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Cost-efficient temperature mediation of DPMS synthesis in flow using continuous flow chemistry

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Abstract: An efficient synthesis of diphenylmethylsilanol (DPMS) utilizing continuous flow chemistry was performed using a coil reactor and an ice bath. The inclusion of careful temperature control minimized the exothermic production of an unwanted dimer. Yields of up to 88% were obtained and dimer formation as low as 2.2% was confirmed by NMR. This material will be used in the formulation to make SX358 and its physical and chemical characteristics will be determined using DSC, DMA, TMA, compression set testing and FTIR.

Introduction:

Siloxane foams are highly versatile and stable materials derived from a polymer containing a silicon-oxygen (siloxane) backbone. These silicon-oxygen bonds play a large role in the most defining property of siloxanes, their thermal characteristics. Siloxane polymers have stability at high temperatures[1] and some of the lowest glass transition temperatures[2] of any type of polymer. This allows siloxane elastomers to be used in a wide range of temperatures[1]. For example PDMS, one of the most widely used siloxane polymers has a glass transition temperature of -123°C and a degradation temperature of 400-650°C. This makes them vital to fields that involve expansive ranges of temperature such as aeronautics and space.

The wide temperature range of siloxanes stem from the unusual characteristics of the siloxane bond that forms their backbones. The siloxane bond is both ionic and has partial double-bond characteristics a result of the overlap of the d-orbitals of silicon with the p orbitals of oxygen[3]. These traits make the siloxane bond considerably stronger than a C-C bond contributing to the high-temperature resistance. The greater length of the silicon-oxygen bond helps lend the polymer its flexibility providing it its very low glass transition temperature. Unfortunately, due to this very low glass transition temperature siloxane polymers are also capable of cold crystallization at a wide range of temperatures[4]. This causes the characteristics of siloxane polymers to slowly change over time as they crystallize.

One method used to prevent the cold crystallization of siloxane polymers is the use of dimethylphenylsilanol (DPMS) as an endcap. DPMS shown in Figure 1 is an organosilanol with two phenyl groups and a methyl group. DPMS is not capable of propagating a radical but can be incorporated into a polymer as an endcap. The bulky aromatic groups on DPMS disrupt the formation of the crystalline structure when included in small percentages. In large percentages the opposite can occur and bulky comonomers like DPMS can induce crystallization[5]. Due to this, most siloxane foam synthesis uses around 5% DPMS in their resin mixes to prevent cold crystallization.

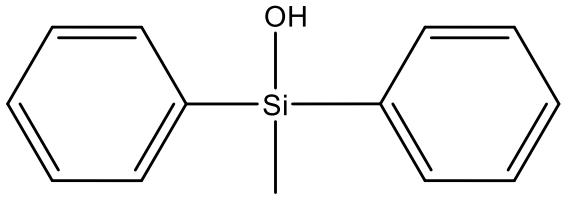

Figure 1: DPMS structure

Polymer characteristics can be tuned by controlling the amount of crosslinking in the samples by terminating propagating radicals with DPMS. The amount of crosslinking in the sample decreases as DPMS content increases[6]. This means crosslinking-dependent properties such as Youngs modulus, tensile strength and brittleness can be altered by changing the amount of DPMS used. Other endcaps can also control the amount of crosslinking, but the use of DPMS as a comonomer can change characteristics that other endcaps don't such as radiological stability. While DPMS has never been experimentally determined to increase the radiological stability of foams, multiple studies[7, 8] have shown that inclusion of aromatic ring systems similar to DPMS can lessen

the effect of ionizing radiation on polymers. These aromatic rings also provide increased thermal stability through their electron withdrawing characteristics[9]. Polymers utilizing DPMS as a comonomer exhibit resistance to cold crystallization and an increase in radiological and thermal stability making them remarkably stable over long periods of time.

