

Lewis Acid Mediated Polymerization of Poly(dimethylsiloxane) Polymers: Investigating Reaction Kinetics Using Both NMR Spectroscopy and Cyclic Voltammetry

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ABSTRACT: Bulk condensation polymerization of (dimethylmethoxy)-*m*-carborane and (dichlorodimethyl)silane occurs in the presence of an $M^{x+}Cl_x$ Lewis acid catalyst. In the literature, $FeCl_3$ is commonly used as the catalyst of choice but little is known about the activation energy and entropy of this polymerization. By monitoring using ¹H-NMR the reaction of a methoxy-terminated poly(dimethylsiloxane) and (dichlorodimethyl)silane the rate determining step in the $FeCl_3$ catalyzed system is determined. The activation energy was calculated to be +43.6 kJ mol⁻¹ and the entropy of the reaction was also calculated. The calculated large entropy of reaction indicates that the transition step is highly ordered. The formation of the electrophile intermediate species in the first

step of the reaction has also been investigated using cyclic voltammetry. To the cyclic voltammetry data Randles-Sevcik fits have been applied to the oxidation peaks to determine the diffusion coefficients for the oxidation of Fe^{2+} to Fe^{3+} . Also, the initial prediction of a reversible reaction Step 1 was shown to be incorrect as the normalized reduction peak maxima increase with scan rate, indicative of an electron transfer-chemical reaction mechanism. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2601–2608, 2012

Key words: poly(dimethylsiloxane); carborane; Lewis acid catalysis; group transfer polymerization; kinetics; nuclear magnetic resonance; cyclic voltammetry; Randles-Sevcik

INTRODUCTION

The syntheses of carborane-siloxane copolymers have been reported in the literature for more than forty years.¹ These copolymers are of interest due to their high thermal stability, relative to siloxane homopolymers. This thermal oxidative resistance is believed to be due to the fact that the carborane cluster unit has significant electron delocalization,² consequently stabilizing the copolymer.³ One of the first methods of producing the copolymers was to use a Lewis acid catalyst, in particular $FeCl_3$ to mediate the reaction of a (dimethylmethoxy)-*m*-carborane with (dichlorodimethyl)silane as shown in Figure 1.⁴ Further use of $FeCl_3$ as the Lewis acid catalyst of choice has recently been discussed^{5–7} in the hope of producing well defined siloxane elastomers with high carborane content. However, the product

of this reaction is not a linear polymer but a cross-linked elastomer where the catalyst is trapped within the matrix of the elastomer network. Cross-linking occurs due to the liberation of HCl from the catalyst, which then reacts with the $-CH_3$ side group on the (dimethyl)siloxane polymer repeat unit, the mechanism of which is discussed by Peters.⁸ This unwanted side reaction can be slowed by keeping the polymerization formulation dry and carrying out the reaction in a nonoxidative environment but for practical applications, this is not always ideal.

Further investigation of the polymerization reaction, when carried out in place of another transition metal chloride would be ideal to determine whether $FeCl_3$ is indeed the optimum catalyst. Hard acid and soft base theory⁹ predicts that the best coupling of Lewis acid and Lewis base comes from hard-hard or soft-soft interactions. By adjusting the metal center in the catalyst the orbital interactions of the subsequent Lewis acid-base pairing will change, affecting the reactivity of the condensation. The production of truly linear polymers would be more advantageous using another catalyst than having to quench the $FeCl_3$ reaction.

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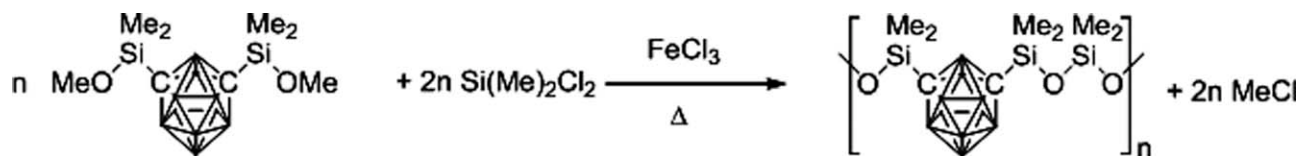


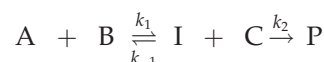
Figure 1 Bulk condensation of (dimethylmethoxy)-*m*-carborane with (dichlorodimethyl)silane in the presence of FeCl_3 .

