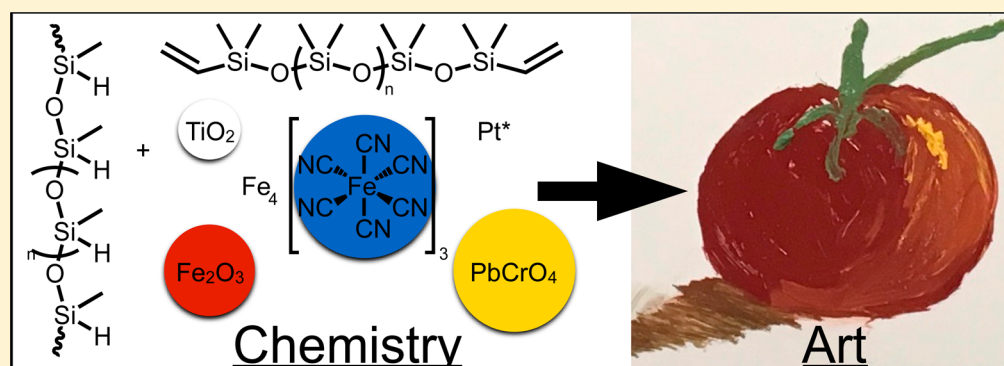


# The Art of Silicones: Bringing Siloxane Chemistry to the Undergraduate Curriculum

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**S** Supporting Information



**ABSTRACT:** Siloxane polymers and silicone materials are major components in most people's daily lives and are important in a wide variety of applications. However, despite their undeniable importance, they are often overlooked in the traditional undergraduate education, as they do not fall neatly into the traditional categories of organic or inorganic chemistry. Even in advanced polymer courses, they are often overlooked despite their value in describing many important polymer concepts. Herein we present three simple experiments to introduce siloxane polymers to the undergraduate education aimed at first-year, upper-level, and non-science-major students. This is prefaced with a brief overview of the history and chemistry of siloxanes and their value as teaching tools in the laboratory and classroom settings.

**KEYWORDS:** First-Year Undergraduate/General, Upper-Division Undergraduate, Polymer Chemistry, Inorganic Chemistry, Hands-On Learning/Manipulatives, Surface Science

## INTRODUCTION

From astronaut boots to potato chips,<sup>1,2</sup> siloxane polymers, commonly called silicones, are among the most important and versatile polymers produced by humankind. In fact, interactions with siloxane polymers are nearly universal in people's daily lives, as they are major components in shampoos, lotions, and pharmaceutical products because of their nontoxicity and biocompatibility.<sup>3-6</sup> Aside from these properties, their excellent thermal and chemical stabilities make them particularly suitable for extreme applications, such as nautical sealants, aerospace equipment, and dielectric barriers.<sup>7-9</sup> Silicones are also important foaming agents in polyurethane cushions found in most chairs and antifoaming agents in paints and coatings.<sup>10,11</sup> One would not be totally incorrect to say that we are literally surrounded by unseen silicones.

However, despite this myriad of applications and their undeniable importance, siloxane polymers are typically omitted from the general undergraduate curriculum and are not mentioned at all in most undergraduate textbooks, being only briefly referred to in advanced polymer texts.<sup>12</sup> This has the unintended consequence of a generally poor understanding of siloxane chemistry by most modern chemists, particularly in

contrast to that of chemists in the 1940s and 1950s. Additionally, the scarcity of suitable laboratory teaching experiments that utilize these materials does not help the situation.<sup>13-15</sup> This absence of silicones is made somewhat forgivable in context of the unique chemical structure of siloxane polymers. A quick glance at the most popular silicone, poly(dimethylsiloxane) (PDMS) (Figure 1A), shows a polymer that exhibits both an "inorganic" backbone and "organic" side chains. This hybrid nature gives rise to its many particular properties but also makes it hard to categorize easily within the spaces of the traditional subject areas.