The anti-aging properties provided by DPMS make it crucial for the synthesis of highly stable siloxane foams such as SX358. SX358 is synthesized by the mixture of a resin and catalyst which causes the resin to begin foaming and cross-linking. The resin used is comprised mostly of polydimethylsiloxane (PDMS) with 5% DPMS, 2% tetra-*n*-propoxysiloxane (TPS), 3% polymethylhydrosiloxane (PMHS) and some filler. The PMHS is used to create the hydrogen gas that forms the pockets in the foam as it reacts with DPMS and PDMS to form crosslinks. The TPS is used to further crosslink the foam as care must be taken to balance foam crosslinking with H_2 gas formation. Without this, large cavities can form in the foam or the resin can fail to foam. Lastly, DPMS is used to prevent cold crystallization and other effects that would slowly change the properties of the SX358 over time.

Despite its importance in key siloxane foams such as SX358 the current synthetic route for DPMS is inefficient. DPMS is synthesized through the hydrolysis of DPMS-Cl under basic conditions shown in figure 2. This hydrolysis is exothermic as it forms energetically favorable HCl which basic conditions are used to offset. While this synthesis is facile and rapid, the DPMS-Cl hydrolysis emits heat which encourages the formation of the dimer side product. DPMS slowly undergoes a dimer-forming reaction even at room temperature[10]. Dimer formation lowers the conversion and efficiency of the reaction. To increase product yield cooling systems are often used to control the reaction conditions and prevent dimer formation.

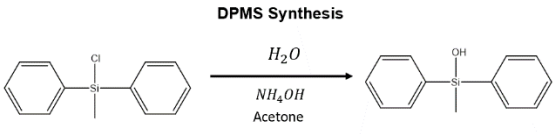

Figure 2: DPMS Synthetic scheme

Continuous flow chemistry systems are highly efficient at controlling reaction conditions, especially temperature. Heat transfer is rapid in flow systems because of the small diameter of the tubing. A small tube diameter means less distance for heat to travel allowing the reaction to cool quickly. The temperature increasing effect of the exothermic reaction is also reduced by the high degree of stoichiometric control over the reaction. Flow systems afford a high degree of stoichiometric control as the reaction volume is fully controlled by the pumping rate[11]. The high heat transfer of the tubing and the precise control over reaction volume allows for a sharp reduction in byproduct formation for the hydrolysis of DPMS-Cl. The increased efficiency provided by flow conditions is supplemented by the continuous nature of flow chemistry allowing easy reaction scale-up.

Other groups have already utilized flow reactor cooling systems to combat the exothermicity of the reaction[12]. The flow systems used micromixer reactor chips and a flow cooling unit to precisely control the stoichiometry and temperature of the reaction. These flow systems were highly successful in reducing the amount of dimer byproduct to around 3%. However, the components that this system utilized are expensive and highly specialized.

To reduce the cost of the reaction, a coil reactor in an ice bath was used instead of a chip reactor in a cooling unit. The same reaction scheme that was used by the previous group was used in this paper (citation?). The temperature of the reactor submerged in the ice bath was approximately 0°C. This mediated the effect of the exothermic reaction without the use of expensive chip reactors or cooling equipment. This method allows for the efficient continuous production of DPMS from DPMS-Cl with inexpensive equipment.

Methods

Materials: DPMS-Cl 98% (1st set of experiments) and DPMS-Cl 97% (2nd set of experiments) were used as received from Sigma Aldrich. Ammonium Hydroxide 28-30% was used as received from Sigma Aldrich. Acetone 99.5% ACS Reagent Grade was used as received from Sigma Aldrich. DI water was obtained using a PURELAB Option Q.

Reactor Setup: DPMS-Cl was pumped through a Vapourtec E-Series Integrated Flow Chemistry System using a peristaltic pump at a flow rate of 0.667 ml/min using acetone as a solvent to prime the lines.

Ammonium hydroxide was pumped through the system at a flow rate of 1.333 mL/min using water as a solvent to prime the lines. After flowing through 50 cm of tubing and into an ice bath the two solutions were mixed. The mixture flowed from the mixer through 32 cm of tubing and into a toothed advanced mixing tube. From there the mixture flowed into a 2mL coil reactor still submerged in the ice bath. The mixture then exited the ice bath flowing 82 cm before exiting the reactor. The residence time of the reaction was 1 minute. Full reactor setup is shown below in Figure 3.