In this study, we focus on the FeCl_3 system using a model reaction as carborane monomers are highly expensive and the cost of completing such a comprehensive study would be excessive. To determine the kinetics, the reaction will be carried out using a methoxy-capped PDMS and will allow us to determine the optimum conditions in which to evaluate the energy of activation for this reaction. The reaction scheme is shown in Figure 2.

To be able to determine the activation energy, the rate determining step must be studied so it is important to discount the least likely rate determining steps first. The third reaction step involving k_3 can be immediately rejected, as gas formation will be rapid due to the instability of the methyl cation. The reaction step involving k_1 and k_{-1} requires the use of electrochemistry to investigate the equilibrium and subsequently determine reversibility of the system. However, during the reaction the catalyst and (dichlorodimethyl)silane will approach equilibrium quickly. This is due to the low levels of catalyst present in the solution restricting the amount of electrophile that can be present at any one time. Reaction Step 2 is most likely to be the rate determining step, as it requires the electrophile to be in the vicinity of the methoxy end-capped group and the electrophile to propagate for longer times as the viscosity of the solution rises with increasing molar mass of poly(siloxane) polymer. In addition, electrophile formation at lower temperatures might be less likely so the intermediate species could be reduced in concentration further. This would suggest that reaction Step 2 would be the rate-determining step.

There are a few complications that should be noted. First, the polymer is also the solvent for the reaction which complicates the measuring of the kinetic behavior. In addition, when measuring the rate constant, normal solution kinetic assumptions may not apply due to the change in viscosity as the reaction proceeds. Moreover, the stability of the electrophile may vary with temperature but this is not predictable and can only be determined by experimentation.

In terms of defining the complex reaction rate the following kinetic analysis may be envisaged,¹⁰ based on the overall reaction.



A simplified reaction rate scheme for the polymerization is shown above where A is (dichlorodimethyl)silane, B is FeCl_3 , I is the electrophile intermediate formed and C is the methoxy capped PDMS. Assuming that [A], [B], and [I] are in equilibrium, the following assumption is then

$$k' = \frac{k_1}{k_{-1}} = \frac{[I]}{[A][B]}$$

and therefore the rate of generation of the product can be described as

$$\frac{d[P]}{dt} = k_2[I][C] = k_2k'[A][B][C].$$

This can be simplified further to the following

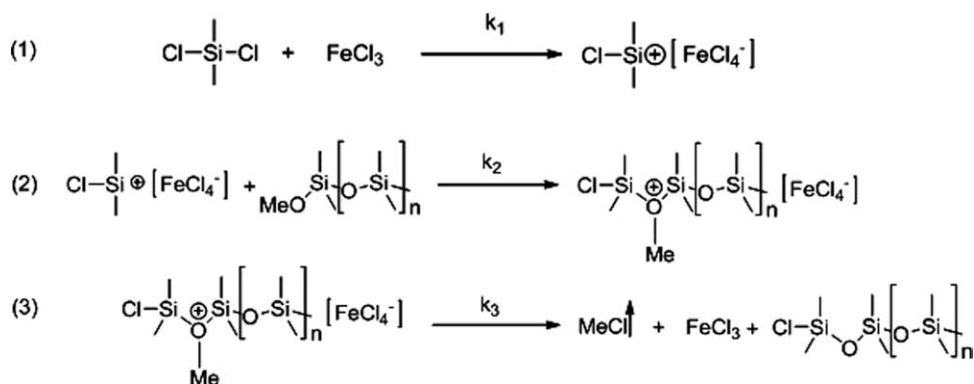


Figure 2 All possible kinetic routes in the polymerization of (dichlorodimethyl)silane and methoxy terminated poly(dimethylsiloxane) polymer mediated by FeCl_3 .

$$\frac{d[P]}{dt} = k''[A][B][C]$$

where the complex rate constant is described as

$$k'' = \frac{k_1 k_2}{k_{-1}}$$

Our model predicts that the formation of the intermediate species is reversible and this needs to be confirmed for our hypothesis to be valid. In addition, in the predicted kinetic model the rate constant obtained in the NMR study will also depend on k_1 and k_{-1} if the hypothesis is valid. This is due to the existence of the pre-equilibrium in the formation of an electrophile intermediate that is only quantifiable through the mathematical model outlined.