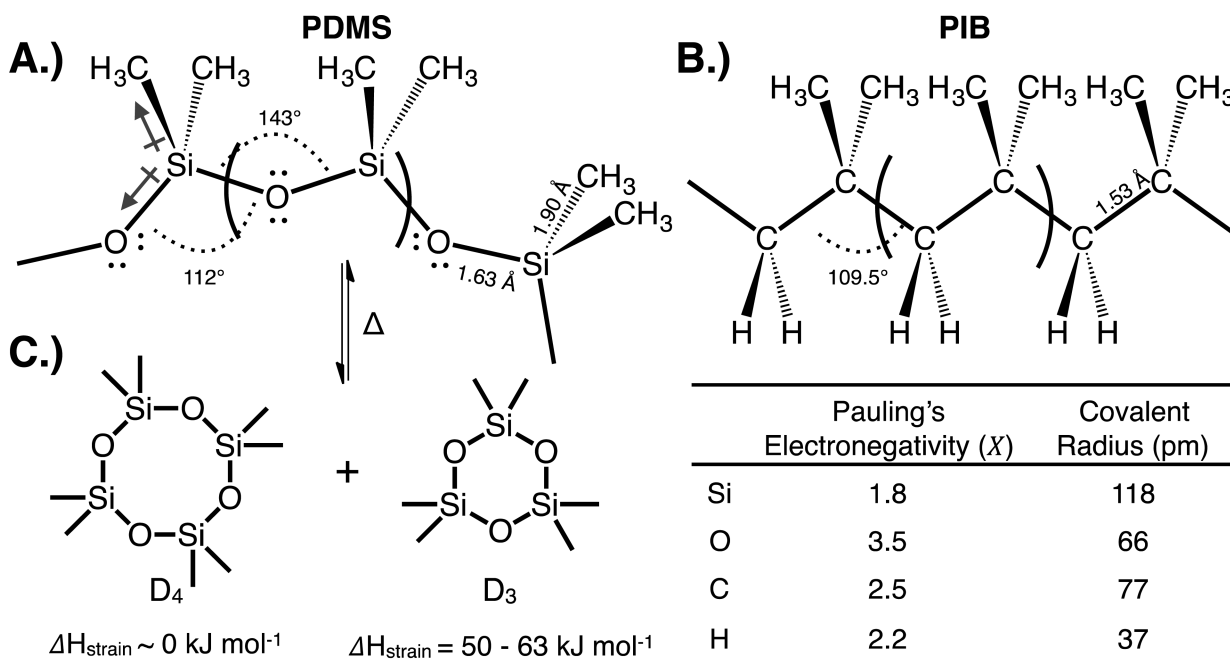
Nevertheless, despite the seeming absence of siloxanes in education, siloxane polymers lie at the crossroads of polymer, materials, organic, and inorganic chemistry and truly highlight the multidisciplinary nature of modern chemistry. They also provide an exceptional teaching opportunity for basic chemical

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**Figure 1.** Molecular comparisons of (A) poly(dimethylsiloxane) (PDMS), (B) poly(isobutylene) (PIB), and (C) the cyclic monomers/thermal degradation products of PDMS. The electronegativities and covalent radii of the constituent atoms are featured in the inset table for convenience.<sup>22</sup>

concepts (bond angles, polarity) and materials topics (hydrophobicity, elasticity). Given their widespread use and applications, we posit these polymers as simple and affordable materials to teach both basic and advanced topics in undergraduate lecture and laboratory courses.

Herein, we discuss the basic properties of silicones with a particular focus on structure–property relationships as useful examples for undergraduate lecture courses. A brief history of silicones emphasizes the impact of historical events and society on the development of chemistry. Finally, three examples of simple experiments are given that highlight the versatile nature of siloxanes to meet a wide variety of students. A simple surface chemistry demonstration with first-year students illustrates the importance of observation and laboratory hygiene. Hydro-silylation reactions for an advanced inorganic chemistry course demonstrate the catalytic cycle and organometallics concepts, while introducing basic concepts of materials engineering and elasticity. Finally, preparation of silicone-based oil paints provides an accessible project for nonscience majors and discusses concepts of homogeneity and heterogeneity. These three experiments are especially designed to account for the differences in facilities between institutions and can be performed without the need for complex instrumentation.

