Photocrosslinked Hydrogel Replication of Small Objects: a Multistep Final Project for Undergraduate Polymer Laboratories

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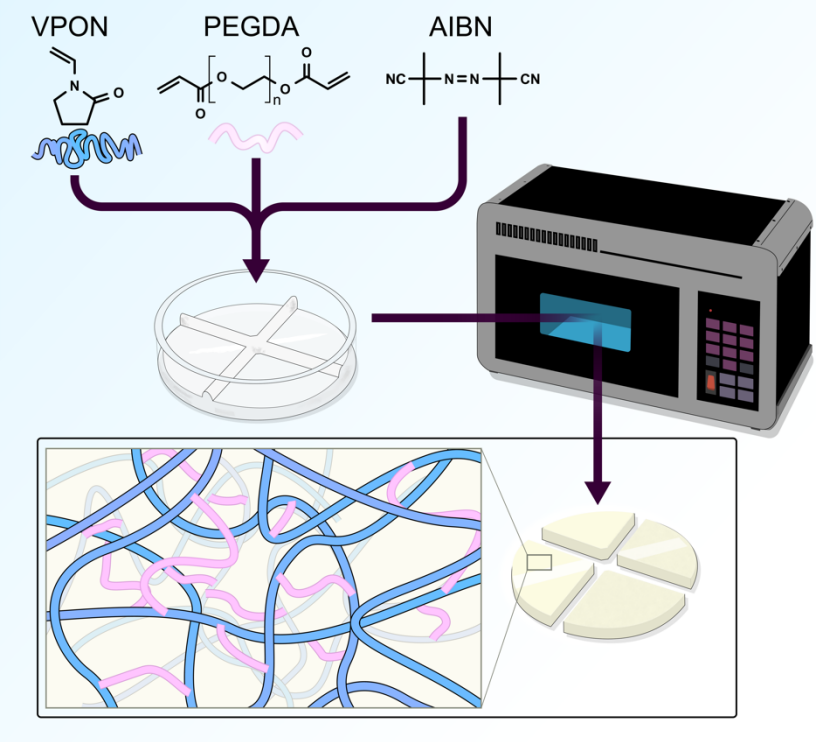
Abstract

We developed a multipart laboratory experiment on the synthesis of free-standing hydrogels for junior to senior undergraduate students. In this experiment series that runs over the course of multiple 3-hour lab periods, small everyday objects belonging to the students are reproduced as hydrogels by first creating negative templates in thermally-cured poly(dimethylsiloxane) molds (PDMS), followed by simultaneous photopolymerization and crosslinking using N-vinylpyrrolidone and poly(ethylene glycol) diacrylate in the molds. After curing at room temperature, the molds are bisected and the objects are recovered. Second, the students optimize the synthesis of poly(N-vinylpyrrolidone)/poly(ethylene glycol) diacrylate (PVPON/PEGDA) hydrogels via UV-induced polymerization in test-batch scale quartered petri dishes. Next, using the optimized hydrogel synthesis and the molds from part one, PVPON/PEGDA replicas of their objects are obtained by simultaneous photopolymerization and

crosslinking in a UV crosslinking device. Finally, students present their results, methodology, and proposals for industrial scaleup to the class. The students are encouraged by steady progress toward their goal of making a freestanding hydrogel replica of their object and applying their knowledge toward developing a reproduceable protocol. They learn to control synthetic parameters including mixing ratios, polymerization time, and UV intensity as well as readjusting their synthesis procedure based on their understanding of structure-property concepts. This experience provides students with an introduction to polymer synthesis and methodologies, familiar to both academic research and industry and builds confidence in their ability to conduct independent research and development.