To obtain any meaningful data from an electrochemical study, it is important that the species of interest will give a peak that is definable before investigating any peak responsible for interrogating the behavior of the intermediate formed. In this instance generation of FeCl_3 electrochemically would be ideal as firstly we could observe a reproducible oxidation of FeCl_2 to FeCl_3 and also FeCl_2 does not react with (dichlorodimethyl)silane so we can be confident that any peaks after the oxidation are solely due to the removal of Fe^{3+} by the (dichlorodimethyl)silane to form the intermediate species as predicted. One problem that becomes apparent from attempting to make electrochemical solutions is the insolubility of FeCl_2 in pure (dichlorodimethyl)silane; in this instance we have to use a solvent to help solvate the chloride salt. This will mean that k_1 will be determined in a electrolytic solvent, which will differ from the actual reaction in which the poly(dimethylsiloxane) acts as its own solvent.

Another reason for generating the FeCl_3 from FeCl_2 is that ferric chloride will form an equilibrium with itself and complex to form the $[\text{Fe}_2\text{Cl}_6]$ dimer.¹¹ In generating small amounts of FeCl_3 , it is hoped that such an equilibrium will not have time to form as the solution will have an excess of (dichlorodimethyl)silane, which will react with all the FeCl_3 generated at the electrode.

EXPERIMENTAL

Materials

Methoxy terminated poly(dimethylsiloxane) was obtained from Fluorochem (United Kingdom). This material was found to have an M_n of 1174 g mol^{-1} by $^1\text{H-NMR}$ spectroscopy through comparison of the relative integrals of the $-\text{OCH}_3$ end group and polymer backbone $-\text{CH}_3$ group. Catalysts and other chemicals used in this project were readily obtained from Sigma Aldrich (United Kingdom).

Synthesis of a PDMS polymer using FeCl_3 catalyst for NMR study

To a 250 mL round bottom flask 8.0 g of methoxy end capped poly(dimethylsiloxane) was added. In a fume hood, (dichlorodimethyl)silane (0.890 g, 6.81 mmol) was weighed and added to the reaction vessel. The reaction vessel was heated up to 80°C in a heating block while stirring. Once equilibrated, FeCl_3 (0.0900 g, 0.547 mmol) catalyst was added such that the total amount was 1% of the total mass of the reactants. At this point, an aliquot of the supernatant solution (0.1 mL) was removed, mixed into deuterated chloroform (2 mL), and filtered into a NMR tube using a pipette filter. During the course of the reaction, similar aliquots were extracted at regular intervals (5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 120, 150, 180, and 210 min). Once the reaction had cooled sufficiently, the remaining material was filtered and collected. The 15 NMR samples were then run on a Bruker 500 NMR spectrometer. ^1H data was collected at 400 MHz, examining the loss of the $-\text{OCH}_3$ peak against reaction time. An example of the data collected at time zero is shown in Figure 3 with interpretation shown in Table I. The change in integral against time was plotted in a graph. The experiment was repeated and data collated showing error between experiments. The experiments were repeated at temperatures varying from 40 to 120°C .

The processing of data was carried out using a batch method as to avoid biasing the integrals obtained in the experiment, the resulting integrals are treated as a quantitative measure of the concentration of the methoxy group in the NMR solution. The change in concentration values are averaged between two experiments then converted to a natural logarithm and plotted against time. In plotting the graph this way, the gradient is equal to the rate constant for the experimental temperature used in the polymerization step.