### Chemistry of Siloxane Polymers

While the chemistry of siloxanes, particularly PDMS, can certainly be found in a number of sources,<sup>16–18</sup> it is useful to look at silicones in the context of undergraduate education. A brief explanation of silicon and silicone nomenclature is given in the Supporting Information. Figure 1 and Table 1 provide scaled comparisons between the chemical structures and physical properties, respectively, of PDMS and its closest carbon-based analogue, poly(isobutylene) (PIB).<sup>19–21</sup> A cursory glance at both of these polymer structures reveals marked differences. First, the Si–O bonds (1.63 Å) and Si–C bonds (1.90 Å) are much longer than the C–C bonds in PIB (1.53 Å). Additionally, the bond angles of the PDMS backbone,

**Table 1.** Physical Properties of Poly(dimethylsiloxane) (PDMS) and Poly(isobutylene) (PIB)

polymer	$T_g$ (°C)	$T_d$ (°C)	density (g/mL)	surface tension (mN/m)	BDE (kJ/mol)
PDMS	–120	~400	0.970	19.8	443 (Si–O)
PIB	–71	~300	0.917	33.6	346 (C–C)

143° and 112°, are much greater than that in PIB (109.5°). This means the constituent atoms of PDMS are much further apart compared with those in PIB.

Another important attribute of siloxane polymers is the large difference in electronegativity between Si (1.8) and O (3.5). While generally considered covalent, the Si–O bond is actually more ionic in nature (51% ionic) according to Pauling's electronegativities.<sup>23</sup> In fact, the ionic nature adds a great deal of flexibility to the siloxane bond and allows the bond angle to easily pass through 180°, much “like a ball and socket joint”.<sup>16,24</sup> The polarity of the siloxane bond also gives rise to the high bond dissociation energy (BDE) of the Si–O bond, which in turn gives siloxanes their comparatively high thermal stability. However, the presence of the methyl side groups and flexibility of the siloxane bonds leads to an effective shielding of the backbone that results in weak intermolecular attractions between the polymer chains.<sup>25</sup> This can be easily seen in the low surface tension of PDMS. Furthermore, the low barrier to intramolecular rotation about the backbone bonds combined with the large distances between the polymer constituents creates more “empty space” (free volume) in PDMS, which is directly related to its extremely low glass transition temperature ( $T_g$ ) of –120 °C and causes PDMS nearly always to be liquid at temperatures between  $T_g$  and the degradation temperature ( $T_d$ ) of ~400 °C.<sup>26</sup>

The preparation of siloxane polymers is also a good method for explaining different mechanisms of polymerization. Scheme 1 shows the two major mechanisms for producing PDMS. Polycondensation of dichlorosilanes offers a step-growth





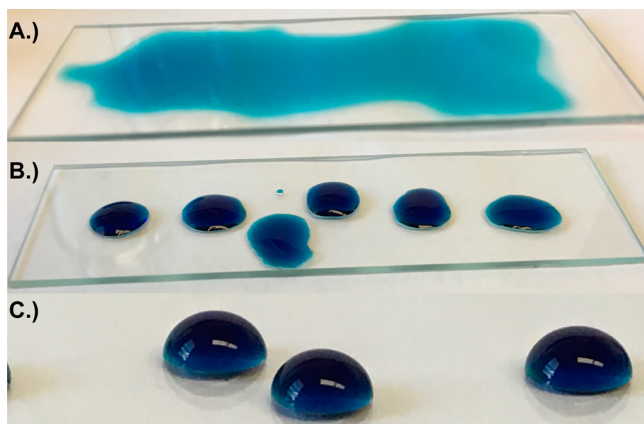
It should also be noted that hydrosilylation reactions are extremely efficient and exothermic. Therefore, it is important that only small amounts of dilute solutions of the platinum catalyst, prepared in advance, should be used in these experiments. As a precaution and to aid the hydrosilylation experiments, the materials should be chilled in an ice bath prior to use. Full experimental details are provided in the [Supporting Information](#).

