

Batteries and a Pinch of Salt: A Simple Toolkit for the Production of Poly(methylsilyne)

Damla Eroğlu,¹ Yusuf Nur,² Umut Sönmez,² Göknuş Bayram,¹
Michael W. Pitcher,² Levent K. Toppare²

¹Department of Chemical Engineering, Middle East Technical University, 06531 Ankara, Turkey

²Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

Received 16 February 2008; accepted 21 December 2008

DOI 10.1002/app.29948

Published online 6 March 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A simple synthesis of poly(methylsilyne) has been developed. The straightforward polymerization reaction can be accomplished using simply a series of batteries and a very simple electrolyte. Poly(methylsilyne) has previously been shown to be a high-purity, high-yield pre-

cursor to stoichiometric silicon carbide. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3519–3521, 2009

Key words: polymer; silicon carbide; poly(methylsilyne); electrochemistry

INTRODUCTION

Silicon polymers are used in a variety of technological applications.¹ One example being that of a pre-ceramic polymer; a polymer which upon heating converts to the desired ceramic.² Using such a methodology, if the polymer is soluble, then ceramic films, fibers, coatings, indeed objects of any size or shape can in theory be produced from the polymer. Recently, a superior polymeric precursor to silicon carbide (SiC) has been reported, poly(methylsilyne) (PMSy).³ The SiC that is produced from this polymer is stoichiometric, and smooth continuous ceramic films can be formed, enabling a variety of possible applications including electronics. The problem is, however, that this Wurtz coupling synthesis requires the application of high-intensity ultrasound, explosive sodium potassium alloy (NaK) as a reducing agent, flammable solvents, and further refluxing with methyl lithium. PMSy and related polymers have also been produced by Vermeulen et al., electrochemically.⁴ The synthesis involves reduction of the appropriate trichloroalkylsilane using a potentiostat or galvanostat as the electrical source, 1,2-dimethoxyethane as the solvent, copper electrodes, and a suitable perchlorate electrolyte. Here, we report an even simpler route for the production of poly(methylsilyne) using the simplest source of electricity and an electrolyte that we could find; namely, a series of 1.5-V batteries and sodium dodecylsulfonate

(SDS), a simple anionic surfactant. Characterization data also indicates that the polymer produced by this method has less Si—O—Si and Si—H impurities than the previous electrochemical method and is comparable in purity to the Wurtz coupling method.^{3,4}

EXPERIMENTAL

Materials

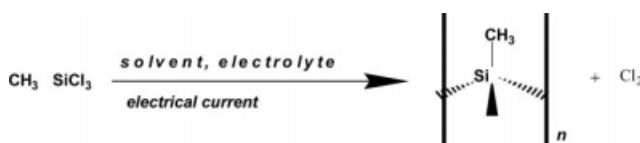
Methyltrichlorosilane (97%) and SDS were purchased from Aldrich (Taufkirchen, Germany) and used as received. Acetonitrile was also obtained from Aldrich and distilled before use. Lithium aluminum hydride was procured from Merck (Darmstadt, Germany) and used as received. 413 stainless steel was used as electrodes. 1.5-V batteries were arranged in series to produce a 6-V electricity source. The synthesis was carried out under an argon atmosphere as methyltrichlorosilane is air sensitive.

Synthesis of PMSy

The electrochemical reactions were carried out in a 25-mL undivided cell. Methyltrichlorosilane (1 mL) was added to the saturated solution of SDS in 5 mL acetonitrile after the cell had been purged with argon gas. The stainless steel electrodes were then connected to the batteries, and then electrolysis was started. After 20 min, the solution becomes yellow indicating the presence of PMSy. Using a syringe, the yellow solution was extracted. Note that due to chlorine gas evolution in the formation of PMSy, this synthesis should be carried out using suitable precautions and ventilation.

Correspondence to: L. K. Toppare (toppare@metu.edu.tr).

Contract grant sponsor: TUBITAK; contract grant number: 107M031.



Scheme 1 General schematic for the production of poly(methylsilylene).

In a two-necked 50-mL round-bottomed flask equipped with stirrer, reflux condenser, and powder addition funnel, LiAlH_4 (0.03 g) was added to the solution (total time about 30 min, 50°C). The reaction mixture was then refluxed for an additional 10 min to ensure complete removal of any unreacted chlorine. This step is again carried out under Argon atmosphere.