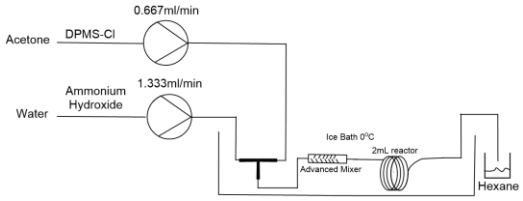

Figure 3: DPMS flow reactor setup

DPMS-OH Synthesis: DPMS-Cl was added to acetone to make a 1.8M solution. Ammonium hydroxide was diluted in water to make a 1.94M solution. Both solutions were reacted in the previously described flow reactor and kept in a 1:2.16 DPMS-Cl to ammonium hydroxide molar ratio using different flow rates. The reaction products were collected in hexane.

Workup: After collection in hexane the reaction was added to a separatory funnel and mixed. After the reaction settled the bottom aqueous layer was removed and an equivalent amount of water was added to the organic layer. The layers were then mixed, allowed to settle, and then separated again. This was repeated twice, once with water and once with brine. The organic layer was then dried using magnesium sulfate while being stirred rapidly. Then the organic layer was removed from the magnesium sulfate and rotovaped until no solvent remained.

Characterization: Product formation was confirmed by TLC and NMR. TLC was performed in solvent systems of 8:1 hexanes to ethyl acetate and 20:1 hexane to ethyl acetate. TLC plates were spotted with a starting material, product and co-spot. TLC plates were visualized using a UV-AC Dual Hand Lamp from VWR at 365nm. NMR was performed using DMSO as the solvent.

Results and discussion

The success of the first three experiments was monitored using thin layer chromatography. Throughout the experiments two characteristic spots were observed, the first had an Rf of around 30 which was indicative of both starting material and product. Other significantly lighter spots were occasionally seen in experiments but were not determined to be significant. The second spot had an Rf of around 70 and was lighter than the first spot indicating byproduct. In the first experiment the second spot was seen in all three lanes which indicated that the starting material was contaminated with byproduct. In the second experiment in the 1.5 bar reaction, only the first spot was seen in all three lanes, however, that was likely due to concentration issues. Both the first and the second spots were seen in the product and co-spot lanes in the following reaction plates however only the first spot was seen in the starting material lane. This indicated that some byproduct had formed in the reaction rather than all of the byproduct coming from the starting material. The first spot being the overlapping product and starting material spots caused difficulties in determining the success and conversion of the reaction. For this reason, TLC was not used for experiments after the third experiment and NMR spectroscopy was used in its place.

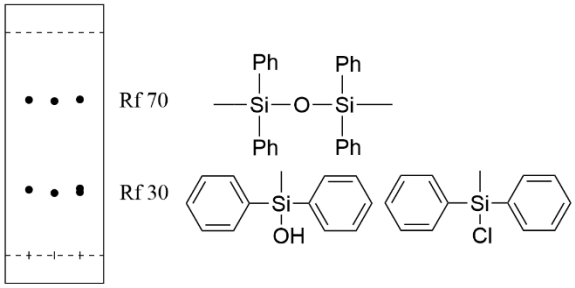

Figure 4: Example spot plate, Lanes from left to right; starting material, product, cospot. Overlapping spots are represented by two spots

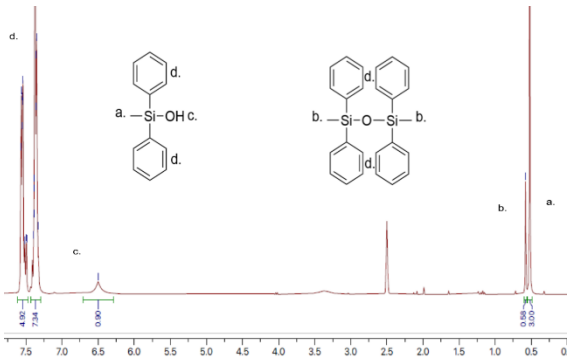

Figure 5: 1H-NMR of DPMS product from contaminated starting material. Signals: a. -CH_3 0.52ppm (s) 3.00, b. -CH_3 0.58ppm (s) 0.58. c. -OH 0.65ppm (s) 0.90 d. Phenyl, 7.34-7.57ppm, (m) 12.26.

