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# Electropolymerization of Polysilanes with Functional Groups

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## 1. Introduction

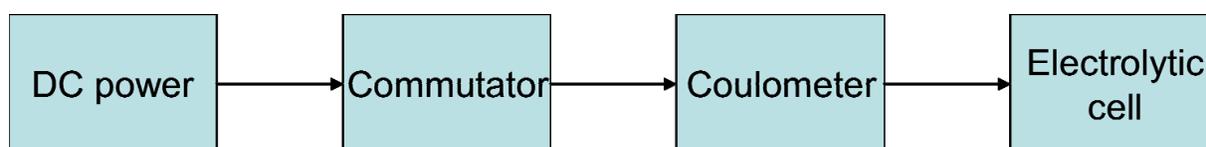
Polysilane (PS) is a kind of polymers with backbone consisting of only silicon atoms. It arouses great attention for its special electronic and optical properties<sup>1</sup>, as well as SiC ceramic precursor<sup>2</sup>. The main method to synthesize polysilane is Wurth coupling reaction which rules out the production of many polysilanes with functional groups for the harsh reaction conditions<sup>3</sup>. Among the various methods for the synthesis of polysilanes<sup>4</sup>, the electrosynthesis technique is gaining importance for its mild and safe condition and aptness of making functional molecules<sup>5</sup>. Shono<sup>6</sup> studied the effects of electrode materials, monomer concentration, amount of supplied electricity, and ultrasonic on the synthesis of polysilanes and related polymers. The concerned monomers bear inert side groups, such as methyl, ethyl, butyl, phenyl. The first attempt of attaching reactive vinyl groups to polysilane by electrosynthesis failed<sup>7</sup>. Our purpose to get high ceramic yield SiC precursor has prompted us searching for ways to introduce cross-linkable groups into polysilane molecules. Using allyl chloride and methyltrichlorosilane (MeSiCl<sub>3</sub>) as monomers, we managed to synthesize polysilane with double bonds<sup>8</sup>, an excellent SiC precursor<sup>9</sup>. To increase the anti-oxidative ablation property of SiC, one way is to adulterate refractory metals M, such as Ti, Zr, Hf, et al., into SiC ceramic<sup>10</sup>. Coordination of M into polysilane molecule needs ligands. Cyclopentadiene (Cp), which is served as ligand for transitional metals, was attached on PS chains, thus zirconium atom was chemically combined with polysilane chain. And a new route to make composite ceramic MC-SiC was invented.

## 2. Electropolymerization of polysilanes

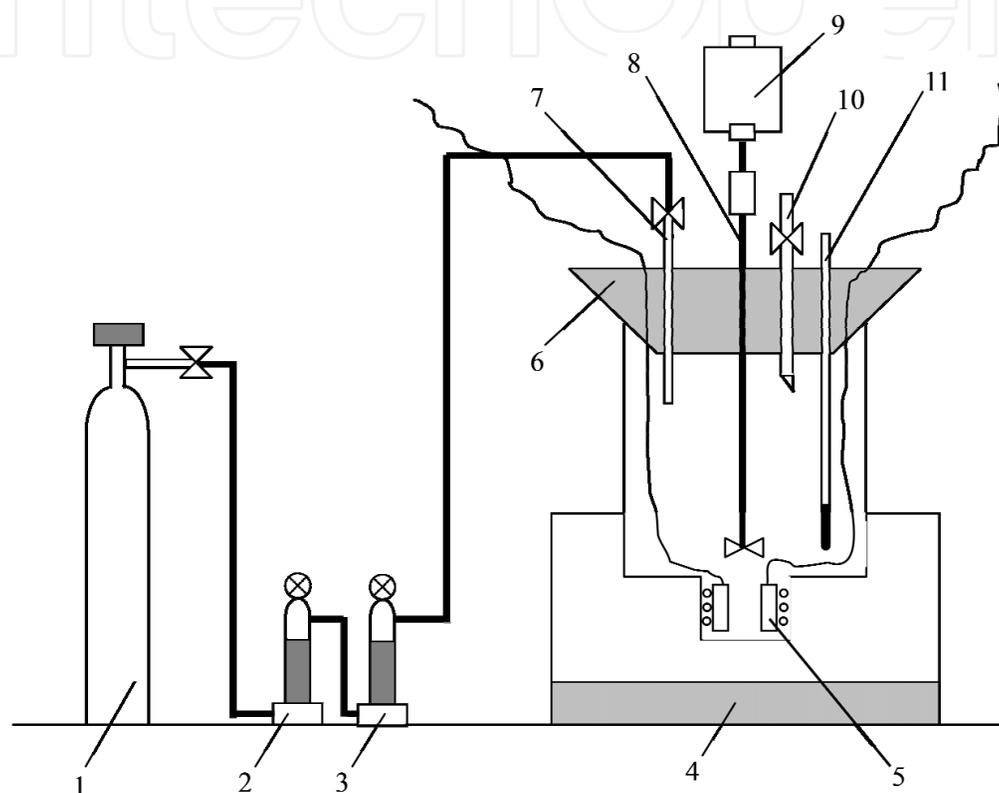
### 2.1 The setup of electrosynthesis

To take advantage of electrosynthesis, many efforts are needed to design the electrolytic apparatus. The paper<sup>6</sup> briefly introduces the setup of electropolymerization. Here we present the details of the apparatus.

The setup consists of four parts (Scheme1). The DC power can operate under two modes: the constant current mode and the constant voltage mode. We usually choose the constant current mode. The commutator can change the polarity of the electrodes in the range of 5 ~ 60 seconds. The supplied electricity is counted by a coulometer. When a predetermined electric volume is reached, it will cut off the electric supply to the electrolytic cell. A detailed description of the cell is plotted in Scheme 2.



Scheme 1. The structure of the setup



Scheme 2. The scheme of the electrolytic cell 1. N<sub>2</sub> bottle (99.99%) 2.drying tower (molecular sieve) 3.drying tower (CaCl<sub>2</sub>) 4.ultrasonic 5.electrode 6. rubber plug 7. N<sub>2</sub> inlet 8.stirrer 9.motor 10.feeding hole 11.thermometer

The rectangle electrodes are 40mm long, 30mm wide and 10mm thick. It is rubbed with emery cloth before use. The space between the two poles is fixed by inserting two hollow polyethylene tubes ( $\Phi$ 4mm), and the electrodes and the tubes are binded together with nylon wire. The power of the ultrasonic (20 kHz) is 100W.

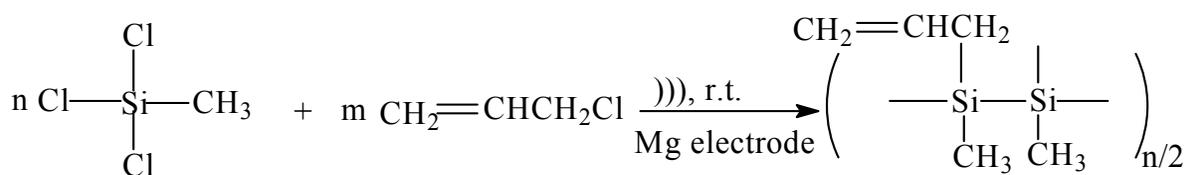
## 2.2 Electropolymerization of polysilanes with double bonds

The introduction of double bonds will increase the ceramic yield, shorten the production period of the C/C-SiC composites, and diminish the mechanical damage to the composites. We will discuss in detail the influential factors in the reaction and characterize the reaction product.

### 2.2.1 Electropolymerization and isolation

The MeSiCl<sub>3</sub> and allyl chloride were put in a compartment cell equipped with Mg cathodes, mechanic stirrer and thermograph. Then THF and LiClO<sub>4</sub> (0.05M) were added. All reactions were carried out under dry nitrogen atmosphere in order to eliminate the oxygen. Constant current electrolysis was applied at room temperature. During the electroreduction the electrolysis cell was sonicated and the polarity of electrodes was periodically alternated. The supplied amount of electricity was counted by a coulometer. Electrolysis was terminated at the desired amount of electricity. Then a quantity of toluene was poured in the cell and adequate gaseous ammonia was introduced to react with the residual Si-Cl. The solution was filtrated to remove MgCl<sub>2</sub> precipitate, and then was vacuum distilled to remove THF in the solvent. Subsequently, the residue was filtrated again to remove insoluble material. Finally, toluene was evaporated at reduced pressure, in each case to yield the light yellow liquid, polysilane with double bonds (EPS1).