## RESULTS AND DISCUSSION

### Hydrophobization of Glass Slides via PDMS

This experiment has been carried out using cohorts of 18 students of mixed science majors in a first-year chemistry laboratory section. Specifically, it was intended to function as a supplement to an observation-driven experiment of chemical reactions (metathesis, precipitation) and reinforce the importance of good observational technique in the laboratory setting, which occurs in the second half of their first semester. However, in principle this experiment could be performed much earlier as well. The week prior to this lab, students prepared clean glass slides for treatment. A few droplets of PDMS (MW  $\sim$  2000 g/mol) were allowed to spread across the glass slides, and then the slides were placed into covered glass Petri dishes, which were placed into an oven at 100 °C for 24 h. This procedure is derived from previously reported results and requires very little preparation time.<sup>42,43</sup>

During the experiment, students were asked to compare the shapes of water droplets on a clean glass slide, a dirty glass slide (here, students rubbed the glass slide with their nitrile gloved fingers), and the PDMS-modified glass slide. Food coloring was added to the water to aid in the observations. In many cases, students opted to take photos of the droplets. [Figure 2](#) shows



**Figure 2.** Water droplets on (A) a clean glass microscope slide, (B) a microscope slide that was made “dirty” by being rubbed with a gloved finger, and (C) a PDMS-treated microscope slide.

images of the three samples of water droplets. Here we can see that water spreads on clean glass (wetting), forms less spread, stable, but irregularly shaped droplets on “dirty” glass (partial wetting), and beads up on the PDMS-modified glass to form droplets shaped as sections of a sphere (nonwetting). More detailed information, including advancing ( $\theta_A$ ) and receding ( $\theta_R$ ) contact angles measured on a contact angle goniometer, is provided in [Table 2](#).<sup>44</sup> Students should observe static contact angles in the range between the advancing and receding contact angles.<sup>45</sup>

**Table 2.** Advancing and Receding Contact Angles of Clean, Dirty, and PDMS-Treated Microscope Slides<sup>46</sup>

Sample	$\theta_A$ (deg)	$\theta_R$ (deg)
Clean slide	— <sup>a</sup>	— <sup>a</sup>
Dirty slide	54	21
PDMS-treated slide	99	56

<sup>a</sup>The water spread on the slide.

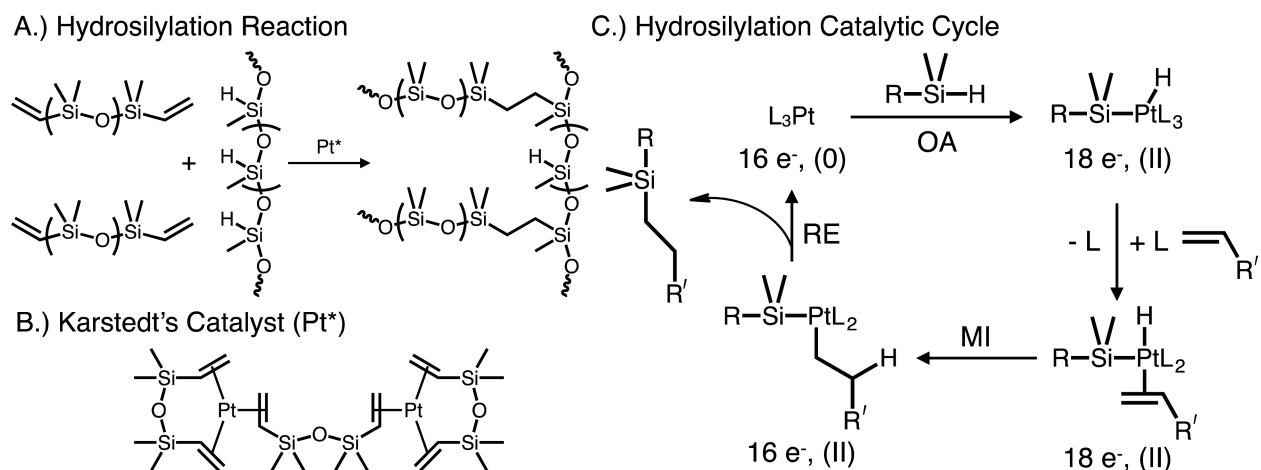
These results are not surprising, but they illustrate several important concepts. First, and most obvious, is how clean glassware appears when interacting with water. While this phenomenon is often described at the beginning of the laboratory course, we found that this important concept was not being substantiated experimentally. Second, by rubbing the glass with their gloved fingers, students can see how easily glassware can be contaminated, even when one is wearing gloves, by the oils from the skin and other contaminants from the laboratory. This, of course, is used to reinforce the reason why one should not handle normal items, like cell phones or doorknobs, while wearing gloves. Similar results can also be derived by rubbing a bare finger on the slides (see the [Supporting Information](#)). Third, it shows how molecular-level events can affect macroscopic properties. While the chemical structure of glass causes water to spread out, changing that surface to PDMS, even as a very thin coating, causes water to bead up. This is the same principle and chemistry found in commercial water repellent sprays for automobile windshields. Finally, this introduces students to multiweek laboratory experiments with minimal effort. Over the last several years, the benefits of more realistic experimental projects have been discussed,<sup>46,47</sup> and this provides a very simple example to meet those needs as well as to introduce authentic practice to students starting in chemistry.<sup>48–50</sup>

