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Synthesis of a Crosslinked Epoxy Resin Medallion in the Organic Chemistry Laboratory

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Abstract Polymer synthesis has a limited inclusion in most organic chemistry lecture curricula, so emphasizing the concepts of polymer chemistry in a laboratory setting gives students hands-on experience in new content and broadens the scope of the class. The details and outcomes of a robust and well-developed laboratory procedure for the synthesis of a crosslinked epoxy network polymer are described. This experiment has been a part of a first-semester, introductory undergraduate organic chemistry laboratory curriculum for more than two decades and has positively impacted over eight hundred students. The experiment had the unique aspect that students cured the resin in a round, seven-centimeter mold, forming a hardened epoxy disk. This disk, or medallion, was decorated in two different ways: first, a design was etched into the mold before curing to form a permanent imprint; second, the final epoxy medallion was decorated, post-cure, with colored permanent markers and glitter glue. After this laboratory experiment, students took home a durable ornament as a memento of their first-semester organic chemistry laboratory course.

Keywords: *interdisciplinary/multidisciplinary, laboratory instruction, organic chemistry, polymer chemistry, second-year undergraduate, upper-division undergraduate, hands-on learning/manipulatives, epoxides, polymerization*

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1. Introduction

Polymer chemistry is rarely introduced in K-12 science classes [1,2] aside from a discussion of plastics and recycling. Polymer synthesis may garner a brief mention in an undergraduate organic chemistry course, particularly in the context of polymerization reactions of alkenes, but polymeric materials are often overlooked in the undergraduate chemistry curriculum as a whole [3,4,5]. Recent guidelines for the ACS-certified undergraduate degree, approved by the American Chemical Society Committee on Professional Training (ACS CPT) in 2015, include the preparation and characterization of polymeric materials [6]. Unfortunately, the ability to teach polymer chemistry content can be a particular limitation at a small, liberal arts school, where the department may not have the students, staffing, or expertise to devote resources towards teaching this material. Moreover, since polymer chemistry is one of the largest sectors in the chemical industry workforce [7], addition of an undergraduate experience in polymer synthesis would benefit any student who may be seeking employment after graduation [8,9].

This gap in the curriculum was addressed by conducting a polymer synthesis laboratory near the end of the first-semester organic chemistry laboratory course. Students in this class were primarily second-year or upper-division undergraduate chemistry or biology majors. This paper describes a polymer laboratory experiment with a particular emphasis on the synthesis of a molded, high temperature, epoxy thermoset resin, one of three reactions included in the polymer laboratory.

2. Overview of the Polymer Lab

The organic chemistry laboratory students met each week for a one-hour pre-laboratory lecture, held several days before the in-laboratory experimental work, which oriented the students to the theoretical, procedural, and safety information for the upcoming laboratory activity. The polymer pre-laboratory lecture described the three polymers that students synthesized in the polymer lab. This pre-lab lecture was particularly critical because two of the reactions, nucleophilic ring opening of an epoxide and amide formation via nucleophilic acyl substitution, were not covered in the classroom until the second semester organic chemistry course. Therefore, a combination of Power Point slides and a pre-laboratory instructional video were utilized to fully describe the reactions and mechanisms.

In the polymer pre-laboratory lecture, the materials were described as follows: Nylon Rope: a nylon-6,10 polymer prepared via interfacial polymerization; Slime: a mixture of aqueous polyvinyl alcohol and sodium tetraborate; and Epoxy: a chemically crosslinked epoxy resin. In the pre-laboratory lecture, the structures and reaction mechanisms of the three polymer types were compared and contrasted to reinforce student understanding of polymer synthesis and materials science. The nylon-6,10 material was described as a linear polymer made by a nucleophilic acyl substitution reaction between two difunctional monomers, a diamine and a diacyl chloride, which released HCl as a by-product. The reaction was conceptually connected to the esterification reaction (or other condensation reaction) that students already knew. Slime was introduced as a polymer made when polyvinyl alcohol (PVA) formed hydrogen bonds and dynamic borate ester links [10] with sodium tetraborate (borax) in aqueous solution. In the Slime experiment, the students were prompted to add differing amounts of borax to investigate the viscosity and properties of the resulting polymer. Procedures for these two laboratory experiments were found online [11,12] and adapted as follows: students measured the length and strength of the Nylon Rope and evaluated the viscosity and properties of the Slime polymers made with differing amounts of borax.

In contrast to the well-known experiments for Nylon Rope and Slime, the synthesis of the high temperature epoxy resin medallion was unique to our laboratories as it was adapted from the graduate research of one of the authors [13]. During the prior graduate research, the reaction stoichiometry was optimized for maximum epoxy strength and durability, and the material was tested as a matrix for high temperature/high performance graphite fiber composites with aerospace applications. The procedure for the undergraduate epoxy laboratory was adapted from this method. Due to the high temperature applications of this particular epoxy material, it was also important to stress to the students that the epoxy resin was inherently different from the first two polymers, Nylon Rope and Slime, since it formed an irreversibly hardened, dimensionally stable thermoset that could not be redissolved or reshaped.

