Poly(phenylmethylsilane) Obtained by Electrochemical Reduction in a Divided Cell Containing a Polymeric Membrane

Roman Dabek[1], Jorge Cervantes[2] and *Arturo Zizumbo[1]

[1]Department of Chemistry, Autonomous University of Coahuila, C.P. 25000, Saltillo, Coahuila, Mexico. azizumbo@alpha1.sal.uadec.mx

[2]Department of Chemistry, University of Guanajuato, C.P. 36050, Guanajuato, Guanajuato, Mexico

SUMMARY: The electrochemical synthesis of poly(phenylmethylsilane) was carried out in a divided cell using a polymeric anion-exchange membrane. The solution contained phenylmethydichlorosilane ($PhMeSiCl_2$), mixed solvent tetrahydrofuran + hexamethylphosphoramide, with tetrabutylammonium perchlorate as support electrolyte. The electrodes were stainless steel as the cathode, stainless steel as the sacrificial anode or platinum as the resistant anode. Poly(phenylmethylsilane) was obtained in yields from 1.5 to 4.5 % from phenylmethyldichlorosilane concentrations equal or higher than 1 M. The number-average molecular mass M_n of poly(phenylmethylsilane) was in the range from 5600 to 9500. A monomodal molecular weight distribution was obtained with a polydipersity Index of 2. The spectra of ^1H, ^{13}C, ^{29}Si NMR and IR were determined. From the ^{29}Si NMR analysis, the poly(phenylmethylsilane) showed a clear difference in the tacticity related to the chemical synthesis of the same polymer. The UV spectra showed a strong absorption in a 331 to 335 nm characteristic for the poly(phenylmethylsilane).

Introduction

Polysilanes have an increasing scientific and commercial interest, due to electronic properties produced by an unusual sigma electron delocalization of Si-Si bond along the backbone. Since the first synthesis of soluble polysilanes by West in 1981 for Wurtz type condensation[1)], some alternative synthesis have been investigated, for example: dehydrogenative coupling[2)], electrochemical reduction[3)], etc.

The Si-Si bond formation has been widely studied by chemical synthesis, but this process is not often reproducible. As an alternative, Hengge achieved the electroreductive formation of

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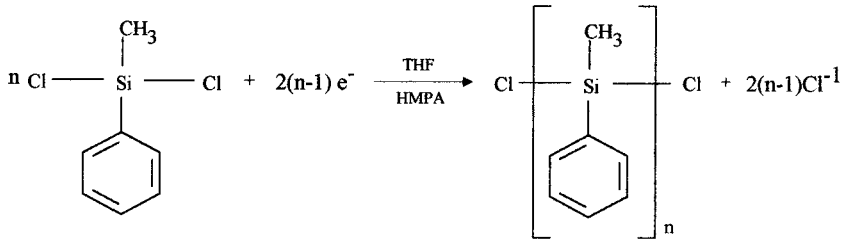
the Si-Si bond, first for the formation of organosilicon compounds[4], and later for polysilanes[5]. Until now, the electrochemical reduction of chlorosilanes is carried out in a single cell[6,7]. However in this method, the main problems are the cleavage of Si-Si bond by anodic oxidation in the anode and the presence of chlorine produced as by-product of electroreduction. Although, electroreduction has been carried out in a divided cell using a diaphragm[8], the process presents clogging and few formation of Si-Si bonds. As a solution to these problems we proposed reductive polymerization using a neutral polymeric separator[9] and thereafter an ion-exchange membrane in a divided cell.

Recently, we have achieved the formation of poly(phenylmethylsilane) (Compound 2), by electrochemical via (Scheme I) in a divided cell using a polymeric separator (Teflon), increasing the molecular weight[9].



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Scheme I

In this paper, we report the electrosynthesis and characterization of poly(phenylmethylsilane) obtained by electroreduction in a divided cell using an anion-exchange polymeric membrane as separator.

