A Polymer Degradation and Remanufacturing Experiment in the High School Classroom

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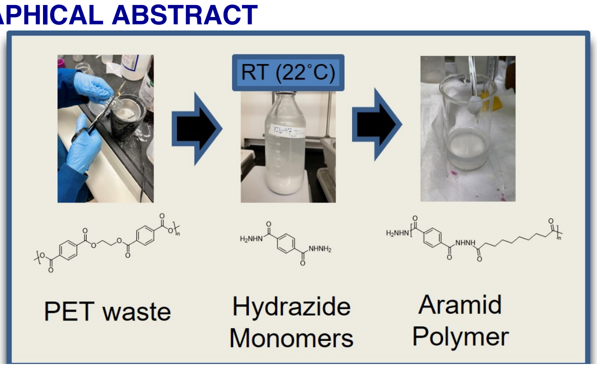
ABSTRACT

Most students enter college without any exposure to polymer science, which leads to the poor understanding and slow implementation of plastics recycling programs in the United States. To address the knowledge gap in chemical recycling, we introduce a 2-part laboratory experiment that was conducted in multiple high schools and public outreach events to demonstrate the depolymerization of PET via aminolysis and the remanufacturing of cleaved PET fragments into a new aramid polymer. Student experiences were evaluated with two post-lab assignments.

GRAPHICAL ABSTRACT



KEYWORDS

High School/Introductory Chemistry, Organic Chemistry, Polymer Chemistry, Hands-on Learning/Manipulatives, and Polymerization

INTRODUCTION

Plastics are ubiquitous materials characterized that are inexpensive to manufacture and have desirable physiochemical properties.[5] Plastics are now mass produced and found in virtually every industry. For example, in 2021 more than 82 million metric tons of polyethylene terephthalate (PET or PETE) alone was produced.[6]

Although exposure to polymer chemistry is limited in the high school classroom,[1] the combination of both the increase of waste plastics and the emergence of promising technologies presents an opportunity to educate the youth our students about chemical recycling.[4] Further, young people need to be able to make informed public policy decisions in the plastics sustainability space. For example, California SB 54 (2022), the Plastic Pollution Prevention and Packaging Producer Responsibility Act, mandates that manufacturers must make/design materials that are at least 65% recyclable/compostable by 2032.[2,3] However, the bill omits consideration of chemical plastics recycling, thus neglecting to account the impact of emerging technologies that promise to produce high quality materials from post-consumer plastics that can't be recycled today.[3,4] Polystyrene is an example of a plastic, generally thought of as single-use, but many convenient methods for its chemical recycling and upcycling are emerging.[4] For the public to make good policy decisions in this space, effective general education in polymer recycling needs to be available at early ages.

In this 2-part experiment, students depolymerize post-consumer PET via aminolysis at ambient temperature and pressure. The resulting products are monomeric and oligomeric acylhydrazides that the students directly use to synthesize new aramid polymers, thereby demonstrating the creation of a new material from waste plastics (Figure 1). Learning outcomes include basic understanding of polymer synthesis/structure, and basic organic chemistry. This experiment is suitable for high school science classes grades 10 and above and introductory/first year undergraduate chemistry courses. The activity may also be adapted as a public outreach demonstration.