After reflux, the apparatus and products of the synthesis were allowed to cool to room temperature, and the lithium aluminum chloride side product was removed by filtration. After evaporation of acetonitrile, yellow PMSy in the form of a solid or waxy-type material was isolated. Sometimes, a further purification step is necessary, and this is done by dissolving the polymer in tetrahydrofuran (THF), adding pentane and then water and shaking the solution. This, when allowed to settle, forms two layers, the bottom water layer with impurities and the top organic layer that contains PMSy. Evaporation of the organic solvents from the organic layer yields pure PMSy.

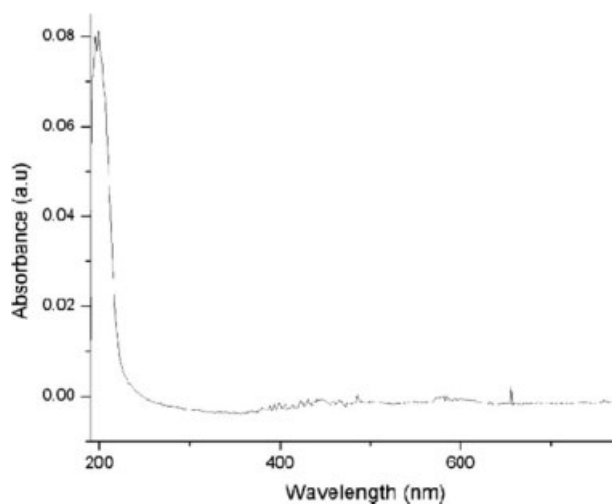


Figure 1 UV/vis spectrum of poly(methylsilylene).

Characterizations of PMSy

An HP8453A UV/visible spectrometer was used to monitor the polymerization reaction. Gel permeation chromatography (GPC) was performed using a Polymer Laboratories PL-GPC 220 system using THF as the solvent and calibrated using poly(styrene) standards. ^1H -nuclear magnetic resonance (NMR) spectra were obtained using a Bruker-Spectrospin Avance DPX 400 Ultra-Shield (400 MHz, CDCl_3 solvent). Fourier transform infrared (FTIR) spectra (THF solution) were collected using a Nicolet 510 FTIR spectrometer.

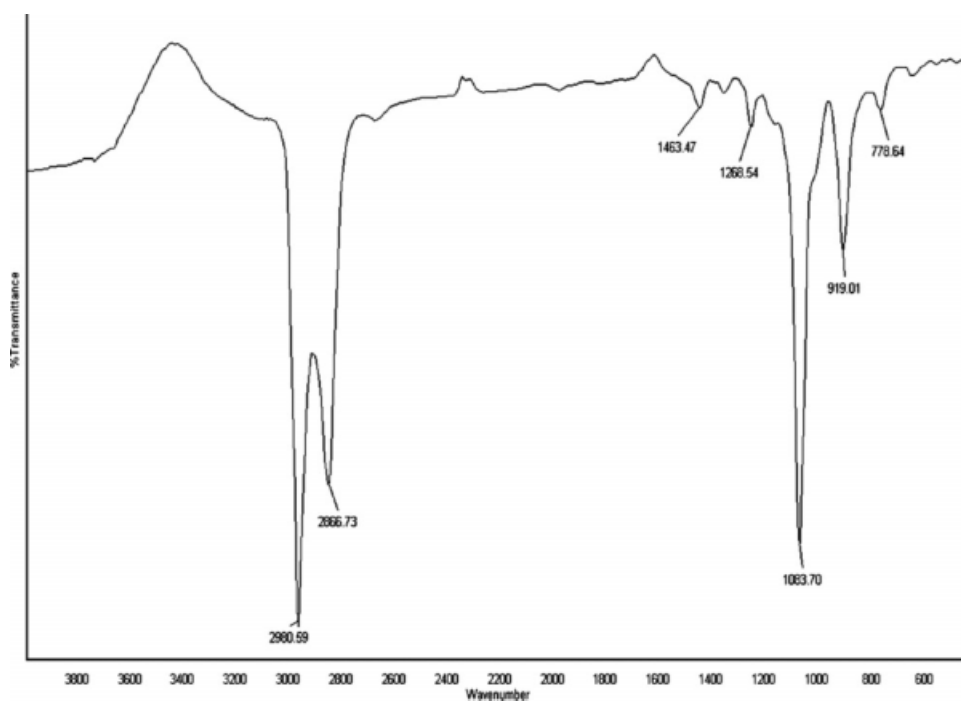


Figure 2 FTIR of the product from the polymerization of methyltrichlorosilane.