Graphical Abstract



Keywords: Upper-Division Undergraduate, Polymer Chemistry, Hands-On Learning, Free Radical Reaction, Polymerization, Laboratory Instruction

Introduction

The commodity nature and vast potential for development of polymers has led to a continuously growing market for students with experience in polymers and a subsequent increase in the number of schools offering degree tracks with a focus in polymers.[1] Polymeric materials may be covered in curricula offered by a range of academic departments including biology, engineering, chemistry, and medicine.[2,3]

As methodologies that were once relegated to research laboratories due to their complexity have become optimized to the point of industrial adoption, more undergraduate chemistry laboratory experiences are being geared toward advanced synthetic strategies such as atom transfer radical polymerization (ATRP) and living polymerization.[4-7] Similarly, the optical properties and industrial flexibility of poly(dimethylsiloxane) (PDMS)-based materials has inspired the development of teaching labs based on the synthesis and characterization of siloxane polymers.[8,9,10,11] Although bulk elastomers have been a primary product of the petroleum industry for decades,[12] hydrogels may be better examples for chemistry course material as they encompass many of the classic essential concepts in polymer chemistry education: radical polymerization, crosslinking, bulk chemical and mechanical properties, macromolecular and network architecture, intuitive structure-property relationships, and applications in familiar and emerging fields.[13,14] For example, hydrogels are being reported as delivery vehicles for hydrophobic biomolecules and tissue repair scaffolds for myocardial infarction damage.[15,16] Their relative youth in comparison to some of the core chemistry disciplines also lends itself to engaging exploratory experiences that feel authentic at the educational laboratory level, such as a recent example of self-healing hydrogels that can be assembled with minimal complication using poly(vinyl alcohol) (PVA) and water.[17]

In this respect, the development of new undergraduate level laboratory experiences incorporating aspects of polymeric hydrogels would be beneficial to the future of polymer research. Equally important, by relating the work done in the teaching laboratory setting to current research with a clear impact potential,[2] students may not only develop interest in the field of polymers but also gain confidence in their ability to make an impact in meaningful research efforts based on their success developing these relatively new systems on a small laboratory scale.

Herein, we report on a laboratory design of hydrogel replication of small objects based on the UV-initiated polymerization of N-vinylpyrrolidone (VPON) crosslinked by poly(ethylene glycol) diacrylate (PEGDA) in poly(dimethylsilxoane) (PDMS) negative templates of the objects. Although PEGDA-PVPON networks have been reported in literature, those studies focused on fundamental kinetic behaviors and molecular orientation during the reaction process.[18,19] Our implementation is geared toward undergraduate students with limited polymer experience and focuses on experimental design and hydrogel synthesis. During this multi-part experiment, students optimize synthetic parameters in test-batch scale quartered petri dishes by varying mixing ratios of the AIBN initiator, VPON monomer, and PEGDA crosslinker to obtain highly crosslinked hydrogels. The poly(dimethylsiloxane), poly(ethylene glycol) diacrylate, and poly(N-vinylpyrrolidone) selected for this laboratory are biocompatible polymers widely used in cutting edge biomedical research ranging from drug delivery to contact lens formulations.[20-25] This lab introduces students to the important concepts of initiator:monomer:crosslinker mixing ratios, UV-initiated polymerization, and the structure-functional relationships of crosslinked elastomers while allowing them to apply their learning in an iterative hypothesis-result-adaptation sequence.

This lab experience is unique and as of yet, no other experimental series based on PDMS molds and object replication using cross-linked polymer networks has been reported to the best of

our knowledge. The students are encouraged to make connections between the hydrogel materials they produce in the lab and their everyday experience by replicating an object of their choosing in a PDMS mold and proposing how the technique could be used to produce a product relevant to the modern world. We believe that the concepts developed in our work can serve as an excellent platform for building valuable knowledge for students, being suitable for entire-semester research projects[26] and independent learning exercises that encourage students to relate the what they are learning to real-world applications like drug research and commercial product development.