Faculty found that the three-experiment polymer laboratory engaged students with its active learning components, including physically testing the Nylon Rope and Slime materials and creatively modifying the epoxy resin mold. The laboratory period was a 3-hour session, during which the epoxy procedure required approximately 1.5 hours to complete. The polymer laboratory was conducted on the last full day of laboratory class for the semester, and the optional decoration of the epoxy medallion occurred during the following week's laboratory cleanup session. The preparation of the epoxy medallion will be fully described in this paper, based on 20+ years of effectively delivering this content in the undergraduate organic chemistry laboratory.

3. Overview of the Synthesis of the High Temperature Epoxy Resin

Students were familiar with retail epoxy adhesives available for home use. However, the epoxy glues sold for residential applications cure at room temperature. In contrast, the epoxy in this experiment was prepared from aromatic monomers, diglycidyl ether of bisphenol A (DGEBA or DER™ 332) and 4,4'-diaminodiphenyl sulfone (DDS), and cured at an elevated temperature to produce a rigid material. The DGEBA/DDS epoxy resin has historically been used as a matrix for strong and lightweight graphite fiber composites, which made it an ideal polymer for student use due to its durability [14-17]. The strength of the material can be attributed to the aromatic monomers; however, use of the aromatic diamine necessitated an elevated curing temperature due to its lower reactivity. DDS is less nucleophilic than an aliphatic diamine, since the nonbonding electrons on the nitrogen atoms are delocalized by interaction with the rings and the conjugated, electron withdrawing sulfone group. The diepoxide and diamine monomers (shown in Figure 1) were combined in approximately a 2:1 molar ratio, respectively. After thorough mixing at 130 °C, the liquid monomeric mixture was poured into a 7-centimeter heavyweight aluminum weighing dish that was optionally modified by etching a design into the aluminum surface.

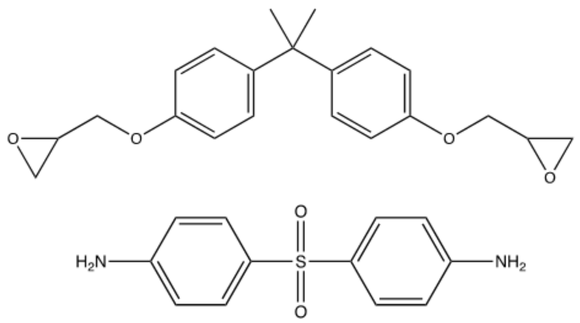

Figure 1. The structures of the monomers: diglycidyl ether of bisphenol A (top) and 4,4'-diaminodiphenylsulfone (bottom)

The epoxy synthesis held a particular attraction for the students, since it provided a dimensionally stable and durable plastic material. The epoxy was de-molded during the subsequent laboratory week, and further decoration of the hard epoxy material was invited as an optional exercise during the end-of-semester laboratory cleanup day. To form an ornament from the epoxy, the instructor drilled a 1/16" hole near the edge of the medallion with careful use of a power drill, and the student attached a ribbon for hanging. Colored permanent markers and/or glitter glue were used to decorate the epoxy medallion. The outcome was a beautiful ornament that students were able to keep as a lasting memento of Organic Chemistry lab.

Overall, the DGEBA/DDS epoxy synthesis has displayed remarkably robust and consistent chemistry for more than twenty years, and there have been very few synthetic issues after the procedure was initially worked out. The full details of the experiment can be found in the Supporting Information. The adaptions that have been made through the years (including adjusting the curing temperature and types of molds) are also described in the Supporting Information. Examples of student-prepared epoxy ornaments are shown in Figure 2.

4. Materials and Procedure

The instructor information, a full list of materials, the student handout, and the procedure can be found in the Supporting Information.

Figure 2. Student-prepared epoxy resin medallions. Credit: Sydney Reynolds (top); Madeleine Leger (middle); Brenna Miller (bottom)

5. Pedagogical Goals of the Epoxy Synthesis Reaction

This engaging polymer chemistry experiment was a novel addition to the organic chemistry laboratory course and provided several curricular benefits for the first-semester organic chemistry course. First, it reinforced the mid-semester lecture topic of macromolecule formation via polymerization reactions, as well as the general chemistry concept of covalent networks. The epoxy laboratory also integrated well with concepts of nucleophiles, electrophiles, ring strain, and the late-semester topic of S_N2 reactions and mechanisms. Moreover, while the introductory S_N2 lecture content focused one step reaction mechanisms, the epoxy reaction mechanism included a second elementary step, a Bronsted-Lowry acid-base reaction, to form the neutral product. The laboratory content also previewed second semester lecture content, such as the reactivity of the epoxide functional group, nucleophilic ring opening of epoxides, compounds with aromatic rings, and reactions of amines as Lewis bases. The mechanism for the amine-induced nucleophilic ring opening reaction of an epoxide is shown in the instructor's materials in the Supporting Information.

