

9-1-2023

Synthesis and characterization of Double-Cross Linked PVPMS Aerogels

Olivia Zill
Winona State University

Follow this and additional works at: <https://openriver.winona.edu/studentgrants2023>

Recommended Citation

Zill, Olivia, "Synthesis and characterization of Double-Cross Linked PVPMS Aerogels" (2023). *Student Research and Creative Projects 2022-2023*. 15.
<https://openriver.winona.edu/studentgrants2023/15>

This Grant is brought to you for free and open access by the Student Research & Creative Achievement Projects at OpenRiver. It has been accepted for inclusion in Student Research and Creative Projects 2022-2023 by an authorized administrator of OpenRiver. For more information, please contact klarson@winona.edu.

*Synthesis and Characterization of Double-Cross Linked
PVPMS Aerogels*

Olivia Zill

Winona State University

05/03/2023

Dr. Kopitzke

Abstract

Aerogels have been rising to the surface as a material of interest for many practical applications. Aerogels are classified as “dried gels with a very high relative pore volume”.¹ Aerogels are typically created through supercritical drying, in which the liquid in a sol-gel is turned into gas without destroying the structure of the gel. The purpose of this research experiment is to create a undergraduate student laboratory for CHEM411 Materials and Synthesis of Characterization in which the students will create polyvinylpolymethylsiloxane (PVPMS) aerogels from vinylmethyldimethoxyxilane (VMDMS) using a new method that has been created using ambient pressure drying rather than supercritical drying.^{7,8} This experiment was successful in created the PVMDMS polymer from VMDMS, and successful in creating the PVPMS hydrogel from the PVMDMS. However, the experiment was unsuccessful in drying the hydrogel into its aerogel form.

Introduction

Aerogels have been rising to the surface as a material of interest for many practical applications. Aerogels are classified as “dried gels with a very high relative pore volume”.¹ The practical applications of aerogels include thermal insulators, electrical conductors, sensors, as well as optical applications and more.²⁻⁵ Aerogels are typically created through supercritical drying, in which the liquid in a sol-gel is turned into gas without destroying the structure of the gel. However this process requires high pressures and temperatures and the solvents used are highly flammable and unsafe at these conditions.⁶

The purpose of this research experiment is to create a undergraduate student laboratory for CHEM411 Materials and Synthesis of Characterization in which the students will create polyvinylpolymethylsiloxane (PVPMS) aerogels from vinylmethyldimethoxyxilane (VMDMS) using a new method that has been created using ambient pressure drying rather than supercritical drying.^{7,8} The method of ambient pressure drying is safer for an undergraduate laboratory and has significantly less risks than the method of supercritical drying. A previous laboratory has been carried out in CHEM411 using the method of

supercritical drying but the aerogels were found to be extremely fragile and brittle. The aerogels created through this new method of ambient pressure drying should result in aerogels that are superflexible, have high superinsulating properties, high hydrophobicity, high transparency, low density, and excellent machinability.^{7,8}

The proposed student laboratory would include both the synthesis and characterization of the PVPMS aerogels, which are both topics that fall under the American Chemical Society's guidelines for topics in Macromolecular, Supramolecular, and Nanoscale (MSN) systems.⁹ Characterization of the resulting PVPMS aerogels would include density, mechanical properties, and infrared spectroscopy (IR). ¹H NMR can also be collected for the polyvinylmethyldimethoxysilane (PVMDMS) polymer and the VMDMS monomer precursor.

Experimental

The first step in this experiment is the radical polymerization of the starting monomer, VMDMS, using di-*tert*-butyl peroxide as the initiator, as seen in Figure 1.