The reaction scheme is shown as follows:



Scheme 3. Electrosynthesis of polysilane with double bonds

Polysilane without double bonds (EPS2) was synthesized in the same way using only MeSiCl<sub>3</sub> as monomer for comparison.

The products were identified using GPC (Agilent1100 American) with THF as solvent, <sup>1</sup>H NMR (AV-500), XRD (D/Max-rc Japan) and FTIR (Thermo Nicolet-AVRTAR370FT-IR). FTIR spectra were measured using KBr method.

The double bond content was determined by bromine addition method<sup>11</sup>.

The measurement of monomer reaction rate is as follows:

Half an hour later after the monomers are plunged into the reaction bottle, the electrodes are charged. A small amount of sample is drawn out at intervals. It is hydrolyzed, and then titrated with sodium hydroxide solution. Therefore, the content of Si-Cl bonds in the bottle is determined. By following the variation of the Si-Cl bonds, we can analyze the reaction rate of the electropolymerization.

### 2.2.2 Influential factors of electrosynthesis

In the following episodes, the various factors influencing the reaction will be discussed in detail.

#### 2.2.2.1 Effect of molar ratios of monomers

The influence of the MeSiCl<sub>3</sub>/allyl chloride ratio on the yield, remaining double bonds, and Mw of polysilanes is shown in Table 1.

The optimum molar ratio of MeSiCl<sub>3</sub>/H<sub>2</sub>C=CHCH<sub>2</sub>Cl was 3/1 where the highest yield, double bonds concentration and molecular weight were reached. The relatively low yield and molecular weight at ratio of 10/1 and 5/1, where allyl chloride was deficient, might be due to the intramolecular reaction of MeSiCl<sub>3</sub>. This reaction led to highly cross-linked structure, which was insoluble in solvent. Only the low molecular weight fraction was

soluble and obtainable as product. As the molar ratio surpassed 3/1, the excessive allyl chloride, acting as end capping agent, blocked the propagation of polysilane chains, resulting in lower molecular weight.

Ratio of (MeSiCl <sub>3</sub> /H <sub>2</sub> C=CHCH <sub>2</sub> Cl)	10/1	5/1	3/1	2/1	3/2
Yield, %	49	51	84	71	79
Retaining ratio of double bonds, %	7.4	9.1	12.6	11.3	8.2
M <sub>w</sub> , Dalton	1625	1974	3749	2293	834
M <sub>w</sub> /M <sub>n</sub>	3.19	3.84	8.26	4.52	1.64

<sup>a</sup> MeSiCl<sub>3</sub> monomer concentration was 1M , 10% theoretical charge was applied, and cathodes were Mg ingots.

Table 1. Effect of molar ratios of monomers<sup>a</sup>

The IR spectra of polysilanes are showed in Fig.1. The polysilane with and without double bonds both have C-H stretching (2960 and 2920cm<sup>-1</sup>) groups, C-H bending (1450 and 1410cm<sup>-1</sup>) groups, Si-CH<sub>3</sub> (1260 and 790cm<sup>-1</sup>), Si-Si (460cm<sup>-1</sup>). These absorptions imply the presence of Si-Si and Si-CH<sub>3</sub> bonds in both polysilanes. The presence of Si-O-Si (1080cm<sup>-1</sup>) linkages was the consequence of the polymers' reactivity toward oxygen during work-up. The absorptions at 1640cm<sup>-1</sup> of C=C stretching groups in the curve (1) indicate the presence of double bonds<sup>12</sup>.

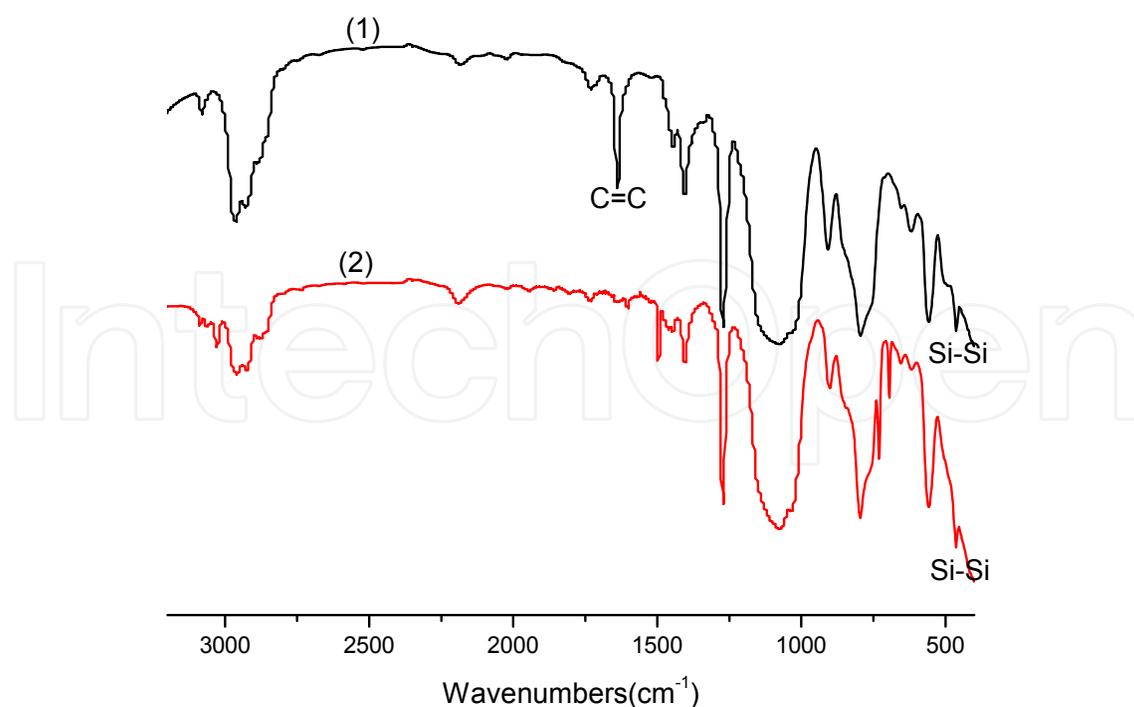


Fig. 1. FT-IR spectra of polysilanes with and without double bonds

1. EPS1: polysilane with double bonds synthesized with the  $\text{MeSiCl}_3/\text{H}_2\text{C}=\text{CHCH}_2\text{Cl}$  ratio of 3:1
  2. EPS2: polysilane without double bonds synthesized with the  $\text{MeSiCl}_3$
- $^1\text{H}$  NMR spectrum of polysilane with double bonds (Fig.2) has four major peaks near  $\delta$  0.09, 0.25, 0.55 and 0.85 ppm, these are chemical shifts of Si- $\text{CH}_3$ . The broad and complication of these peaks are due to the complex structures around the Si- $\text{CH}_3$  groups. The observed peaks near  $\delta$  5.8, 5.1-5.2, and 3.8-3.9 are the characteristic chemical shifts for Si-allyl moiety<sup>13</sup>. This proves the presence of double bonds in polysilane.

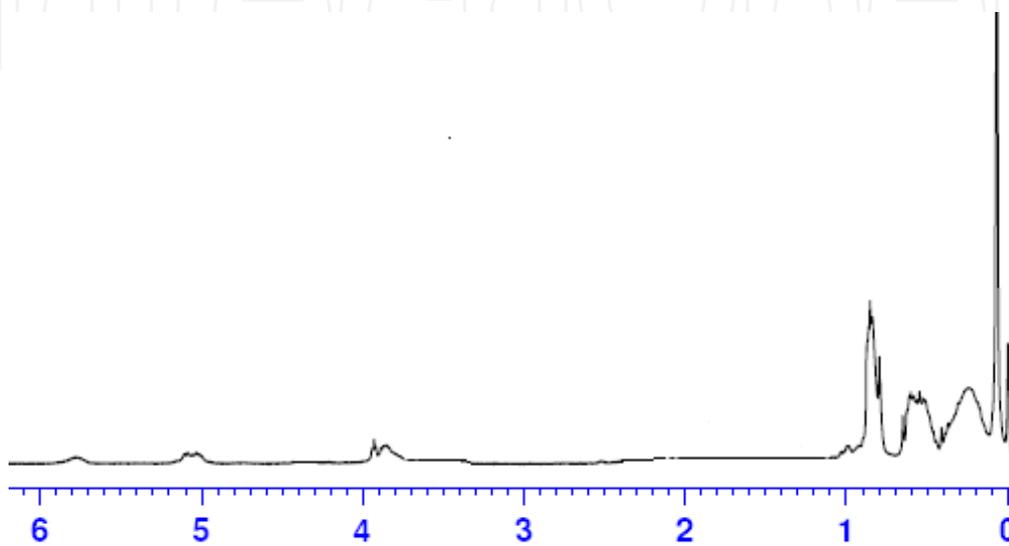


Fig. 2.  $^1\text{H}$  NMR spectrum of polysilane with double bonds

The following experiments were performed on  $\text{MeSiCl}_3$ /Allyl Chloride ratio of 3:1.

