\[
\begin{align*}
\text{Cl} & \quad \text{Si} & \quad \text{Cl} \\
\text{Cl} & \quad + & \quad \text{H}_2\text{C} & \quad = & \quad \text{C} & \quad \text{Si} & \quad \text{OEt} & \quad \text{Si} & \quad \text{OEt} \\
\text{Na/Toluene} & \quad & \quad \text{Si} & \quad \text{H}_2 & \quad \text{C} & \quad \text{SiMe} & \quad & \quad \\
\end{align*}
\]

**Scheme 4:** Preparation of PCS 3

The product was obtained as two fractions, one as a viscous liquid with brown colour which was soluble in toluene and a white solid which was insoluble in all solvents. The molecular weight was determined for liquid fraction by GPC technique using polystyrene as standard and toluene as solvent. The liquid oligomer had a molecular weight \(M_n = 650, M_w = 854\) from GPC.

The insoluble polycarbosilane was analysed with TG-DTA, XRD analysis, FT-IR spectroscopy, \(^{13}\text{C}\) NMR spectroscopy and \(^{29}\text{Si}\) NMR spectroscopy.

Infrared spectrum of PCS 3 exhibited peaks at 2967 cm\(^{-1}\) corresponding to C-H stretching in Si-CH\(_3\), 1642 and 1414 cm\(^{-1}\) due to C-H stretching or CH\(_2\) deformation in Si-CH\(_3\), 1258 cm\(^{-1}\) to Si-CH\(_3\) deformation, 1076 cm\(^{-1}\) to CH\(_2\) wagging in Si-CH\(_2\)-Si, 777 cm\(^{-1}\) due to Si-CH\(_3\) wagging and Si-C stretching.

The peaks assigned to Si-O-Si bonds are observed, peak around 1030 cm\(^{-1}\) was observed as superimposed on 1076 cm\(^{-1}\) which was due to the Si-O stretching of Si-OH bond. This peak intensified with prolonged air exposure, polymer might have oxidised during the handling and recording processes.
Figure 8: $^{29}$Si CP-MAS NMR spectrum of PCS 3

$^{29}$Si CP-MAS NMR spectrum of PCS3 is shown in Figure 8. Chemical shifts are based on tetramethylsilane as internal standard. In the spectrum, the peak around 17.11 ppm was assigned to be due to the resonance of Si-O-Si unit, which would have resulted by the oxidation of the polymer, peak at -12.15 ppm was due to the resonance of Si in the (CH$_3$)$_2$Si(CH$_2$)$_2$ linkage, peak around -26.79 ppm corresponded to (CH$_2$)$_2$Si Si unit, peak around -57.39 ppm corresponded to the Si-Si linkage which was formed by the consequence of head to head polymerization.
Figure 9: $^{13}$C NMR spectrum of PCS 3

Figure 9 presents the solid state $^{13}$C-NMR spectrum of PCS 3. It exhibits two major broad peaks around 6.92 ppm and -2.71 ppm, which are mainly assigned to the signal of SiSiCH$_3$ units and Si-CH$_2$ respectively. The absence of signal around 60 ppm indicates the absence of unreacted alkoxy group in the prepared polymer.

2.2.5. Preparation of polycarbosilane from trichloromethylsilane and trimethoxyvinylsilane (PCS 4)

Polycarbosilane was prepared by the sodium metal mediated copolymerization of trimethoxyvinylsilane with trichloromethylsilane in a ratio of 1:1. The monomer to sodium metal ratio was retained as 1:1. The reactions were done in toluene, as solvent and under nitrogen atmosphere.
Synthesis and Characterization of Polycarbosilane

Scheme 5: Preparation of PCS 4

The product was obtained as two fractions, one as a viscous liquid which was soluble in toluene and a white solid which was insoluble in all solvents. The molecular weight was determined for the liquid fraction by GPC technique using polystyrene as standard and toluene as solvent. The liquid oligomer have a molecular weight Mn = 596, Mw = 992 from GPC. The liquid fraction was discarded.

The insoluble polycarbosilane was analysed with TG-DTA, XRD pattern, FT-IR spectroscopy, $^{13}$C NMR spectroscopy and $^{29}$Si NMR spectroscopy.