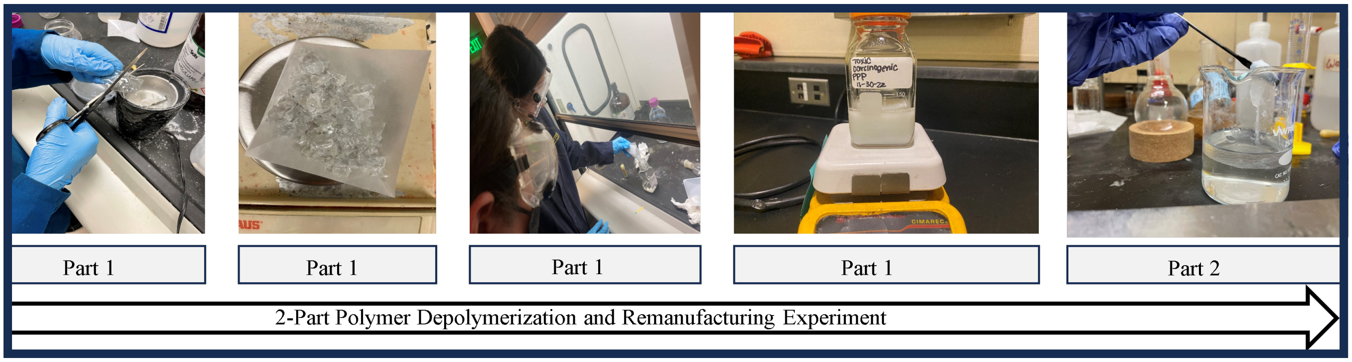


Figure 1. Overall, 2-part PET depolymerization and remanufacturing experiment

POLYMERS

Polymers are macromolecules that consists of repeating subunits (monomer) joined together by a characteristic linking bond.[7] There may be more than one type of monomer in some polymers;[7] for example, polyethylene terephthalate (PET) is made up of two monomers, ethylene glycol and terephthalic acid. These monomers alternate between ester bond linkages in the resulting polymer's chemical structure. The type of polymeric linkage classifies the polymer: since PET is made up of ester linkages, it is considered a polyester. Polyesters are a type of condensation polymers because water is condensed out of the material upon polymerization, and PET is the only of these among the main six classes of recyclable plastics. Another class of condensation polymers is aramids, which are polymers made up of aromatic amide linkages, as in Kevlar.[8]

CHEMICAL RECYCLING

Plastics can conventionally be recycled by mechanical or thermal methods.[9] These involve sorting, washing, and/or melt processing thermoplastics. However, melt processing is often frustrated by impurities or immiscibility among batches of polymer that produce lower quality second-cycle materials.[9] In the case of PET, some of these second cycle materials are not suitable for food packaging, so they are used in applications such as clothing, carpeting, and engineering resins.[9] Contamination is also a large enough issue that some governments have implemented programs to maintain homogeneity of the reclaimed PET feedstock such as California's Redemption Value (CRV) specifications for bottle recycling.[10]

Alternatively, chemical recycling breaks polymeric linkages to yield isolatable monomeric units that are suitable for remanufacturing into new high-quality plastics.[11] For example, IBM has recently commercialized this their VolCat system, which enables the renewability of PET.[11] VolCat does not require sorting or washing and produces high purity monomers.[11] The European market has emerged as a global model for implementing chemical plastics recycling. Major firms such as Loop Industries, Eastman, and Carbios are investing over $1 billion to construct and support three new PET chemical recycling plants in France.[12]

There are many ways to depolymerize PET with reagents that target its polymeric ester bond. These include acid solution (acidolysis), alcohols (alcoholysis, as in VolCat), amines (aminolysis), glycols (glycolysis), and water (hydrolysis).[9] While glycolysis, methanolysis, and hydrolysis are industrially more popular than aminolysis, they are strategically analogous, because they all target the ester bond with their respective nucleophiles.[9] This laboratory experiment will use hydrazine to cleave PET. While PET depolymerization experiments have appeared in this journal,[9,13] these require high temperatures and materials poorly suited to high school.[9,13] One uses potassium tert-butoxide or potassium hydroxide in refluxing pentanol.[13] Another utilizes an *N*-heterocyclic carbene for a transesterification reaction of PET with ethylene glycol in refluxing tetrahydrofuran.[9] Neither of these demonstrate remanufacturing of PET fragments. Our procedure exploits the potent nucleophilicity of hydrazine at low concentrations (< 3 wt%) for the aminolysis of PET in aqueous ethanol at room temperature (Figure 2). In a few hours, PET will suspend into a thick white haze that comprises the resulting hydrazide fragments. These fragments are repolymerized into a new polymer using sebacoyl chloride (Figure 3). We nickname this material “Yourlar”, because it’s similar, but distinct, from Mylar (biaxially-oriented PET) or Kevlar. The depolymerization reaction can take up to 72 hours to complete, but it need not be monitored during this period. Introducing and starting the reaction require less than 1 hour. The subsequent repolymerization can also be done within a separate one hour session, which makes this experiment suitable for high schools that have a typical one hour science period.

MATERIALS AND EQUIPMENT

To demonstrate our experiment, we put students in groups of 4-6. In part 1, each group used a mechanical grinder (coffee grinder), mass balance, scissors, fume hood, stir bar, stirrer, and a 250 mL glass media bottle. The grinder, fume hood and balance were shared. Chemicals involved were PET waste (sourced from student lunch boxes), hydrazine monohydrate, NaOH, ethanol, and deionized water.

During part 2 each group used basic laboratory glassware and a fume hood. Chemicals involved are NaOH, sebacoyl chloride, and hexane. Students should not prepare stock solutions of hydroxide, hydrazine, or sebacoyl chloride; these should be prepared by a trained individual.