Student understanding of the epoxy reaction mechanism was assessed on the written laboratory final using the sample question provided in the Supporting Information. In Semester I of 2018-2019, the average score was 2.1/4 (n=47). While this score was lower than optimum, it likely reflected the fact that the students had not yet been introduced to ring opening reactions in the lecture portion of the course. The most common incorrect answer depicted the mechanism as a Bronsted-Lowry acid-base reaction with the primary amine serving as the proton donor and the epoxide oxygen serving as the proton acceptor.

6. Hazards and Safety Precautions

The DGEBA and DDS monomers are skin irritants. DGEBA has weak estrogenic effects and is a skin sensitizer [18]. DDS is an FDA-approved drug but is considered harmful if swallowed with an oral LD_{50} of 375 mg/kg in mice [19]. Neither monomer is considered to be a human carcinogen.

Disposable protective gloves must be worn while weighing out the monomers and they must be mixed in the hood. Any student with known skin sensitivities should wear chemically resistant gloves such as Silver Shield® gloves. However, because the reaction stoichiometry is approximately 2:1 DGEBA:DDS, and the material achieves an almost 85% cure rate after 110 minutes at 170°C [20] the material is highly crosslinked and the monomers are fully incorporated into the final material.

The reaction is completed at an elevated temperature, so care must be exercised when handling the heated test tube, oil bath, and monomeric mixture. The hot oil bath must be used in the hood. Heat retardant gloves must be worn to remove the test tube of monomeric mixture from the hot oil bath and while wiping the oil from the outside of the test tube. The transfer of monomeric mixture from the test tube to the heated mold must be done in the hood, and heat retardant gloves must be worn to transfer the filled mold to the laboratory oven.

Students must use caution when peeling/removing the aluminum mold from the epoxy medallion, post-curing, as the cut aluminum edges can be sharp.

The only laboratory accident in over twenty years of delivering this content occurred a student dropped his test tube containing the epoxy mixture onto the floor. After the spill cooled, the instructor was able to remove the epoxy and glass shards from the floor with a paint scraper.

7. Conclusion

This preparation of a crosslinked epoxy resin was well-optimized and ran smoothly. It was combined in a 3-hour laboratory period with two other classic experiments: Nylon Rope and Slime. Academically, the polymer laboratory helped to address a gap in the undergraduate chemistry curriculum by introducing students to the discipline of polymer chemistry and giving them first-hand experience in the synthesis and properties of polymeric materials. The pedagogical goals of instructing the students in the new reaction mechanisms were met by dissemination of the laboratory content via a pre-laboratory lecture, an instructional video, and experimental work. These pedagogical goals included reinforcing first-semester topics of the S_N2 reaction mechanism and concepts of nucleophiles, electrophiles, and Lewis and Bronsted-Lowry acid-base theory. The second-semester topics of ring opening reactions, the epoxide functional group, reactivity of aromatic compounds, and a new reactivity pattern for an amine were also introduced. The concept of using difunctional monomers to synthesize a high molar mass polymeric material was also introduced, and the relationship between the laboratory syntheses and commercial plastics was emphasized in pre-laboratory materials. The final experimental outcome of the epoxy synthesis, a decorated epoxy ornament, provided students with a long-lasting memento of their organic chemistry laboratory experience.

Acknowledgements

The authors thank the University of Indianapolis Chemistry Department for supporting the developmental work for the epoxy laboratory. Several former students shared photos of their epoxy ornaments: Kristopher Butler, Megan Hay, Michaela Heil, Juliette Landon, Madeleine Leger, Brenna Miller, Sydney Reynolds, and Dana Youssef. Not all of these photos could be used due to space considerations.

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Instructor Materials & Student Handout

A. Instructor Materials

Introduction:

The synthesis of an epoxy network using an aromatic amine, 4,4'-diaminodiphenyl sulfone (or 4-aminophenyl sulfone), and a diepoxide (the diglycidyl ether of bisphenol A, or DGEBA) is described here. This procedure yields a high temperature epoxy material, molded into the shape of a medallion, and provides a durable plastic ornament that can be taken home by the students. More details on the applications of this chemistry are provided in the student handout.

The reaction stoichiometry is approximately 1 part diamine:2 parts diepoxide, which ensures that extensive crosslinking will occur as each primary amine functionality of the DDS could potentially react with two epoxide moieties to yield a tertiary amine. This reaction utilizes an aromatic amine compound, which is less reactive than an aliphatic amine, so the epoxy material cures (polymerizes) at 170 °C, unlike many epoxies purchased for home use which cure at room temperature.

Information on the historical aspects of epoxy chemistry and its current applications can be found online for inclusion in the pre-laboratory lecture, if desired.

The epoxy procedure is done as an individual lab so that each student can take home his/her epoxy resin, which can be optionally decorated to form an ornament. The required materials are listed below. The synthesis of the molded epoxy resin occurs in one lab period late in the semester; the de-molding and optional decoration of the epoxy resin occurs in a subsequent lab period (for example, during the lab cleanup at the end of the semester).