The FT-IR spectrum of the polymer has the corresponding peaks of the polycarbosilane. Peak at 1453, 1270, 1082, 783 cm$^{-1}$ are clearly seen in the spectrum which corresponded to the CHSiCH$_3$ and SiC. The spectrum showed a peak at 2929 cm$^{-1}$ which was corresponding to the C-H stretching, 1635, 1453 cm$^{-1}$ due to Si-CH$_3$ stretching, 1270 cm$^{-1}$ corresponding to Si-CH$_3$ deformation, 1082 cm$^{-1}$ due to CH$_2$ wagging in Si-CH$_2$-Si bond and 783 cm$^{-1}$ due to Si-CH$_3$ wagging.

1032 cm$^{-1}$ seen as superimposed on 1082 cm$^{-1}$ was due to the Si-O stretching of Si-OH bond. The peaks assigned to Si-O-Si bonds (around 1032
cm$^{-1}$) are observed, which intensified with prolonged air exposure, polymers might have oxidised during the handling and measuring processes.

Figure 10: $^{29}$Si CP-MAS NMR spectrum of PCS 4

$^{29}$Si CP-MAS NMR spectrum of the PCS 4 is presented in figure 10. Spectrum gives a clear idea about the structure of the polycarbosilane. Peaks are mainly distributed in two regions. Peak around -10.45ppm corresponds to CH$_3$Si(CH$_2$)$_2$ linkage and -48.77 ppm peak is of Si-Si linkage; formed by the head to head polymerization of the monomers. A small peak at 18.79ppm corresponds to Si-O-Si linkage which might be formed by the oxidation of the polymer.
Figure 11: $^{13}$C NMR spectrum of PCS 4

Figure 11 presents the solid state $^{13}$C-NMR spectrum of PCS 4. It exhibits two major broad peaks around 6 and 20 ppm, which are mainly assigned to the signal of SiSiCH$_3$ units and CH$_2$-CH$_2$ respectively. The absence of signal around 60 ppm indicates the absence of unreacted alkoxy group in the prepared polymer.

2.2.6. Preparation of polycarbosilane from Diethoxymethylvinylsilane (PCS 5)

Polycarbosilane was prepared by the sodium metal mediated homopolymerization of diethoxymethylvinylsilane. The monomer to sodium metal ratio was maintained as 1:1. The reaction was done in toluene, as solvent and under nitrogen atmosphere.
The product was obtained as two fractions, one as a viscous liquid which was soluble in toluene and a white solid which was insoluble in all solvents. The molecular weight was determined for liquid fraction by GPC technique using polystyrene as standard and toluene as solvent. The liquid oligomer had a molecular weight $M_n = 690$, $M_w = 872$ as obtained from GPC.

The insoluble solid polymer was used for further studies. It was analysed with TG-DTA, XRD analysis, FT-IR, $^{13}$C NMR and $^{29}$Si NMR spectroscopy.

Infrared spectrum of PCS 5 has the peaks at 2961 cm$^{-1}$ corresponding to C-H stretching in Si-CH$_3$, 1647 and 1407 cm$^{-1}$ due to C-H stretching or CH$_2$ deformation in Si-CH$_3$, 1264 cm$^{-1}$ due to Si-CH$_3$ deformation, 1095 cm$^{-1}$ due to CH$_2$ wagging in Si-CH$_2$-Si, 790 cm$^{-1}$ due to Si-CH$_3$ wagging and Si-C stretching.

The peak at 1031 cm$^{-1}$ was seen as superimposed on 1095 cm$^{-1}$ which was the peak assigned to Si-O-Si bond (around 1031 cm$^{-1}$) observed in the polymer, since this peak intensified with continuous air exposure; polymers might have oxidised during the handling and recording processes.
Figure 12: $^{29}$Si CP-MAS NMR spectrum of PCS 5

$^{29}$Si CP-MAS NMR spectrum of the PCS 5 is shown in figure 12. Peak around -10.15 ppm corresponds to CH$_3$Si(CH$_2$)$_2$ linkage and -25.67 ppm peak is due to the CH$_2$SiCH$_2$ group, a peak around -57.16 ppm which is an evidence for Si-Si linkage; formed by the head to head polymerization of the monomers.

Figure 13: $^{13}$C NMR spectra of PCS 5
The solid state $^{13}$C NMR spectrum of PCS 5 (shown in figure 13) exhibits only one resonance signal centered at 20 ppm, which is a broad signal ranging from 10 ppm to 30 ppm. This is mainly assigned to the signal of CH$_2$-CH$_2$ unit. There is no signal around 120 ppm and 60 ppm, which indicate the absence of unreacted vinyl groups and alkoxy groups in the prepared polymer.

