

Electrochemical Synthesis of Poly(methylsilyne) and Investigation of the Effects of Parameters on the Synthesis

Damla Eroglu,¹ Yusuf Nur,² Goknur Bayram,¹ Levent K. Toppare²

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

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

Received 12 August 2009; accepted 2 May 2010

DOI 10.1002/app.32725

Published online 1 July 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This study aims to synthesize poly(methylsilyne) by electrochemical reduction of methyltrichlorosilane at a constant potential of -6 V, while investigating the effects of parameters such as the nature of the electrode, solvent and supporting electrolyte, the monomer/solvent ratio, and the reaction time on the properties of the products. The polymer was characterized by $^1\text{H-NMR}$ (Proton Nuclear Magnetic Resonance Spectroscopy), FTIR (Fourier Transform Infrared Spectroscopy), UV-Visible Spectroscopy, and TGA (Thermogravimetry Analysis). Copper (Cu) electrodes were used as stainless steel introduced impurities into the system. In an electrolytic media consisting of acetonitrile (AN), sodium dodecyl sulfate (SDS), and Cu electrodes, increasing the monomer/solvent ratio and the reaction time affected the system negatively based on the purity of poly

(methylsilyne) in the final product. Reproducible results were only achieved in an electrolytic media containing 1,2-dimethoxyethane (DME) and tetrabutylammonium perchlorate (TBAP). In this system, the purity of the products was less dependent on monomer/solvent ratio and reaction time. The color and the $^1\text{H-NMR}$, FTIR, and UV-Visible spectra proved that the product is poly(methylsilyne). In addition, the significantly high-average decomposition temperature obtained from TGA results revealed that the polymer is a good candidate as an additive for improving thermal stability and flame retardancy in thermoplastics. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3049–3057, 2010

Key words: preceramic polymers; poly(methylsilyne); electrochemistry; synthesis; inorganic polymers

INTRODUCTION

As ceramic materials like silicon carbide are commonly used in many applications as hard, light-weight, temperature, and wear resistant materials, preceramic polymers that can be converted into silicon-based ceramics upon pyrolysis, have been widely studied.^{1,2} These preceramic polymers are also used in the synthesis of cellular porous ceramic foams¹ and as additives in common thermoplastics to improve their flame retardancy and thermal properties.^{3–7}

Silicon-based preceramic polymers gained great importance for the last 30 years since production of silicon carbide by polymer pyrolysis is the most efficient and successful method.¹ Polysilanes, $[\text{SiR}_2]_n$, are high-yield precursors of silicon carbide, and they are commonly studied because of their potential applications as conducting polymers, photoresist materials, and nonlinear optical materials.^{8,9} Polysi-

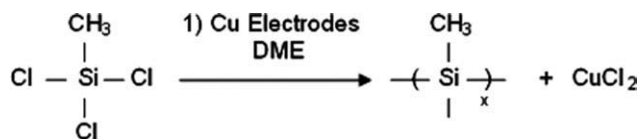
lynes, $[\text{SiR}]_n$, in other words network polysilanes, are a relatively new class of preceramic polymers. They were first synthesized in 1988 by Bianconi and Weidman.¹⁰ They exhibit a broad UV band that tails into the visible region unlike the polysilanes and hence, they have interesting visible absorption and emission characteristics.^{11,12} The polysilanes and related polysilynes are generally synthesized by the reductive coupling of dichlorosilanes and trichlorosilanes via Wurtz synthesis which utilizes alkali metal reducing agents in high-boiling solvents.^{9,10,13–17}

Poly(methylsilyne), $[\text{SiCH}_3]_n$, is a relatively new member of poly(alkylsilyne) family, and it is a promising silicon carbide precursor with its optimum Si : C ratio of 1 : 1 and solubility in common nonpolar organic solvents.² In literature, poly(methylsilyne) is synthesized by a modified sono-chemistry² and also by electrochemical polymerization of methyltrichlorosilane, which does not require high-boiling solvents or alkali metal reducing agents.^{11,12} In our previous study, poly(methylsilyne) was synthesized electrochemically using simply a series of batteries with an anionic surfactant as the supporting electrolyte in small-scale (25 mL undivided cell).¹⁸

In this study, poly(methylsilyne) was produced by electrochemical polymerization (Scheme 1) under constant supply of -6 V in larger scale (200 mL undivided cell) and the effects of parameters such as

Correspondence to: G. Bayram (gbayram@metu.edu.tr).

Contract grant sponsor: The Scientific and Technological Research Council of Turkey (TUBITAK); contract grant number: 107M031.



Scheme 1 Electrochemical synthesis of poly(methylsilylene).

the electrode, solvent and supporting electrolyte types, monomer/solvent ratio and reaction time were investigated. A comprehensive characterization was made in terms of $^1\text{H-NMR}$, FTIR, UV-Visible Spectroscopy, SEM, and TGA analyzes.

EXPERIMENTAL

Materials

Methyltrichlorosilane ($\geq 97\%$) was purchased from Aldrich (Taufkirchen, Germany) and used as received. The solvents; acetonitrile, AN (dried, max. 0.005% H_2O) and 1,2-dimethoxyethane, DME (anhydrous, 99.5%), were obtained from Merck (Darmstadt, Germany) and Aldrich, respectively. Sodium dodecyl sulfate, SDS (ACS reagent, $\geq 99.0\%$) (Aldrich) and tetrabutylammonium perchlorate, TBAP ($\geq 98.0\%$) (Fluka) were used as the supporting electrolytes. Lithium aluminum hydride, LiAlH_4 , purchased from Merck was used to convert the remaining Si-Cl bonds into Si-H bonds. Toluene (extra pure) that was used in the purification of the polymer was obtained from Merck.