#### 2.2.2.2 Effect of monomer concentration

Under different monomer concentrations, the polysilanes were synthesized with 5% theoretical electricity. As shown in Table 2, the yield and molecular weight of the polysilanes became lower with increase of concentration. When the concentration was higher,  $\text{MeSiCl}_3$  was apt to polymerize with itself, forming giant three dimensional networks, which would precipitate from solution.

Monomer concentration	1M	2M	3M
Yield, %	93	72	49
$M_w$ , Dalton	1723	861	474
$M_w/M_n$	4.89	2.29	1.33

Table 2. Effect of monomer concentration

The following experiments were performed at 1M monomer concentration.

#### 2.2.2.3 Effect of electrode materials

The electrode materials have a profound influence on the formation of polysilanes. As Table 3 shows, the entry using Mg anode and cathode gave the highest molecular weight and

yield. Aluminum was less effective than Mg, and Cu the worst. It was said that Mg played some important roles in the formation of the Si-Si bond<sup>6</sup>. Although details of the role of Mg in the mechanism of formation of the Si-Si bond are not clear now, the unique reactivity of Mg electrode is undoubtedly shown in this reaction.

Electrode materials	Mg-Mg	Mg-Al	Al-Al	Mg-Cu
Yield, %	85	78	34	18
$M_w$ , Dalton	3952	1099	898	512
$M_w / M_n$	8.67	3.36	2.12	1.63

<sup>a</sup> The polysilane were synthesized with 10% theoretic electric charge and interval time 17s.

Table 3. Effect of electrode materials <sup>a</sup>

The following experiments were performed with Mg electrodes.

#### 2.2.2.4 Effect of the amount of electricity

The molecular weight was monitored at the different amount of electricity during the reaction process (Fig. 3). The molecular weight went up rapidly before 3% theoretical electricity ( $1440C \cdot mol^{-1}$ ) and entered a linear increasing period afterwards. This suggests that electrochemical synthesis of polysilane is a step-growth polymerization.

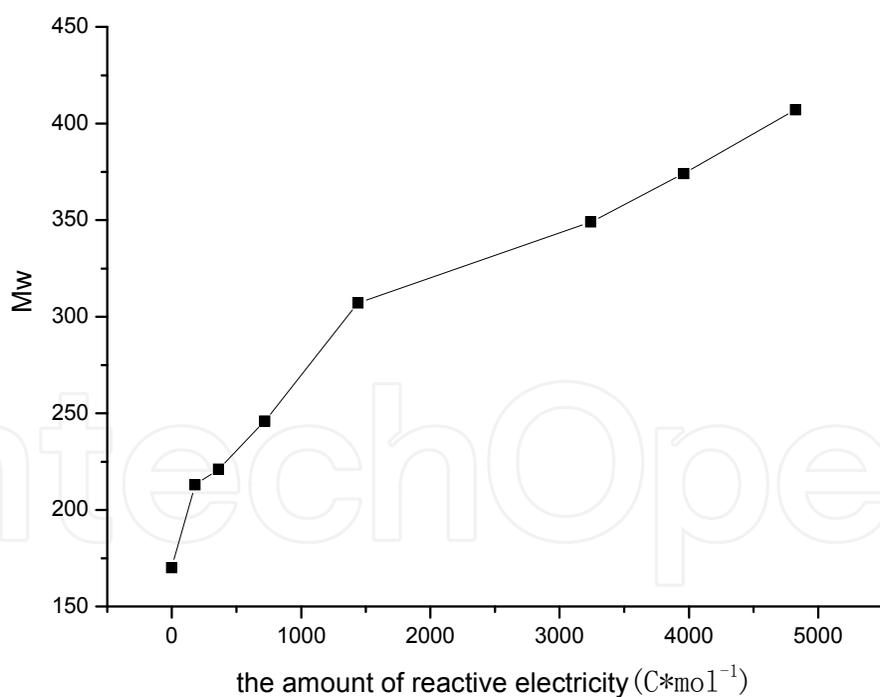


Fig. 3. The change of molecular weight of polysilane with the amount of electricity increasing

The amount of electricity is one of the most important factors to control the formation of Si-Si bond. The polymers, synthesized with different proportion of theoretical electricity, are

listed in Table 4. With increase of the amount of electricity, the molecular weight rose stepwise and the molecular weight distributions became broader. The broader  $M_w / M_n$  might be due to the heterogeneous reaction condition and multiple reaction paths<sup>14</sup>. The results indicate that the polysilanes with different molecular weight can be obtained by controlling the amount of electricity.

The amount of electricity	5% theoretic electricity	7.5% theoretic electricity	10% theoretic electricity
Yield, %	87	92	85
$M_w$ , Dalton	1723	2687	3952
$M_w / M_n$	4.89	6.58	8.67

Table 4. Effect of the amount of electricity

### 2.2.2.5 Effect of interval time

The electroreduction was carried out under ultrasound with different interval times of 8s, 17s and 26s, respectively. As shown in Fig. 4, the molecular weights of the products became higher with decreasing of the interval time. It could be explained that the alternation of anode and cathode might overcome the difficulty of keeping the electric current at a suitable level due to the increase of the voltage between anode and cathode with progress of the reaction<sup>6</sup>. The maximum voltage was relatively lower at shorter interval time. The lower voltage reduced the possibility of side reactions, thus benefiting the propagation of Si-Si bonds.

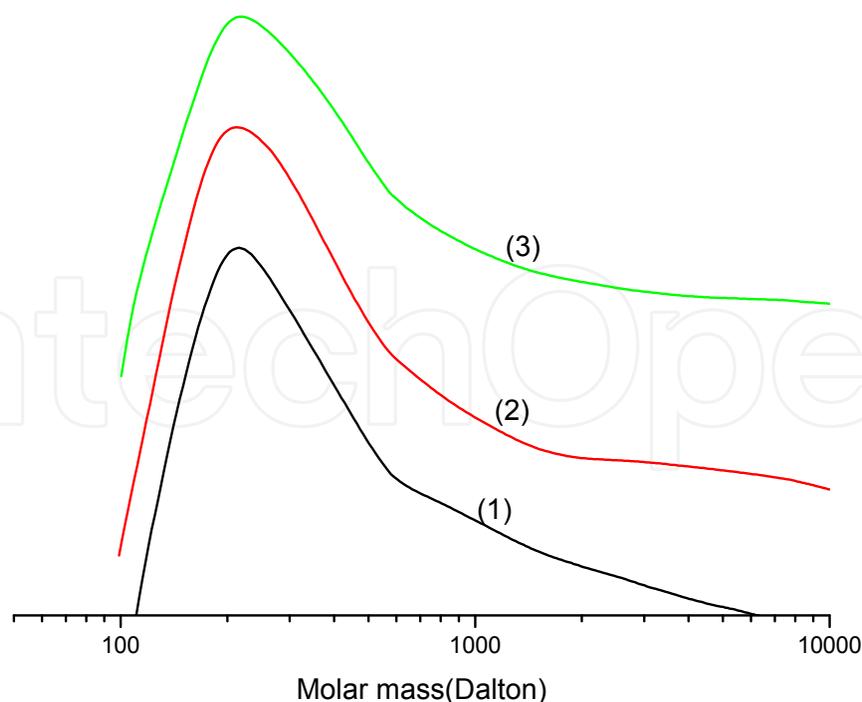


Fig. 4. Effect of interval time on the products' GPC spectra (1)  $\overline{M}_w = 2432$ , interval time 26s; (2)  $\overline{M}_w = 3031$ , interval time 17s; (3)  $\overline{M}_w = 6980$ , interval time 8s;

### 2.2.2.6 Effect of the concentration of supporting electrolyte

The increase in the concentration of supporting electrolyte resulted in the growth of molecular weight and yield (Table 5). Higher concentration of supporting electrolyte brought on lower electrode voltage to maintain constant current, thus reducing side reaction. The 0.05M concentration seemed reasonable because the acquired molecular weight and yield were satisfying, and even higher concentration leads to higher cost as the recovery of costly  $\text{LiClO}_4$  is difficult.

