

The reaction rate of polysilanes prepared by electroreduction with different monomers and additives

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여러 가지 모노머와 첨가제를 가지고 전기환원법에 의해 제조된 폴리실란의 반응속도

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Abstract: In this study, polysilanes were synthesized by electroreduction with different monomers such as $\text{CH}_3\text{HSiCl}_2$, PhSiCl_3 , CH_3SiCl_3 and $(\text{CH}_3)_2\text{SiCl}_2$ by Mg electrodes under ultrasonic radiation. The effects of monomers and additives (*p*-dibromobenzene (DBB), naphthalene (NAPH) and anthracene (ANTH)) on the reaction rate were investigated. Polymerization of PhSiCl_3 among the four monomers showed the highest rate. *p*-dibromobenzene (DBB) was proved the most effective additive. Based on the observations, some possible reaction mechanisms of the polymerization were proposed.

요 약: 본 연구에서 초음파 조사하에서 Mg 전극을 사용하여 $\text{CH}_3\text{HSiCl}_2$, PhSiCl_3 , CH_3SiCl_3 및 $(\text{CH}_3)_2\text{SiCl}_2$ 와 같은 여러 가지 모노머를 가지고 전기환원법에 의하여 폴리실란을 합성하였다. 또한 반응속도에 있어서 모노머와 첨가제 (*p*-dibromobenzene (DBB), naphthalene (NAPH) 및 anthracene (ANTH))의 효과를 연구하였다. 네 종류의 모노머중에서 PhSiCl_3 의 고분자화 반응은 아주 높은 반응속도를 보였다. 또한, *p*-dibromobenzene (DBB)는 가장 좋은 첨가제로 입증되었다. 이들 관찰에 근거하여 이들의 고분자화 반응에서 가능한 반응 메커니즘을 제시하였다.

Key words : polysilane, electroreduction, reaction rate, monomers, additives

1. Introduction

The special intrinsic properties make polysilanes

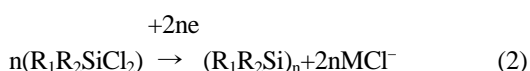
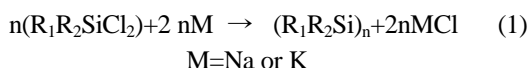
promising candidates for various applications such as photoresists,¹⁻⁴ optoelectronic devices,⁵⁻⁸ non-linear optical materials,^{9,10} precursors of thermally stable

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ceramics, silicon carbide fibers^{11,12} and components of anti-oxidation of carbon/carbon composites.¹³ As this reason, several synthetic pathways had been developed which include Wurtz coupling reaction^{14, 15} (eq. 1) and electrochemical reductive reaction¹⁶⁻¹⁹ (eq. 2).



Compared with Wurtz reaction, electrochemical reduction reactions had attracted more attention because of its mild reaction conditions. Masanobu and Atsutaka^{20,21} have studied the roles of some preliminary optimizations such as monomer, supporting electrolyte, solvent, additive, cathode material, current density, electricity, concentration and temperature on the yield of polysilanes. However, the studies on the reaction rate of electrochemical reaction had seldom been reported. In this paper, we had studied the effects of the monomers and additives on the electroreduction rate of polysilanes.

2. Experimental Section

2.1. Materials

Mg cathodes were polished with emery paper and washed with acetone. Solvent tetrahydrofuran (THF) was dehydrolyzed with metallic sodium, distilled and stored under 4Å molecular sieve. LiClO₄ was used as supporting electrolyte. All the monomers (CH₃HSiCl₂, PhSiCl₃, CH₃SiCl₃ and (CH₃)₂SiCl₂) and additives (p-dibromobenzene (DBB), naphthalene (NAPH) and anthracene (ANTH)) were purchased from Shanghai Chemical Co., Ltd.

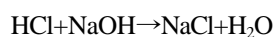
2.2. Electropolymerization

Electropolymerization was carried out in a 500 mL cell equipped with a pair of Mg electrodes (12.00 cm²), which was dried at 323 K in vacuo for 3 h. Supporting electrolyte LiClO₄ (1.07 g), the monomers and THF (150 mL) were added into the cell under an atmosphere of nitrogen. The electroreduction was

carried out under constant current of 90 mA, and anode and cathode were alternated with the interval of 17 second. Ultrasound (20 kHz) was applied to the reaction mixture during the electroreduction.