Experimental

Materials

$PhMeSiCl_2$, and HMPA were supplied by Aldrich, THF was supplied by EM Science. A commercial anion-exchange membrane, RAI-1025 (δ = 77 μm) was used. Prior to use, THF was dried by refluxing over metallic sodium with benzophenone and then distilled under a nitrogen atmosphere. HMPA was used from a sealed fresh flask. Bu_4NClO_4 was prepared with Bu_4NBr and $Mg(ClO_4)_2$, was dried in a vacuum stove at 120 °C for 8 hrs, and then was stored in a dessicator. $PhMeSiCl_2$ was distilled before each electroreduction reaction.

Electrolytic Cell

A divided cell using an anion-exchange membrane for electrolysis of $PhMeSiCl_2$ was used. The cell construction and characteristic were described in our previous paper[9]. Resistant platinum or a sacrificial stainless steal was used as anodes and stainless steal as cathode. A THF solution of equal concentration of Bu_4NClO_4 (0.2 M) was transferred into a catholyte (5 ml) and anolyte (7 ml). $PhMeSiCl_2$ (1 M) and HMPA (1 ml) were added only for the catholyte. The electrolytic solution was magnetically stirred only in the catholyte for the entire electroreduction. Constant voltage electrolysis (45 V) was supplied at ambient conditions for about 24 hrs while current was monitored. The electroreduction cell and other equipment were placed in a glove box under nitrogen atmosphere.

Separation and Characterization of Products

After electrolysis, insoluble solids were separated by filtration of a catholyte solution with a filter paper (pore, 0.5 μm). Ethanol was added to the filtrated solution until a precipitate is formed. The precipitate was centrifuged and separated from the solution. The oligosilanes, and remaining monomer ($PhMeSiCl_2$) were dissolved by the ethanol and no other treatment was made to the solution. The solid precipitate was purified with THF and reprecipitated from ethanol 3 times, then poly(phenylmethylsilane) was dried in a vacuum stove for 4 hrs before the characterization. The electrochemical synthesis afforded a poly(phenylmethylsilane) in the form of white solid powder. After purification, it was soluble in THF and Toluene.

The chemical structure of purified poly(phenylmethylsilane) was determined by GPC, NMR, IR, and UV spectroscopy. IR spectrum was run for a solid poly(phenylmethylsilane) in a Perkin Elmer 1710 Spectrometer with an ATR accessory. UV spectrum was determined in THF solution (0.1 mg/ml) in a Beckman DU 650 spectrometer. ^{1}H, ^{13}C and ^{29}Si NMR spectra were obtained in d-chloroform solvent (90 mg/ml) in a Varian Unity-plus NMR spectrometer of 300 MHz. GPC chromatograms were run in THF (1 mg/ml) using polystyrene standards (PL Polymer Laboratories) in a Water 150C chromatograph with a refractive index detector.

Results and Discussion

Poly(phenylmethylsilane) by electrochemical synthesis was obtained using either a resistant Pt anode or a sacrificial stainless steel anode. Although the number of Faraday/mol feed was

low (0.19 to 1.15), poly(phenylmethylsilane) was obtained in moderate yields (1.5 to 4.3 %) and number-average molecular weight (5600 to 9500), and polydispersity among 2. Polysilanes were obtained for concentrations equal or higher than 1M. In our experience we note also that the addition of HMPA was necessary to obtain a high molecular weight mass because under the same conditions when HMPA was not added to electrolytic solution in the catholyte, polysilane was not obtained. This is in accordance with best results obtained by other researchers when they had used HMPA as trapping agents of chlorine ions.