Background of the experiment

We have developed these laboratory experiments to serve as a "final project" series of two to three 3-hour classes in a semester-long course for junior to senior undergraduates. The experimental series was implemented in classes numbering from 20 to 39 students working in groups of 3 and was developed over 3 semesters. After reading a supplementary prelab document on the course website and taking an online quiz on the fundamentals of polymer hydrogels and photoinitiated reactions, the students create negative templates of an object using a PDMS mold system. While the PDMS mold cures, the students develop the protocol to produce a hydrogel material with physical properties in line with the purpose of their object. Along the way, the fundamental aspects of the effects of crosslink density as a function of mixing ratios and reaction time on the final properties of the PVPON-PEGDA hydrogels are explored as the students try to produce test batches of the hydrogels with varying levels of rigidity in plastic petri dishes.

Their learning is assessed first by their ability to produce a freestanding hydrogel using their own optimized procedure in the final class, by an in-class presentation in which they propose a commercialization of their concepts, and by their performance on relevant questions on a final

exam. Encouraging the students to present creative and entertaining applications leads to an in-class discussion of the actual real-life merits and pitfalls of such ideas, and their gained knowledge is evaluated at this point by their ability to answer questions posed by the class and the instructor. The main criteria are: their understanding of the basic properties of crosslinked hydrogels, their understanding of the purpose of each reagent and ability to demonstrate schematically the structure of the hydrogels they produce, and their ability to predict how desired changes in the physical properties of the hydrogels would be achieved through changes of the synthetic procedure.

The main framework, which starts with creating a negative mold of the object in thermally-cured poly(dimethylsilxoane) (PDMS) and subsequently photopolymerizing/crosslinking monomers to form a freestanding hydrogel, was inspired by recent report in Nature Communications.[27] In the work referenced above, PDMS molds were used to prepare nanoscale PEGDA hydrogel probe tips for atomic force microscopy (AFM). Our adaptation of this concept involves changing the hydrogel composition by adding VPON monomer and 2,2′-azobis(2-methylpropionitrile) (AIBN) initiator resulting in simultaneous VPON polymerization and crosslinking by PEGDA under irradiation with a 254 nm UV light. We are motivated by the fact that the presence of the PVPON should increase rigidity compared to PEGDA-only hydrogels, while the AIBN initiator is less expensive and less sensitive to water or oxygen than the phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide used in the original procedure. The procedure introduced here demonstrates that the content of the lab has merits at the forefront of polymer research and also raises open-ended questions about the network architecture and reaction behaviors of the PVPON-PEGDA system, which in turn promote discussion between the students and the instructor. Figure 1 shows an overview of the PVPON-PEGDA hydrogel formation process used in the multipart lab. The entire methodology, materials list, and detailed experimental

procedures are given in the supporting files (Supporting information: Materials, methods, and detailed procedures).

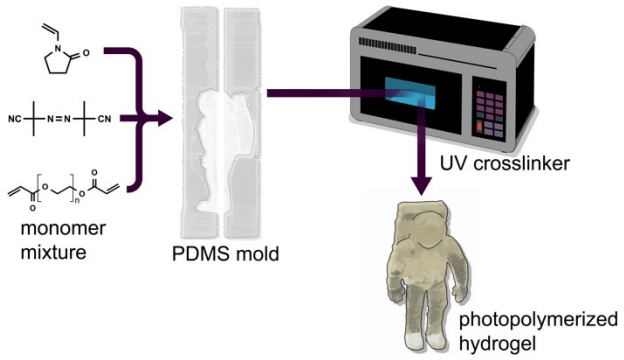


Figure 1. An overview of the UV-photopolymerization and object replication. The typical mixing ratio was between 10-50 mg/mL AIBN in 2 mL VPON added to 2 mL of 2.5-15 v/v% PEGDA (700 Da Mn) in VPON. 60 s of UV irradiation formed freestanding hydrogel replicas that the students removed from the PDMS molds.