To determine the kinetics of the reaction, NMR was chosen as the method of analysis. The signal at 3.5 ppm sits distinctly away from other peaks and can be easily monitored. NMR of the resulting polymer can be achieved by dissolving an aliquot of the reacting polymer into CDCl_3 and filtering. Monitoring of the reaction by NMR could be achieved by choosing any of the various active nuclei (^{13}C , ^{29}Si , and ^{17}O) however for reduced analysis time $^1\text{H-NMR}$ is selected. The reaction progress is followed by the loss in the $-\text{OCH}_3$ peak signal with respect to time. Although not a direct measure of concentration, the resulting integrals give rise to the following relationship

$$R_{\text{OMe}} = \frac{I_t}{I_0}$$

where R_{OMe} is the relative concentration of methoxy group, I_t is the integral at time t and I_0 is the integral at time zero.

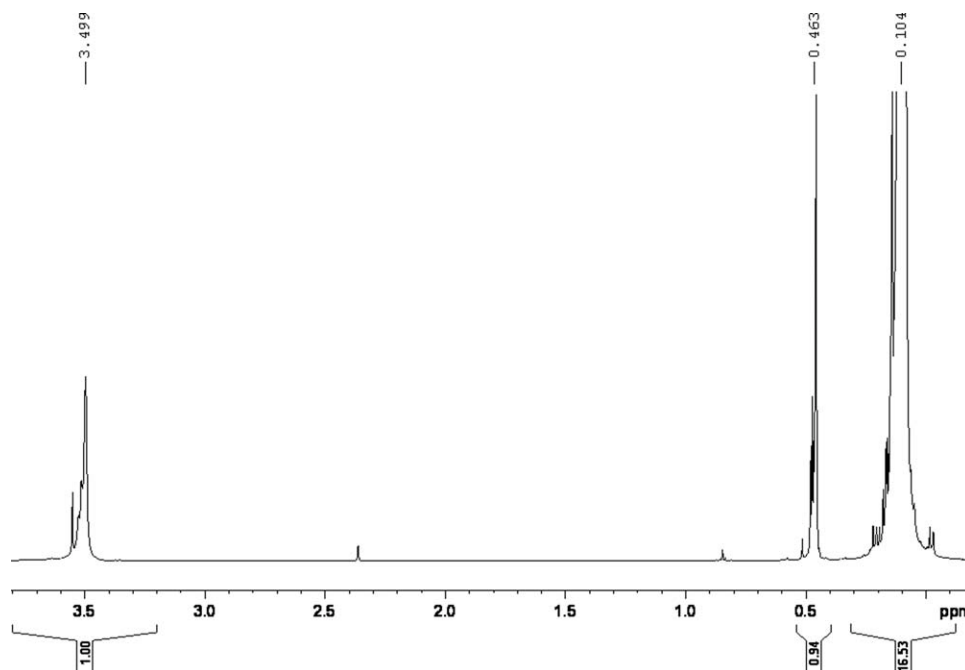


Figure 3 ^1H NMR plot of reaction solution at time $t = 0$.

Preparation of FeCl_2 solutions for electrochemical study

Five solutions were made up in separate 50 mL standard flasks for the electrochemical study. A 20.0 mM aqueous solution of FeCl_2 (0.127 g) in 0.100M KCl (0.745 g); a 0.100M solution of tetrabutylammonium chloride, TBACl, (0.829 g) in THF; a 0.100M solution of TBACl (0.829 g) with 0.100M (dichlorodimethyl)silane (0.605 mL) in THF; a 20.0 mM solution of FeCl_2 (0.127 g) with 0.100M of TBACl (0.829 g) in THF, and a 20.0 mM solution of FeCl_2 (0.127 g) with 0.100M of TBACl (0.829 g), and 0.100M (dichlorodimethyl)silane (0.605 mL) in THF. The cyclic voltammetry was carried out using an Autolab eco-chemie PSTAT10 and GPES3 software package. The working electrode used was a platinum disc, the counter electrode was a platinum mesh and the reference electrode was an Ag/AgCl electrode. Each solution was degassed in the electrochemical cell before the experiment was begun and the solutions were scanned at various rates from 10 mVs^{-1} through to 1.6 Vs^{-1} between the voltage limits of -0.5 V to $+1.75$ V. The data was then plotted as voltage (ref. Ag/AgCl) against current. The

results obtained in the electrochemical experiments using cyclic voltammetry were analyzed using the Randles-Sevcik equation¹² at 298 K described as:

$$i_p = -(2.69 \times 10^5) \times n^{3/2} \times C_o \times D^{0.5} \times v^{0.5}$$

where i_p is the peak current density (A cm^{-2}), n is the number of electrons, C_o is the concentration of electro-active species (mol cm^{-3}), D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), and v is the scan rate (V s^{-1}).