Molecular Weight

The chromatogram of polyphenylmethylsilane (Fig. 1) shows the molecular weight distribution from a representative run obtained in a divided cell using an RAI-1025 membrane. The number-average molecular weight was of 8649, the weight-average molecular weight was of 16387 and a polydispersity index of 2. We can observe that a monomodal molecular weight distribution was obtained. A monomodal Poly(phenylmethylsilane) distribution obtained for electrochemical via differs from polysilanes obtained from chemical via where a bimodal distribution was reported[10]. The monomodal evidence suggests that one mechanism may be involved in the chain extension. We had also noted the same fact in our previous paper for the electrosynthesis in a divided cell using a neutral polymer separator (Teflon)[9].

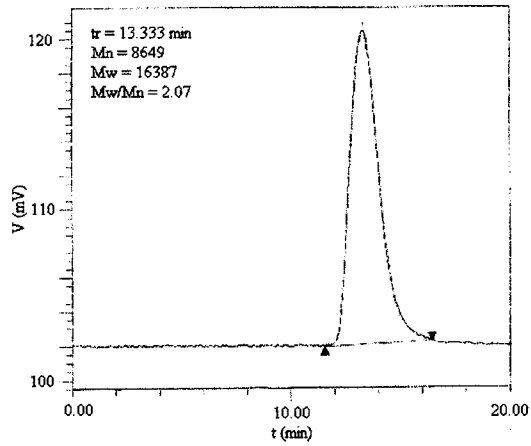

Fig. 1: GPC chromatogram of $(PhMeSi)_n$ run in THF solution.

Due to a monomodal distribution obtained and the average degree of polymerization (n) of 72, we assume that cyclosilanes were not formed. Thereafter, in comparison with electrochemical synthesis in a single cell[11], the molecular weight of poly(phenylmethylsilane) in a divided cell was increased.

^{29}Si NMR Spectrum

The ^{29}Si spectrum of poly(phenylmethylsilane) (Fig. 2) obtained by electroreduction differs from the one obtained by the chemical synthesis[12]. It shows mainly the three line patterns characteristic of poly(phenylmethylsilane) with some resonances between the lines (-39.3, -40.1 and -41.4 ppm). According to Wolf and coworkers[12], the signals are assigned to the isotactic (mm), syndiotactic (rr) and heterotactic (rm) triads respectively. However, the intensity ratio of the triads is nearly a statistical distribution (30%: 25%: 45%) close to the 1: 1: 2 (25: 25: 50) expected for an atactic polymer. Maxka and coworkers[13] have observed the same tendency where they obtained the poly(phenylmethylsilane) by a different chemical route than the Wurtz coupling. The explanation given to this difference is related to some effects in the polymer, which has nearly a random distribution of the triad sequence.

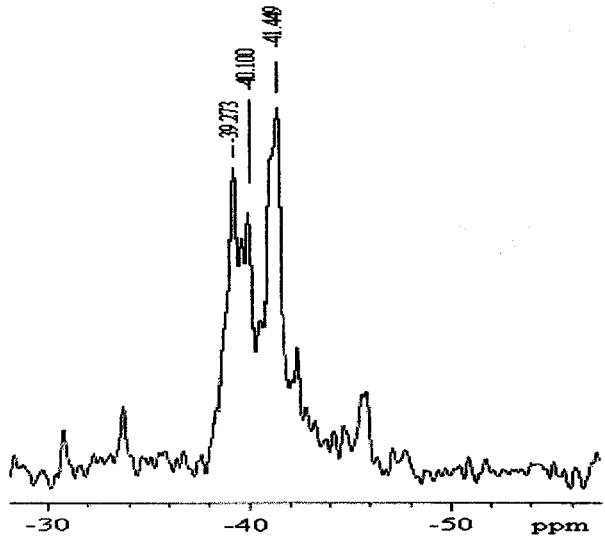

Fig. 2: ^{29}Si spectrum of $(PhMeSi)_n$ run in d-chloroform solution (Acquisition time, 2.291 sec; number of scan, 16644).