While we have found that this experiment illustrates the above-mentioned points well, it also reinforces other topics found in the lecture component of this course, specifically the acidic nature of inorganic oxides. In particular, the mechanism of this reaction relies on the acidity of surface silanols to cleave the siloxane bonds and subsequently form covalent bonds.<sup>42</sup> Finally, while this has not been performed by these authors, we suggest this as an excellent companion piece to the superhydrophobicity experiment proposed by Verbanic et al.<sup>51</sup> for a more in-depth discussion of surface properties and hydrophobicity.

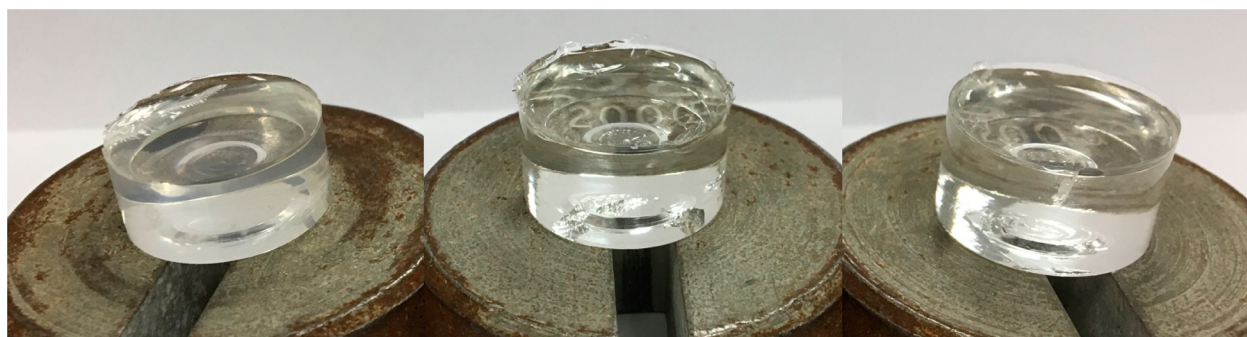
### Hydrosilylation of Siloxane Polymers

This experiment was designed for a capstone advanced inorganic chemistry course with small cohorts of students. The design philosophy for the entire laboratory sequence was six mini-projects to be performed over the course of the semester. Most of the experiments were multiweek syntheses and characterizations, and students were expected to work in groups on more than one (typically two) experiments within an allotted lab time (3 hours) to simulate more realistic research conditions. This particular experiment appears midsemester in the sequence to tie polymer chemistry into inorganic chemistry and was envisioned as a modern update of and companion to the classic “silly putty” experiment found in most inorganic laboratory textbooks.<sup>52,53</sup> Students were tasked with preparing three separate silicone materials with different cross-link densities via hydrosilylation and testing their material properties by examining their changes under different weights.





**Figure 3.** (A) Platinum-catalyzed hydrosilylation reaction of vinyl-terminated PDMS and poly(hydridomethylsiloxane). (B) Structure of Karstedt's catalyst. (C) Catalytic cycle for the platinum catalyst in the hydrosilylation reaction.



