

Synthesis and characterization of polysilane with double bonds by an electrochemical method

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Polysilanes with double bonds have been synthesized by the electroreduction of trichloromethylsilane and allyl chloride in a single compartment cell. The polymers have been characterized using FTIR, GPC and ¹H NMR. The effects of monomer ratio, monomer concentration, electrode materials, the electrode's interval time and the amount of electricity supplied were investigated. The results indicate that the ideal molar ratio of MeSiCl₃/allyl chloride is 3:1 with a Mg electrode material. The molecular weight and yield of polysilanes became higher with an increase of the charge passed, a shortening of the electrode's interval time, and a decrease of the monomer concentration.

Key words: Polysilane, Double bonds, Synthesis, Electrochemical

Introduction

Polysilanes have attracted considerable attention due to their usefulness as precursors for thermally-stable ceramics [1] or materials for microlithography [2]. The general method of preparing polysilanes is through the condensation of organo-dichlorosilane with alkali metal (the Kipping method). However, this method has difficulties in controlling the unit-structure, molecular weight and molecular weight distribution, and in polymerizing monomers with functional groups [3]. The method cannot be easily industrialized because of the risk of involvement of alkali metals.

Recently it has been demonstrated that compounds with Si-Si bonds are produced in good yields by the method of electroreduction in an undivided cell using a sacrificial metal anode [4–6]. The electrochemical reactions were carried out with moderate reaction conditions. However, polysilanes with double bonds have not been referred to. In this paper, the details of the electrochemical synthesis of polysilanes with double bonds are described, including the ratio and concentration of monomers, the effects of the electrode material, the electrode's interval time and the amount of charge supplied.

Experimental Procedure

Raw materials

Trichloromethylsilane (MeSiCl₃) and allyl chloride were

used as received. Toluene and tetrahydrofuran (THF) were purified by distillation with sodium. LiClO₄, the supporting electrolyte, was dried at 623 K for 2 h. Magnesium electrodes (30 × 50 × 10mm) were polished with emery and washed with acetone.

Electropolymerisation and isolation

The MeSiCl₃ and allyl chloride were put in a compartment cell equipped with a stirrer and thermograph. Then THF and LiClO₄ were added. All reactions were carried out under a dry nitrogen atmosphere in order to eliminate the oxygen [5]. Constant current electrolysis was applied at room temperature. The electricity supplied was measured by a coulometer. During the electroreduction the electrolysis cell was sonicated (20 kHz) and the polarity of electrodes was alternated. Electrolysis was terminated when the desired amount of electricity had been supplied. Then a quantity of toluene was poured in the cell and adequate NH₃ was introduced to react with the residual Si-Cl. The solution was filtered and vacuum distilled twice. The resulting polymer was a light yellow liquid.

Characterization

The products were identified using GPC (Agilent1100 American), ¹H NMR (AV-500), and FTIR (Thermo Nicolet-AVRTAR370FT-IR). FTIR spectra were measured using the KBr method.

Results and Discussion

Effect of molar ratios of monomers

The influence of the molar ratio of MeSiCl₃ and allyl chloride on the yield, M_w , and remaining double bonds

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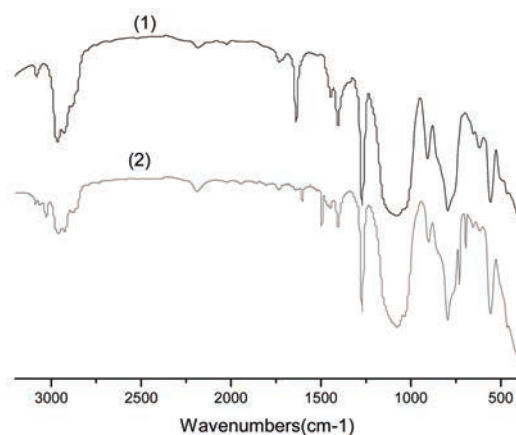
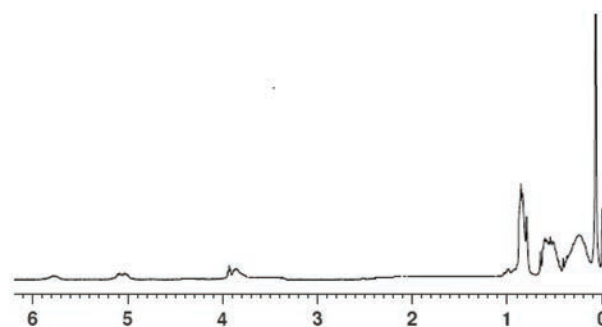
Table 1. Effect of molar ratios of monomers on the yield, M_w , and remaining double bonds of pol