Electrochemical synthesis of poly(methylsilylene)

The electrochemical reduction of methyltrichlorosilane was carried out in a 200 mL undivided cell. After the supporting electrolyte was added to the cell and cleaned electrodes (2.5×7.5 cm plates as both electrodes) were placed, cell was closed and purged with argon. Then, the solvent and the monomer were injected into the cell. Finally, the electrodes were connected to the power source, and the electrolysis was started. The reaction was carried out at a constant potential of -6 V^{11-12,18} under argon

atmosphere. After the electrolysis, the solution was stirred over 100 mg of LiAlH_4 for 3 h under argon atmosphere. The solution was then filtered using filter paper, and the product was obtained after the solvent was evaporated. The products synthesized using SDS as the supporting electrolyte were not purified because of the low presence of SDS in the products (as SDS has a very low solubility in AN, all the excess SDS were filtered before the evaporation of AN). The products that are synthesized using TBAP were purified by first dissolving in toluene, then filtering the undissolved impurities using a filter paper and finally evaporating the solvent of the solution containing the polymer.

During the electrochemical synthesis of poly(methylsilylene), copper or 413 No. stainless steel plates were used as the electrodes and AN or DME were used as the solvents. Two different supporting electrolytes were used throughout the experiments, SDS and TBAP. In addition, the monomer/solvent ratio (volume ratio) was changed as 1/5, 1/10, and 1/20. Finally, the effect of reaction time was investigated with 30 min, 1 h and 4 h of electrolysis times. The experimental parameters are tabulated in Tables I and II.

The reaction mechanism of the synthesis of poly(methylsilylene) was not investigated in this study; however, a reaction mechanism analogous to the formation of the linear polysilanes from dichlorosilane monomers were proposed previously in the literature for the electrochemical synthesis of poly(methylsilylene).¹² In their study, Vermeulen et al. proposed that electrochemical synthesis of polysilylenes are composed of both electrode and thermal processes.¹²

Characterization of poly(methylsilylene)

The polymer was primarily characterized by its yellow color that is distinctive for polysilylenes.^{10-12,18} The products were characterized by $^1\text{H-NMR}$ and FTIR. UV-Visible Spectroscopy, SEM, and TGA analyzes were used for further characterization and carried out only for the products with the best $^1\text{H-NMR}$ and FTIR results. $^1\text{H-NMR}$ spectra were

TABLE I
Experimental Parameters of the Electrochemical Synthesis

	PMS-D-SS	PMS-D-CU	PMS1/5	PMS1/10	PMS-D-1/5	PMS-D-1/10	PMS-D-1/20
Electrode type	SS	Cu	Cu	Cu	Cu	Cu	Cu
Solvent type	DME	DME	AN	AN	DME	DME	DME
Supporting electro. type	TBAP	TBAP	SDS	SDS	TBAP	TBAP	TBAP
Supporting electro. amount	1.88 g	1.88 g	0.400 g	0.400 g	2.052 g	1.88 g	3.59 g
Monomer amount	5 mL	5 mL	10 mL	5 mL	10 mL	5 mL	5 mL
Solvent amount	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL	100 mL
Monomer to solvent ratio	1/10	1/10	1/5	1/10	1/5	1/10	1 mL/20 mL
Reaction time	30 min	30 min	30 min	30 min	30 min	30 min	30 min

TABLE II
Experimental Parameters of the Electrochemical Synthesis

	PMS30M	PMS1H	PMS4H	PMS-D-30M	PMS-D-1H	PMS-D-4H
Electrode type	Cu	Cu	Cu	Cu	Cu	Cu
Solvent type	AN	AN	AN	DME	DME	DME
Supporting electro. type	SDS	SDS	SDS	TBAP	TBAP	TBAP
Supporting electro. amount	0.400 g	0.400 g	0.400 g	1.88 g	1.88 g	1.88 g
Monomer amount	5 mL	5 mL	5 mL	5 mL	5 mL	5 mL
Solvent amount	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL
Monomer to solvent ratio	1/10	1/10	1/10	1/10	1/10	1/10
Reaction time	30 min	1 h	4 h	30 min	1 h	4 h

obtained in deuterated chloroform using a Bruker-Spectrospin Avance DPX 400 Ultra-Shield (400 MHz). FTIR spectra were collected by IR Prestige-21 SHIMADZU FTIR spectrometer (THF solution on KBr pellet). UV-Visible spectra were obtained on a HP8453A UV-Visible spectrometer using cyclohexane as the solvent. For the SEM analysis, a low voltage JEOL JSM-6400 scanning electron microscope was used. TGA was performed using a SHIMADZU 60H-DTG machine at nitrogen atmosphere, in the temperature range from room temperature to 800°C with the heating rate of 20°C min⁻¹.