2.2.7. Halide Estimation

The quantitative chlorine estimation of the polycarbosilanes was done by modified Volhard’s method$^{27}$. The chlorine estimation was done for all the synthesized polycarbosilanes except PCS 5. All other polycarbosilanes gave expected results for the estimation and the results are listed in table 1.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PCS 1</th>
<th>PCS 2</th>
<th>PCS 3</th>
<th>PCS 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine (mmol/g)</td>
<td>3.9</td>
<td>5.1</td>
<td>4.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>

2.2.8. Thermal properties of polycarbosilanes

In order to investigate the thermal behaviour of the polycarbosilanes; the TG-DTA analysis was done. The polycarbosilanes were subjected to temperature scan from 50 to 1000°C in N$_2$ atmosphere at a rate of 20°C/min. The result is illustrated in figure 14.

![Thermogravimetric analysis of polycarbosilanes](image)

**Figure 14:** Thermogravimetric analysis of polycarbosilanes
In the TGA curve, 3% weight loss below 300°C is attributed to the vaporization of low molecular weight oligomers. From 300-800°C the weight loss is due to the release of gaseous products such as methane and hydrogen during the conversion of the Si-Si bond to Si-C bond. No obvious weight loss was observed in the range of 800-1000°C. High temperature stability is attributed to substantial cross-linking in PCS.

The TGA residues of the polycarbosilanes are given in table 2.

**Table 2: TGA residue of the polymers**

<table>
<thead>
<tr>
<th>Entry</th>
<th>TGA residue at 1000°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCS 1</td>
<td>89</td>
</tr>
<tr>
<td>PCS 2</td>
<td>68</td>
</tr>
<tr>
<td>PCS 3</td>
<td>54</td>
</tr>
<tr>
<td>PCS 4</td>
<td>86</td>
</tr>
<tr>
<td>PCS 5</td>
<td>38</td>
</tr>
</tbody>
</table>

From the TGA curves it is clear that out of the five polycarbosilanes, PCS 1 and PCS 4 have highly cross-linked structure. PCS 1, polycarbosilane prepared by the thermolysis of polysilane gave high char yield. It has low volatile substituents because it had under gone thermolysis prior to analysis. During thermolysis the low volatile fractions might have undergone evaporation and hence high char yield. Polycarbosilane prepared by the homopolymerization of diethoxymethylvinylsilane (PCS 5) have low char yield. This may be because of the less cross-linked nature of the polymer. Other polymers PCS2 and PCS3 gave average char yield.
2.2.9. X-Ray diffraction analysis

X-ray diffraction analysis of all the polycarbosilanes was performed. The sample was scanned over the range of 20°-90° angles with an increment of 0.05° angle and with the rotation speed of 5°/min.

![X-Ray Diffraction Pattern](image)

**Figure 15:** X-Ray Diffraction pattern of the polycarbosilanes

The XRD pattern of the polycarbosilanes clearly reveals their amorphous nature; which can be explained due to the cross-linked structure of the polymers.

2.2.10. Surface Area Analysis

Nitrogen gas adsorption methods are commonly employed to determine surface area and pore size distribution of solids. The polycarbosilanes are subjected to surface area analysis by BET surface area analyzer. Results are tabulated (table 3).
Table 3: Results of BET surface area analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET</td>
<td>Langmuir</td>
</tr>
<tr>
<td>PCS 1</td>
<td>333.3</td>
<td>506.2</td>
</tr>
<tr>
<td>PCS 2</td>
<td>229.4</td>
<td>458.5</td>
</tr>
<tr>
<td>PCS 3</td>
<td>203.6</td>
<td>397.8</td>
</tr>
<tr>
<td>PCS 4</td>
<td>679.3</td>
<td>1171.2</td>
</tr>
<tr>
<td>PCS 5</td>
<td>154.2</td>
<td>275.2</td>
</tr>
</tbody>
</table>

The high surface area of PCS 4 is attributed to its high cross-linked structure. And PCS 4 has mesoporous nature also. The thermogravimetric analysis results are in good agreement with these results. From the surface area results it is clear that the homopolymer prepared from diethoxymethylvinylsilane has low surface area which can be explained because of its less cross-linked nature.