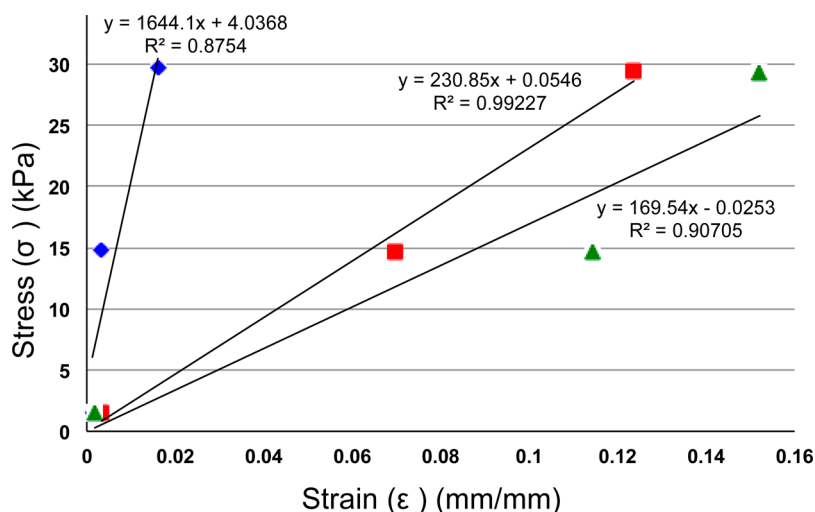
**Figure 4.** Silicone materials with decreasing cross-link density (left to right).

Figure 3 shows the hydrosilylation reaction of vinyl-terminated PDMS (v-PDMS) and poly(hydridomethylsiloxane) (PHMS) and the platinum catalyst utilized in these reactions, Karstedt's catalyst. Here the processes of oxidative addition (OA), ligand exchange ( $-L/+L$ ), migratory insertion (MI), and reductive elimination (RE) are all well-demonstrated. The electron count and oxidation number are provided beneath each structure as well. While the use of a platinum catalyst may not seem cost-effective, in fact extremely little is needed to perform these reactions. Students mix the v-PDMS (MW  $\sim 6000$  g/mol) and PHMS (MW  $\sim 2000$  g/mol) in 3:1 and 2:1 molar ratios with 50  $\mu\text{L}$  of a dilute platinum catalyst solution in toluene (2.20 mM Pt) in polystyrene vials to achieve different cross-linking densities based on previously reported techniques.<sup>54</sup> Students should stir the components gently to avoid the formation of air bubbles in the samples. The use of higher-molecular-weight v-PDMS has been attempted for this experiment, but seldom has it afforded a workable material without extensive bubble formation. It is likely that using a commercial silicone kit, like Sylgard 184, would avoid this. However, we have avoided using these kits for reasons discussed later in the text.

As a control and contrast to these "soft" materials, an extremely cross-linked silicone was prepared using a 1:2 molar ratio of tetramethylcyclotetrasiloxane and tetramethyltetravinylcyclotetrasiloxane following the procedure reported by Zheng and McCarthy.<sup>55</sup> As previously stated, some care should be taken when mixing these materials as the hydrosilylation reaction is extremely exothermic. For this reason, the starting

materials are chilled in an ice bath prior to mixing, and excess platinum catalyst should be avoided. The mixed product is chilled in an ice bath and allowed to warm to room temperature. Following this, the solid samples are allowed to cure at 60  $^{\circ}\text{C}$  for 24 h and are then isolated by carefully cracking the plastic vials. Additional details are provided in the [Supporting Information](#). Using hard objects, such as spatula, should be avoided in removing the samples, as they often damage the sample surfaces, which can affect the measurements.

Using the pure polymers as starting materials, rather than commercially available PDMS elastomer mixtures, allows for a more pure polymer material without additional fillers, like silica nanoparticles. However, these commercially available mixtures, such as Sylgard 184, would suit this experiment as well and should not affect the desired outcomes.<sup>56,57</sup> Figure 4 shows the silicone materials after isolation from the plastic vials. In principle, the samples look nearly identical, but the differences in cross-linking density can be easily felt by squeezing them. One of the benefits of this experiment is the ability for students to see the tangible effects of small amounts of catalyst on a reaction. The starting materials are low-viscosity silicones, which in turn become monolithic solids. As the catalytic cycle (Figure 3C) for Karstedt's catalyst has been well-studied,<sup>58</sup> it also provides a good connection to lecture topics, particularly on organometallics. Additionally, the infrared spectra of these materials have been well-characterized, and the peaks for Si-H (2158  $\text{cm}^{-1}$ , stretching; 756  $\text{cm}^{-1}$ , bending), the vinyl group



**Figure 5.** Stress–strain curves of a lightly cross-linked silicone (triangles), a medium cross-linked silicone (squares) and an extremely cross-linked silicone (diamonds).