RESULTS AND DISCUSSION

The effect of electrode type

The use of stainless steel and copper electrodes on the properties of the polymer synthesized were investigated in the electrolytic media containing AN as the solvent and SDS as the supporting electrolyte. When stainless steel electrodes were used in the electrolysis, with increasing reaction time or monomer/solvent ratio, products with unusual colors were obtained. The dark colors obtained in these products are explained by the impurities coming

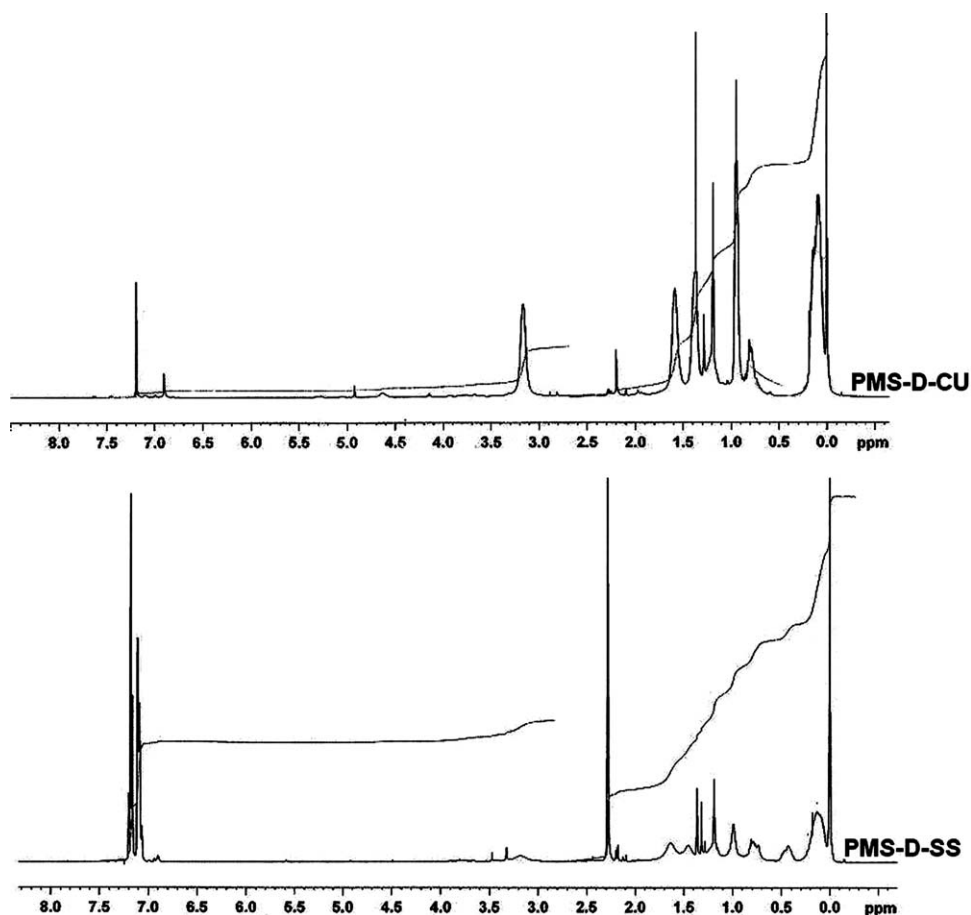


Figure 1 1H-NMR spectra of poly(methylsilyne) with different electrode types; copper electrodes (PMS-D-CU) and stainless steel electrodes (PMS-D-SS) in DME.

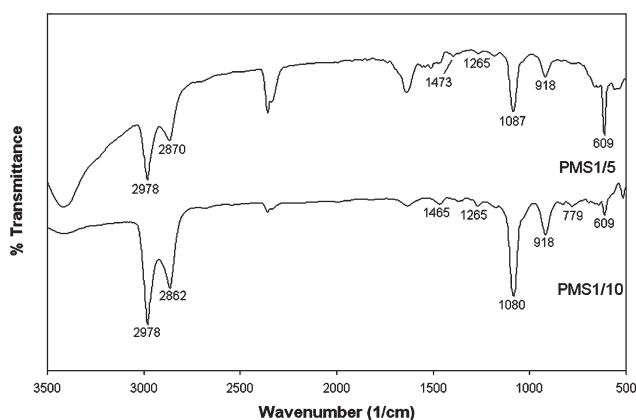


Figure 2 FTIR spectra of poly(methylsilylene) with different monomer/solvent ratios; 1/5 (PMS1/5) and 1/10 (PMS1/10) in AN.

from the stainless steel electrodes during electrolysis, especially with increasing reaction time. When copper electrodes were used in the electrolysis such problems were eliminated. The products obtained for each reaction time and monomer/solvent ratio have yellow color as expected.

The effect of electrode type in the medium containing DME and TBAP was studied for stainless steel electrodes (PMS-D-SS) and copper electrodes (PMS-D-CU). Each time a reaction time of 30 min and monomer/solvent ratio of 1/10 were employed. When the physical properties of the samples are compared, it was seen that PMS-D-SS has also yellow color unlike the samples with stainless steel electrodes in AN.

In the $^1\text{H-NMR}$ spectra of the samples (Fig. 1), the characteristic poly(methylsilylene) peak, which is a broad, significant peak between 0–0.4 ppm (Si-CH_3) was observed. This reveals that poly(methylsilylene) was successfully synthesized in both experiments.^{11–12,18} It can be concluded that stainless steel electrodes do not cause a significant problem in the product as the reaction time is short.