The diffusion coefficients were measured for a range of samples to determine the rate at which the species of interest were moving on to the surface of the electrode. The shape of the cyclic voltammogram helps determine the reversibility of the system.

RESULTS AND DISCUSSION

The results obtained from the NMR integrations were then plotted for different temperatures as shown in Figure 4. Table II shows the rate constants obtained and error in best fit line for each pair of runs. NMR studies of the copolymerization revealed that the concentration of methoxy group on the PDMS reduced over time according to first order kinetics. Only the first nine data points of the experiment were carried forward into these plots as the initial rate method applied to these results. At reaction times greater than 1 hour, undesirable effects start to occur. The viscosity of the solution becomes significant and this has a greater influence on the mobility of electrophile, reducing the reaction rate. At higher temperatures, (dichlorodimethyl)silane can

TABLE I

Assignment of ^1H NMR for Spectrum Shown in Figure 3

^1H NMR Chemical Shift (δ)	Integral Value	Peak identification
3.49 (s)	1.00	$-\text{OCH}_3$ terminal group
0.46 (s)	0.94	$\text{SiCl}_2(\text{CH}_3)_2$ reactant
0.11 (multi)	16.53	$\text{SiO}-(\text{CH}_3)_2$ backbone

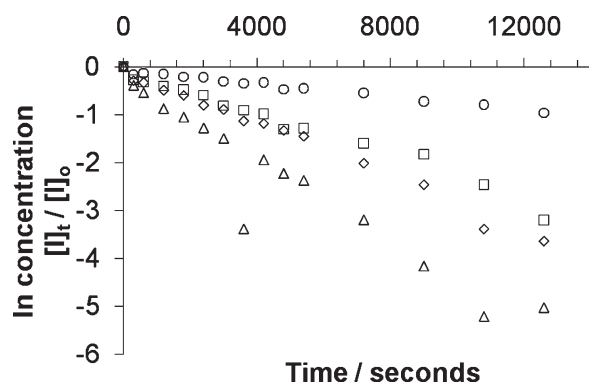


Figure 4 Plot of natural log of the fraction of the $-\text{OCH}_3$ integral present at time t as a function of reaction time. Circles are reaction at 60°C , squares are reaction at 75°C , diamonds are reaction at 80°C , and triangles are reaction at 90°C .

distill from the reaction vessel. In addition, a temperature study was conducted and an Arrhenius plot was obtained that encompassed data points from 40 through to 120°C as shown in Figure 5. In the plot, three regions were observed which could each be explained by experimental observation. In region A, there is a slow increase in size of the rate constant where it was observed that the catalyst was only partially soluble at lower temperatures, which lead to slower reaction rates. Region B is the Arrhenius region in which the reaction rate almost doubles with each 10°C increase in temperature. In region C, the reaction rate significantly fails to increase further, most likely caused by the distillation of reactant material at elevated temperature.

The Arrhenius region was extracted from the data, replotted as shown in Figure 6, and the activation energy obtained. The activation energy of the FeCl_3 catalyst was found to be $+43.6 \text{ kJ mol}^{-1}$. Further extrapolation of the data back to the y-axis reveals the frequency factor for the reaction defined as $\ln A$. This was used to calculate the activation entropy of the reaction¹³ according to the following equation

$$\Delta S^\ddagger = R \left(\ln A - \ln \left(\frac{kT}{h} \right) - 1 \right)$$

TABLE II
Rate Constants at Various Temperatures Including Best Fit Value

Temperature ($^\circ\text{C}$)	Rate constant $k \times 10^{-4} \text{ (s}^{-1}\text{)}$	R^2 best fit value
40	0.50	0.79
60	0.69	0.98
75	2.55	0.90
80	2.92	0.92
90	5.10	0.75
100	6.62	0.74
120	6.89	0.75