The NMR spectra of the product shown in Figure 4 showed complete conversion of starting material and around 8% production of dimer side product. Conversion was determined using the singlet at an integration of 6.5 which corresponds to the alcohol on DPMS-OH. This signal was integrated with respect to the methyl group peak which yielded an integration of 0.9. This combined with the production of side product and allowing for slight error in measurement suggested full conversion of starting material into product. The production of dimer side product was measured through the measurement of the signal at 0.52ppm respective to the signal at 0.58ppm. The signal at 0.52ppm represented the methyl peak on DPMS-OH while the signal at 0.58ppm represented the two methyl groups on the dimer. The integration of these signals was compared with respect to the number of hydrogens they represent. It was determined that around 8% dimer byproduct was produced.

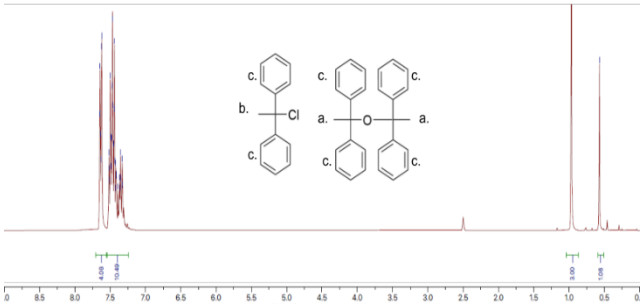

Figure 6: Contaminated DPMS-Cl NMR. Signals: a. CH_3, 0.57ppm, (s) 1.08. b. CH_3, 0.97ppm, (s) 3.00, d. Phenyl, 7.33-7.65ppm, (m) 14.57.

The high amount of dimer produced may have indicated reaction failure, however, because of the observations made on the spot plate from the first experiment an NMR was run on the starting material. This NMR spectra shown in Figure 5 had four major signals, Two groups of overlapping phenyl signals at a shift of between 7.33 and 7.65, a methyl signal at 0.97 for the DPMS-Cl methyl group and a methyl signal at 0.57 where the dimer methyl group peaks resided. Comparing the integrations of the methyl peaks it was determined that approximately 13% dimer byproduct was present in the starting material. Since the starting material was old it was hypothesized that over time water from the air reacted with DPMS-Cl in the container which dimerized through a nucleophilic substitution of the chlorine in the starting material. The difference between the amount of dimer byproduct in the product and starting material is likely due to byproduct being lost in the workup. As the old DPMS-Cl was contaminated with dimer a new bottle of DPMS-Cl was used for all future experiments. NMR was used to confirm the purity of the new bottle of DPMS-Cl.

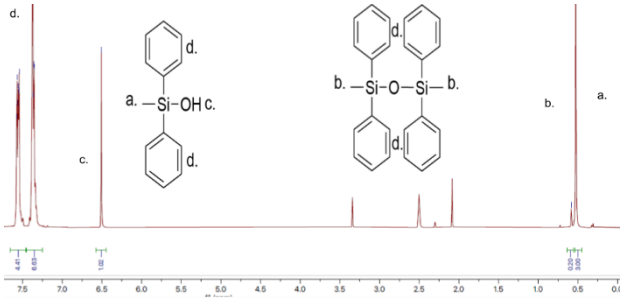

Figure 7: [1]H-NMR of DPMS product from large scale synthesis using new bottle. Signals: a. -CH_3 0.52ppm (s) 3.00 b. -CH_3 0.58ppm (s) 0.2 c. -OH 6.51ppm, 1.03. d. phenyl, 7.35-7.57, (m) 11.04