The effect of monomer/solvent ratio

The effect of monomer/solvent ratio in the system with AN and SDS was investigated for the samples with the feed ratios of 1/5 (PMS1/5) and 1/10 (PMS1/10). Cu electrodes were used in each trial with a reaction time of 30 min. PMS1/5 yielded a yellow oil whereas PMS1/10 a yellow solid. Therefore, it can be concluded that by replacing stainless steel electrodes with the copper electrodes, the effect of monomer/solvent ratio on the color of the product was eliminated. However, it can be seen that the decrease in monomer/solvent ratio still creates a difference in the physical properties. Poly(methylsilylene) was synthesized both as an oil and a solid in litera-

ture, because of the differences in the molecular weights of the products.^{2,11,12}

The FTIR and $^1\text{H-NMR}$ spectra of the samples are shown in Figures 2 and 3, respectively. The FTIR spectra of the products are very similar to the results in literature revealing all the expected peaks for poly(methylsilylene) at 2978, 2862 cm^{-1} (C-H , Si-CH_3); 1473, 1265 cm^{-1} (C-H , Si-CH_3); and 918 cm^{-1} (SiH_2).^{2,12} An intense peak around 1080 cm^{-1} is observed in the FTIR result. This intense Si-O-Si band is also present in the FTIR result of poly(methylsilylene) in the studies in literature and generally explained by the reactivity of the monomer towards oxygen.^{2,11,12} The intensity of the peak is not an indication of the excess amount of this bond. Even small amounts of Si-O-Si will give an intense absorption at this region.¹⁹

The characteristic Si-CH_3 peak can be seen in both $^1\text{H-NMR}$ spectra between 0 and 0.4 ppm. In addition, there are peaks around 3 and 5 ppm corresponding to Si-H and Si-H_2 bonds in the polymer. When the two results are compared, PMS1/10 sample with a lower monomer/solvent ratio has a spectrum with a more significant Si-CH_3 peak. In addition, the peaks observed around 6.17 ppm for PMS1/5 sample (probably because of SiHCl and SiOH impurities) are not observed for PMS1/10

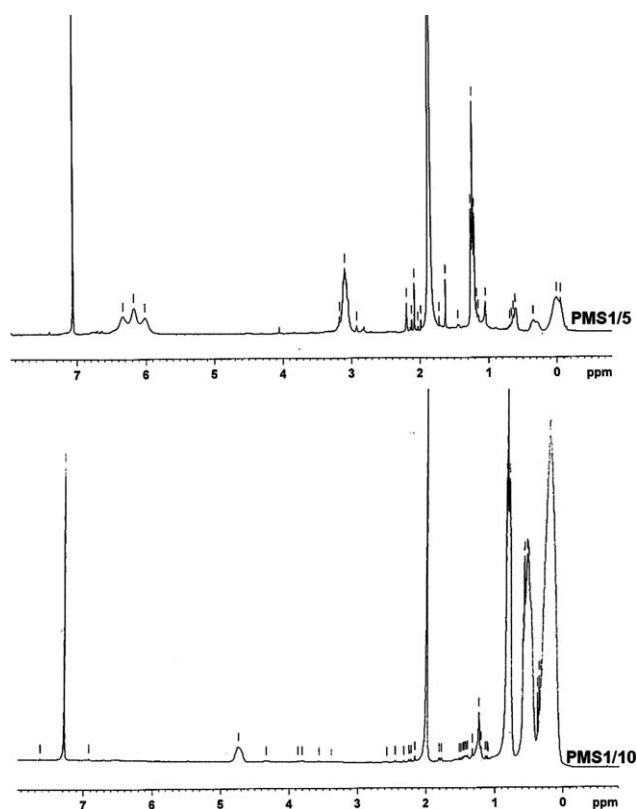


Figure 3 $^1\text{H-NMR}$ spectra of poly(methylsilylene) with different monomer/solvent ratios; 1/5 (PMS1/5) and 1/10 (PMS1/10) in AN.