Materials and Equipment (per one lab student):

Safety glasses
Gloves
1 test tube (25 x 150 mm, VWR International # 10545-928)
DER™ 332 (slightly warmed to 35 °C, 16.0 g) – also known as diglycidyl ether of bisphenol A, DGEBA, or 2-[[4-[2-[4-(oxiran-2-ylmethoxy)phenyl]propan-2-yl]phenoxy]methyl]oxirane (IUPAC) – can be purchased from Sigma Aldrich
4,4'-diaminodiphenylsulfone (6.0 g) – also known as 4-aminophenylsulfone or 4-(4-aminophenyl)sulfonylaniline (IUPAC)
Plastic weigh boats
Hot plate & oil bath (135 °C) – can be shared by two students
Ring stand and clamp(s)
Thermometer
Wooden skewer for stirring (wooden chopsticks work)
Two heavyweight aluminum weighing dishes (VWR International #25433-089)
Lab oven (preheated to 170 °C, timed to turn off 2 hours after lab period ends)
Decorating materials (completed in the following week's lab):
Safety glasses
Needle-nose pliers or standard pliers (to peel the aluminum away from the cured epoxy resin)
Power drill with small (1/16") drill bit
Wood block to protect the lab bench from the drill
Ribbon (thin plastic ribbon of the type that curls for wrapping presents)
Glitter paint, glitter glue pens, craft glue, glitter
Colored permanent markers

Table of Reagents:

The chemical reagents for this synthesis are shown in Table A1. Before the lab period, students must review the SDSs for reagents and complete the "Hazards" information on the table.

Table A1. Table of reagents for the epoxy synthesis

Chemical Reagent (see structures above)	CAS #	Molar Mass (g/mol)	Amount Needed (g)	Moles Needed	Hazards
4,4'-diaminodiphenyl sulfone (DDS)	80-08-0	248.30	6.0	0.0242	
DER™ 332 (DGEBA)	1675-54-3	340.42	16.0	0.0470	

Reaction Chemistry:

The reaction schematic for the formation of the crosslinked epoxy network is shown in Figure A1. The exact details of the mechanism are discussed in prelab content provided by the instructor.