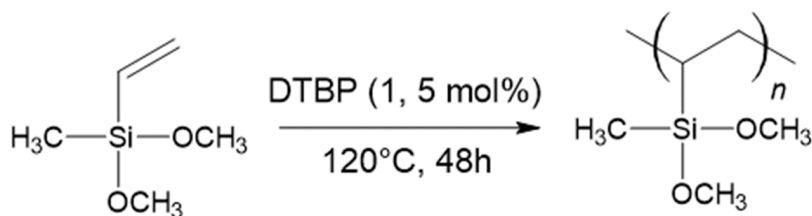


Figure 1. Radical Polymerization of VMDMS

To carry out this step, the VMDMS is combined with the DTBP in a hydrothermal reactor and the hydrothermal reactor is then flushed with Argon to create an oxygen-free setup. The hydrothermal reactor is then placed into a temperature-controlled



Figure 2. Hydrothermal Reactor

oven at 120°C for 48 hours. A picture of a hydrothermal reactor in Figure 2. This reaction was carried out at varying volumes (1 mL, 3mL, 5mL, 6mL) and varying mol % of DTBP (1%, 5%) when attempting this step. The final results of this step should be a clear and viscous liquid.

At first, there was no temperature-controlled oven available for use for this step so a regular convection oven was used. A few attempts were also carried out using an oil-bath setup. There was also no argon originally available so the setup of the reaction mixture in the hydrothermal reactor was first done in a glovebox. Eventually, argon was purchased and a temperature-controlled oven was found and those were used for the experiment from that point on.

The second step in the experiment is the hydrolytic polycondensation of the PVMDMS polymer to turn it into a hydrogel. In this step tetramethylammonium hydroxide is used as the catalyst. As seen in Figure 3.

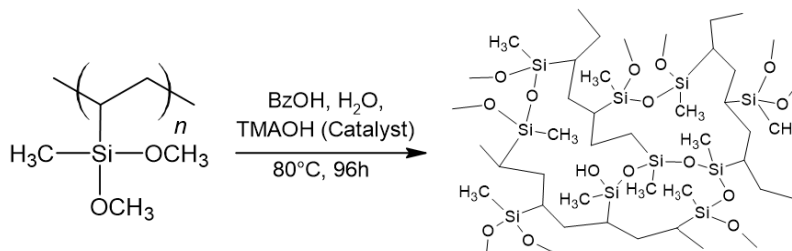


Figure 3. Hydrolytic Polycondensation of PVMDMS with TMAOH

Once the hydrothermal reactor was taken out of the oven, for a 3 mL VMDMS scale, 8.97 mL benzoic acid (BzOH), 0.727 mL water, and 0.054 mL TMAOH were added to the polymer in that order, and the mixture was stirred for approximately 5 minutes. Once the mixture was done stirring, it was then transferred into polypropylene containers. The containers were then placed back into the temperature-controlled oven at 100°C for 4 days, in which the gel formed within the first hour and cured for the rest of the time.

The third step in the experiment was to put the resulting gels through solvent exchange in order to remove and residual water, BzOH, or other chemicals. To do so, the hydrogel is soaked

in isopropyl alcohol (IPA) overnight at 60°C three times. This was done by just filling up the polypropylene containers with the IPA. In one attempt, the hydrogels were transferred to a larger container and all soaked together.

The fourth and final step of the experiment was the ambient pressure drying step that turns the hydrogel into its aerogel form. To do so, a small hole was made in the top of the polypropylene containers, and they were allowed to dry at room temperature for 2-5 days and then in the temperature-controlled oven at 80°C for 4 hours. One other method of ambient pressure drying is able to be done without solvent exchange by replacing the BzOH in step two with IPA instead. Then the hydrogel after step two is just dried at room temperature for 2-5 days until dry.

For characterization, ¹H Nuclear Magnetic Resonance (NMR) was collected for both the starting monomer VMDMS and the synthesized polymer PVMDMS. Fourier Transform Infrared Spectroscopy (FTIR) was collected for the final PVPMS aerogel. The color of the aerogels were also observed.

Results and Discussion

Various attempts were made for the first two steps of the reaction using the glovebox/convectional oven and oil bath setups. A table of the attempts as well as their results is seen below.