( $1650\text{ cm}^{-1}$ ), and the resulting  $\text{CH}_2$  ( $1408\text{ cm}^{-1}$ ) are clearly visible.<sup>59</sup>

One of the well-known properties of silicone materials is their elasticity. This is typically characterized by the material's Young's modulus,  $E$ ,<sup>60</sup> for small stress–strain values and can be qualitatively felt simply by “squishing” the materials with one's fingers. We note that typically tensile measurements are utilized in determining Young's modulus, since there is often a deviation from ideal behavior under compression, especially under large stresses and strains.<sup>61,62</sup> In this experiment, only small stresses (kPa) and strains are utilized to avoid this deviation, but it is expected should larger stresses (MPa) be used. For the students' experiment, several standard weights are placed on top of the silicone materials (Figure S5), and the changes in height are measured. The Young's modulus is then obtained from the slope of the stress versus strain plot (Figure 5) on the basis of the expression shown in eq 1:

$$E = \frac{\sigma}{\epsilon} = \frac{mg/A}{\Delta h/h_0} \quad (1)$$

where  $\sigma$  is the stress,  $\epsilon$  is the strain,  $m$  is the mass of the standard weight in kilograms,  $g$  is the gravimetric constant ( $9.8\text{ m/s}^2$ ),  $A$  is the surface area of the top of the silicone sample in meters squared,  $h_0$  is the initial height of the sample without a weight in meters, and  $\Delta h$  is the change in the height under compression.

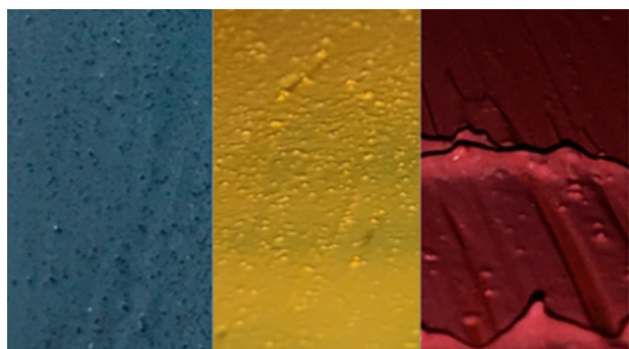
For each of these measurements, a caliper was used to measure the differences in height in millimeters, but a traditional ruler would also be suitable. There is some inherent error associated with these measurements, which can arise from not having a perfectly smooth, flat surface for the weights, as well as any air bubbles that may be present in the sample. However, students can still assess the effect of cross-linking on the material's elasticity from the gathered moduli data. Figure 5 presents stress–strain curves for the three samples shown in Figure 4. The slope of each fitted trend line is the material's Young's modulus. As expected, the Young's modulus decreases with decreasing cross-linking. In other words, materials with lower Young's moduli are more elastic (deform more easily under stress), whereas high-modulus materials resist deformation. Here the moduli for the highly cross-linked, medium cross-linked, and lightly cross-linked silicones were 1.64 GPa,

230 kPa, and 170 kPa, respectively. For comparison, the literature value for the extremely cross-linked control silicone has been reported to be  $1.59 \pm 0.16\text{ GPa}$ .<sup>55</sup> Through this characterization, students can tie together the topics of catalysis, cross-linking, and mechanical properties to highlight the multidisciplinary nature of chemistry.