2.3. Detection of the reaction rate

The reaction rate was characterized by measuring the decreasing rate of Si-Cl bonds in the solution. Therefore the remaining of Si-Cl bonds was monitored during the electrolysis and it was determined as following principle (equation 3)^{22,23}:



To determine the remaining of Si-Cl bonds in the solution, partial reactant was drawn out from reactor and injected into a conical flask. Then distilled water (100 mL) without CO₂ was added into the conical flask. Sealed the flask and stirred for 15 minutes at room temperature. The solution was titrated with NaOH standard solution with 1~2 drops of phenolphthalein indicator. Finally, the percent of remaining Si-Cl bonds were calculated using the equation 4:

$$\text{Cl}\% = (\text{N} \times \text{V} \times 35.5) \times 100 / (\text{W} \times 100) \quad (4)$$

Where N (mol/L) is the molar concentration of NaOH standard solution; V (mL) is the volume of NaOH standard solution consumed; W (g) is the weight of the reactant drawn out from reactor.

2.4. Separation and characterization of the samples

The reaction was terminated after arrived at the assigned amount of charge. Toluene (100 mL) was

Table 1. The preparation conditions and the samples code

Sample	Type of monomer	Additive
EPS1	CH ₃ HSiCl ₂	no
EPS2	CH ₃ SiCl ₃	no
EPS3	PhSiCl ₃	no
EPS4	(CH ₃) ₂ SiCl ₂	no
EPS5	CH ₃ HSiCl ₂	DBB
EPS6	CH ₃ HSiCl ₂	NAPH
EPS7	CH ₃ HSiCl ₂	ANTH

added into the conical flask and excess NH_3 was introduced to quench the remaining of Si-Cl bonds. The reactants solution was filtrated and distilled twice to obtain yellow oil product. The products of different reaction with different monomers are listed in Table 1 respectively.

The polymers were characterized by IR, UV-VIS spectroscopy, ^1H NMR (AV-500). IR spectra were recorded on an AVATAR 370 FT-IR spectrometer; UV spectra were recorded using an obtained with a Shimadzu UV-2501PC spectrometer.

3. Results and Discussion

All the yellow oil products EPS1, EPS2, EPS3 and EPS4 from the reactions are soluble in common organic solvents, such as, toluene, THF, methylene chloride. However, the polymeric product from $(\text{CH}_3)_2\text{SiCl}_2$ by the Wurtz reaction are usually insoluble. The IR spectra of polysilane were shown in Fig. 1. All the polysilanes revealed C-H stretching (2960 and 2920 cm^{-1}) groups, C-H bending (1450 and 1410 cm^{-1}) groups, Si- CH_3 (1260 and 790 cm^{-1}), Si-Si (460 cm^{-1}). These absorptions imply the presence of Si-Si and Si- CH_3 bonds in all polysilanes.

The UV absorption spectra were not identical for the polymers with different reaction conditions, which were showed in Fig. 2. Compared with our previous work,^{24,25} we found that these products were polysilanes: The UV absorption spectrum of EPS1 only had a narrow absorption band at approximate 216 nm ; this is the typical symbol of linear

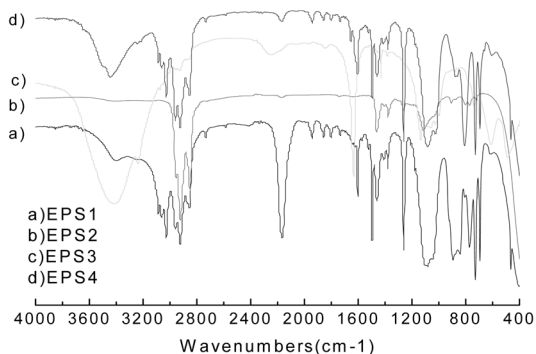


Fig. 1. FT-IR spectra of polysilanes.

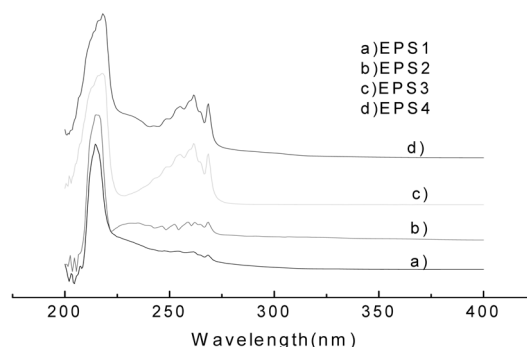


Fig. 2. UV spectra of polysilanes.