Table 1. Attempts before Temperature-Controlled Oven

<u>Sample # and Type</u>	<u>Amount VMDMS (mL)</u>	<u>Mol % DTBP (%)</u>	<u>Results of Step 1</u>	<u>Results of Step 2</u>
1, glovebox/oven	1.00	1	Not very viscous, pale yellow color, cap was loose	No gel, just a yellowish viscous liquid
2, glovebox/oven	1.00	1	Formed a crystalline solid, yellow/gold color	N/A
3, glovebox/oven	1.00	1	Somewhat solidified liquid, yellow color	N/A
4, argon/oven	1.00	1	Not very viscous, yellow color	N/A
5, argon/oven	3.00	5	Completely solid, yellow color	N/A
6, argon/oil bath	3.00	5	Dark yellow color, not very viscous	No gel
7, argon/oil bath	3.00	5	Sample completely evaporated	N/A
8, argon/oil bath	3.00	5	Viscous, pale yellow color	No gel

Only a few of the attempts from the glovebox/oil bath/argon setups seen in Table 1 were able to be carried on to the second step, and none of the mixtures resulted in the formation of the PVPMS hydrogel. In sample 7, when the sample mixture completely evaporated, it is assumed that the seal on the hydrothermal reactor must not have been completely shut. In other samples such as samples 2, 3, and 5 when the sample formed a solid or somewhat solidified, it is possible

that the container within the hydrothermal reactor had residual acid or old product on it and thus the samples reacted with it while in the oven.

Once the temperature-controlled oven was found to be used, it was setup and from that point on it was used for the rest of the samples. The sample volume amounts and the results of the first two steps can be seen in Table 2.

Table 2. Temperature-Controlled Oven Samples

<u>Sample #</u>	<u>Amount</u> <u>VMDMS (mL)</u>	<u>Mol % DTBP</u> <u>(%)</u>	<u>Results of Step</u> <u>1</u>	<u>Results of Step</u> <u>2</u>
9	3.00	5	Clear viscous liquid	Formed a gel
10	6.00	5	Clear viscous liquid	Formed a gel

For both samples using the temperature-controlled oven, a clear viscous liquid was obtained after the polymerization step, and a sample was collected for ^1H NMR and dissolved in CDCl_3 . The ^1H NMR spectra of the VMDMS monomer and sample 9 of the PVMDMS polymer are seen in Figures 4 and 5.