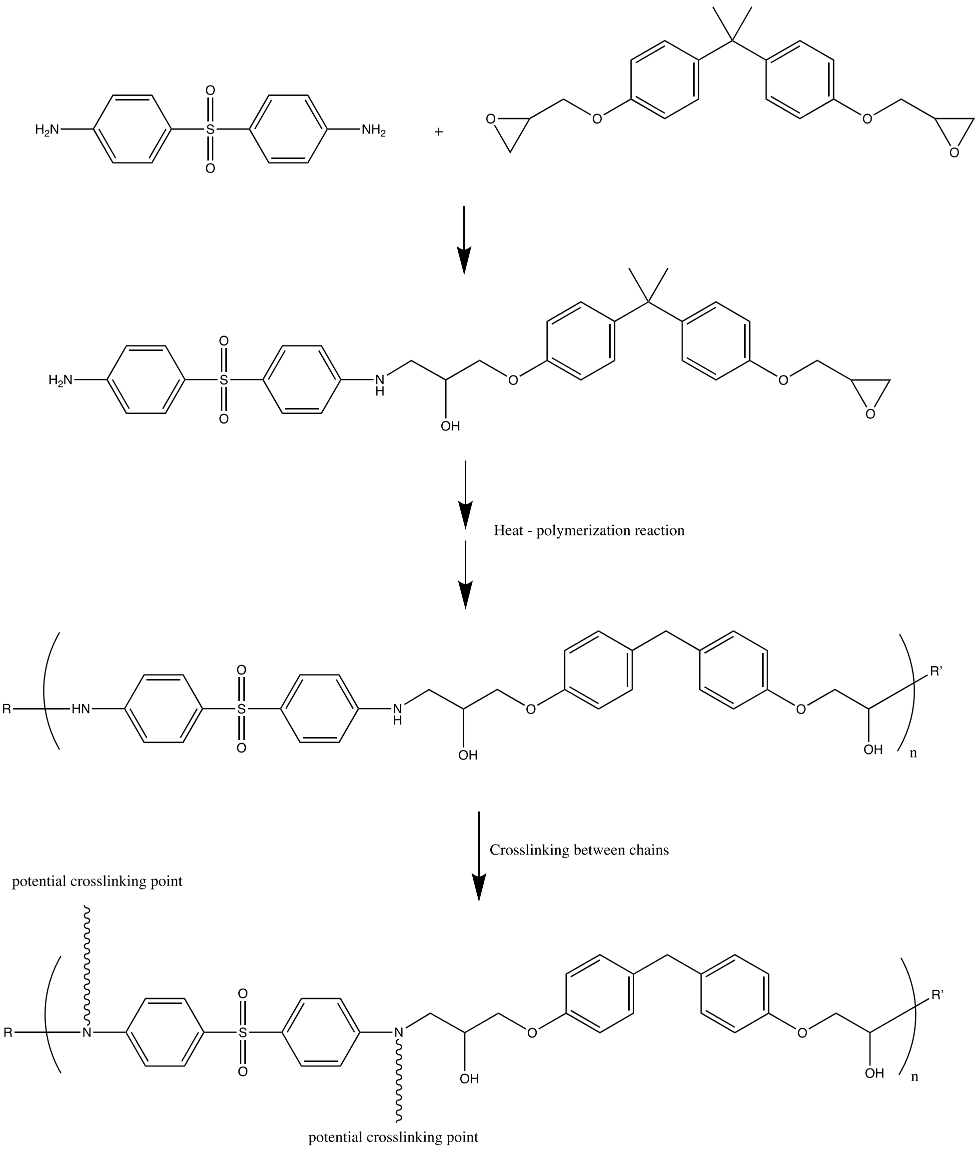


Figure A1. The reaction for the synthesis of the crosslinked epoxy resin.

Procedure:

This procedure provides details and reagent amounts for one laboratory participant.

Place a beaker containing mineral oil on a hot plate and heat until the mineral oil bath has a temperature of 130°C. Wearing gloves, weigh 16.0 g of DER 332 diepoxide directly into a large test tube (supported on the balance by an Erlenmeyer flask). This diepoxide is semi-liquid, semi-solid at room temperature (it should be warmed gently by placing on top of the oven for at least 1 hour prior to lab). Clamp the test tube in the 130°C oil bath – note what happens to the diepoxide as it is heated. Weigh out 6.0 g of the diamine, 4,4'-diaminodiphenyl sulfone, into a plastic weigh boat. Add this carefully to the warm epoxide using a powder funnel. Wear gloves and try to avoid getting the diamine on the walls of the test tube. Any diamine powder on the test tube walls must be pushed into the mixture at the bottom of the test tube. Continue heating the mixture and stir (using a wooden stick) until the diamine is completely dissolved in the diepoxide (**the solution must be clear**). Continue to heat and stir for another 10 minutes. While the mixture is heating, you may etch a picture into the bottom (reverse side) of the heavyweight aluminum dish, using a pen or spatula, if desired. This dish will be used as the epoxy "mold". If you draw on the bottom of the aluminum mold, make sure the bottom of your mold is pushed flat and put your decorated mold inside another aluminum weigh dish so it doesn't leak. Place the mold on the hot plate in advance of the transfer so that it is heated. Using heat retardant gloves and taking care not to burn yourself, take the test tube out of the oil bath, wipe the outside with a paper towel, and pour the reaction mixture into the heated mold (be careful that oil from the bath doesn't get into the mold). Place your uncured epoxy resin/mold into an oven preheated to 170°C. At this temperature, the epoxy will take approximately two hours to cure.

Clean up:

The wooden stick can go in the trash. It is nearly impossible to clean up after epoxy synthesis, so throw the test tube in the "broken glass" container.

Safety:

The DGEBA and DDS monomers are skin irritants. DGEBA has weak estrogenic effects and is a skin sensitizer (allergen). DDS is an FDA-approved drug but is considered harmful if swallowed with an oral LD_{50} of 375 mg/kg in mice. Neither monomer is considered to be a human carcinogen.

Disposable protective gloves must be worn while weighing out the monomers and they must be mixed in the hood. Any student with known skin sensitivities should wear chemically resistant gloves such as Silver Shield® gloves. However, because the reaction stoichiometry is approximately 2:1 DGEBA:DDS, and the material achieves an almost 85% cure rate after 110 minutes at 170 °C, the material is highly crosslinked and the monomers are fully incorporated into the final material.

The reaction is completed at an elevated temperature, so care must be exercised when handling the hot test tube, the hot oil bath, and the monomeric mixture. The hot oil bath must be placed in the hood. Heat retardant gloves must be worn to remove the test tube of monomeric mixture from the hot oil bath and while wiping the oil from the outside of the test tube. The transfer of monomeric mixture from the test tube to the heated mold must be done in the hood, and heat retardant gloves must be worn to transfer the filled mold to the lab oven.

After the polymerization reaction is complete, students must use caution when peeling/removing the aluminum from the epoxy medallion, as the cut aluminum edges can be sharp.

Post-Laboratory Questions:

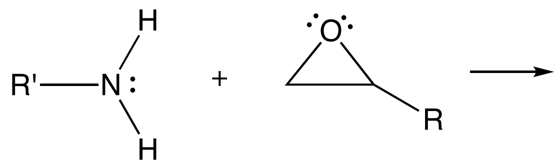
1) The epoxy network is "chemically crosslinked". What does this mean? How does crosslinking affect a polymer’s properties?
2) The cured epoxy resin has pendant hydroxyl (OH) groups along the polymeric chain. Do you suppose that this contributes to the epoxy's "goodness" as an adhesive? Why?
3) When we synthesized Nylon-6,10 (the Nylon Rope), HCl was a by-product of the polymerization reaction. Are there any by-products of the epoxy cure? Why does that make epoxy good for home use?