	Molar ratio of (MeSiCl ₃ /H ₂ C=CHCH ₂ 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_w	1625	1974	3749	2293	834
M_w/M_n	3.19	3.84	8.26	4.52	1.64

of polysilanes is shown in Table 1. MeSiCl₃ monomer concentration was 1 M and a 10% theoretical charge was applied. The optimum molar ratio of MeSiCl₃/H₂C=CHCH₂Cl was 3:1 as the highest yield, the double bond concentration and molecular weight were reached at this point. The relatively low yield and molecular weight at ratios of 10:1 and 5:1 might be due to the intramolecular reaction of MeSiCl₃, which leads to a highly cross-linked structure and insolubility in the solvent when there is inadequate allyl chloride. Only a section of low molecular weight was left in the solvent. When the molar ratio surpasses 3:1, the excess allyl chloride, acting as an end capping agent, blocks the propagation of polysilane chains, resulting in a lower molecular weight.

The IR spectra of polysilane with double bonds are shown in Fig. 1. The polysilane with and without double bonds both revealed C-H stretching (2,960 and 2,920 cm⁻¹) groups, C-H bending (1,450 and 1,410 cm⁻¹) groups, Si-CH₃ (1260 and 790 cm⁻¹), Si-Si (460 cm⁻¹). These absorptions imply the presence of Si-Si and Si-CH₃ bonds in both polysilanes. However, in the curve (1) the absorptions at 1,640 cm⁻¹ of C=C [7] stretching groups and at 3,080 cm⁻¹ of =C-H groups indicated the presence of double bonds.

The ¹HNMR spectrum of polysilane with double bonds

**Fig. 1.** FT-IR spectra of polysilane with and without double bonds (1)EPS1: polysilane with double bonds synthesized with a MeSiCl₃/H₂C=CHCH₂Cl molar ratio of 3:1; (2) EPS2: polysilane without double bonds synthesized with MeSiCl₃.**Fig. 2.** ¹HNMR spectrum of polysilane with double bonds.

(Fig. 2.) presented four major peaks near δ 0.09, 0.25, 0.55 and 0.85 ppm; these were chemical shifts of Si-CH₃ [7]. The broad and complication of these peaks were due to the complex structures around the Si-CH₃ groups. The observed peaks near δ 5.8, 5.1-5.2, and 3.8-3.9 were the characteristic chemical shifts for Si-allyl moiety [8].

Effect of monomer concentration

With different monomer concentrations the polysilanes were synthesized with 5% of the amount of theoretical electricity. As shown in Table 2, the yield and molecular weight of the polysilanes became lower with an increase of monomer concentration. This is because MeSiCl₃ is apt to polymerize with itself to form giant three dimensional networks, which will precipitate from solution, when the concentration is higher. So the following experiments were performed at 1 M monomer concentration.

Effect of electrode materials

Polysilanes were synthesized with 10% theoretical electric charge and a time interval of 17 s. As shown in Table 3; the electrode materials have a profound influence on the formation of polysilanes. The entry using a Mg anode and cathode gave the highest molecular weight and yield. Al is less effective than Mg and Cu is the worst. It is

Table 2. Effect of monomer concentration on the yield and M_w of polysilanes

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

Table 3. Effect of electrode materials on the yield and M_w of polysilanes

	Electrode Materials			
	Mg-Mg	Mg-Al	Al-Al	Mg-Cu
Yield, %	87	78	34	18
M_w	1979	1099	898	512
M_w/M_n	4.93	3.36	2.12	1.63

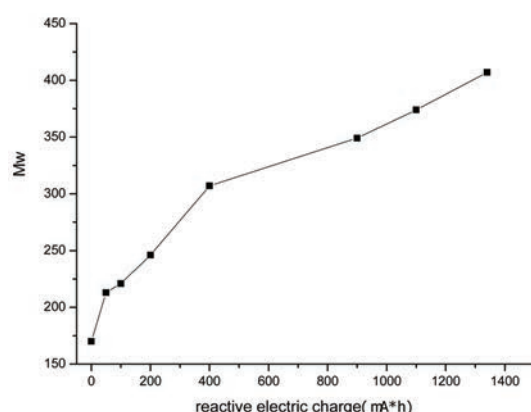


Fig. 3. The molecular weight of polysilane as a function of the reactive electric charge.

said that Mg plays some important roles in the formation of the Si-Si bond [9]. 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 [10, 11].