#### Preparation of Silicone Oil Paints

This experiment was proposed as a senior thesis project for a nonscience major and was performed over the course of a semester. The outcomes of this project were procedures to make silicone oil paints as artistic media and the preparation of several small pieces of art. These procedures have since been adapted for an elementary nonmajor science course (Science and Art) to explain the components and purposes of paints in a single laboratory experiment. The chemistry of this reaction is identical to that in the previous experiment, and the procedure utilizes a 1:1 molar ratio of  $\nu$ -PDMS (6000 g/mol) and PHMS (2000 g/mol) as the binder and the traditional inorganic powders of Prussian blue [ $\text{Fe}_7(\text{CN})_{18}$ ], chrome yellow ( $\text{PbCrO}_4$ ),<sup>63</sup> and red ochre ( $\text{Fe}_2\text{O}_3$ ) along with P25 titania ( $\text{TiO}_2$ ) as pigments. Students are given the procedure found in the Supporting Information and asked to mix the materials together. Again, cooling the components prior to mixing helps with the application of the paint without worry of premature cross-linking.

The three pigments were chosen for several reasons. Most obviously, they are the three primary colors and can be used to make secondary colors. They also illustrate the differences between dyes and pigments, where dyes are typically aqueous solutions and pigments are solid particles. Third, these pigments have been utilized in several famous paintings, including van Gogh's *Starry Night* and *Sunflowers*. Red ochre is one of the oldest pigments known to humankind and has been found in Paleolithic sites at Pech Merle in France. The particles themselves also exhibit different properties. Prussian blue tends to form aggregates that make dispersion slightly more difficult. Improper mixing can easily lead to heterogeneous coatings (Figure 6). This is seen in the heterogeneity in both the color (dark spots) and texture, where the Prussian blue sample displays both discolorations and a rough texture. The chrome yellow sample in Figure 6 shows a uniform color but still has a rough texture. On the other hand, red ochre is generally a very



**Figure 6.** Degrees of heterogeneity in silicone paints decreasing from left to right.

fine powder that is easily mixed with the silicone to produce very homogeneous mixtures. This allows students to directly observe the effects of heterogeneity on the texture and quality of the paints that they have made. Using titania also brings in modern paint applications.<sup>64</sup> Titania is the most widely used white pigment in the world and is found in nearly every paint currently produced. Students can easily see why this is the case, since titania is both extremely white and does not let light through the samples. Furthermore, the use of titania is not limited to paints. Campbell et al.<sup>65</sup> have previously reported the compounding of titania in silicone materials for the preparation of fluorescent and magnetic materials in undergraduate experiments.

During the experiment, students are given the “recipe” for making the paints and are generally permitted to experiment with making their own colors. Ceramic tiles are used as easy, cheap substrates for the paintings (Figure 7A), but canvas is also an option (Figure 7B). As can be seen from Figure 7, students will often stick to the primary colors, but many will branch out into secondary colors if time permits. The more artistically inclined have even experimented with brush strokes using both the spatula and a paint brush (Figure 7C).

Aside from the concepts of heterogeneity and paint composition, this experiment introduces many non-science-major students to basic laboratory practices to which they may not have otherwise been exposed, including using balances and

preparing mixtures. Because of the low stakes of the experiment, errors in mixing can often be turned into educational experiences. For example, using the incorrect amount of v-PDMS could lead to a painting that is either too hard and cracks or is too soft and tacky. Being able to unite actions with the resulting outcomes is an essential skill, regardless of discipline.

However, perhaps the strongest benefits of this experiment are twofold. First, it shows how something as commonplace as paint can have very deep science behind it, and in fact, a lot of time and research is put into these materials. Second, it dispels the notion that the sciences are necessarily boring and intimidating but rather shows that science can be a fun and rewarding experience.

## CONCLUSION

Despite many misconceptions about these materials, siloxane polymers offer many opportunities for students across different levels of experience and disciplines. Their unique chemical attributes make them excellent examples for explaining fundamental concepts of chemistry and truly highlight the interdisciplinary nature of the field. Their nontoxicity makes them ideal candidates for simple laboratory course experiments that do not require the use of expensive instrumentation. Being ubiquitous, commonplace materials, siloxanes and silicones deserve a place in our undergraduate curriculum, and it is time for these fascinating polymers to achieve greater popularity within our general education of undergraduate chemistry students.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00769.

Detailed experimental procedures and a brief discussion of silicone nomenclature (PDF, DOCX)

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**Figure 7.** Student silicone paintings on (A) 4 in. × 4 in. ceramic tiles, (B) 3 in. × 6 in. stretched canvas showing all colors, and (C) different brush strokes on canvas.



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## Notes

The authors declare no competing financial interest.

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