2.3. Conclusion

Preparation of five polycarbosilanes was done successfully. Halogen estimation was done by Volhard’s method. The polycarbosilanes were characterised using various analytical techniques such as UV-Vis DRS, TG-DTA, X-ray diffraction analysis, FT-IR spectroscopy, $^{13}$C NMR spectroscopy, $^{29}$Si NMR spectroscopy and surface area analysis. From the results of analytical data the structure of polycarbosilanes was deducted. All the polycarbosilanes are of highly cross-linked structure and amorphous in nature. All of them possess high temperature stability and high surface area. The polycarbosilanes, except PCS 5, are capable of further functionalization. The functionalization of polycarbosilanes can be used to make use of the polycarbosilanes in a variety of applications.
2.4. Experimental

2.4.1. Preaparation of polycarbosilane

2.4.1.1. Preparation of polycarbosilane 1 (PCS 1)

2.4.1.1.1. Preparation of polymethyl silane

Trichloromethylsilane was used as the monomer. Sodium metal (1.2g, 54.375mmol) in anhydrous toluene (50mL) was refluxed and stirred vigorously to make a dispersion. Trichloromethylsilane (6.4mL, 54.375mmol) was added drop wise. The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 12h. It was cooled and the suspension obtained was filtered, washed with methanol and dried. The whole process was carried out under Nitrogen atmosphere. Yield: 47%.

2.4.1.1.2. Thermolysis of polymethylsilane to polycarbosilane

The polysilane obtained by the Wurtz coupling of trichloromethylsilane was taken in a silica crucible and was heated upto 400°C in a muffle furnace for 4h. A colourless powder was obtained. The polysilane has undergone Kumada rearrangement and gave cross-linked polycarbosilane.

2.4.1.2. Preparation of PCS 2

In a 250mL round bottom flask, the Sodium metal (2.5g, 108.75mmol) in anhydrous toluene (50mL) was refluxed and stirred vigorously to make dispersion. A mixture of trichloromethylsilane (6.4mL, 54.375mmol) and chlorodimethylvinylsilane (7.4mL, 54.375mmol) was added drop wise. The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 12h. It was cooled and the obtained suspension was filtered, washed with methanol and dried. The whole process was carried out under Nitrogen atmosphere. Yield: 48 %.
2.4.1.3. Preparation of PCS 3

In a 250mL round bottom flask, the Sodium metal (2.5g, 108.75mmol) in anhydrous toluene (50mL) was refluxed and stirred vigorously to make dispersion. A mixture of trichloromethylsilane (6.4mL, 54.375mmol) and diethoxymethylvinylsilane (10.24 mL, 54.375mmol) was added drop wise. The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 12h. It was cooled and the obtained suspension was filtered, washed with methanol and dried. The whole process was carried out under Nitrogen atmosphere. Yield: 14g (47%).

2.4.1.4. Preparation of PCS 4

In a 250mL round bottom flask, the Sodium metal (2.5g, 108.75mmol) in anhydrous toluene (50mL) was refluxed and stirred vigorously to make dispersion. A mixture of trichloromethylsilane (6.4mL, 54.375mmol) and trimethoxyvinylsilane (8.13mL, 54.375mmol) was added drop wise. The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 12h. It was cooled and the obtained suspension was filtered, washed with methanol and dried. The whole process was carried out under Nitrogen atmosphere. Yield: 50 %.

2.4.1.5. Preparation of PCS 5

In a 250mL round bottom flask, the Sodium metal (1.2g, 54.375mmol) in anhydrous toluene (50mL) was refluxed and stirred vigorously to make dispersion. Diethoxymethylvinylsilane (10.24 mL, 54.375mmol) was added drop wise. The reaction was highly exothermic. After the addition of monomer, the reaction mixture was refluxed for 12h. It was cooled and the obtained suspension was filtered, washed with methanol and dried. The whole process was carried out under Nitrogen atmosphere. Yield: 60 %.
2.4.4. Estimation of chlorine capacity of the polymers

Chlorine analysis was done by the modified Volhard’s method. The polycarbosilane (250mg) was heated with pyridine (2.5mL) for 1 h at 100°C, and the suspension was diluted with acetic acid: water (1:1) (25mL). The halide was displaced by the addition of Con.HNO₃ (5mL) and precipitated with a measured excess of standard AgNO₃ solution. AgCl that was formed was coated with toluene, and the excess AgNO₃ was back titrated with standard NH₄SCN solution, using ferric alum [FeNH₄(SO₄).12H₂O] as indicator. A red colour due to the formation of Fe(SCN)₃, indicates that an excess of SCN⁻ is present and that the end-point has been reached.

2.5. References