Answer key for post-laboratory questions:

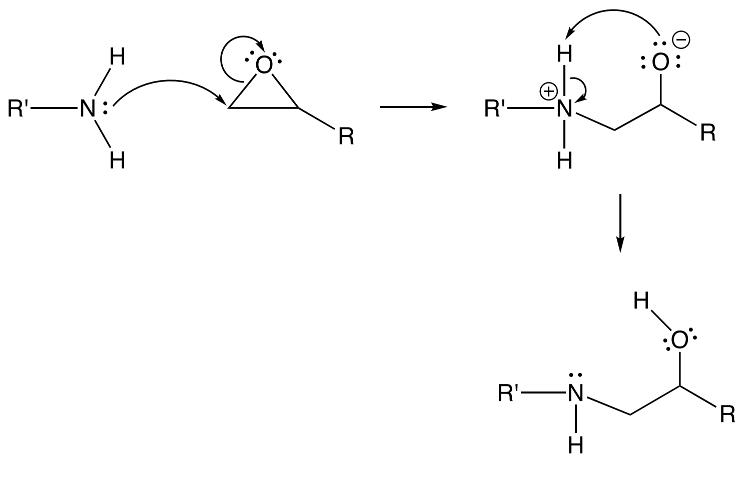
1) A chemically crosslinked network is one in which the polymer chains have links between them. Crosslinking forms a rigid material since the chains can’t slide past one another. A crosslinked polymer is often called a “thermoset” for this reason.
2) The pendant hydroxyl group along the polymeric chain allows the epoxy polymer to hydrogen bond with other materials. This contributes to the epoxy’s ability as an adhesive, since the hydrogen bond is a strong intermolecular force.
3) The epoxy has no by-products when cured (all atoms are incorporated into the final polymer). This makes the epoxy a good adhesive for home use because there is no opportunity for environmental contamination due to liberated by-products.

Sample question for a written laboratory assessment:

In the reaction to form an epoxy polymer, an amine reacts with an epoxide. Using arrows, show the electron movement of the first step of the reaction to form the reaction intermediate. Then, show the reaction to form the products of the reaction. Include all nonbonding electrons and formal charges in your response. (4 points)



Answer key for the written laboratory assessment sample question:



Historical Development of the Epoxy Resin Synthesis Procedure

The epoxy resin experimental conditions were optimized by trial and error through the years by evaluating the effect of curing temperature, types of molds and mold-release agents, and methods of decoration. Some of the variations tried before adoption of the final reaction procedure and conditions are described here.

Curing Temperature

While the initial lab procedure involved heating the diepoxide/diamine mixture for 2 hours at 200 °C, curing at this temperature produced epoxy resins with a strong yellow tint. Curing the resin at 170 °C yielded an almost colorless final epoxy medallion with no apparent decrease in the strength of the material. According to the literature, the material achieves an almost 85% cure rate after 110 minutes at 170 °C. This degree of cure seems to give the medallions sufficient strength for durability.

Molds and Mold-Release Agents

Different molds and mold-release agents were evaluated during the development of the epoxy synthesis lab experiment. Some of the mold-release agents tested were: Teflon™-based sprays, silicone sprays, and Teflon™ coatings on molds (such as Teflon™-coated baking pans). None of these materials worked as mold-release agents; in fact, the epoxy adhered so strongly to the Teflon™-coated baking pans that it pulled the layer of Teflon™ off of the pan.

Some substrates evaluated as molds included: thin gauge aluminum weigh dishes, silicon candy molds, and cookie molds – again, the epoxy adhered to all of these and would not release. The best mold for the epoxy was found to be a heavy-weight aluminum weigh dish which had two benefits: first, an image can be inscribed into the bottom of the dish (this image will be permanently imbedded into the polymer surface); second, the heavy-gauge dish can be completely removed/peeled away from the polymer with the help of pliers, leaving a clean and smooth surface.

Other Synthetic Issues

The chemistry of this lab is quite robust and reproducible and yields consistent results year after year. However, lapses in lab technique by the students have caused minor inconsistencies. First, some epoxy medallions came out of the oven with a greasy surface – this likely can be attributed to contamination with oil from the oil bath when the polymer was transferred from the test tube to the aluminum dish. This grease can be easily washed away with acetone to reveal the epoxy medallion. When students rushed and did not thoroughly mix their reactants before pouring the reaction mixture into the mold, the cured epoxy resins were cloudy/hazy. Finally, if the students accidentally punched a hole in the weigh dish/mold when drawing an image in the bottom of the mold, the pan would leak in the oven unless it was placed into a second dish. Note that the secondary dish can be recycled from year to year.

B. Student Handout

Introduction:

Epoxies are well known adhesives that were first developed in the 1940's. We are most familiar with the types of epoxies available in the hardware store, which are used around the house for projects involving gluing wood, metal, ceramics, and glass. Epoxies are often used as structural materials – when fully crosslinked, the epoxy network is hard, tough, and chemically resistant. Composite bicycle frames, golf clubs, and tennis rackets contain an epoxy component. The aerospace industry also uses epoxy/graphite fiber composite materials for airplane parts.