We recommend using 4 L amber glass bottles to collect waste. There should be at least two types of waste containers for this experiment, respectively collecting aqueous base and organic waste. The former will comprise excess stock solution from part 1. The latter will primarily consist of unused sebacoyl chloride and hexane.

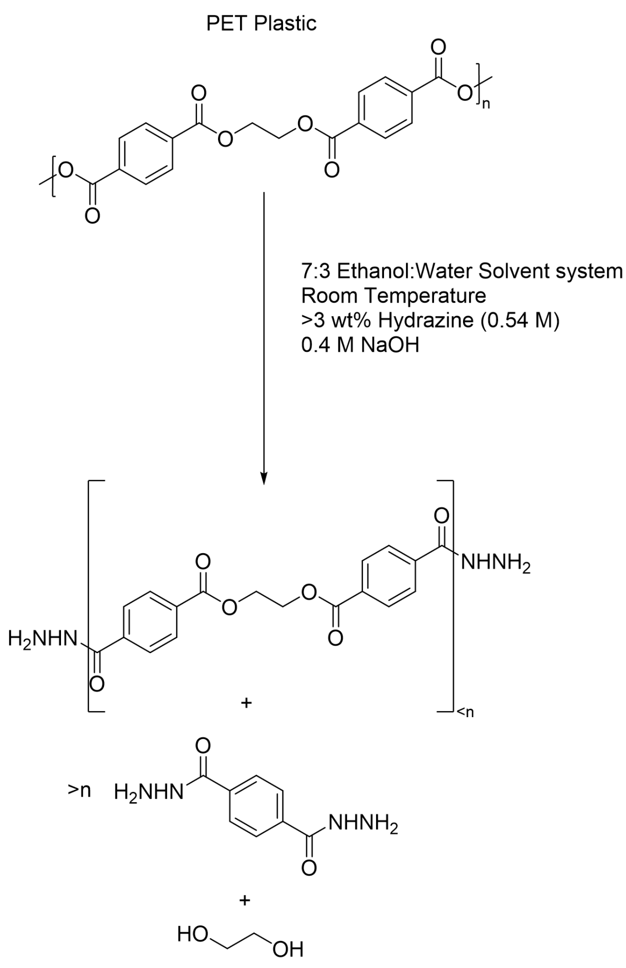


Figure 2. Ambient temperature and pressure PET depolymerization with hydrazine.

EXPERIMENTAL PROCEDURE

Part 1

The PET reactor solution (prepared ahead of time by a trained chemist) comprises 70% v/v aqueous ethanol, 0.4 M NaOH, and 0.84 M hydrazine (< 3 wt%). The system is designed to digest 1.5 g of PET polymer per every 2.68 g of hydrazine. Therefore, every 100 mL of this system should digest 1.5 g of PET. We suggest preparing to decant 100 mL from this stock solution for each group. The solution should remain in the fume hood or proper storage.

The first step of the demo is to cut up PET bottles. Students are instructed to use scissors to cut the PET smaller than 2-inch squares. These go in the coffee grinder until the material is a fine powder. Each group will then weigh out 1.5 g of this powder for upcycling.

Groups then charge a 250 mL glass media bottle with 1.5 g of plastic powder and a stir bar. Stock solution (100 mL, 0.84 M hydrazine in 70% ethanol) is distributed into the media bottle in the fume hood. Bottles are then carefully capped and taken out of the fume hood to be labeled "3 wt% hydrazine, toxic, do not open." Media bottles are then set on a stir plate until the contents become a homogenous white liquid. The reaction may take as long as 72 hours to complete. No heating is needed.

Part 2

Students continued with part 2 when the reaction appears as a thick white suspension. Part 2 of the demo was done in the fume hood, because of the volatile chemicals involved. Having only one fume hood in each of our classrooms, we had one group at a time proceed through part 2, which fit comfortably into our one-hour class periods. To begin, a student should carefully transfer 50 mL of the completed part 1 reaction suspension into a 150 mL beaker. Sodium hydroxide (30 mL, 1.5 M) is then added, causing the solution to appear clear. Other students then took turns gently layering sebacoyl chloride (0.15 M in hexane) over the aqueous solution in the beaker. A translucent film was then observed in the interfacial layer between the two immiscible liquids as in popular nylon synthesis demonstrations.[14]

Students were instructed to wait at least one minute after layering the solutions for the polymer film to develop. They could then use a stir rod or scoopula to drag the polymer out of solution. The polymer can then be placed on a petri dish or weighing boat to dry in the fume hood. Finally, students can then characterize the color and mechanical nature of the polymer. Simply prodding the aramid polymer with the stir bar can reveal its brittle nature. Finished groups were then instructed to work on the post-lab assignment and the next group was called up to the fume hood. Detailed information and photographs are available under section 1, Supporting Information I.