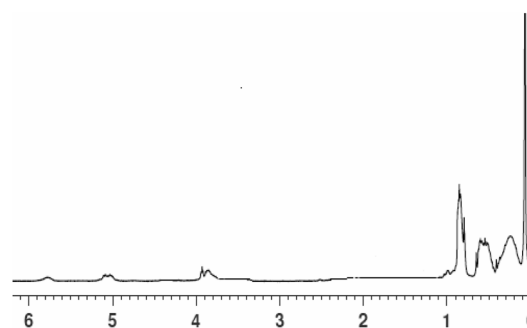


Fig. 3. ^1H NMR spectrum of polysilane.

polysilanes.²⁶ Small broad peaks in the range of 240 – 260 nm were observed in absorption spectra of EPS2, EPS3 and EPS4, those peaks absorbance are contributed to branched polysilanes.²⁷

Fig. 3 shows the ^1H NMR spectrum of polysilane. See from Fig. 3, there were four major peaks near δ 0.09 , 0.25 , 0.55 and 0.85 ppm ; these were chemical shifts of Si- CH_3 .²⁸ The broad and complication of these peaks were due to the complex structures around the Si- CH_3 groups. The observed peaks near δ 5.8 , 5.2 , and 3.9 were the characteristic chemical shifts for Si-H.²⁹

The electrolysis reaction rate of four monomers without additive was not identical (shown in Fig. 4). The decreasing rate of Si-Cl bonds stands for the reaction rate. As a whole, the electrolysis reaction rate of $\text{CH}_3\text{HSiCl}_2$, CH_3SiCl_3 and PhSiCl_3 descends along with the amount of charge increased. At initial stage, the reaction rate with $\text{CH}_3\text{HSiCl}_2$, CH_3SiCl_3 and PhSiCl_3 showed relatively higher rate compared with the reaction with $\text{CH}_3\text{HSiCl}_2$. Overall, the

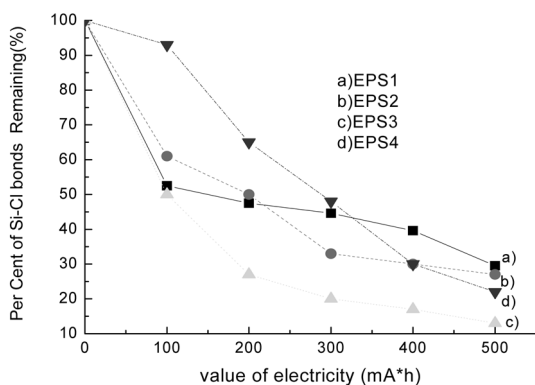


Fig. 4. Influence of monomers on the electropolymerization without additive.

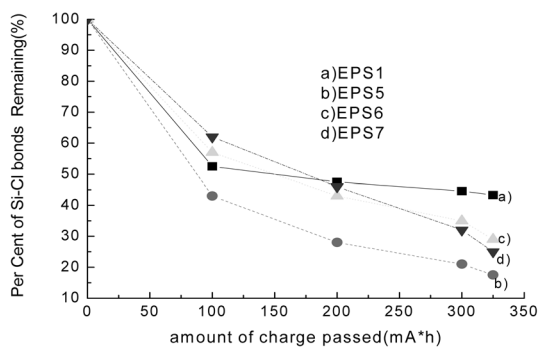


Fig. 5. The effect of additives on the electropolymerization

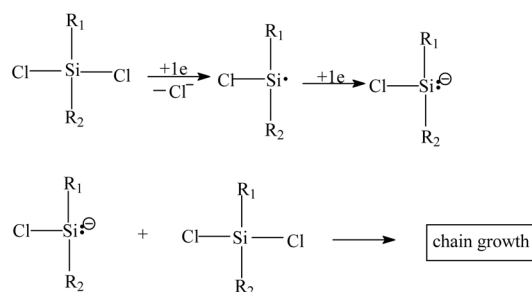
reaction rate of PhSiCl_3 among the four reactions was the fastest, which because of the electrons transfer and radical anion stabilization by aromatic ring. When the value of electricity arrived at 100 mA·h, the percent of Si-Cl bonds remaining with the monomers $\text{CH}_3\text{HSiCl}_2$, CH_3SiCl_3 , PhSiCl_3 and $(\text{CH}_3)_2\text{SiCl}_2$ was 52.5%, 61%, 50% and 93% respectively. Beyond 100 mA·h, all the reaction rates of electrolysis slowed down except for $(\text{CH}_3)_2\text{SiCl}_2$. At 500 mA·h, the reaction rates were very slow and the percent of Si-Cl bonds remaining was 29.5%, 27%, 13% and 25% respectively. So the practical function of electrolysis is small after passed 10% theory charge.