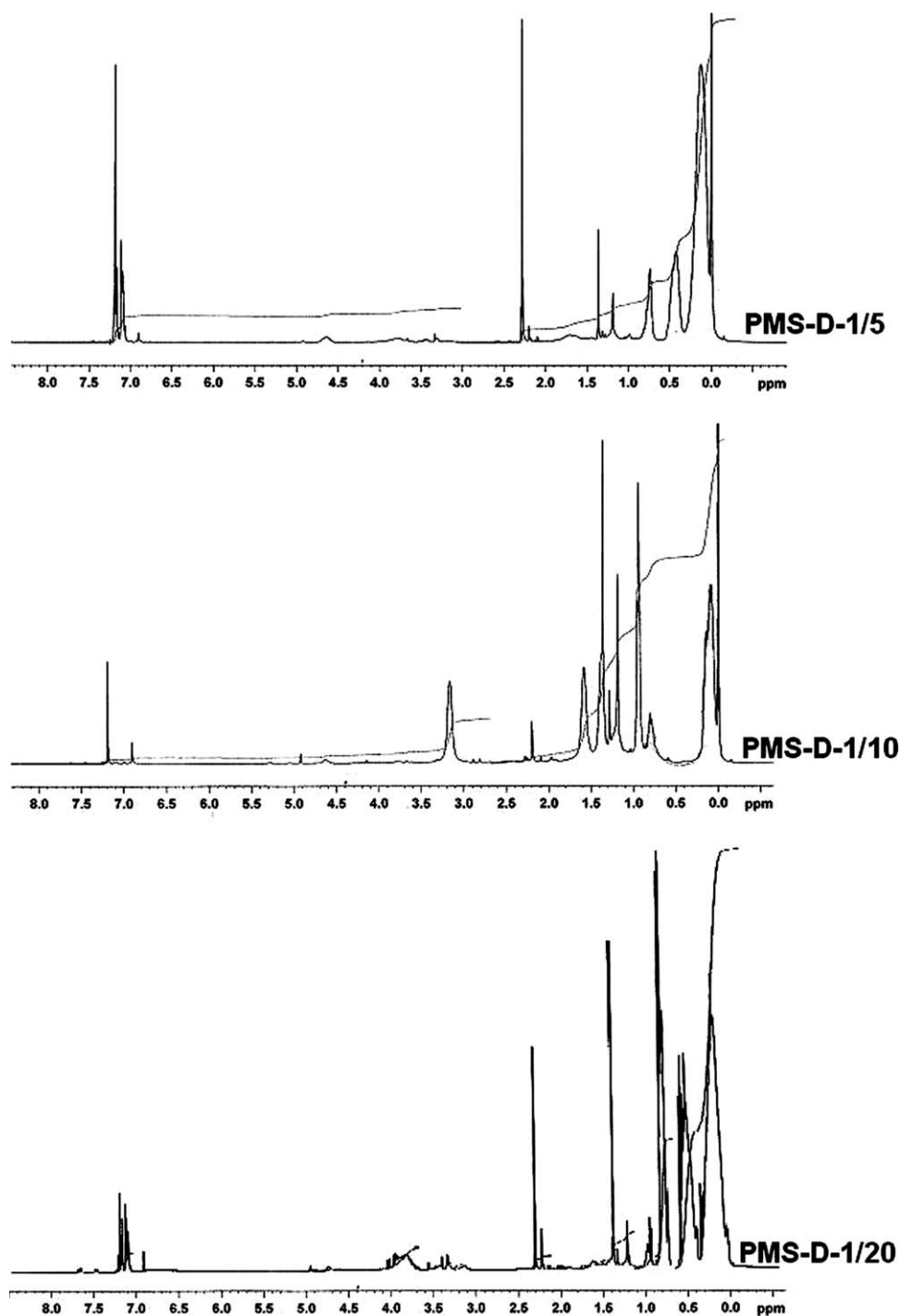


Figure 4 ¹H-NMR spectra of poly(methylsilylene) with different monomer/solvent ratios; 1/5 (PMS-D-1/5), 1/10 (PMS-D-1/10), and 1/20 (PMS-D-1/20) in DME.

sample. Both spectra exhibit some peaks corresponding to AN, SDS, and CHCl₃ around 2 ppm, 0.8 ppm, and 7 ppm, respectively.

As a result of the FTIR and ¹H-NMR spectra of the products, it was concluded that in the electrolytic medium with AN, SDS, and Cu electrodes, decreasing the monomer/solvent ratio has a positive effect on the purity of the product.

The effect of monomer/solvent ratio in a medium with DME, TBAP, and Cu electrode was investigated for samples with monomer/solvent ratios of 1/5 (PMS-D-1/5), 1/10 (PMS-D-1/10), and 1/20 (PMS-D-1/20). Each run was allowed for a reaction time of 30 min. From the ¹H-NMR results shown in Figure 4, it can be concluded that all three samples exhibit a broad significant Si—CH₃ peak between 0 and 0.5

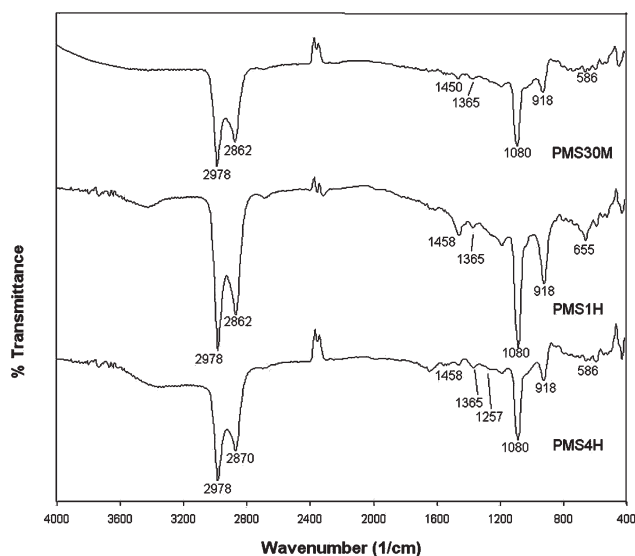


Figure 5 FTIR spectra of poly(methylsilylene) with different reaction times; 30 min (PMS30M), 1 h (PMS1H), and 4 h (PMS4H) in AN.

ppm. This proves that the polymer was successfully synthesized for each monomer/solvent ratio. Therefore, monomer/solvent ratio has no significant effect in an electrolytic medium containing TBAP and DME.

The effect of reaction time

The effect of reaction time was investigated for the samples with reaction times of 30 min (PMS30M), 1 h (PMS1H), and 4 h (PMS4H) in a medium containing AN, SDS, and Cu electrodes. All the feed ratios were 1/10, because in the previous trials this ratio gave the best $^1\text{H-NMR}$ results. All the products have yellow colors as expected for polysilynes. The FTIR and $^1\text{H-NMR}$ spectra of the polymers can be seen in Figures 5 and 6, respectively. The FTIR results are very similar to each other exhibiting all the expected peaks. From the $^1\text{H-NMR}$ spectra of the polymers, it can be concluded that with increasing reaction time, the significance of Si-CH_3 peak decreases. This shows that increasing the reaction time in this system has a negative effect on the synthesis, which is most probably because of the increase in the impurities introduced by the decomposition of the electrodes.

In the electrolytic media containing DME, TBAP, and Cu electrodes, the effect of reaction time was also investigated with reaction times of 30 min (PMS-D-30M), 1 h (PMS-D-1H), and 4 h (PMS-D-4H). Monomer/solvent ratio was taken as 1/10 for each experiment. When the physical properties of the samples are compared, it is seen that PMS-D-1H and PMS-D-4H have an orange color whereas PMS-D-30M has a yellow color. This is most probably because of differences in the molecular weights of the polymers aroused by longer reaction time.