Concentration of supporting electrolyte ( $\text{LiClO}_4$ )	0.05M	0.03M	0.005M
Yield, %	91	81	72
$M_w$ , Dalton	3031	1309	665
$M_w/M_n$	7.89	2.56	1.42

Table 5. Effect of concentration of supporting electrolyte

### 2.2.2.7 The rate of electrosynthesis of polysilane

As shown in Fig.5, the EPS1 with double bonds has similar reaction tendency as the EPS2 without double bonds. About 30% ~ 40% Si-Cl had consumed at 0 mA\*h of electricity because of the Grignard reaction between monomers and Mg in THF. The rate of electrosynthesis was relatively quicker in 0~100 mA\*h range. The reaction finished as the amount of electricity reached 400 mA\*h (30% of the theoretical amount of electricity). The EPS1 with double bonds reacted faster than the EPS2 without double bonds. At the same electricity volume, the Si-Cl content of EPS1 was 10% ~ 15% less than that of EPS2. The reason for this is that the allyl chloride might change into allyl anion by gaining electrons, then the obtained allyl anion initiates the anion polymerization of polysilane, thus increasing the reaction rate.

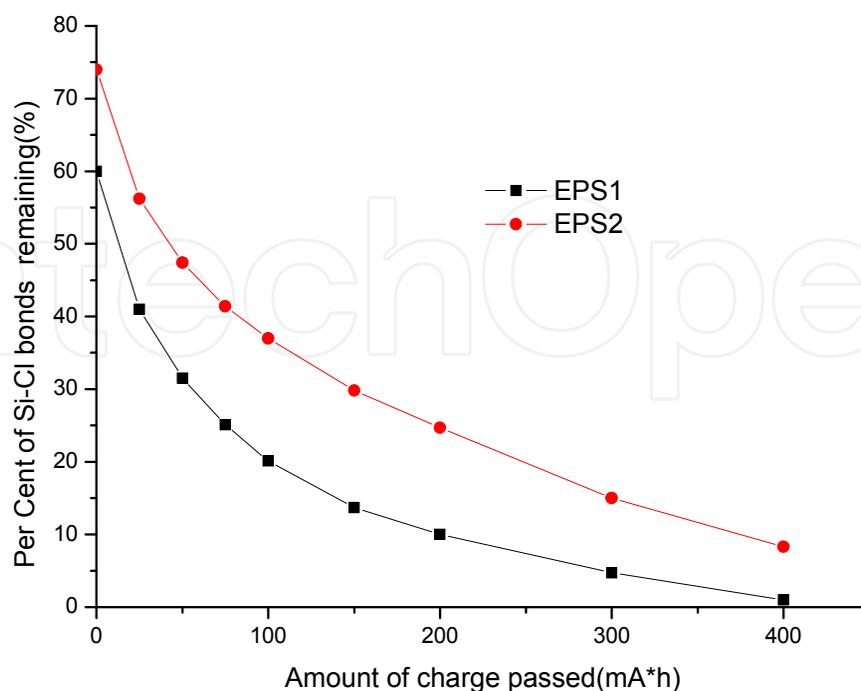


Fig. 5. Reaction Rate of EPS1 and EPS2 by Electroreduction

### 2.2.2.8 Comparison of the rates of electrosynthesis with and without electricity

The result above indicates polymerization can happen without electricity. To evaluate the role of electricity in the synthesis, the synthetic reactions of EPS1 and EPS2 with and without electricity were pursued (Fig. 6). The Si-Cl content in the case of electricity (curve b and d) is 5% ~ 13% less than that without electricity (curve a and c). In the whole electrosynthesis, the Grignard reaction between monomers and Mg ingot is in the majority, its ratio being as high as 80% ~ 90%. This result implies that the amount of charge passed could be much lower than that of the theoretical one to fulfill the electrosynthesis.

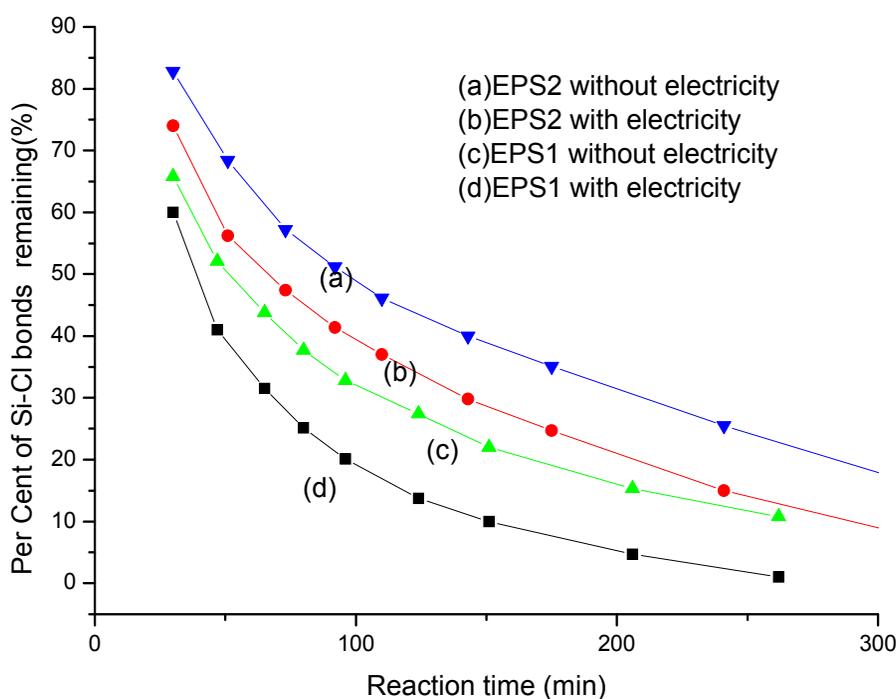


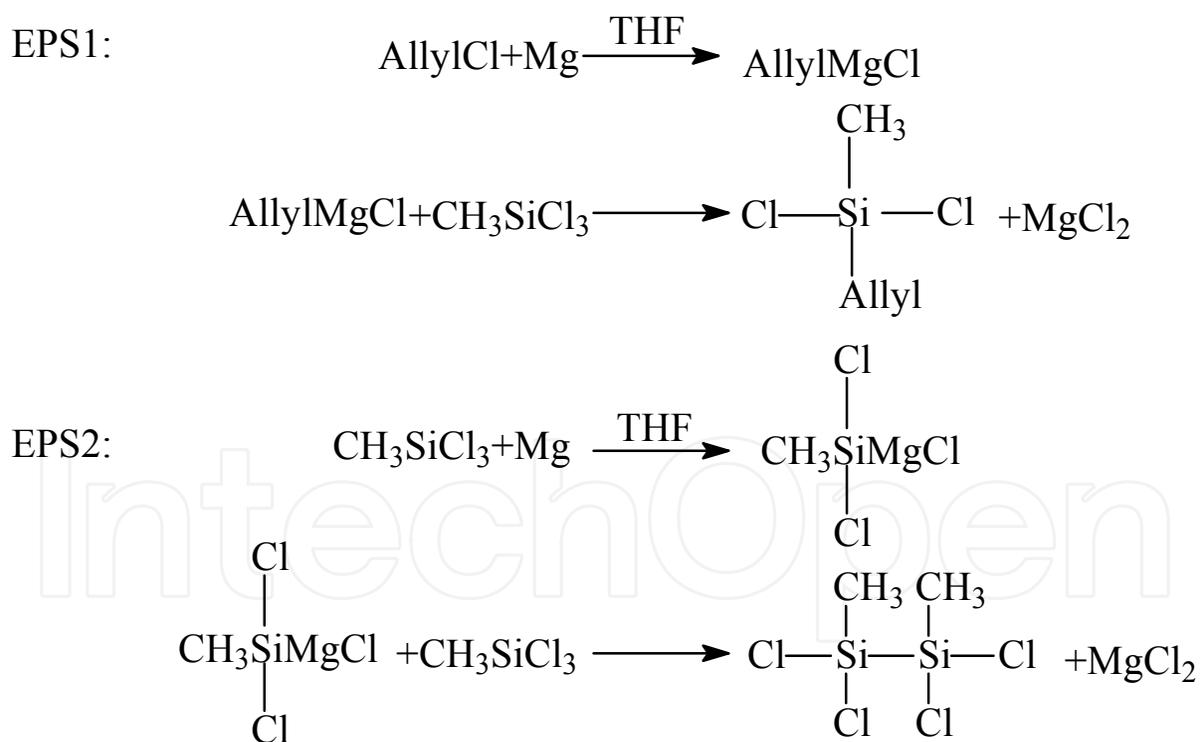
Fig. 6. Reaction rate of EPS1 and EPS2 with and without electricity