Hazards

VPON, PEGDA, and AIBN are mild irritants and should be kept in a fume hood until the photoinitiated reaction. Sylgard 184 silicone elastomer kit is harmful if swallowed or inhaled, and can cause skin, eye, and respiratory irritation. The Sylgard 184 Silicone Elastomer kit components should be mixed in a fume hood. UV light at any intensity is dangerous to tissues and the eyes. A cover or shield must be used when the UV light is on. The AIBN-VPON-PEGDA prepolymer solutions may heat rapidly upon UV irradiation; care should be taken to prevent burns in the moments after the photoinitiated reaction.

Results and Discussion

The online prelab portion introduces students to some examples of hydrogels from everyday life, followed by the basics of photoinitiated polymerization and the relationships between crosslinking and hydrogel properties. An overview of the project involving descriptions of the PDMS mold formation using Sylgard 184 and VPON hydrogel synthesis is also given along with some guidelines for the VPON:PEGDA:AIBN mixing ratios. The students are instructed to bring a variety of small objects (up to 3 inches) to be used in the PDMS molds in the first lab. As the Sylgard 184 mixture takes at least 24 hours to fully cure into a crosslinked solid at room temperature, the students work in parallel during the first lab to start testing the effect of the VPON:PEGDA:AIBN mixing ratio against their expectation for the rigidity of the resulting hydrogel elastomer.

Development stage: UV-photopolymerization in petri dishes

At this stage we find that the students express general enthusiasm for the project and start to become excited to test their ideas about mixing ratios and use the UV-crosslinker to begin photoinitiated polymerization reactions in the petri dishes. This iterative portion of the lab allows the students to challenge their understandings of the effects of altering reaction parameters on the properties of the PEGDA-crosslinked PVPON final product. The process of choosing a mixing ratio and UV exposure time, evaluating the properties of the resulting PVPON-PEGDA gels, and reformulating the mixture teaches students that they can strategically approach a desired result through the application of their gained knowledge of elastomers, crosslinking density, and polymer synthesis. In fact, a recent article discussing crosslinked polymethacrylate esters produced via photoinitiation as a teaching lab has revealed the importance of introducing students to

photochemistry and shown that photoinitiated radical reactions and polymer synthesis is a complimentary educational pairing.[1]

The students set out to find a mixing ratio of VPON, PEGDA, and AIBN that produces a PVPON-PEGDA hydrogel with elastomeric properties, but quickly find that the product can be either completely free-flowing or extremely brittle if the mixing ratio is not optimized. For each reaction, the students kept notes on the mixing ratio and recorded observations on the hydrogel produced from the photopolymerization reaction before moving on to the next test batch. Figure 2 depicts a typical quartered petri dish with the results from 4 different mixing ratios after photopolymerization. Reaction observations from the students in the most recent semester are shown in Table S-1 (Supporting Information: Instructor notes and table of student observations). The student observations are summarized as follows: the mixing ratios with 10 mg/mL of AIBN did not sufficiently crosslink in the 20 s reaction time to be freestanding, while those with <50 mg/mL became brittle. Students noticed that increasing either PEGDA or AIBN volumes from 0.1 mL to 0.6 mL and from 10 to 100 mg/mL, respectively, increased robustness of the hydrogels. Some students reported that the hydrogel burned in the UV crosslinker at 120 mJ/cm^{2}s intensity at AIBN concentrations above 50 mg/mL as well. All found that increased concentrations of PEGDA created hydrogels that were not flexible. Indeed, increasing crosslinker and initiator concentration increases crosslink density which is known to result in a stiffer material.[28,29] There was no observable effect of the PDMS molds interacting with the prepolymer solution, given that the resulting hydrogels were as easily removed from the molds as they were from the plastic petri dishes.