All samples exhibit the expected broad Si-CH_3 peak in the $^1\text{H-NMR}$ spectra (Fig. 7). In the medium containing AN and SDS, increasing the reaction time affects the product purity. This negative effect was

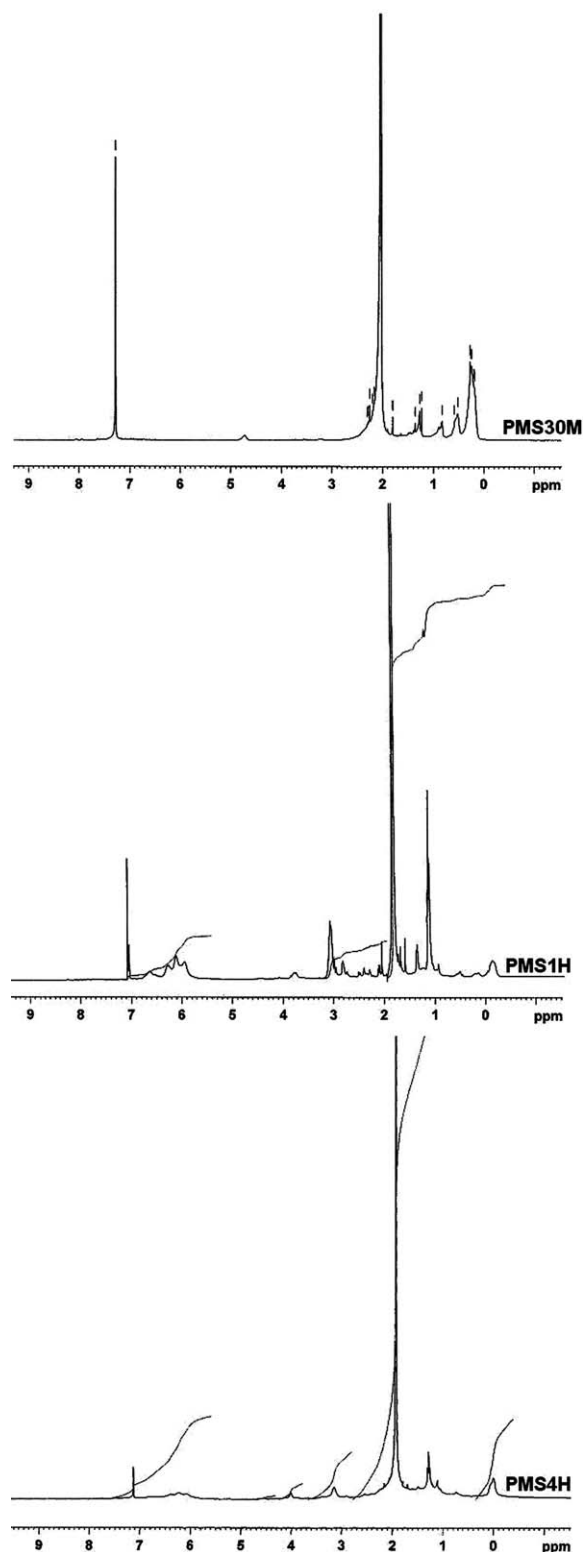


Figure 6 $^1\text{H-NMR}$ spectra of poly(methylsilylene) with different reaction times; 30 min (PMS30M), 1 h (PMS1H), and 4 h (PMS4H) in AN.

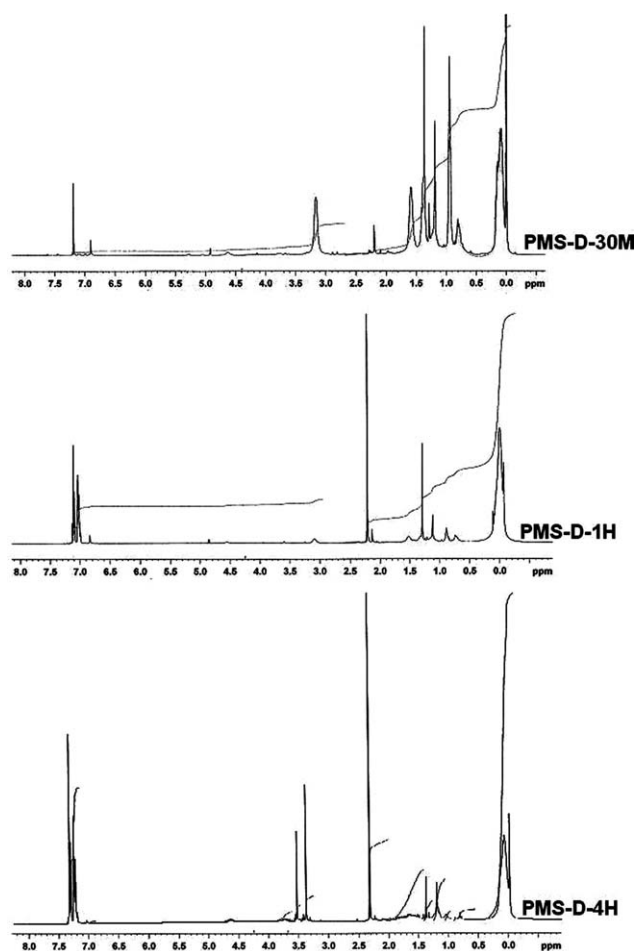


Figure 7 $^1\text{H-NMR}$ spectra of poly(methylsilylene) with different reaction times; 30 min (PMS-D-30M), 1 h (PMS-D-1H), and 4 h (PMS-D-4H) in DME.

eliminated in the system with DME and TBAP, as most probably the impurities coming from the decomposition of electrodes were minimized.