Most readily available epoxies that can be purchased at the local home improvement store will cure (polymerize and crosslink) at room temperature for ease of household use. These epoxy preparations contain an aliphatic diamine component (Tube A) that reacts with a diepoxide (Tube B). Today we will synthesize an epoxy network using an aromatic diamine, 4,4'-diaminodiphenyl sulfone (or 4-aminophenyl sulfone), and a diepoxide (the diglycidyl ether of bisphenol A, or DGEBA) manufactured by Dow Chemical Company and sold under the tradename DER™ 332. This procedure yields a high temperature epoxy material with applications as a resin for graphite fiber-reinforced composite materials, as an embedding medium, or for encapsulation processes.

The chemical reagents for this synthesis are shown in Table B1, and a reaction schematic for the formation of the crosslinked epoxy network is shown in Figure B1. Note that the reaction stoichiometry is approximately 1 part diamine to 2 parts diepoxide, which ensures that crosslinking will occur. Also, while a home-use hardware store epoxy glue will cure at room temperature, this reaction utilizes aromatic amine compounds which are less reactive than the aliphatic amine compounds, so this epoxy material will cure (polymerize) at 170 °C.

Before the lab period, complete the "Hazards" information on the Table of Reagents and review all prelab content information provided by the instructor.

Table B1. Table of Reagents for the epoxy synthesis

Chemical Reagent	CAS #	Molar Mass (g/mol)	Amount Needed (g)	Moles Needed	Hazards
4,4'-diaminodiphenyl sulfone (DDS)	80-08-0	248.30	6.0	0.0242	
DER™ 332 (DGEBA)	1675-54-3	340.42	16.0	0.0470	

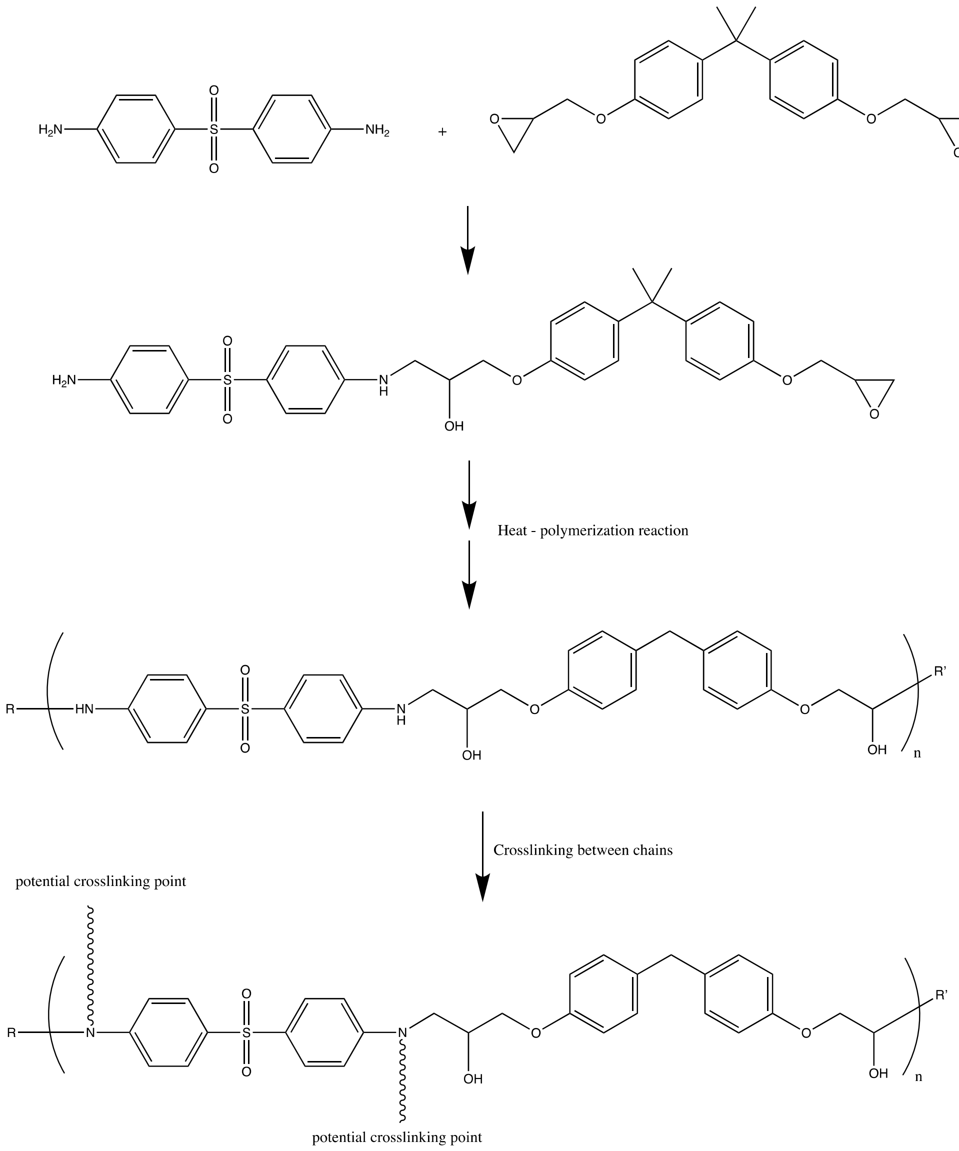


Figure B1. The reaction for the synthesis of the crosslinked epoxy resin.