^{13}C NMR Spectrum

The spectrum of ^{13}C (Fig. 3) shows some signals around of 77 ppm that they correspond to the resonances for the carbons of d-chloroform. In this spectrum appears 136.3, 135, 133.2, 129.4, 127.5, and 127.2 ppm resonances attributed to aromatic ring carbons, and -6.2 ppm due to methyl carbons. The structure is consistent with the resonances reported by Hammegg and coworkers[14] for poly(phenylmethylsilane).

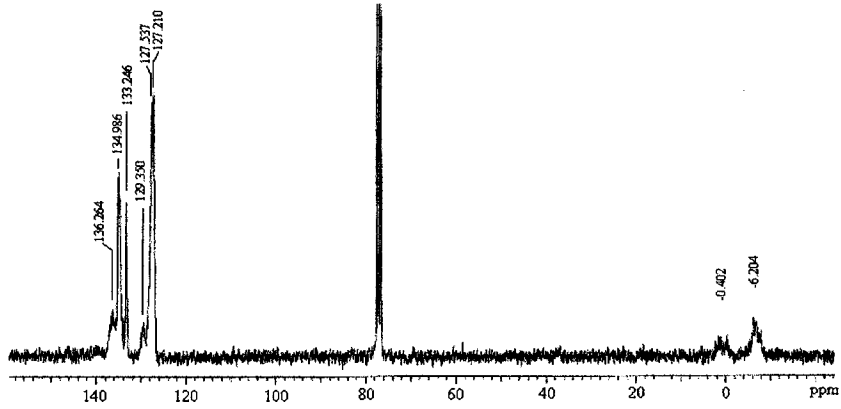

Fig. 3: ^{13}C spectrum of $(PhMeSi)_n$ run in d-chloroform solution (Acquisition time, 1.814 sec; number of scan, 72576).

As we reported in our previous paper[9], there was a possibility of decomposition of the electrolyte (Bu_4NClO_4) in the electrolytic solution due to high voltage applied to the electroreduction reaction. As a result of this decomposition, some imperfections could be present in the backbone of the polysilane because of the interaction of decomposition compounds from secondary reactions with the electroactive silane compounds produced during electroreduction. Thus, we may assign the other resonance (–0.4 ppm) to an insertion of methylene groups into the backbone of poly(phenylmethylsilane) for the decomposition of electrolyte (Bu_4NClO_4) during electrosynthesis.

^{1}H NMR Spectrum

The spectrum of ^{1}H (Fig. 4) shows a sharp signal in 7.3 ppm that corresponds to the proton of hydrolyzed d-chloroform. This spectrum is consistent with the structure for a poly(phenylmethylsilane) reported by Trujillo[15] with a broad resonance in 6.7 ppm for a 5 aromatic protons, and a broad resonance in –6 ppm for a 3 methyl protons. Similar to the ^{13}C spectrum, there are other peaks around 1.5 ppm, attributed again to an insertion of methylene

groups into the backbone during electrolysis. Also a peak appears in 3 ppm that may be due to chloration of methylene groups.