### 2.2.3 On the reaction mechanism

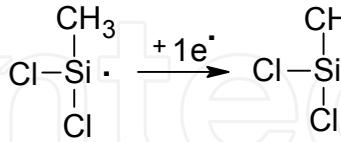
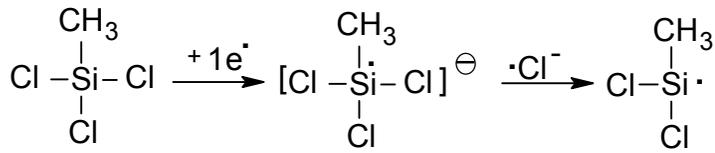
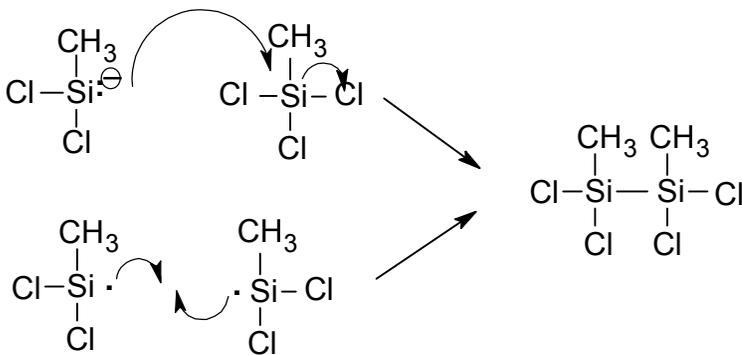
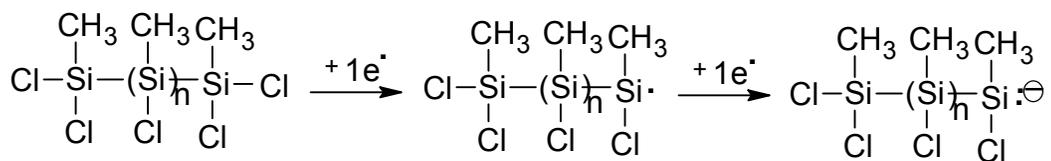
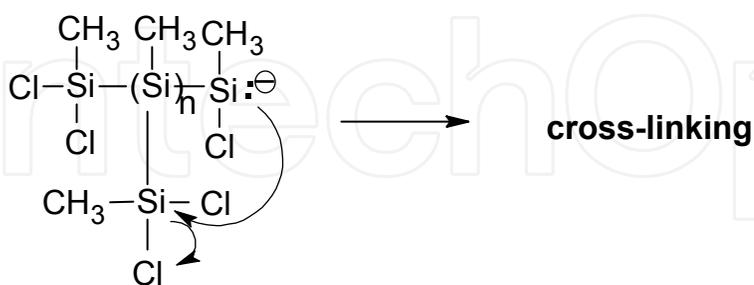
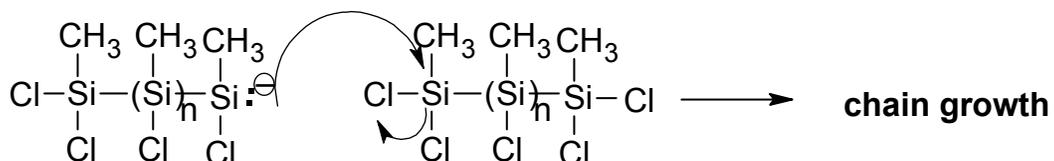
The reaction mechanism for synthesis of polysilane through Wurtz route has been studied in the past few decade<sup>15</sup>. However, the mechanism by electrochemical route is scarcely reported<sup>16</sup>. According to above-mentioned, we speculate the mechanism might be divided into two parts. The first part is the Grignard reaction mechanism (Scheme 4). The monomers can react with Mg to form Grignard reagent, which again react with  $\text{CH}_3\text{SiCl}_3$  to produce a large molecule. The process repeats to form polysilane.

Another part is the electropolymerization mechanism (Scheme 5). The reactions include the electrode reaction and thermal reaction. First, the monomer gains an electron, being reduced to anion. The anion changes to silicon radical by eliminating chlorine anion, which can react

with magnesium ion from sacrificing anode. The formed silicon radical might gain another electron to change into silicon anion intermediate. This intermediate reacts with other monomers by nucleophilic substitution to form oligomers, which can also be reduced to silicon anions. In the process of chain elongation, the delocalization of the electron along the chain makes it easier for the reduction of the oligomer. The thermal process includes the nucleophilic substitution of silicon anion with monomer or oligomer, and the coupling reaction between radicals. The nucleophilic substitution may happen intramolecularly or intermolecularly. The intramolecular one leads to cross-linking, while the intermolecular makes the chain to grow.



Scheme 4. The proposed reaction mechanism for Grignard reaction of  $\text{CH}_3\text{SiCl}_3$

**Electrode Processes 1: Monomer Reactions****Thermal Processes 1: Nucleophilic Substitution****Electrode Processes 2: Oligomer Reactions****Thermal Processes 2****Intramolecular****Intermolecular**Scheme 5. Proposed reaction mechanism for electropolymerization of  $\text{CH}_3\text{SiCl}_3$

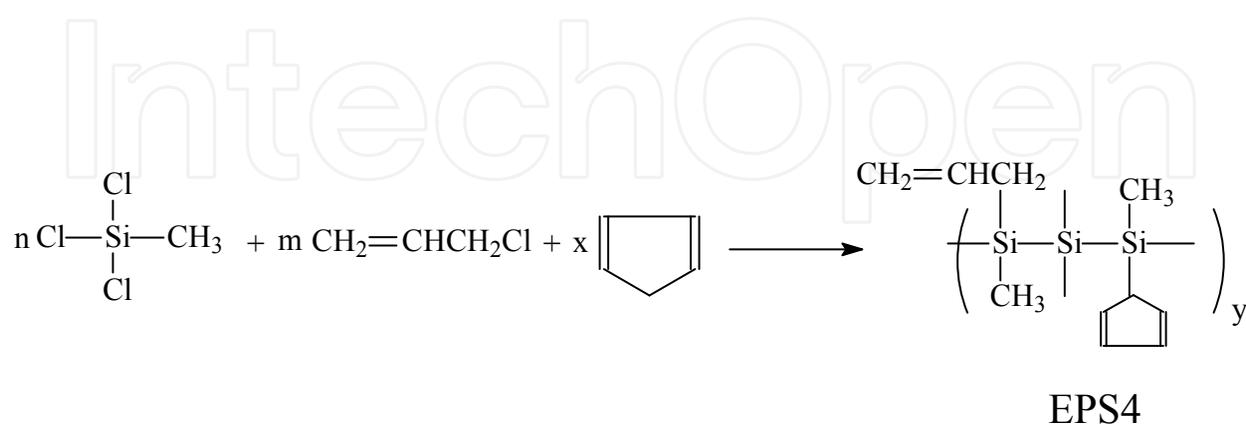
### 2.3 Electropolymerization of polysilanes with refractory metals