The electrolysis reaction rates of $\text{CH}_3\text{HSiCl}_2$ with additives are similar (shown in Fig. 5). The electrolysis reaction rates of $\text{CH}_3\text{HSiCl}_2$ are comparative if additive putted into or not before the amount of charge arrived at 100 mA·h, but the reaction rates

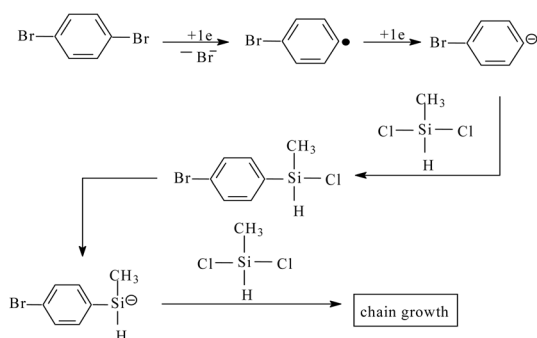
were about 10 times faster with additives after 100 mA·h. After the amount of charge arrived at 100 mA·h, the electrolysis reaction rate of $\text{CH}_3\text{HSiCl}_2$ with DBB, NAPH and ANTH are all more quick than no additive. Of the three additives, DBB was the most effective one which showed highest rate. When the amount of charge arrived at 10% of theory value, the percent of Si-Cl bonds remaining with DBB, NAPH, AN and no additive are 17.5%, 27%, 29% and 43.3% respectively. Compared with the percent of Si-Cl bonds remaining (29.5%) without additive at 500 mA·h, the function of additives on the electrolysis of $\text{CH}_3\text{HSiCl}_2$ is remarkable.

The mechanism of the formation of linear σ -conjugated polysilanes by Wurtz reaction had been widely studied^{26,27} However, the reaction mechanism for the electrochemical synthesis of polysilanes had scarcely been investigated.³⁰ It has been proposed that electrochemical polymerization should follow a similar mechanism as Wurtz coupling reaction. Herein, we proposed a possible mechanism for the electrochemical synthesis of the linear polymers which is shown in Scheme 1.^{17,30} The monomer gets one electron to form anion species, this anions then react with monomer, producing silyl anion, which can go on with more monomers. Thus the propagation reaction begins and more anions propagate into polymers.

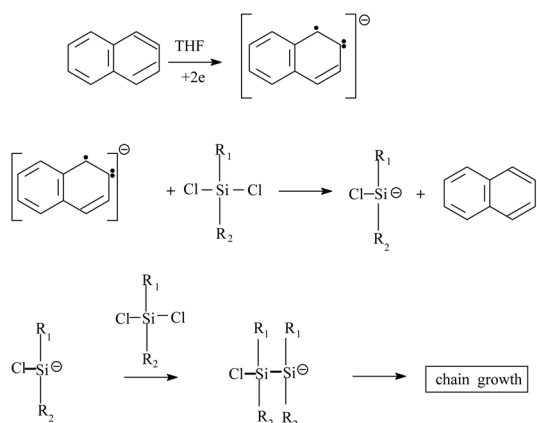
The corresponding reaction mechanisms for electropolymerization of $\text{CH}_3\text{HSiCl}_2$ with DBB or NAPH were proposed in Scheme 2-3.^{17,30} Based on the above mechanisms, the aromatic group facilitates electron transfer and stabilizes the radical anion. So



Scheme 1. Proposed reaction mechanism for electropolymerization of $\text{R}_1\text{R}_2\text{SiCl}_2$ ($\text{R}_1=\text{CH}_3$, $\text{R}_2=\text{CH}_3$ or H)



Scheme 2. Proposed reaction mechanism for electropolymerization of $\text{CH}_3\text{HSiCl}_2$ with DBB.



Scheme 3. Proposed reaction mechanism for electropolymerization of $\text{CH}_3\text{HSiCl}_2$ with NAPH ($\text{R}_1=\text{CH}_3$, $\text{R}_2=\text{H}$)

the reaction of phenyltrichlorosilane with Mg electrode is fastest one among the four reactions. The same phenomena had also been observed in Miller and coworker's²⁶ studies. Good electrons acceptor makes DBB easy to form anion, which can initiate the propagation of the reaction. So the net effect with DBB had greatly increased the reaction rate. Different with DBB, NAPH and ANTH accelerate the reaction rate by function as electron transmitters.

4. Conclusions

The reaction rate of polymerization of $\text{CH}_3\text{HSiCl}_2$, CH_3SiCl_3 , PhSiCl_3 and $(\text{CH}_3)_2\text{SiCl}_2$ by electroreduction were not identical. Polymerization of PhSiCl_3 among the four monomers showed the highest rate. Without

additive, the percent of Si-Cl bonds remaining for $\text{CH}_3\text{HSiCl}_2$ were 29.5% when electricity reached 15.5% of theoretic value. However, the percent of Si-Cl were 17.5%~29% when electricity arrived at 10% of theory value with additives. The additives DBB, NAPH and ANTH all can accelerate the reaction rate. DBB accelerate the reaction by initiate the propagation of the reaction, however NAPH and ANTH function as electron transmitters.

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