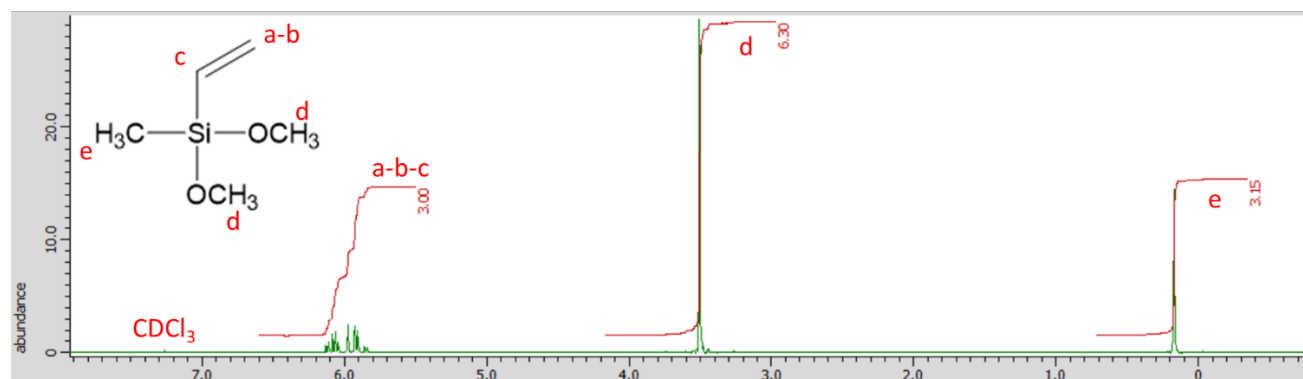


Figure 4. ^1H NMR of VMDMS

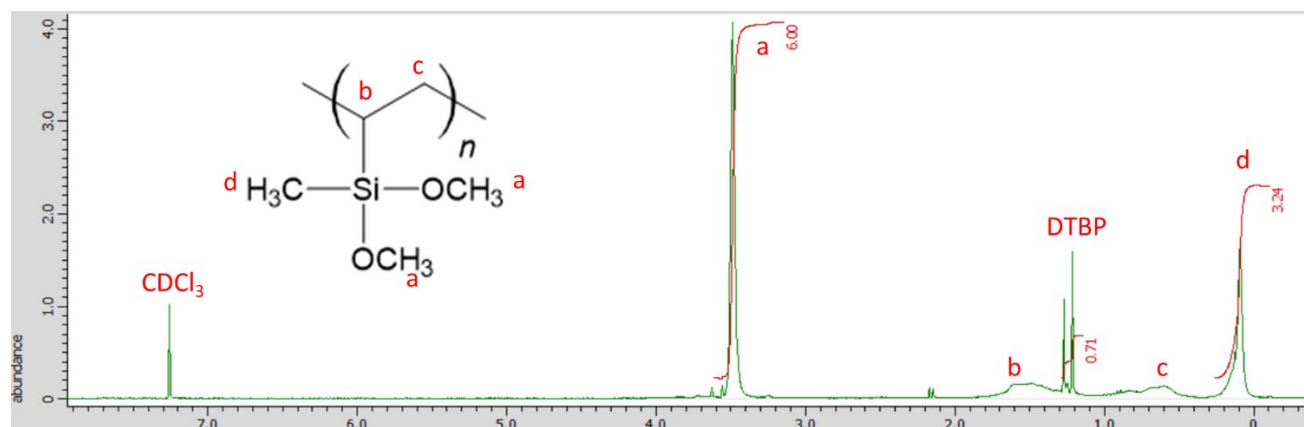


Figure 5. ¹H NMR of PVMDMS

As can be seen by the peak labeling in Figure 4, the grouping of peaks labeled a/b/c around 6.0 ppm correspond to the C-H₂ hydrogens seen in the structure of VMDMS. These peaks disappear in the PVMDMS spectrum in Figure 5 as the C=C double bond disappears with the polymerization. Instead, there is the appearance of two broad peaks around 1.6 ppm and 0.6 ppm correspond to the new C-H₃ bonds present in the PVMDMS polymer. There is the presence of a strong doublet peak around 1.3 ppm that is likely due to DTBP end groups on the polymer, however it is unsure as to why it is displaying as a double rather than a singlet, as would be expected.

Since samples 9 and 10 were successfully able to form the hydrogel, they were then put through the IPA solvent exchange and then the ambient pressure drying. Figure 6 shows the coloration of the hydrogel and a picture of one of the solvent exchanges.

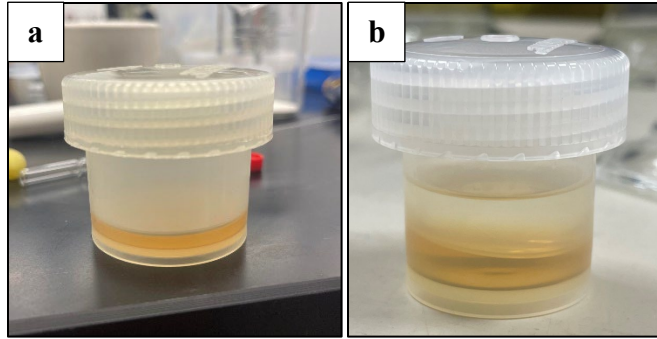


Figure 6. a) PVPMS hydrogel b) Solvent exchange of PVPMS aerogel with IPA

After the solvent exchanges, the hydrogels of samples 9 and 10 were then subjected to ambient pressure drying. Figure 7 shows the PVPMS aerogels obtained after the drying process. Solid FTIR was collected and is seen in Figure 8. The aerogels retrieved in this experiment displayed a yellow color, and were firm/solid and cracked easily. The PVPMS aerogels obtained by Zu et al following this same method were found to be highly flexibly and strong, as well as displayed a light blue color, meaning that the aerogels made in this experiment were not made successfully.