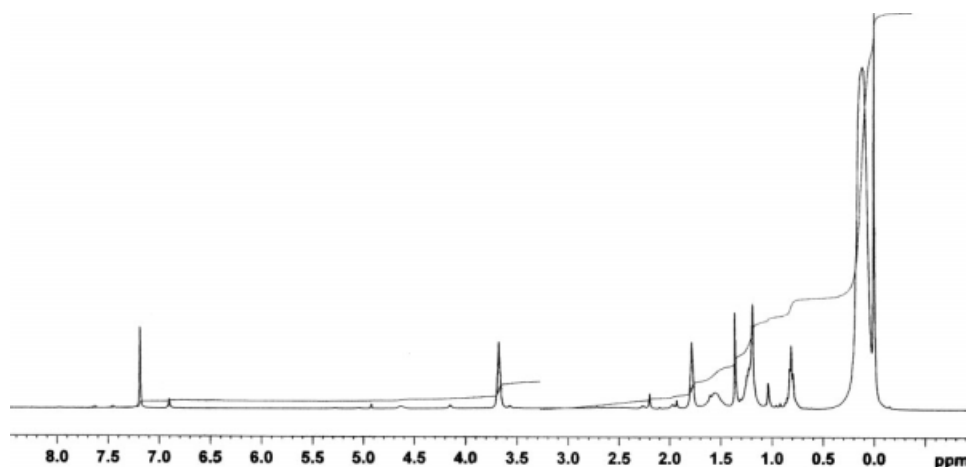


Figure 3 $^1\text{H-NMR}$ of the poly(methylsilylene).

RESULTS AND DISCUSSION

The simple application of electricity, in the form of a series of four 1.5-V batteries (total 6 V), to a mixture of methyltrichlorosilane and SDS in acetonitrile, produces the distinctive yellow color of PMSy. A general reaction scheme is shown in Scheme 1.

Indeed, PMSy and all these types of polymers have a unique UV/visible spectrum given in Figure 1, which consists of a broad intense absorption in the UV tailing down to the visible; identical spectra are seen in this work.

The presence of a polymeric product is confirmed by GPC. The number-average molecular weight is about 6000. Tests for the presence of chlorine/chloride prove negative, and any other elemental analysis is precluded because of the well-known difficulties encountered when analyzing these types of polymers and other ceramic precursors.^{5,6}

The FTIR spectrum is shown in Figure 2 and is almost identical to the one reported in the Wurtz coupling synthesis of PMSy; indicating little Si—O—Si and Si—H impurities.

They are also known to have broad NMR resonances due to a random network structure of the polymer backbone. $^1\text{H-NMR}$ is shown in Figure 3 and gives the expected broad Si—CH₃ resonance between 0 and 0.5 ppm and no appreciable amounts of either SiH₂, SiH (~ 3.5 ppm) or SiHCl, SiOH (>5 ppm), and electrolyte.

All these data are consistent with the other two reports of the synthesis of PMSy and confirm the presence of high-purity PMSy.^{3,4}

Of course, this synthesis could become chemically even more rudimentary by using an electrolyte such as sodium chloride or lithium bromide. However, there are problems with this; that is, whichever electrolyte is employed has to be soluble in the solvent used, and therein lies the difficulties we have faced in attempting such a move. Water is an obvious candidate, but methyltrichlorosilane rapidly hydrolyzes in the presence of water and any attempt at polymerization is futile; indeed, this is why the acetonitrile has to be distilled before use. Very simple ionic salts are also soluble in solvents like ether; however, ether is not a suitable solvent as it is not stable when 6 V of electricity is applied. Further work is continuing in this area.

CONCLUSION

Here, we have described an attractive method for the synthesis of poly(methylsilylene). As the polymer is soluble, this makes the production of silicon carbide of any possible shape.

References

1. Nur, Y.; Seyyidođlu, S.; Pitcher, M. W.; Toppare, L. K. *J Macromol Sci Pure Appl Chem* 2008, 45, 358.
2. Seyferth, D. *Adv Chem Ser* 1995, 245, 131.
3. Pitcher, M. W.; Joray, S. J.; Bianconi, P. A. *Adv Mater* 2004, 16, 706.
4. Vermeulen, L. A.; Smith, K.; Wang, J. *Electrochim Acta* 1999, 45, 1007.
5. Young, R. S. *Analyst* 1982, 107, 721.
6. Bradley, H. B. *Standard Methods of Chemical Analysis*, 6th ed.; D. Can Nostrand Company: Princeton, 1962; Vol. 1, p 963.