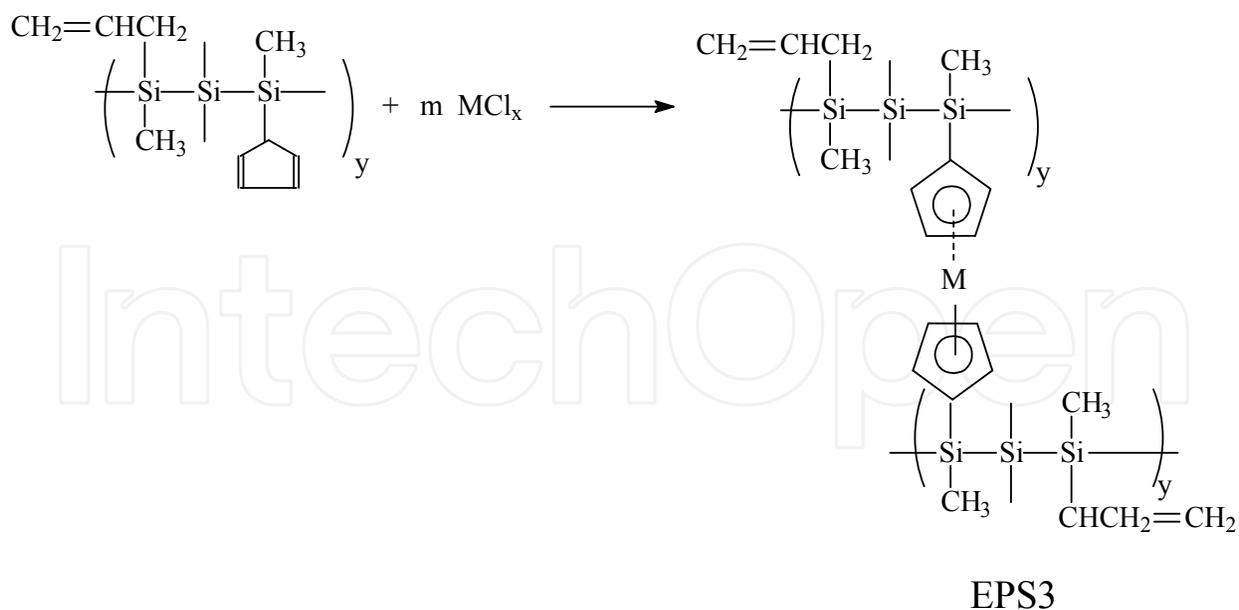
The study of refractory-metals-containing SiC through polymer-derived ceramic (PDC) method is of interest<sup>17</sup>, because the introduction of refractory metals M (such as Ta, Ti, Zr, Hf, Nb, Mo et al.) can enhance the heat-resistance property and the anti-oxidative ablation property of SiC ceramic. The methods of introducing M metals can be divided into two classes. One way to obtain M containing ceramic precursors is by pyrolysis of polycarbosilane (PCS) or polysilacarbosilane (PSCS) with organometallic compounds, such as  $M(\text{acac})_n$ ,  $M(\text{OR})_n$ ,  $\text{Cp}_2\text{MCl}_2$ <sup>18-20</sup>. Another way is by condensation of Si-H containing polymethylsilane with  $\text{MCl}_n$ <sup>21</sup>, or by copolyrolysis of polydimethylsilane with  $M(\text{OR})_n$ <sup>22</sup>. The polymers used in above methods are synthesized by Wurtz reaction, which is featured by the relatively high cost and harsh reaction conditions. Our success in synthesis of polysilane with double bonds has prompted us to fabricate polysilane with refractory metals. By attaching cyclopentadienyl (Cp) ligand to the side chains of PS, the M atoms can be chemically combined with the Cp through  $\eta^5 \pi$  bonds.

#### 2.3.1 Electrosynthetic procedure of polysilane containing zirconium

Into the electrolytic cell were plunged  $\text{MeSiCl}_3$ , allyl chloride, and cyclopentadiene in the molar ratio of 1:1/3:1/5. THF was used as solvent,  $\text{LiClO}_4$  as supporting electrolyte, and magnesium ingot as electrodes. After deairing and inputing nitrogen three times, start stirring and ultrasonic. Set the interval time 10 seconds. The reaction was carried out at constant current mode.  $\text{ZrCl}_4/\text{THF}$  solution was charged into the cell as the passed electricity reached 90% of the predetermined electrical amount. It took about 8 hours to finish the electrosynthesis. Then 200ml toluene was poured into the cell, and ammonia gas was introduced to eliminate the remaining Si-Cl groups. After pressure filtration plus vacuum distillation two times, the Zr-containing polysilane EPS3, a black liquid, was obtained. As a comparison, the polysilane EPS4 was synthesized in the same procedure without adding  $\text{ZrCl}_4/\text{THF}$  solution.

The reaction is schemed as follows:





Scheme 6. Electrosynthesis of polysilane containing refractory metals

### 2.3.2 Characterization of the Zr-containing polysilane

The EPS3, being synthesized with the monomers of  $\text{MeSiCl}_3$ , allyl chloride, cyclopentadiene and  $\text{ZrCl}_4$  in the ratio of 1:1/3:1/5:1/5, had the element contents (Wt%): 48.8%Si, 42.6%C, 4.1%Zr and a little oxygen. The retaining ratio of double bonds was 10.8% and the product yield was 71.2%.

The GPC analysis result and viscosity of EPS2 and EPS3 is listed in Table 6. As a result of the introduction of Zr increased the size of the polysilane. Both the EPS2 and EPS3 can dissolve in toluene, THF and chloroform.

Sample	$\overline{M}_w$ / (Dalton)	$\overline{M}_w / \overline{M}_n$	Viscosity/(mPa.s/25°C)
EPS2	1723	1.89	75
EPS3	3749	3.24	125

Table 6. Molecular weight and Shear viscosity of EPS2 and EPS3

The IR absorption of EPS3 at  $1405\text{cm}^{-1}$  corresponds to Si-Cp<sup>23</sup> and the  $1640\text{cm}^{-1}$  peak corresponds to the C=C stretching(Fig.7).

The UV maximum absorptions of EPS3 and EPS4 shift to red, being broadening and higher, compared with EPS2 (Fig.8). The first reason for this phenomenon is the delocalization of the double bonds of the allyl groups, which increases the  $\sigma$ - $\pi$  conjugation between the backbone and the side groups. Next the Cp group can conjugate with the main chain, making it bigger the whole conjugation system of the molecule. Thus the electron-transfer energy is lowered, causing significant spectral red shifts into the accessible UV region. Furthermore, the big  $\pi$  bond formed between Zr and Cp makes the conjugation system even wider, leading to still broader adsorption peak.