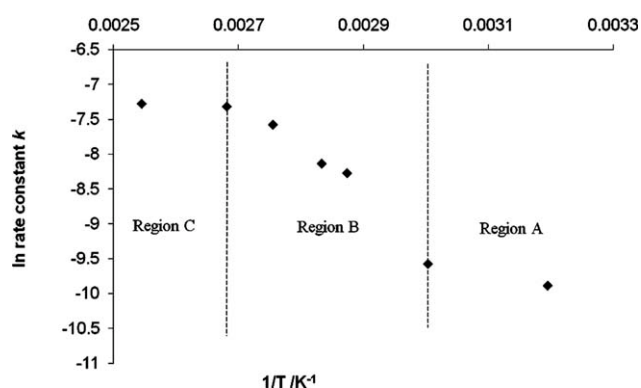


Figure 5 Overall Arrhenius plot of rate constant from 40°C through to 120°C against reaction rate.

The value calculated for the reaction was taken from a temperature in the Arrhenius region (80°C) giving a value for $\Delta S^\ddagger = -198.2 \text{ J K}^{-1} \text{ mol}^{-1}$. The value is large and negative, which indicates that the transition state is much more ordered than the original reactants, as befits the proposed mechanism in reaction Step 2.

To complete the kinetic study, an analysis of reactions involving steps of k_1 and k_{-1} were investigated. The first electrochemical study involved testing the reversibility of FeCl_2 to FeCl_3 in aqueous KCl solution. Figure 7 shows the oxidation and reduction peaks at various scan rates. Clear diffusion controlled peaks were obtained for both oxidation and reduction reactions with a peak-to-peak separation of 120 mV (independent of scan rate). The latter indicates that the electron transfer process is slow for this reaction. The diffusion coefficient for the Fe^{2+} was obtained using Randles-Sevcik equation and is shown in Table III. Ideally for the next series of cyclic voltammetry experiments the solubility of the FeCl_2 in (dichlorodimethyl)silane would allow us to measure the cyclic voltammogram without an additional solvent. However, the solubility of the FeCl_2 is poor in (dichlorodimethyl)silane even at elevated temperatures $> 80^\circ\text{C}$. To overcome this, THF

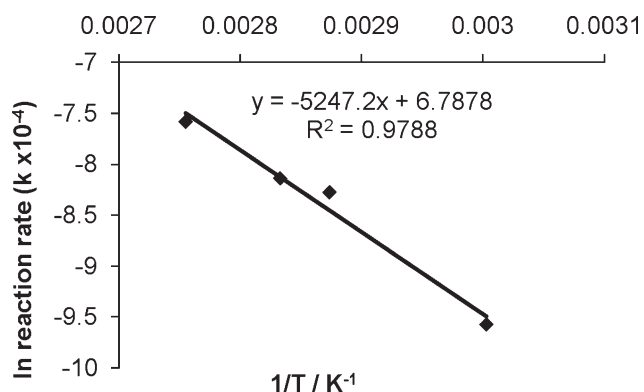


Figure 6 Arrhenius region plotted between the temperature range of 60 – 90°C against natural log of reaction rate.

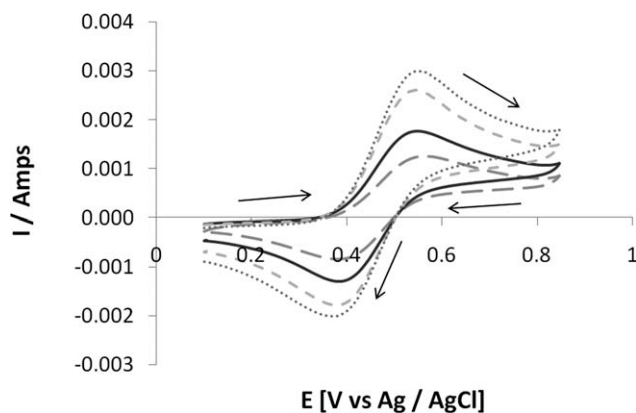


Figure 7 20 mM solution of FeCl_2 in 0.1M KCl solution. Scan rates show are 20 mVs^{-1} (long dash), 40 mVs^{-1} (solid line), 80 mVs^{-1} (short dash), and 120 mVs^{-1} (dotted line). The cyclic voltammogram shows the oxidation of FeCl_2 to FeCl_3 and its reduction in the reverse peak.