Materials per lab participant:
Safety glasses
Gloves
1 test tube (25 x 150 mm, VWR International # 10545-928)
DER™ 332 (slightly warmed to 35 °C, 16.0 g) 4,4'-diaminodiphenylsulfone (6.0 g) (also known as 4-aminophenylsulfone)
Plastic weigh boats
Hot plate & oil bath (135 °C) – can be shared by two students
Ring stand and clamp(s)
Thermometer
Wooden skewer for stirring (wooden chopsticks work)
Two heavyweight aluminum weighing dishes (VWR International #25433-089)
Lab oven (preheated to 170 °C, timed to turn off 2 hours after lab period ends)
Decorating materials (completed in the following week's lab):
Safety glasses
Needle-nose pliers or standard pliers (to peel the aluminum away from the cured epoxy resin)
Power drill with small (1/16") drill bit
Wood backing/block to protect the lab bench from the drill
Ribbon (thin plastic ribbon of the type that curls for wrapping presents)
Glitter paint, glitter glue pens, craft glue, glitter
Colored permanent markers
Procedure: (This is enough for one student—each student should make his/her own)

Place a beaker containing mineral oil on a hot plate and heat until the mineral oil bath has a temperature of 130 °C. Wearing gloves, weigh 16.0 g of DER 332 diepoxide directly into a large test tube (supported on the balance by an

Erlenmeyer flask). This diepoxide is semi-liquid, semi-solid at room temperature (it should be warmed gently by placing on top of the oven for at least 1 hour prior to lab). Clamp the test tube in the 130 °C oil bath – note what happens to the diepoxide as it is heated. Weigh out 6.0 g of the diamine, 4,4'-diaminodiphenyl sulfone, into a plastic weigh boat. Add this carefully to the warm epoxide using a powder funnel. Wear gloves and try to avoid getting the diamine on the walls of the test tube. Any diamine powder on the test tube walls must be pushed into the mixture at the bottom of the test tube. Continue heating the mixture and stir (using a wooden stick) until the diamine is completely dissolved in the diepoxide (**the solution must be clear**). Continue to heat and stir for another 10 minutes. While the mixture is heating, you may etch a picture into the bottom (reverse side) of the heavyweight aluminum dish, using a pen or spatula, if desired. This dish will be used as the epoxy "mold". If you draw on the bottom of the aluminum mold, make sure the bottom of your mold is pushed flat and put your decorated mold inside another aluminum weigh dish so it doesn't leak. Place the mold on the hot plate in advance of the transfer so that it is heated. Using heat retardant gloves and taking care not to burn yourself, take the test tube out of the oil bath, wipe the outside with a paper towel, and pour the reaction mixture into the heated mold (be careful that oil from the bath doesn't get into the mold). Place your uncured epoxy resin/mold into an oven preheated to 170 °C. At this temperature, the epoxy will take approximately two hours to cure.

Clean up: The wooden stick can go in the trash. It is nearly impossible to clean up after epoxy synthesis, so throw the test tube in the "broken glass" container.

Safety: The DGEBA and DDS monomers are skin irritants. DGEBA has weak estrogenic effects and is a skin sensitizer (allergen). DDS is an FDA-approved drug but is considered harmful if swallowed with an oral LD_{50} of 375 mg/kg in mice. Neither monomer is considered to be a human carcinogen.

Disposable protective gloves must be worn while weighing out the monomers and they must be mixed in the hood. Any student with known skin sensitivities should wear chemically resistant gloves such as Silver Shield® gloves. However, because the reaction stoichiometry is approximately 2:1 DGEBA:DDS, and the material achieves an almost 85% cure rate after 110 minutes at 170 °C, the material is highly crosslinked and the monomers are fully incorporated into the final material.

The reaction is completed at an elevated temperature, so care must be exercised when handling the hot test tube, the hot oil bath, and the monomeric mixture. The hot oil bath must be placed in the hood. Heat retardant gloves must be worn to remove the test tube of monomeric mixture from the hot oil bath and while wiping the oil from the outside of the test tube. The transfer of monomeric mixture from the test tube to the heated mold must be done in the hood, and heat retardant gloves must be worn to transfer the filled mold to the lab oven.

After the polymerization reaction is complete, use caution when peeling/removing the aluminum from the epoxy medallion, as the cut aluminum edges can be sharp.

Post-Laboratory Questions:

1) The epoxy network is "chemically crosslinked". What does this mean? How does crosslinking affect a polymer's properties?
2) The cured epoxy resin has pendant hydroxyl (OH) groups along the polymeric chain. Do you suppose that this contrib
3) When we synthesized Nylon-6,10 (the Nylon Rope), HCl was a by-product of the polymerization reaction. Are there any by-products of the epoxy cure? Why does that make epoxy good for home use?