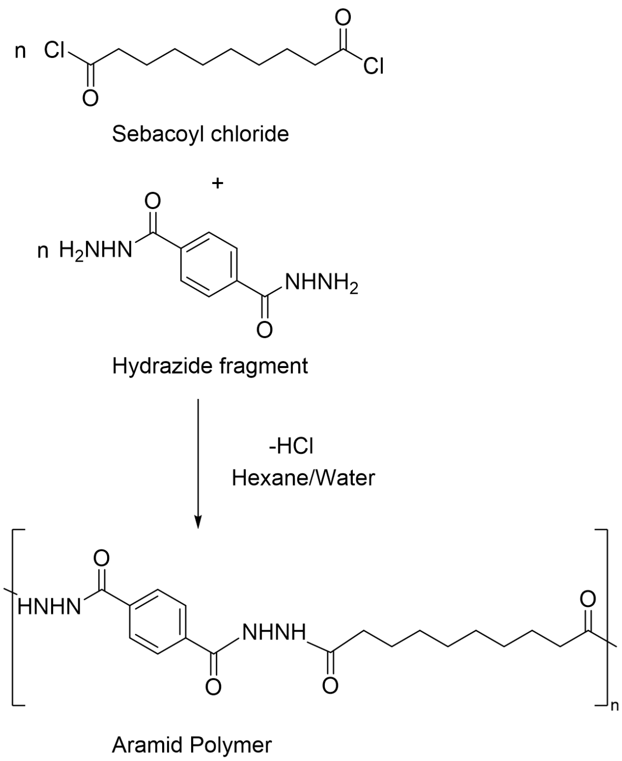


Figure 3. Aramid polymer synthesis using hydrazide fragments and sebacoyl chloride.

HAZARDS

Hydrazine is flammable and a known carcinogen with acute toxicity.[15,16] It is especially toxic if inhaled, ingested, or absorbed through the skin.[16] However, it is well established that its aqueous solutions have greatly reduce toxicity. Furthermore, the partial pressure of 5 wt% hydrazine over an aqueous hydrazine solution at room temperature is below the US NIOSH IDLH level.[15] Therefore, it is appropriate to use a well monitored < 3 wt% hydrazine solution for this experiment without fear of inhalation toxicity.[15]

Sebacoyl chloride is also acutely toxic and will cause damage if ingested or absorbed through the skin.[16] It should only be manipulated in the fume hood with gloves. Adipoyl chloride may be used as an alternative, because it is less toxic.[18] However, both chemicals are very corrosive and adipoyl chloride is still dangerous to inhale or contact without PPE.[17,18]

Sodium hydroxide is caustic and toxic, and ethanol and hexane are flammable.[19,20,21] These materials are handled regularly in high schools, with care to avoid contact or inhalation. We required personal protective equipment (PPE) including lab coats, goggles, and gloves for all participants.

In consideration of the high hazards involved in this experiment we suggest having at least one trained individual in the classroom/laboratory per every 10 students. We generally worked with 15-25 students per class section, so we had at least three trained individuals to supervise the classroom. Trained individuals may be the instructor, lab assistants, and/or faculty. Anyone under the age of 18 should not be considered a trained individual.

Waste materials generated in this demonstration must be properly disposed by a local waste manager. We dispose materials through LA City SAFE centers, USC Environmental Health and Safety, or Enviroguide.

STUDENT DEMOGRAPHICS AND PUBLIC OUTREACH

This experiment was successfully conducted in two private high schools in Los Angeles County. Experiments were conducted with 10th and 11th graders during their 1-hour chemistry classes. Prior to starting the experiment, we gave a presentation to familiarize students with the basics of lab safety, polymeric structures, and chemical polymer recycling. This content can be found in the Supporting Information II. When students returned for part 2, we prepared another presentation to review the depolymerization reaction and introduce interfacial polymerization (Supporting Information II).