was used as the solvent to ensure dissolution of the electrolyte and electro-active analyte. A background scan using a solution of TBACl electrolyte in THF was produced to show that no peaks appear in the voltage limits of interest. Again, a second background scan using a THF solution incorporating (dichlorodimethyl)silane and TBACl shows that no peaks are observed in the voltage range of interest. When 20 mmol of FeCl_2 was added to a solution containing the electrolyte in THF peaks for the oxidation and for reduction of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ center were observed similar to that of Figure 7. As before, the diffusion coefficient was extracted from a voltage scan rate dependence and application of the Randles-Sevcik equation. The value obtained is given in Table III. The decrease in D here compared to that in aqueous solution suggests that the diffusion species in the less polar THF solvent is much larger than in water.

When (dichlorodimethyl)silane, FeCl_2 and electrolyte are present in the same solution the oxidation of Fe^{2+} to Fe^{3+} is observed (peak A) and in continuing to scan in a positive direction a second peak is observed, which is only present when FeCl_3 and (dichlorodimethyl)silane are present (peak B), shown in Figure 8. Here the oxidation and reduction peaks associated with $\text{Fe}^{2+}/\text{Fe}^{3+}$ (at 0.3 V and 0.15 V, respectively) are still present peak to peak separation increases substantially with scan rate, giving a

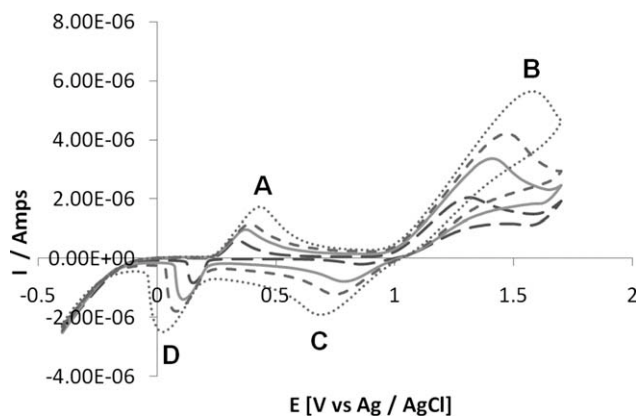


Figure 8 20 mM FeCl_2 , 0.1M (dichlorodimethyl)silane and 0.1M TBACl in THF. Scan rates shown are 40 mVs^{-1} (long dash), 120 mVs^{-1} (solid line), 200 mVs^{-1} (short dash), and 400 mVs^{-1} (dotted line).

500 mV separation at a scan rate of 400 mV s^{-1} . This indicates that the reaction has become even more electrochemically irreversible in the medium (THF). Furthermore, although the shape of the oxidation peak at A retains the diffusion controlled reaction shape, the reverse reduction reaction at D does not. The shape of the peak at D suggests that the Fe^{3+} species generated at the electrode surface in this region becomes rapidly exhausted, due to continuing chemical reaction with the (dichlorodimethyl)silane.

The size of peak B is three times greater than peak A, which indicates it could be associated with a multi-electron process. This could be due to the destabilization of the iron center by the (dichlorodimethyl)silane liberating the three chloride ligands on the metal center. The oxidation process peak B is linked to the reverse reduction process at peak C and both give diffusion controlled shapes. In such a case, we can normalize the curves by dividing by $v^{1/2}$ in which case, all the curves should superimpose shown in Figure 9. However, due to the above-mentioned electrochemical irreversibility of the reactions taking place here, this does not occur and there is still a shift to higher potentials with increasing scan rate. The oxidation current maxima, however, do become similar (as for peaks A and D) if irreversibility is taken into account. What is significant although here is that, the normalized reduction current maxima increases with scan rate. Such a

TABLE III
Diffusion Coefficients and Associated Errors for Varying Solutions Containing FeCl_2