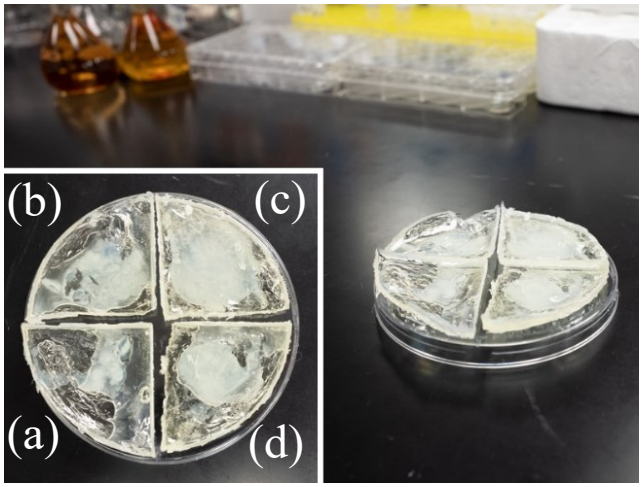


Figure 2. Quartered petri dish and the photocrosslinked hydrogels prepared using different mixing ratios. These hydrogels represent the initial stages of development when the students first started working with the materials and understanding their properties. There is an observable difference in the opacity of the mixtures of differing VPON:PEGDA:AIBN ratios where (a) through (c) represent increasing the PEGDA from 0.1-0.3 mL in 4 mL of VPON and (d) represents an increase in AIBN from (c) from 25 to 50 mg/mL.

This experiment provides teaching opportunities that can be used to reinforce the fundamental theories concerning the relationships between initiator concentration and polymer molecular weight, and those of crosslinking density and rigidity/swelling capability. To simplify discussions, the reactivity ratio of PEGDA and VPON monomers may be assumed to be close to 1, as the propagation rate constant of VPON on the bulk phase initiated by AIBN at 50 °C has been reported to be in the range[30] of 1000 M^{-1} s^{-1} while that of various long chain acrylates was reported

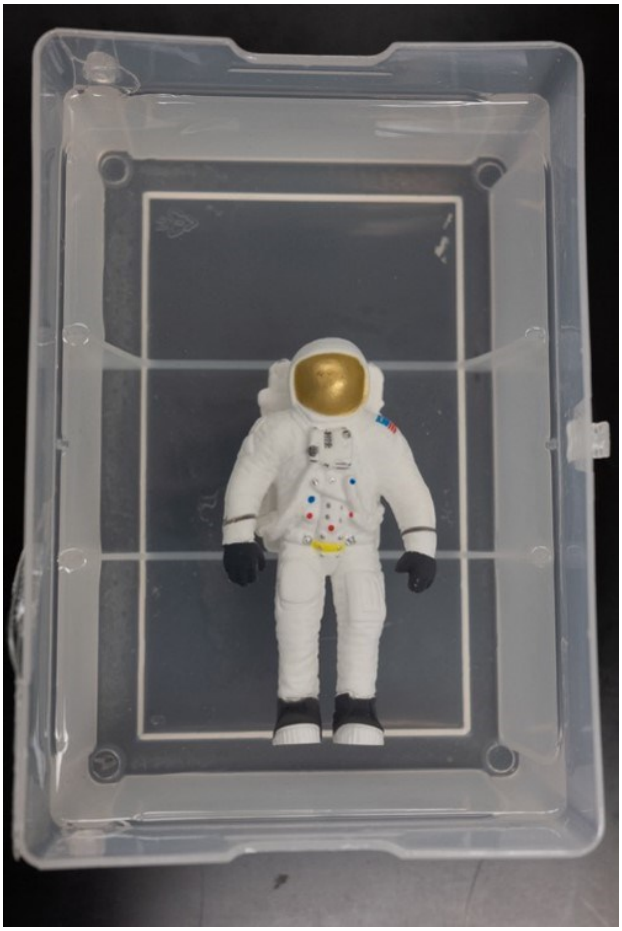


Figure 3. The object (2-inch tall) to be molded was submerged in the Sylgard 184 silicone elastomer mixture in a plastic container. This image was taken 24 h after placing the figurine within the molding liquid after the removal of residual air bubbles.

to be in a similar (900-1200 M^{-1} s^{-1}) range.[31] However, though it has been well known for decades that the reaction solvent exerts a strong effect on the polymerization rate of VPON,[31,32,33] the effects of the particular comonomer (PEGDA) used in this study have not been established in

detail. While an in-depth discussion of these concepts was not implemented in our lab, one could be implemented to expand the scope of this lab into a complex quantitative analysis series.