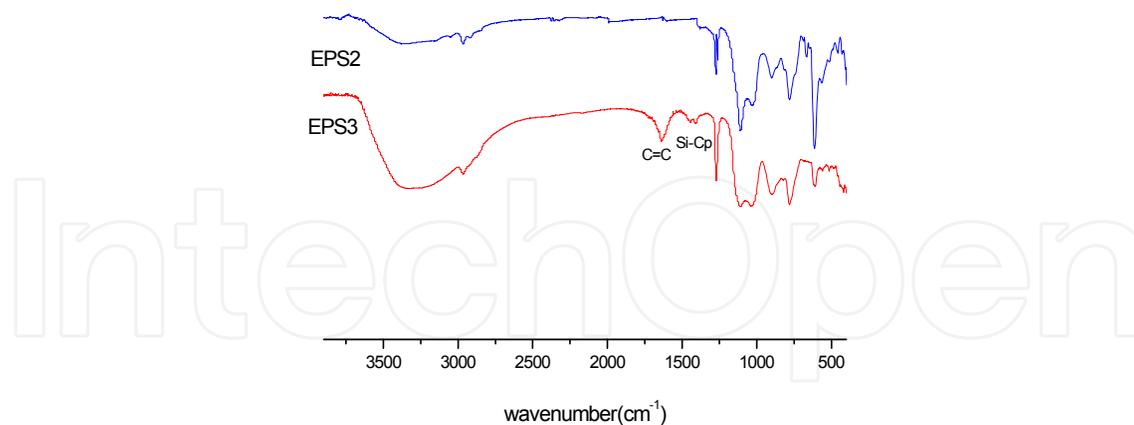


Fig. 7. FT- IR spectrum of EPS2 and EPS3

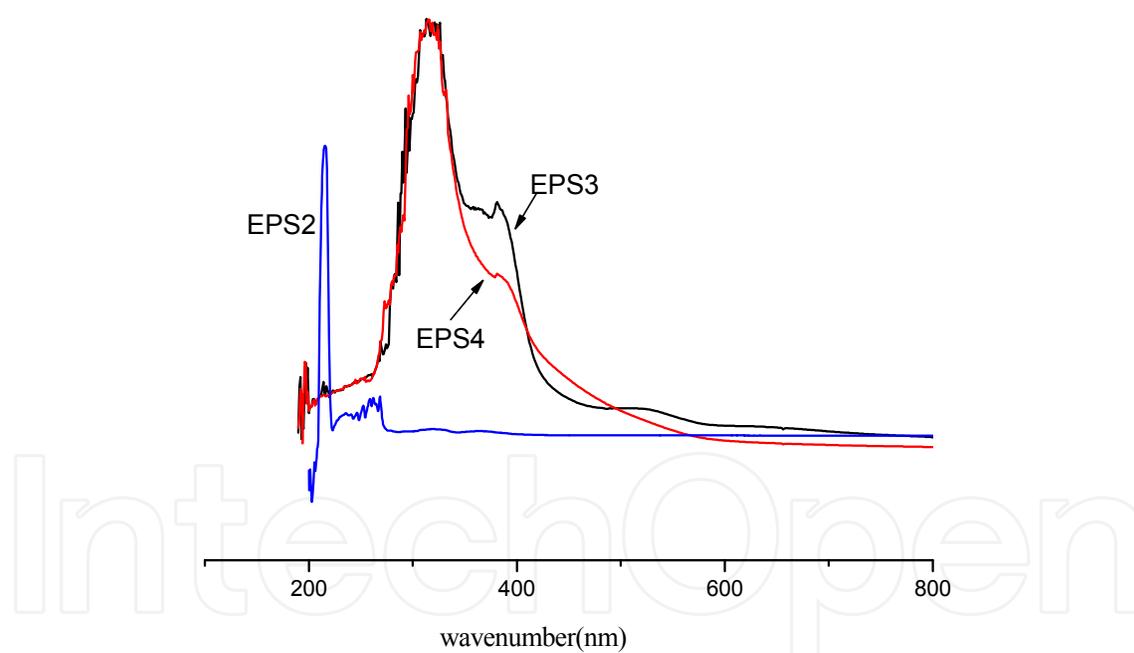


Fig. 8. UV spectra of EPS2, EPS3 and EPS4

The chemical shift  $\delta=4.9-5.1$ ,  $5.8$  and  $1.5$  on the  $^1\text{H-NMR}$  spectrum of EPS3 (Fig.9) correspond to the primary, secondary and tertiary H of the allyl group<sup>13</sup>. The spectral peak at  $\delta=5.5$  and  $6.0$  belongs to the H of Cp group attaching to Zr elements<sup>24, 25</sup>.

The above results prove that EPS3 has the predesigned structure. With Cp groups as a bridge, the refractory metals can be chemically attached to the backbone of the chain. As a result, the polysilane with both double bonds and hetero-elements has been invented.

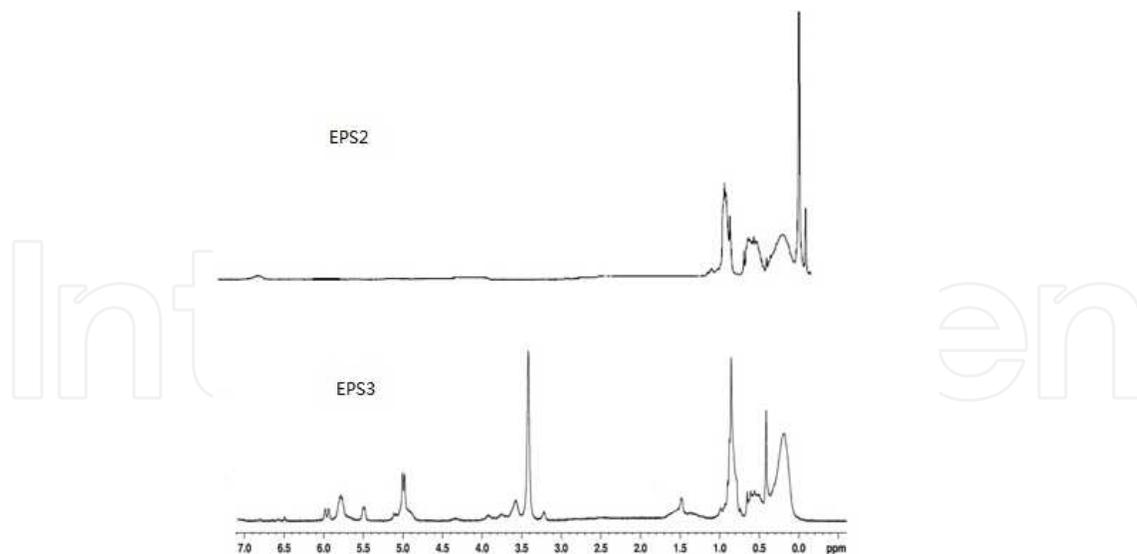


Fig. 9.  $^1\text{H}$ -NMR spectra of EPS2 and EPS3

### 3. Ceramization of polysilanes with functional groups

#### 3.1 The procedure of cross-linking and ceramization

The samples were loaded onto the sample holders. The cross-linking was carried out under dry nitrogen atmosphere at  $130^\circ\text{C}/12\text{h}$  plus  $200^\circ\text{C}/3\text{h}$ . The samples' weights before ( $m_0$ ) and after ( $m$ ) cross-linking were measured so that the mass retaining ratio ( $m/m_0$ ) can be obtained. Ceramization was carried out in a sealed alumina tube furnace in flowing argon gas at  $25\text{--}1300^\circ\text{C}$ , with a heating rate  $1^\circ\text{C}/\text{min}$  and a dwell time of 3h. The crucible loaded with sample was weighed before and after pyrolysis so that ceramic yield may be calculated.

#### 3.2 The cross-linking and pyrolysis of polysilanes with functional groups

The mass retaining ratio of EPS1 was much higher than that of EPS2 (Table 7), and was close to that of EPS1/DVB (1/0.5). It could be inferred that the double bonds on EPS1 had played important role in the cross-linking processes and were the cause of high mass retaining ratio. The ceramic yields of self-cross linking samples were dramatically higher, compared with specimens having DVB as curing agent. DVB might form inhomogeneous structure during curing process, leading to lower ceramic yield<sup>26</sup>. Therefore, it is not necessary to add curing agent to polysilane with double bonds, which is on its own a good ceramic precursor. The Zr-containing EPS3 also had a high mass retaining ratio and a moderate ceramic yield.

Sample	Mass retaining ratio	Ceramic yield
EPS1(self-cross linking)	97.5%	73.4%
EPS1+DVB (1:0.5)	99.1%	47.3%
EPS2(self-cross linking)	66.1%	70%
EPS2+DVB (1:0.5)	76.7%	40%
EPS3(self-crosslinking)	86.5%	65.5%
EPS3+DVB (1:0.5)	89.1%	60.1%

DVB: Divinylbenzene, as curing agent.

Table 7. Mass retaining ratio and Ceramic yield of EPS1, EPS2 and EPS3

XRD pattern of the pyrolyzed product of EPS1 at 1300°C (Fig. 10) shows broad peaks of  $\beta$ -SiC ( $2\theta = 35.6^\circ, 60^\circ, 71.8^\circ$ ). That of EPS3 (Figure 11) shows the existence of  $\beta$ -SiC, ZrC, Si and SiO<sub>2</sub>.

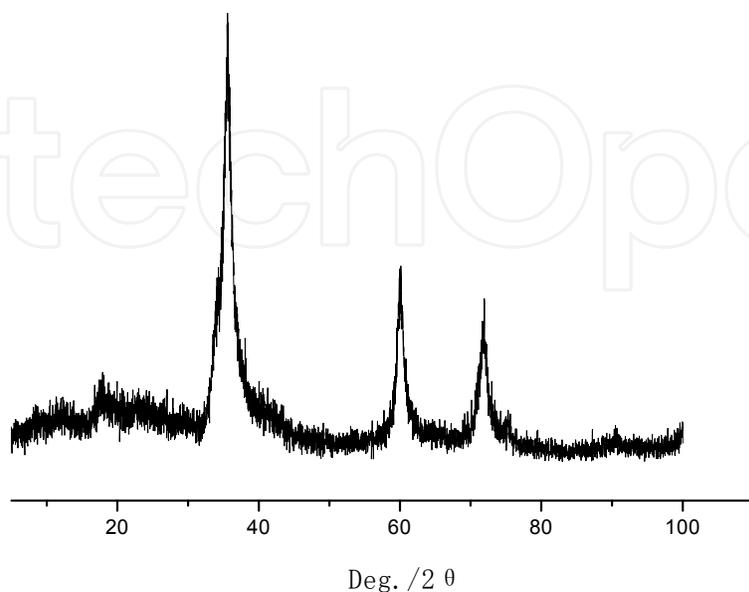


Fig. 10. XRD spectrum of EPS1's pyrolyzed product

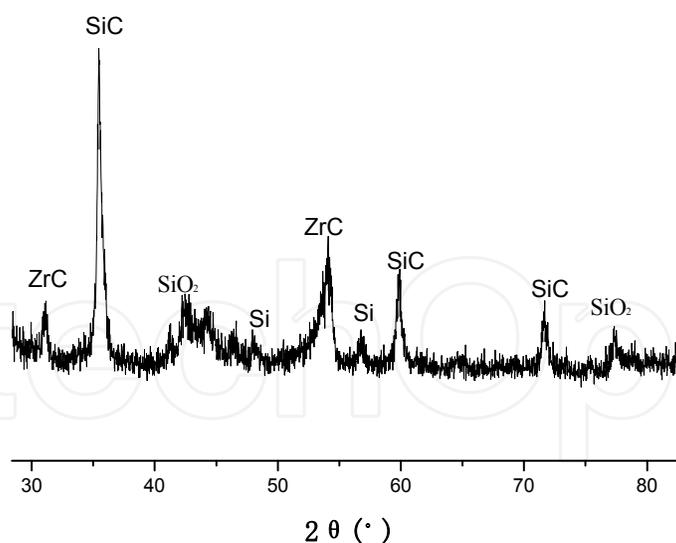


Fig. 11. XRD pattern of ceramic from EPS3

### 3.3 Improvement of the anti-oxidative ablation property of C/C composites by using polysilanes with functional groups