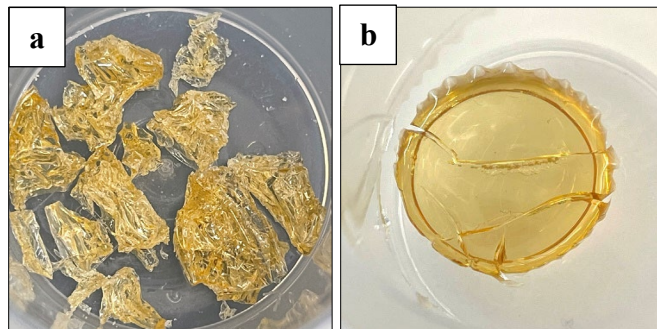


Figure 7. a) Sample 9 PVPMS Aerogel b) Sample 10 PVPMS Aerogel

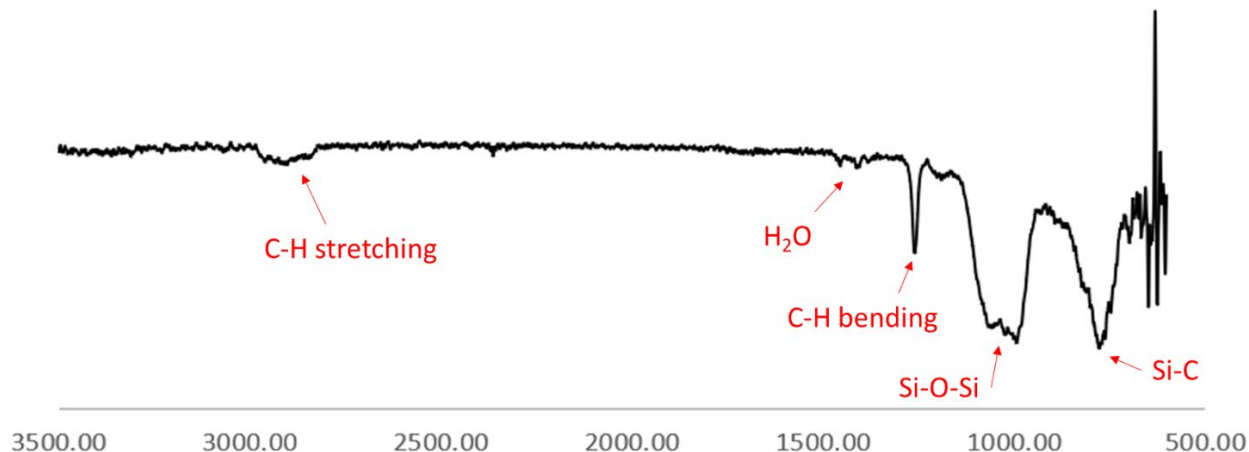


Figure 8. FTIR Spectrum of PVPMS Aerogel

Compared to the expected structure of the PVPMS aerogel, there are peaks that present in the collected FTIR spectrum. However, some of the peaks are not as strong/sharp as are to be expected. The C-H stretching peak around 2900 cm^{-1} is expected to be a little bit stronger than is seen, and the Si-O-Si peak is expected to be sharper. There is also a small peak around 1450 cm^{-1} that corresponds to a presence of water in the structure, which should not be there. The peak corresponding to the Si-C bond should also be sharper than is shown.

One attempt was done to try the ambient pressure drying with no solvent exchange, however the sample dried up completely in the oven and shattered and was unsuccessful.