Application stage: object replication in PDMS molds

After completing the development phase with the petri dishes, the students move on to create 1:1 replicas of their original objects using their newly-formulated photopolymer synthesis protocol and the PDMS molds from the first lab. While the Sylgard 184 mixture can cure in < 3 hours with heat, we have found that letting the molds cure at room temperature allows the near-unavoidable air bubbles that form in the viscous mixture after pouring and mixing to escape. Figure 3 shows an example of a completely bubble-free mold after the curing process. A container with some flexibility permits easier removal of the PDMS mold after curing. The PDMS mold must be cut carefully to separate the mold into two halves that can be rejoined into a single well-sealed unit as seen in Figure 4. If done carefully, the objects can be returned to the students in perfect condition.

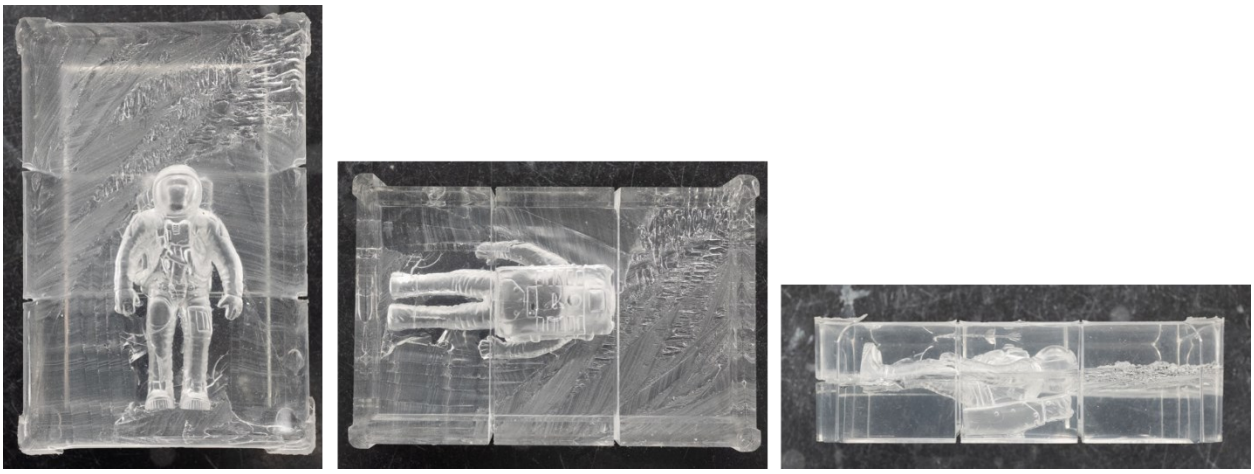


Figure 4. The empty mold (a negative replica) viewed from different angles after cutting along the coronal plane with a utility razor and removing the figurine. Careful cutting allowed the PDMS mold to reseal along the cut and retain the VPON/PEGDA/AIBN solution during the photopolymerization procedure. The monomer solution was poured through a small hole near the middle of the backpack portion of the figurine when the mold was used for the photopolymerization procedure.