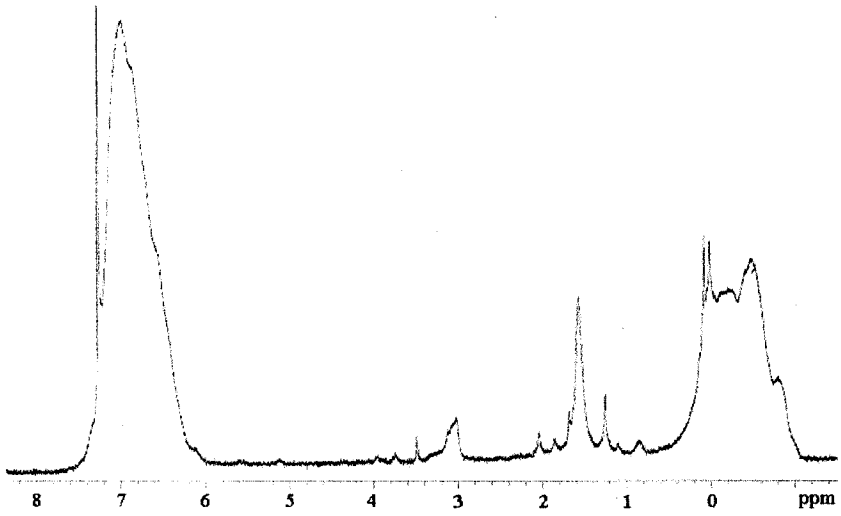

Fig. 4: ^{1}H spectrum of $(PhMeSi)_n$ run in d-chloroform solution (Acquisition time, 3.739 sec; number of scan, 64).

UV Spectrum

The ultraviolet absorption spectrum (Figure 5) shows an absorption wavelength λ_{max} near to 331 nm, characteristic for high linear poly(phenylmethylsilane).

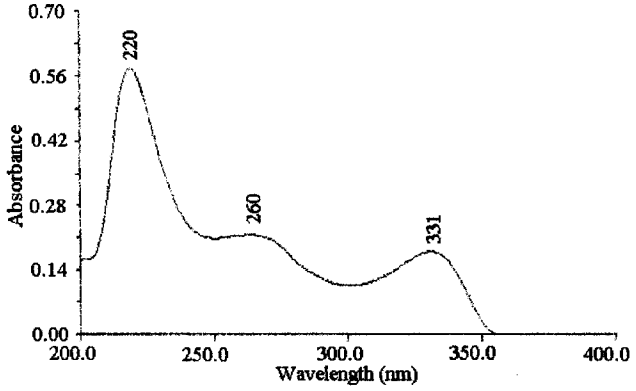

Fig. 5: UV spectrum of $(PhMeSi)_n$ run in THF solution.

Although Chen and coworkers[16] reported the presence of wavelengths near to 220, 260 for isomers of $(PhMeSi)_5$ and $(PhMeSi)_6$, we believe that wavelengths near to 220 and 260 nm may be present due to an interaction between tactacity configuration, and we have assigned them to high linear poly(phenylmethylsilane). The assignment for these bands in UV spectrum for linear polysilane was likewise consistent with monomodal distribution of the GPC chromatogram.

IR Spectrum

In the IR spectrum of poly(phenylmethylsilane) (not shown in this publication) appears the frequencies of 1425 and 1097 cm^{-1} for Ph-Si bond, and 1244 cm^{-1} for Me-Si bond. There was not formation of Si-H in 2130 cm^{-1}. And, due to the size of the band between 1000-1100 cm^{-1}, there was a formation of a few Si-O bonds. In our previous paper[9], we reported the possibility of a decomposition of the electrolyte (Bu_4NClO_4) due to high voltage applied in the electrolysis (45 V). Therefore, we suppose that the formation de Si-O bond in the polysilane chains may be formed for the reduction of the Bu_4NClO_4. This is in accord with the same observation of Kunai and coworkers[17]. This fact was not observed with electrolytes, which do not contain oxygen in their compounds used in the electrochemical reduction like: Bu_4NBF_4[17], or Bu_4NBPh_4[18].

Conclusion

The electroreductive formation of Si-Si bonds for high poly(phenylmethylsilane) were carried out successively in a divided cell using a anion-exchange membrane as a separator. The molecular weights were as expected higher than those obtained in the same condition but without a separator (undivided cell). The structure of linear poly(phenylmethylsilane) was confirmed by NMR, IR, UV spectroscopy and GPC chromatography. The ^{29}Si spectrum showed a nearly random distribution of a triad sequence (mm, rr, and mr). Also, real structure of poly(phenylmethylsilane) chains show some imperfections in the backbone like Si-O bond, and methylene groups due to the decomposition of one component in the electrolytic solution (Bu_4NClO_4) for the high voltage (45 V) applied during electroreduction in our conditions.

Acknowledgements

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