Conclusion

In conclusion, the VMDMS monomer was able to be successfully polymerized into the PVMDMS polymer as seen visually and by the ^1H NMR spectrum. The polymer was then able to be successfully synthesized into the PVPMS hydrogel. However, the ambient pressure drying step was unsuccessful in drying the PVPMS hydrogel into the PVPMS aerogel. Future directions for this research include attempting different initiators for the polymerization step, trying different scales mol % of the initiator, as well as attempting the other ambient pressure drying method as well as other methods in order to successfully dry the hydrogel into the aerogel. Then, this experiment could be optimized for a student laboratory for CHEM411 Synthesis and Characterization of Materials.

References

- (1) Pierre, A. C.; Pajonk, G. M. Chemistry of Aerogels and Their Applications. *Chem. Rev.* **2002**, *102* (11), 4243–4266. <https://doi.org/10.1021/cr0101306>.
- (2) Kehrle, J.; Purkait, T. K.; Kaiser, S.; Raftopoulos, K. N.; Winnacker, M.; Ludwig, T.; Aghajamali, M.; Hanzlik, M.; Rodewald, K.; Helbich, T.; Papadakis, C. M.; Veinot, J. G. C.; Rieger, B. Superhydrophobic Silicon Nanocrystal–Silica Aerogel Hybrid Materials: Synthesis, Properties, and Sensing Application. *Langmuir* **2018**, *34* (16), 4888–4896. <https://doi.org/10.1021/acs.langmuir.7b03746>.
- (3) Aghajamali, M.; Iqbal, M.; Purkait, T. K.; Hadidi, L.; Sinelnikov, R.; Veinot, J. G. C. Synthesis and Properties of Luminescent Silicon Nanocrystal/Silica Aerogel Hybrid Materials. *Chem. Mater.* **2016**, *28* (11), 3877–3886. <https://doi.org/10.1021/acs.chemmater.6b01114>.
- (4) *High Performance Lithium–Sulfur Batteries with a Sustainable and Environmentally Friendly Carbon Aerogel Modified Separator | ACS Sustainable Chemistry & Engineering*. <https://pubs-acsc-org.wsuproxy.mnpals.net/doi/10.1021/acssuschemeng.7b02322> (accessed 2023-02-08).
- (5) Noroozi, M.; Panahi-Sarmad, M.; Abrisham, M.; Amirkiai, A.; Asghari, N.; Golbaten-Mofrad, H.; Karimpour-Motlagh, N.; Goodarzi, V.; Bahramian, A. R.; Zahiri, B. Nanostructure of Aerogels and Their Applications in Thermal Energy Insulation. *ACS Appl. Energy Mater.* **2019**, *2* (8), 5319–5349. <https://doi.org/10.1021/acsaem.9b01157>.
- (6) *Aerogel.org » Supercritical Drying*. <http://www.aerogel.org/?p=345> (accessed 2023-03-23).
- (7) Zu, G.; Kanamori, K.; Shimizu, T.; Zhu, Y.; Maeno, A.; Kaji, H.; Nakanishi, K.; Shen, J. Versatile Double-Cross-Linking Approach to Transparent, Machinable, Supercompressible, Highly Bendable Aerogel Thermal Superinsulators. *Chem. Mater.* **2018**, *30* (8), 2759–2770. <https://doi.org/10.1021/acs.chemmater.8b00563>.
- (8) Zu, G.; Shimizu, T.; Kanamori, K.; Zhu, Y.; Maeno, A.; Kaji, H.; Shen, J.; Nakanishi, K. Transparent, Superflexible Doubly Cross-Linked Polyvinylpolymethylsiloxane Aerogel Superinsulators

via Ambient Pressure Drying. *ACS Nano* **2018**, *12* (1), 521–532.

<https://doi.org/10.1021/acsnano.7b07117>.

(9) ACS Committee on Professional Training. ACS Guidelines and Evaluation Procedures for Bachelor's Degree Programs: Macromolecular, Supramolecular, and Nanoscale Systems in the Curriculum, **2015**.

<https://www.acs.org/content/dam/acsorg/about/governance/committees/training/acsapproved/degreeprogram/macromolecular-supramolecular-nanoscale-supplement.pdf> (accessed 2023-02-10).