NMR was used to determine byproduct formation in the reactions that utilized the new bottle of DPMS-Cl. The NMR of the product from the final scale-up is shown in Figure 6. The integrations of the phenyl signals at 7.55ppm and 7.36ppm added up to 11.04, which almost matches the expected total number of signals in those peaks, 10. The alcohol signal at a shift of 6.5ppm had an integration of 1.03, the accuracy of these integrations to expected integrations indicates a high degree of purity. The comparison of integrations between the methyl signals at 0.58ppm and 0.52ppm indicated approximately 3% dimer formation. This calculated 3% dimer formation is equivalent to previously mentioned work that

utilized a cooling unit[12]. This indicates that the heat produced by the hydrolysis of DPMS-Cl on a 2M concentration scale can be mediated by an ice bath.

The products of the later reactions were also analyzed through ^{12}C-NMR to confirm the structure of the product. There were 5 distinct signals for 5 total non-identical carbons. One of these carbons at a shift of 0.5 was the methyl group carbon. The other four shifts between 128 and 139 which corresponded to the four unique phenyl carbon shifts. ^{12}C-NMR was especially beneficial for identifying the phenyl group carbons as they had overlapped in the ^{1}H-NMR. The four phenyl groups, two with twice the height of the other two showed the expected pattern for monosubstituted aromatic rings.

After both ^{1}H-NMR and ^{12}C-NMR confirmed the full conversion and low dimer production the reaction scale-up using the final reaction conditions was performed. Scale-up was performed by creating solutions of a greater volume and running the flow reactor longer. The yields from the reactions which used the final reaction conditions are shown in the table below.

Table 1: Reaction scale up yield percentages.

Reaction Scale (mmol)	DPMS-Cl Conc. (M)	NH_4OH Conc. (M)	Reagent to Base Ratio	% Yield
17.7	1.8	1.94	1:2.16	71.02
36	1.8	1.94	1:2.16	68.87
108	1.8	1.94	1:2.16	88.07

Approximately 70% yield was achieved for both the 17.7 and 36 mmol scales. The 17.7 mmol scale reaction was run for 20 minutes and the 36 mmol scale reaction was run for 40 minutes. At 70% yield the rate of product generation was roughly 0.63 mmol/min. Based on the NMR results the 70% yield was not caused by incomplete reaction but likely by product loss in the workup. The yield for the final 108 mmol experiment was 88% over a span of 120 minutes. The rate of product generation in this experiment was 0.8 mmol/min. The increased yield for the longest reaction is likely due to improvement in workup, timing, and experimental technique. The yield in addition to the lack of byproduct formation in the final reaction and the length of the reaction show that the ice bath is an effective tool for the synthesis of DPMS in both the long-term and the short term.

Conclusions:

Diphenylmethylsilanol was synthesized using an ice-bath cooled flow system. The synthesis achieved yields of up to 88% and was performed on 0.1 molar scale. The optimized reaction allowed for a production rate of 0.8 mmol/min. Comparable amounts of byproduct formation to previous experimentation that utilized cooling reactions were achieved as confirmed by ^{1}H-NMR and ^{12}C-NMR. The high yields of the reactions and minimal byproduct formation show that a reaction system using an ice bath and a coil reactor is a cost-effective and efficient method for the synthesis of DPMS.

Future Directions

To confirm the usefulness of the DPMS produced in flow using an ice bath reactor SX358 foam will be synthesized using the DPMS synthesized using the ice bath. This SX358 will be mechanically characterized using DSC, DMA, TMA and FTIR. The DSC will be used to confirm that the DPMS synthesized using the method outlined in this paper can prevent cold crystallization. The DMA, TMA and compression set testing will confirm that the mechanical characteristics of the foam align with literature values. FTIR will be used to determine the chemical composition of the foam.

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Notes

The authors declare no competing financial interest in this work

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