To adapt this experiment as a public demonstration we recommend only displaying the part 1 PET depolymerization reaction (100 mL, 0.84 M hydrazine in 70% ethanol). We delivered this demo to two separate outreach events in Southern California. The first outreach event was the 2022 Annual Avalon Harbor Underwater Cleanup. The second outreach event was during the 2023 Polytechnic School Pet and Hobby Show. Here we worked in conjunction with an Eagle Scout project to depolymerize PET waste the youth collected from an Arroyo Seco watershed cleanup. We did not adapt part 2 as a public outreach demonstration.

DISCUSSION

Post-lab assignments were given to every student after part 1 and part 2 of the experiment. Most students completed their post-lab assignments in the same period as the experiment. Assignment 1 familiarizes students with polymeric structures and commodity plastics. Most students easily answered questions 1-3 and 5 correctly. Many students struggled with question 4, identify bonds broken and formed in the balanced equation of the reaction, but wrote striking details that demonstrated critical thinking: they were able to recognize that there are two reactive centers in the scheme, and others wrote that two equivalents of hydrazine per repeating unit are needed to yield monomeric chemicals. Surprisingly, few students specifically mentioned which bonds were broken/formed, but they understood that the polymeric ester linkage is where the chain is being broken. For this reason, we encourage reviewing the assignment with the class and allowing students to make these observations with their peers.

Post-lab assignment 2 was designed to reinforce the concept of interfacial reaction. Students should understand that they used the hydrazide fragments from the part 1 reaction to synthesize an aramid polymer using interfacial polymerization. Students answered questions 1, 2, and 4 with ease. Question 3 (where did the polymerization occur) was also easily answered, as each student had an opportunity to pour hexane over the aqueous monomer solution. Question 5 (what are the byproducts; what's the role of NaOH) was the most challenging question. Most students were able to identify that HCl is a byproduct of this reaction, but they did not recognize that HCl can deactivate the nucleophilicity of the hydrazide fragments or that NaOH neutralizes it. To maximize learning outcomes, students should be familiar with acid base chemistry and functional groups, which are topics typically encountered in a high school chemistry curriculum.

Some students inquired about the potential uses of the aramid polymer product. Whilst our aramid is novel, it has no industrial use. We explained it is structurally like commercial aramids such as Mylar, but it's not MY-lar, so we call it "YOUR-lar". The primary objective of this experiment was to demonstrate to students that it's possible to chemically recycle plastic waste and make new materials from them. In both schools we found students to be curios and deeply engaged. They understood the concept of chemical conversion and its advantages.

CONCLUSION

The procedures and experiences described in this text should enable instructors to demonstrate chemical PET recycling in a high school classroom. A procedure that requires no heat or pressure is unique, which makes this experiment appropriate for this setting.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.3c00692

Detailed information of the procedures and equipment used are in the supporting information. Post lab worksheets are also available on this same document.

Supporting Information I:

(Suppoting Information I DOCX)

Furthermore, students were prefaced with a presentation prior to the experiment. Attached is the presentation content.

Supporting Information II:

(Supporting Information II PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information I

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1a. General Procedures: Materials and Equipment

Hydrazine monohydrate was supplied by Oakwood Chemical. Ethyl Alcohol (Kopetk), sodium hydroxide (Macron fine chemicals) and Hexanes (Supelco) were purchased through VWR. Sebacoyl chloride was supplied by TCI America. Deionized water was purified in house using a Millipore system. We recommended DI water, but bottled drinking water is equivalently effective. PET bottle plastic was procured from the waste. The mechanical grinders used were Quiseen 2.5 oz one touch electric coffee grinders (Model no. Q-CG001)

1b. Procedure with Graphics

Images were acquired at the USC department of Chemistry, Flintridge Prep, and Polytechnic School. We encourage the use of these images.

Part 1

Stock reactor solution should be prepared by the instructor ahead of time. This stock solution comprises 70% v/v aqueous ethanol, 0.4 M NaOH, and 0.84 M hydrazine (< 3 wt%). The system is designed to digest 1.5 g of PET polymer per every 2.68 g of hydrazine. Therefore, every 100 mL of this system should digest 1.5 g of PET plastic. We suggest that the total volume of the stock solution should be 100 mL per student group. The stock solution should always be within a fume hood or properly stored. Details on the ratio between hydrazine to PET plastic are found in section 2, Supporting Information I.