The poor oxidation resistance of C/C composites restricts its usage in oxidized environments. To improve its oxidative ablation resistance, the matrix of C/C composites is

modified with SiC ceramic<sup>27</sup>. The introduction of SiC can be achieved by the chemical vapor infiltration (CVI) and the polymer infiltration and pyrolysis (PIP)<sup>28</sup>. PIP has aroused much interest due to its low manufacturing temperature, ability for the design of precursor molecules, simplicity of formation and feasibility of fabricating complex components. The main precursors for SiC at present are polycarbosilane and polysilane (PS)<sup>4</sup>. The C/C-SiC composites were manufactured using PS with double bonds by the PIP technique<sup>9</sup>. The C/C-ZrC-SiC composites were prepared using Zr-containing polysilane. The ablation behavior of the C/C-SiC composites and C/C-ZrC-SiC composites were measured.

The used C/C composites with a density of 1.29 g/cm<sup>3</sup> were made by CVI of bulk needled carbon felt and temperature treatment at 2 300 °C. The C/C-SiC composites and C/C-ZrC-SiC composites were densified by the following procedure: C/C composites → vacuum + pressure infiltration of precursor → cross-linking → pyrolysis → sintering. The process was repeated several times. The maximum density of the obtained C/C-SiC and C/C-ZrC-SiC composites were 1.75 g/cm<sup>3</sup> and 1.69 g/cm<sup>3</sup>, respectively.

The specimens, with a size of ø30 mm×10 mm, were flushed vertically with a H<sub>2</sub>-O<sub>2</sub> torch flame. The inner diameter of the nozzle tip was 4.68 mm. The distance between the nozzle tip and specimen surface was 15.8 mm. The pressure and flux of oxygen were 1.55 MPa and 2.1 L/min, and for hydrogen, they were 0.18 MPa and 1.68 L/min, respectively. The ablation time was 180 s.

The thickness of the specimen before ablation (d1) was measured with a micrometer (precision 0.01 mm), and the mass (m1) was measured with an analytical balance (precision 0.1 mg). After ablation, the thickness at the lowest point (d2) and mass (m2) were measured. For the ablation time of t, the linear ablation rate was calculated by (d1-d2)/t, and the mass ablation rate was calculated by (m1-m2)/t.

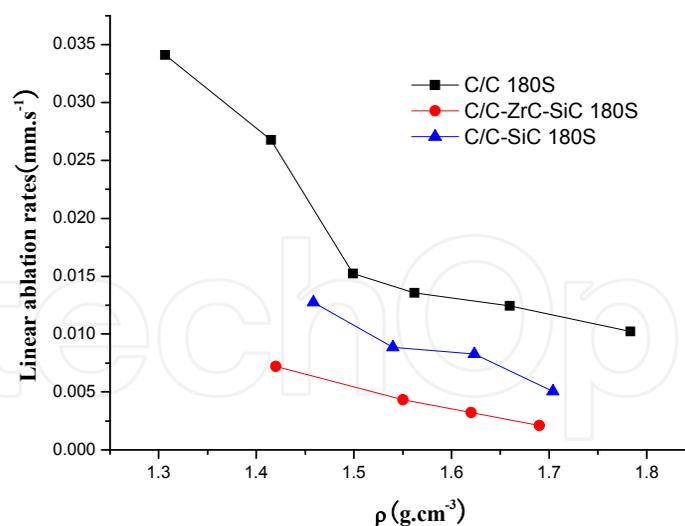


Fig. 12. Linear ablation rate of specimens

The ablation test results are depicted in Fig.12 and Fig.13, which show that the linear and mass ablation rate of the C/C-SiC and C/C-ZrC-SiC were lower than that of the C/C composites at the same density. With the increase of infiltration times, the density of C/C-SiC specimens increased, and the ablation rate decreased. The linear ablation rates of the 1.75 g/cm<sup>3</sup> C/C-SiC and 1.69 g/cm<sup>3</sup> C/C-ZrC-SiC specimen were 21.7% and 20.6% those of

the 1.78 g/cm<sup>3</sup> C/C specimen, respectively. And the mass ablation rates of the 1.75 g/cm<sup>3</sup> C/C-SiC and 1.69 g/cm<sup>3</sup> C/C-ZrC-SiC specimen were 78.6% and 31.6% those of the 1.78 g/cm<sup>3</sup> C/C specimen, respectively. Therefore, introduction of SiC into C/C composite greatly improved its oxidative ablation-resistive property, and the adulteration of Zr element enhances the effect even more. It is worthwhile to investigate the impact of attaching refractory metals, such as Ta, Zr, Hf, Th, et al. solely or combinatorially to polysilanes on the anti-oxidative ablation property of the C/C composites.

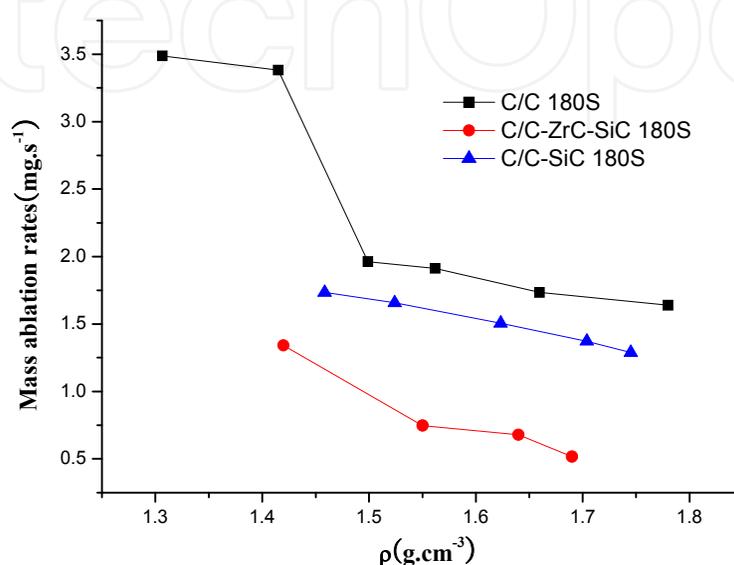


Fig. 13. Mass ablation rate of specimens

#### 4. Conclusions

The electroreduction MeSiCl<sub>3</sub> and Allyl chloride monomers carried out with Mg electrodes in a single compartment cell gave polysilane with double bonds. The preferred MeSiCl<sub>3</sub>/Allyl chloride ratio was 3:1. The molecular weight and yield of the products were affected by the concentration of monomer, the amount of electricity, the electrode's interval time and concentration of supporting electrolyte. By introducing cyclopentadienyl ligands as side groups of polysilanes, the polysilanes with refractory metals were obtained by the combination of Cp with the metal elements. The synthesized polysilanes with self-curable ability and high ceramic yields are excellent ceramic precursors.

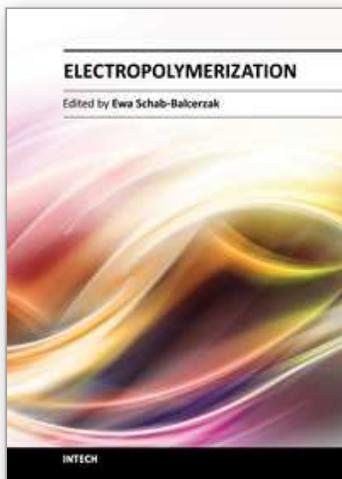
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In recent years, great focus has been placed upon polymer thin films. These polymer thin films are important in many technological applications, ranging from coatings and adhesives to organic electronic devices, including sensors and detectors. Electrochemical polymerization is preferable, especially if the polymeric product is intended for use as polymer thin films, because electrogeneration allows fine control over the film thickness, an important parameter for fabrication of devices. Moreover, it was demonstrated that it is possible to modify the material properties by parameter control of the electrodeposition process. Electrochemistry is an excellent tool, not only for synthesis, but also for characterization and application of various types of materials. This book provides a timely overview of a current state of knowledge regarding the use of electropolymerization for new materials preparation, including conducting polymers and various possibilities of applications.

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