From here, the students prepare a large-scale batch of their optimized AIBN-VPON-PEGDA mixture from the development phase to be used for replication of their objects. The AIBN-VPON-PEGDA mixture is poured into the resealed PDMS molds and placed in the UV-crosslinker for an extended time of 60 s. In our experience, the need to compress the mold with elastic bands varied with the geometry of the cuts and size of the cavity. The optical clarity of the PDMS allows the UV light to reach the reaction mixture efficiently and it subsequently undergoes polymerization and crosslinking to form a solid elastomeric hydrogel of PEGDA-crosslinked PVPON with the exact shape, contour, and outer texture of their original object. The reaction produces enough heat to make the replica dangerous to touch for the first few minutes, so a cool down period of 3-5 minutes was implemented after the photopolymerization. The hydrogel

elastomer releases cleanly from the PDMS surface but should be removed delicately to avoid tearing.

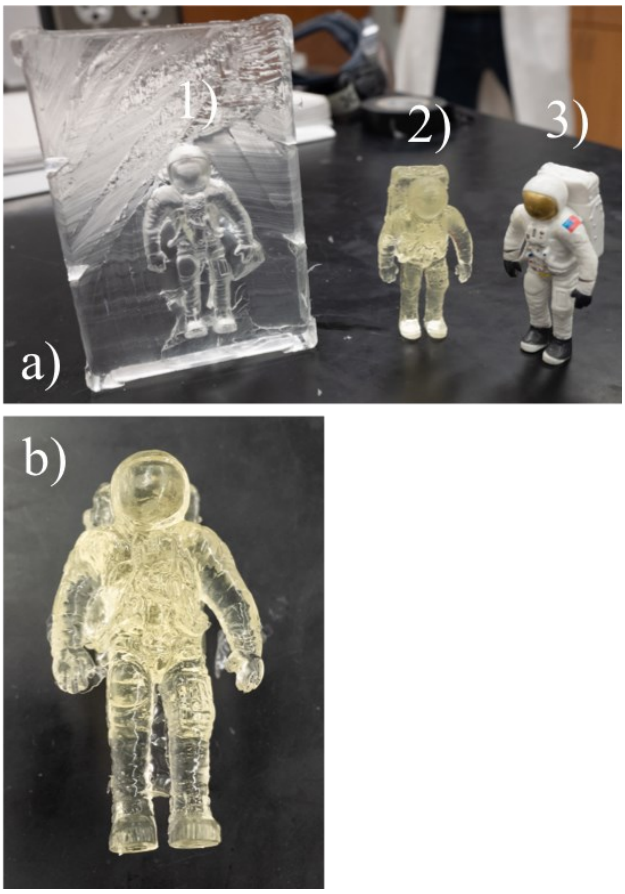


Figure 5. a) The photocrosslinked PVPON-PEGDA replica of the figurine. b) The PDMS mold (1) next to the freestanding PVPON-PEGDA hydrogel replica (2) of the astronaut figurine (3).

Figure 5 shows an example of the freestanding PVPON-PEGDA hydrogel replica alongside the original object and the PDMS mold. If the PVPON-PEGDA hydrogel is damaged in the removal process, another can be created easily by simply pouring another batch of the initiator/prepolymer mixture in the clean PDMS mold and running the photopolymerization

reaction again. Since it only takes a few minutes from start to finish, students usually ran through the process multiple times to fine-tune their procedure or create multiple replicas.

Figure 6 shows an additional examples of PVPON-PEGDA hydrogel, which is an exact replica of the initial object. The figure clearly show that this method allows for exact replication of an object in fine detail.

Figure 6. PVPON-PEGDA hydrogel replication of a key. The exact form of the key was retained by the PDMS mold, and the resulting clear hydrogel elastomer even retained the cross-hatching of the top section after photopolymerization.

As water uptake with these highly crosslinked systems is slow, students were instructed to soak their product in water until the next lab meeting to assess the characteristic swelling of the hydrogels. While quantitative measurements of the hydration were not pursued due to the length

of the course, students observed a visual change to the opacity of the PVPON-PEGDA gels and significant softening of their test hydrogels from the petri dishes. However, due to the high degree of crosslinking chosen by the students in our study, the swelling was limited to a roughly 20% increase in hydration in the highest cases. This portion of the lab could be expanded to include quantitative measurements of the swelling behaviors and perhaps a set of class data could be used to understand the relationship between the amount of crosslinker used and the swelling properties of the hydrogels.