Solution	Electrode Area (cm^2)	Diffusion Coefficient $\text{cm}^2 \text{ s}^{-1}$ (1×10^{-7})	Error $\pm \text{cm}^2 \text{ s}^{-1}$ (1×10^{-7})
20 mM FeCl_2 in 0.1M KCl	0.38	22.4	1.25
20 mM FeCl_2 and 0.1M TBACl in THF	0.002	0.415	0.00689
20 mM FeCl_2 , 0.1M $\text{Si}(\text{Me}_2\text{Cl}_2)$, and 0.1M TBACl in THF Peak A	0.002	0.578	0.00875

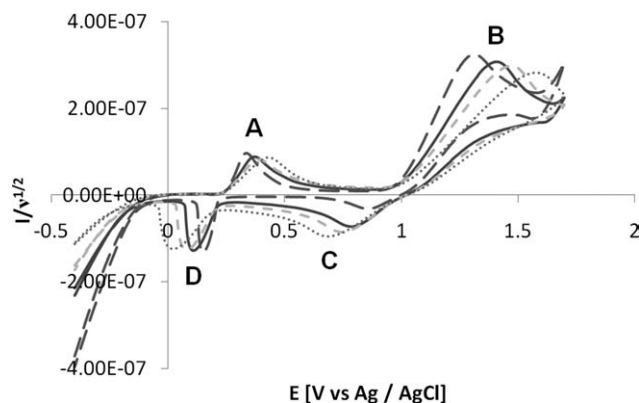
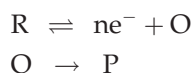


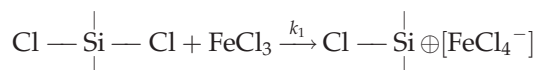
Figure 9 20 mMol FeCl_2 , 0.1M (dichlorodimethyl)silane and 0.1M TBACl in THF. Current has been divided by the square root of the scan rate. Scan rates shown are 40 mVs^{-1} (long dash), 120 mVs^{-1} (solid line), 200 mVs^{-1} (short dash), and 400 mVs^{-1} (dotted line).

behavior is anomalous for an EC (electron transfer-chemical reaction) mechanism. Thus, an oxidation of R, the intermediate species [I] gives rise to the following process shown as



This yields the species O, which can undergo chemical reaction to give an electrochemically inactive species P. The amount of O available for the reverse reduction process to give peak C depends on the rate of the chemical reaction of O converting to P. If the latter process is very fast, then there will never be any O available to give the peak C. However, for very slow conversion of O to P, the reverse reaction will not be affected at all except at the very slow scan rates. The reality for the first step of the kinetic model is the (dichlorodimethyl)silane is consumed in the electrochemical step, thus giving rise to the irreversible process.

In the context of our system, the effect of this is to change the kinetic equation associated with the overall reaction shown in Figure 2. The initial reaction Step 1 proceeds as shown:



where the rate of the reaction is now solely dependent on k_2 and the kinetics are as follows:

$$\frac{d[\text{P}]}{dt} = k_2[\text{I}][\text{C}]$$

In this instance the amount of species [I] will be small in line keeping with steady state approxima-

tion. Therefore, the rate change in the equation collapses to a first order equation as was confirmed in the resulting NMR plots of concentration of the methoxy capped PDMS, that is,

$$\frac{d[\text{P}]}{dt} = k_2[\text{C}]$$

CONCLUSIONS

The results of the study have been the first to quantify the activation energy the polymerization of (dichlorodimethyl)silane and methoxy capped PDMS using a FeCl_3 catalyst in relating to the reaction involving a silyl methoxy capped *m*-carborane monomer. The large entropy of reaction indicates that the transition state in Step 2 is highly ordered and most likely the rate determining step. Further work investigating the activation energy of other Lewis acid catalysts is desirable due to the crosslinking problem encountered with the use of FeCl_3 . Also repeating the study using the *m*-carborane reaction would be desirable to prove whether the reactions are truly comparable, however the cost of *m*-carborane starting material is a barrier to completion of this study.

The electrochemical study disproved the initial prediction that the first step in the reaction mechanism was reversible. The normalized reduction current maxima increase with scan rate which is indicative of an EC mechanism, the Fe^{3+} is being consumed by the (dichlorodimethyl)silane. Further work also includes simulation of the electrochemical data to determine at what scan rate the chemical reaction involving the (dichlorodimethyl)silane starts to affect the electrochemical redox process.

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