The effect of supporting electrolyte type

In the medium with AN and Cu electrodes, the effect of supporting electrolyte type was investigated for the samples containing SDS (PMSSDS) and TBAP (PMSTBAP). Both experiments were performed with a monomer/solvent ratio of 1/10 and a reaction time of 30 min. The most significant effect of the supporting electrolyte type on the synthesis was the increase in the current. The current, which is lower than 0.01 A for PMSSDS sample, increases up to 0.09 A for PMSTBAP. Therefore, using TBAP instead of SDS increases the current by nearly 10 times. When the $^1\text{H-NMR}$ results of the samples are compared, it is seen that peaks, because of to TBAP (0.5–1.6 ppm) suppress the expected Si–CH₃ peak in the spectrum since TBAP was significantly present in the product. This problem does not occur in the samples with SDS since its amount in the product is very limited

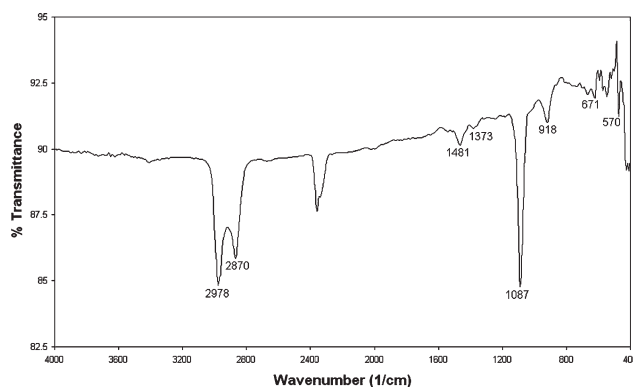


Figure 8 FTIR spectrum of poly(methylsilylene).

due to its low solubility in AN. Therefore, purification is required for the samples with TBAP to observe the expected Si–CH₃ peak in NMR results.

Reproducibility of the method

In the system containing AN and SDS, $^1\text{H-NMR}$ and FTIR results prove that the polymer synthesized is poly(methylsilylene) for a monomer/solvent ratio of 1/10 and a reaction time of 30 min. However, this system has problems in terms of reproducibility as the products synthesized with the same method have significantly different colors. Also $^1\text{H-NMR}$ results revealed differences in Si–CH₃ peaks. These problems in the reproducibility of the electrochemical polymerization were not observed for the medium with DME and TBAP. There may be two reasons for that. The first reason is the low current (0.01 A) passing through the electrolyte containing SDS. SDS was used as the supporting electrolyte because it is a simple anionic surfactant, which does not create a significant amount of impurity in the end product because of its low solubility. However, as it is not soluble in AN, the electrolytic media does not have enough ionic conductivity. Second, it is suspected that AN and LiAlH₄ give an undesired reaction during stirring introducing unwanted

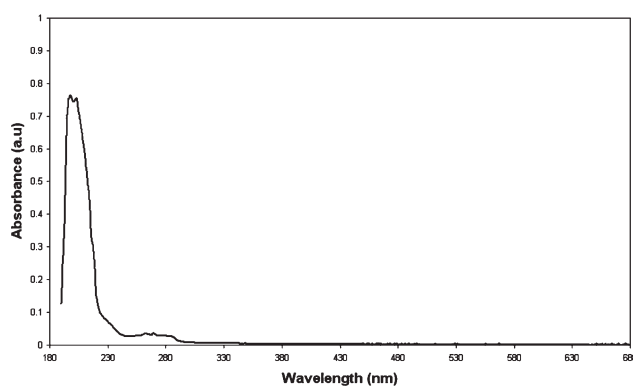


Figure 9 UV-Visible spectrum of poly(methylsilylene).

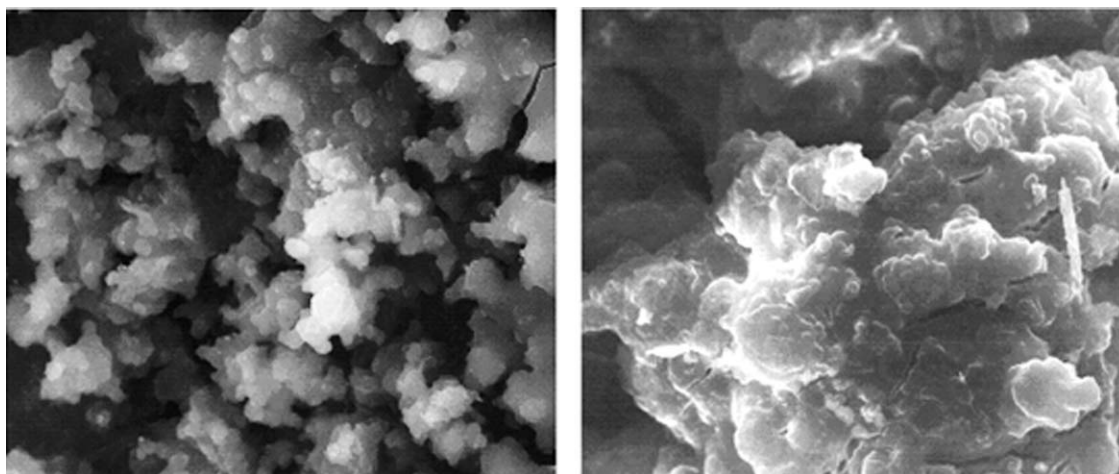


Figure 10 SEM micrographs of poly(methylsilylene) at x5000 magnification.

impurities which affects the reproducibility of the method.