The first step of the chemical recycling process is to increase the surface area of plastic by cutting it up. Students are instructed to meet with their group and use the scissors to cut the PET waste plastic until the PET is no larger than 2 inches on every side. Then groups proceed with using the coffee grinder to shred the plastic until it is grainy (Figure S1)

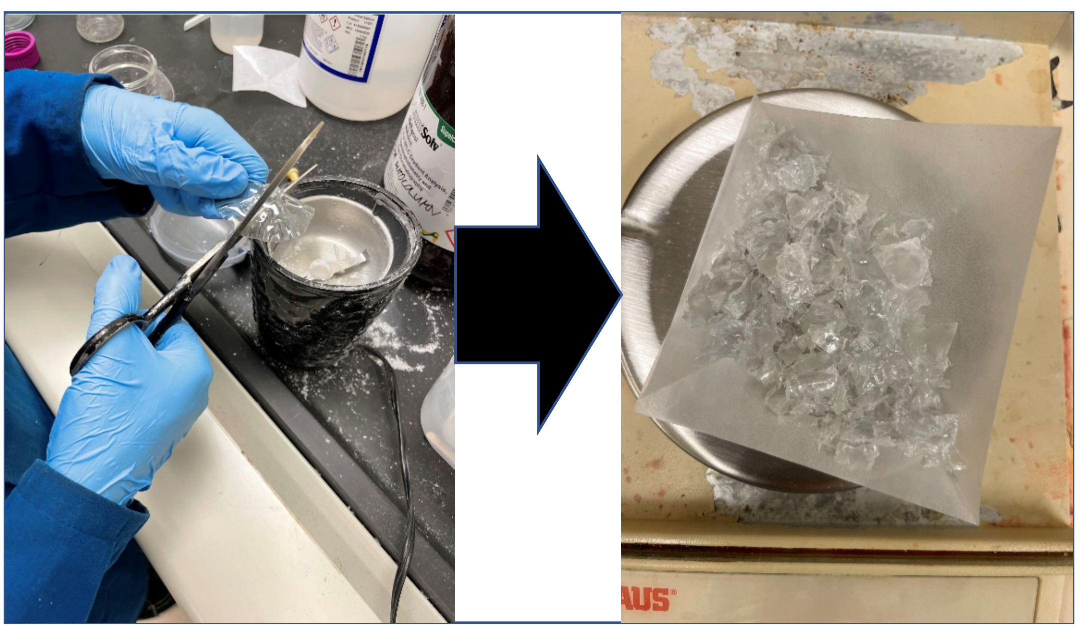


Figure S1: Cutting and shredding the PET to an appropriate size

Each group should then weigh out 1.5 g of plastic. Excess plastic is collected and put in the waste. Groups then obtain a 250 mL glass media bottle. The 1.5 g of plastic and a stir bar are placed in the bottle to indicate that group is ready to receive stock solution. Stock solution is only added in the fume hood (Figure S2).

Figure S2: Decanting stock reaction solution under the fume hood

Each group should receive 100 mL of the stock solution to digest their 1.5 g of plastic. Bottles are then carefully capped and taken out of the fume hood to be labeled. Labels must display "< 3 wt% hydrazine, toxic, do not open". Media bottles are then placed on a stirrer and allowed to react until the contents become a uniform white suspension (Figure S3). *Do not turn on the heat*: this could cause ethanol or hydrazine to partition out of the bottle and create a safety hazard.