Reporting stage: in-class presentations/proposals

The project ends with the students presenting potential industrial applications of the methodology they mastered in the lab creating photocrosslinked PVPON-PEGDA hydrogels. The knowledge they accumulate during the experimental procedure fuels their creativity and critical thinking and we found that they formulated many inventive uses for their hydrogels. Since hydrogels are able to efficiently retain water, one group of students proposed that their system could be mixed with soil to improve the water uptake of plants, making them less susceptible to drought conditions. Another group wanted to incorporate their hydrogels into diapers to improve the absorbent properties, and many groups proposed some generalized implantable hydrogels for biomedical engineering. Several students recognized the potential medical advantages of hydrogels for drug encapsulation and delivery, as well as for topical wound treatment. Most of the students focus on the concept of hydrophilic encapsulation or other water-based applications even though the swelling behaviors were not fully quantified in our lab. In this case, we suggest guiding the formulation of the hydrogels toward something with a much lower crosslink density

in future iterations of this lab to allow the students to explore quantitative water uptake measurements more akin to the hydrogels they read about in their research for the presentations.

At this stage we found that the students were able to demonstrate a thorough understanding of the structure-property relationships of crosslinked elastomers and hydrogel materials based on their experience in the development stages of the lab. We evaluated this aspect by asking them questions during their presentations that required them to apply the following main concepts: 1) that increasing the amount of crosslinker in the reaction mixture increases the crosslink density of the final product. This in turn increases the rigidity and decreases the water uptake potential. 2) that increasing the reaction time and/or initiator amount increases the degree of monomer conversion which can limit leakage of monomer from the final product. 3) that large-scale reactions may not proceed if the UV light cannot effectively reach the full depth of the reaction vessel. Other topics were explored when relevant, such as how changing the molecular weight of the crosslinker would affect the mesh size of the network and how this would alter the properties of the finished product. 25% of their grade for the presentation depended upon their correct representation of the chemical structures of the reagents and a schematic of the structure of the crosslinked hydrogel product, 25% came from their ability to articulate the finer points and details of their proposal during questions from other students, 25% came from their demonstrated understanding of the structure-property relationships during the question/answer discussion portion (guided by the instructor), and 25% depended on the overall presentation quality. For the final exam, a publication from a high impact factor research paper[34] was distributed along with the test (see SI, example questions from a final exam) and questions pertaining to hydrogels and their properties were presented to the students. Examples of the questions from one of the semesters the experiment was implemented can be seen in the supporting file (Supporting Information:

Example questions from a final exam). All questions had equal weight and partial credit was given on the open-ended questions for answers that demonstrated solid logic. The students scored an average of 87.4±7.3% (n=24 students) on the final exam which demonstrates that the main educational goals were achieved.

Conclusion

We developed a series of junior to senior level undergraduate laboratory experiments involving the replication of a small object chosen by students as a freestanding hydrogel elastomer to serve as a "final project" series of two to three 3-hour classes in a semester-long course. Students seemed to genuinely become interested in the lab due to the involvement of an object familiar to them and the freedom to explore their own project direction with instant feedback from the photopolymerization reaction. Based on our experience with undergraduate students from a wide variety of backgrounds in chemistry and engineering, we believe this is a framework that can be easily incorporated into a polymer chemistry course and encourages students to apply their creativity to newly learned materials and develop confidence in the scientific methodology that forms the basis of research.

Associated content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website: materials, methods, and detailed procedures for all experimental steps (DOCX); instructor notes and table of student observations (DOCX); and example questions from a final exam (DOCX).

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Notes

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