FTIR, UV-visible, SEM and TGA results of poly(methylsilylene)

Further characterization results are given for the electrolyte containing DME and TBAP with a monomer/solvent ratio of 1/10 and a reaction time of 30 min since poly(methylsilylene) was produced in this media with no reproducibility problems.

The FTIR spectrum of the polymer (Fig. 8) is very similar to the ones in literature showing the expected C—H (Si—CH₃) peaks at 2978, 2870, 1481 and 1373 cm⁻¹, SiH₂ peaks at 918 cm⁻¹ and Si—C peak at 671 cm⁻¹. The peak at 1087 ppm corresponding to Si—O—Si is expected due to the reactivity of the polymer toward oxygen.

The UV-Visible spectrum (Fig. 9) with a broad UV band tailing down the visible region around 400 nm exhibits the characteristic behavior of polysilylenes. This UV-Visible spectrum proves the branched structure of the polymer, because linear polysilanes have a completely different spectrum with two sharp absorption peaks.^{13,15}

The SEM micrographs of poly(methylsilylene) are shown in Figure 10. In terms of morphology, it can be seen from the figure that the polymer is made up of particles which are irregular in shape and form as agglomerates.

The molecular weight of poly(methylsilylene) was tried to be calculated using GPC method for each sample, however reasonable results could not be obtained. The reason of the failure of GPC is most probably the remnants of supporting electrolyte in the polymer. Calculation of molecular weight using Mark-Houwink-Sakurada Equation was also considered, however as poly(methylsilylene) is a relatively new polymer, the K and a values are not present in the literature for this polymer.

Silicon-based preceramic polymers are commonly studied in literature to improve the flame retardancy properties and thermal stabilities of thermoplastics.³⁻⁷ Hence, to show the potential use of poly(methylsilylene), thermogravimetry analysis was performed. TGA curve of the polymer is shown in Figure 11. Poly(methylsilylene) has a very high-thermal stability with an average decomposition temperature of 730°C. The ceramic yield of SiC is significantly dependent on the ramp rate and the physical properties of the polymer.² The pyrolysis conditions that were used to prepare SiC films in the literature² are greatly different than the conditions in TGA. Therefore, the final ceramic yield of TGA cannot be compared with the SiC yield as a result of pyrolysis. However, when the ceramic yield of the polymer around 500°C (Fig. 11) is considered, the ceramic yield is around 90%, which is very high as expected. Although this value is still lower than the theoretical value, because the product also includes low-molecular weight oligomers.² This result shows that poly(methylsilylene) can be a good candidate as an additive for thermoplastics to improve their thermal properties.

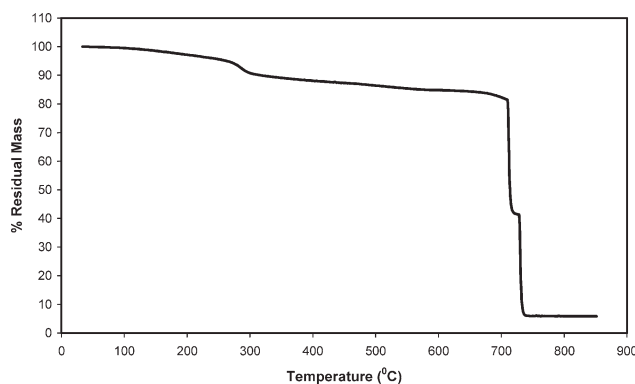


Figure 11 TGA curve of poly(methylsilylene).

CONCLUSIONS

The synthesis of poly(methylsilyne) by the electrochemical reduction of methyltrichlorosilane was studied based on the effects of the parameters in the synthesis. Parameters such as the electrode material, supporting electrolyte, solvent, monomer/solvent ratio and reaction time were studied. For the electrolytic media containing AN, SDS, and stainless steel electrodes, with increasing monomer/solvent ratio and reaction time, unusual dark colors were obtained for the products. These differences in the colors of the products were attributed to the impurities arising from the decomposition of stainless steel anode with increasing reaction time. This problem was not observed for the electrolyses with Cu electrodes.

For the electrolyte with AN, SDS and copper electrodes, increasing the monomer/solvent ratio and the reaction time affected the product purity. The reason for this negative effect was attributed to the impurities resulting from the decomposition of the electrodes with increasing time. Although the polymer was synthesized successfully with these reaction conditions, reproducibility could not be maintained.

The effect of supporting electrolyte was also examined. The low current for SDS electrolyte was probably one of the reasons in reproducibility. With the use of TBAP, a better supporting electrolyte, the current increased significantly.

DME was also used as the solvent since a reaction between AN and LiAlH_4 affected the reproducibility. It was observed that in the electrochemical synthesis with DME and TBAP, successful results were obtained after purifying the product with toluene. The properties of the products were less dependent on the monomer/solvent feed ratio and the reaction time unlike for the system with AN and SDS.

The reaction yield could not be determined for different reaction conditions since the polymer could

not be completely separated from the supporting electrolyte for the products both synthesized using SDS and TBAP.

Finally, it was concluded that the polymer has a very high-thermal stability, which can be used for improving the thermal and flame retardant properties of thermoplastics in future.

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