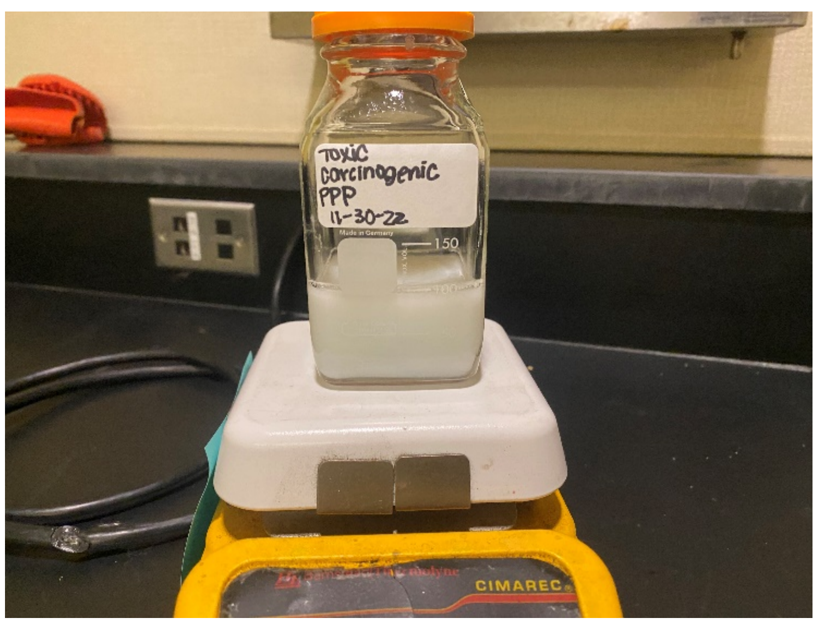


Figure S3: Completed part 1 reaction

Part 2

Students continued with part 2 when the reaction appeared as a uniform white suspension. This typically takes at least 72 hours from the start of stirring. Students must perform part 2 in the fume hood. If there is only one fume hood, have one group work at a time.

Have one student carefully decant 50 mL of the completed reaction suspension into a separate 150 mL beaker. Add NaOH (30 mL, 1.5 M) to adjust the pH of the suspension. The result should appear as a clear solution (Figure S4).

Figure S4: Interfacial polymerization in hexane and water

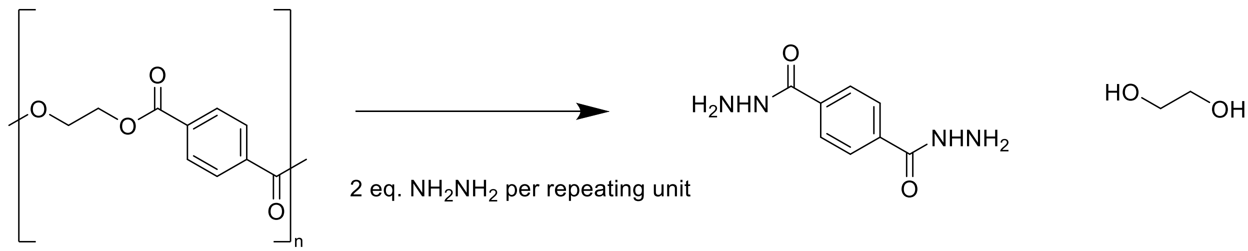
Finally, allow another student to gently layer sebacoyl chloride (0.15 M in hexane) over the aqueous solution in the beaker. Polymerization will take place in the interfacial layer between the two immiscible solvents (Figure S4). Instruct students to wait at least one minute for the polymer film to develop in the interfacial layer, then encourage students to use a stir rod or scoopula slowly to drag the polymer out of solution (Figure S5). Students are directed to place the polymer on a petri dish or weigh boat to dry, but do not remove it from the fume hood. Students can then characterize the color and mechanical properties of the polymer and see how it is distinguishable from PET.

Figure S5: Part 2 aramid polymer

2. Hydrazine wt% Calculation

Terephthalic acid makes up roughly 74% of the mass in PET. For complete monomerization there needs to be two eq. of hydrazine per every repeating unit in PET. Therefore, the theoretical amount of hydrazine needed is given by (1).

$$(1)\ Theoretical\ mol\ of\ Hydrazine = \frac{2\ x\ (Mass\ of\ PET)\ x\ (0.74)}{164\ g/mol}$$



Therefore 1.5 grams of polymer needs 0.67 g of hydrazine. For best results, optimized conditions use an excess of x4 this amount of hydrazine. Therefore, 1.5 grams of polymer should need 2.68 g of hydrazine.

We recommend making a 3 wt% solution to stay below US NIOSH IDLH limits.

$$Hydrazine\ wt\%\ in\ hydrazine\ monohydrate = 64\ wt\%$$

$$Density\ of\ 70\ mass\ \%\ of\ ethanol\ in\ water = 0.863\ g/mL$$

(Source: Washburn, E. W., Ed., *International Critical Tables of Numerical Data of Physics, Chemistry, and Technology*, Vol. 3, McGraw-Hill, New York, 1926–1932.)

Hydrazine needed in a 3 wt% 100 mL solution of 70% v/v ethanol solution:

$$\frac{2.68\ g\ of\ hydrazine}{86.3\ g\ of\ ethanol\ solution + \ 4.187\ g\ of\ hydrazine\ monohydrate} * 100\% = \ 3\ wt\%$$

The resulting solution should be 0.8375 M. Every group should receive 100 mL of the stock solution. Scale up appropriately.

3. Molecular Characterization of Polymer

The resulting aramid polymer is not soluble in most solvents including acetonitrile, acetic acid, chloroform, ethyl acetate, ethanol, hexane, water, dimethyl sulfoxide, dimethyl formamide, and methanol.