Effect of electric charge

The molecular weight was monitored at different electric charge during the reaction process. As shown in Fig. 3, the molecular weight goes up rapidly before 3% of the theoretical electric charge (400 mA*h) and enters a linearly increasing period afterwards. This suggests that the electrochemical synthesis of polysilane with double bonds is a step-growth polymerization.

The electric charge is a significant factor in the electrochemical synthesis of polysilane. The polymers synthesized using different proportions of theoretical electric charge and listed in Table 4. With an increase in the electric charge the molecular weight raised obviously 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 [12]. The results indicate that polysilanes having different molecular weight can be obtained by controlling the amount of electric charge.

Effect of time interval

The electroreduction was carried out in an ultrasonic bath with an Mg anode and cathode. The electrodes were alternated with intervals of 8 s, 17 s and 26 s. As the

Table 4. Effect of electric charge on the yield and M_w of polysilanes

	Electricity		
	5% Theoretical Electric charge	7.5% Theoretical Electric charge	10% Theoretical Electric charge
Yield, %	87	92	85
M_w	1723	2687	3952
M_w/M_n	4.89	6.58	8.67

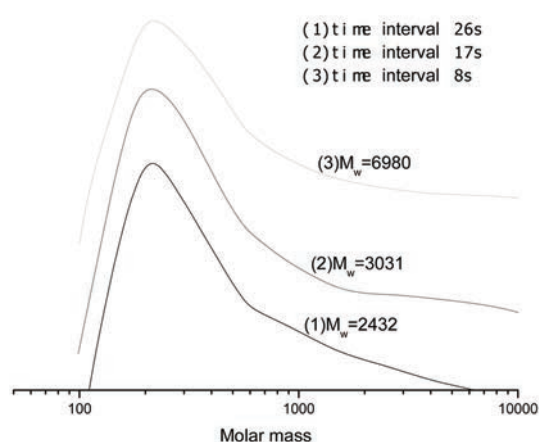


Fig. 4. Effect of time interval on the GPC spectra of the products.

Table 5. Effect of the concentration of the supporting electrolyte on the yield and M_w of polysilanes

	Concentration of the Supporting Electrolyte (LiClO ₄)		
	0.05 M	0.03 M	0.005 M
Yield, %	91	81	72
M_w	3031	1309	665
M_w/M_n	7.89	2.56	1.42

results show in Fig. 4, the molecular weights of the products became higher with a decrease in the time interval. This can be explained by the fact that the alternation of the anode and cathode can overcome the difficulty of keeping the electric current at a suitable level due to the increase of the voltage between the anode and cathode with the progress of the reaction [13]. A shorter interval led to relatively lower maximum voltage, thus reducing the possibility of side reactions and creation the propagation of Si-Si bonds.

Effect of the concentration of supporting electrolyte

The influence of the supporting electrolyte on polymerization is summarized in Table 5. An increase in the concentration of the supporting electrolyte resulted in a growth of the molecular weight and yield. This might be explained that a higher concentration of the supporting electrolyte brought on a lower electrode voltage to maintain a constant current, thus reducing side reaction. The 0.05 M concentration seems reasonable because the acquired molecular weight and yield are satisfaction, and an increase in concentration leads to a high cost as the recovery of costly LiClO₄ is difficult.

Conclusions

Polysilanes with double bonds were achievable using Mg electrodes with MeSiCl₃ and allyl chloride monomers. The preferred MeSiCl₃/allyl chloride molar ratio was 3:1. The yield and molecular weight of the polysilanes became lower with an increase of the monomer concentration.

The entry using Mg anode and cathode gave the highest molecular weight and yield. With an increase of electric charge the molecular weight increased obviously and the molecular weight distributions became broader. The molecular weights of the products became higher with a decrease of the time interval. An increase in the concentration of the supporting electrolyte resulted in a growth of the molecular weight and yield.

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