(Soon to be FTIR)

Figure S6:

4. Part 1 Post-lab Worksheet

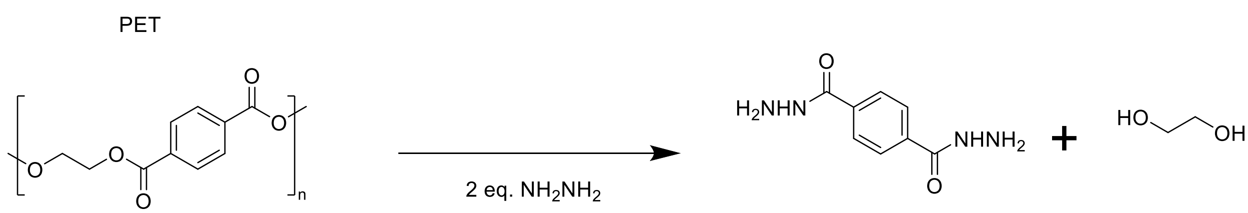
1.) What is the term for a molecule constructed from many repeating monomers?

2.) What does PET stand for and what are the two monomers that make it up?

3.) We know that recycling codes refers to different types of common plastics.

If “1” refers to PET. To which plastics do “2” and “3” refer?

4.) In the depolymerization reaction that you did, which bonds are broken and which bonds form? How does this represent depolymerization?



5.) You may notice that one of the products from this reaction is ethylene glycol. What are some uses of ethylene glycol?

Answer Key:

1.) Polymer

2.) Polyethylene terephthalate- ethylene glycol and terephthalic acid

3.) HDPE and PVC, respectively

4.) Carbon-oxygen single bond is broken to form carbon-nitrogen bond. The former

carbon-oxygen bond was the attachment to the main polymer backbone. This bond was replaced to make this specific repeating unit no longer a part of the polymer.

5.) Freezes at -12 ^{o}C, used as antifreeze, heat transfer agent, polymer precursor, etc.

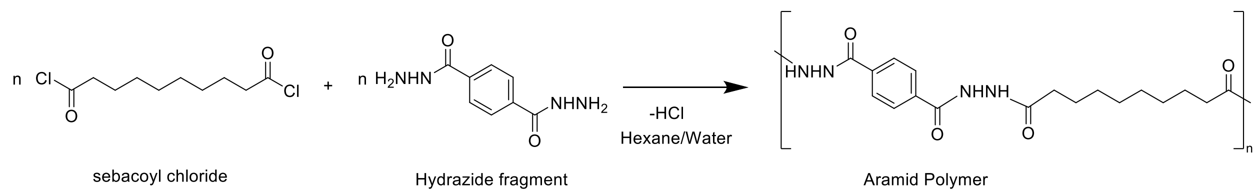
5. Part 2 Post-Lab Worksheet

1. Justin had to make 400.0 mL of a 2.00 M solution of sodium hydroxide. How many grams of NaOH did he need to make 2.00 M NaOH for a 400 mL solution?

2. What does it mean for liquids to be immiscible? What are some examples of immiscible liquids?

3. Where in your reactor did the polymer form and why? Did it form in the aqueous layer, hexane layer, or in between?

4. Where did the hydrazide fragment come from?



5. Challenge: Are there any byproducts in this polymerization? What might have been the role of NaOH?

Answer Key

1.) 32 g of NaOH

2.) Oil and water, gasoline and water, benzyl alcohol and water (Lava Lamp)

3.) Interfacial layer, the only region where the two comonomers meet

4.) PET depolymerization reaction

5.) HCl is produced for every new polymer linkage. The role of NaOH is to adjust the pH of the solution to prevent protonation of the amine, which would deactivate the reaction.

Supporting Information II

A Polymer Degradation and Remanufacturing Experiment in the High School Classroom

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PET Chemical Recycling Demo

Y. Justin Lim, Brandon Wong, Katie Macfee, Alexa Cueva, E. Aaron Martinez, Cameron Paxton, Robin Barnes, Eric Kleinsasser, Travis Williams

The problem with plastics

- In 2018, 360 million tons of plastics have been manufactured and is expected to surpass 500 million tons in 2025
- Roughly 60% of plastics waste is not recycled
  - These plastics end up in landfills or become incinerated
    - Incineration uses substantial energy and produces harmful byproducts
- Remolding and mechanical recycling greatly reduce the material durability

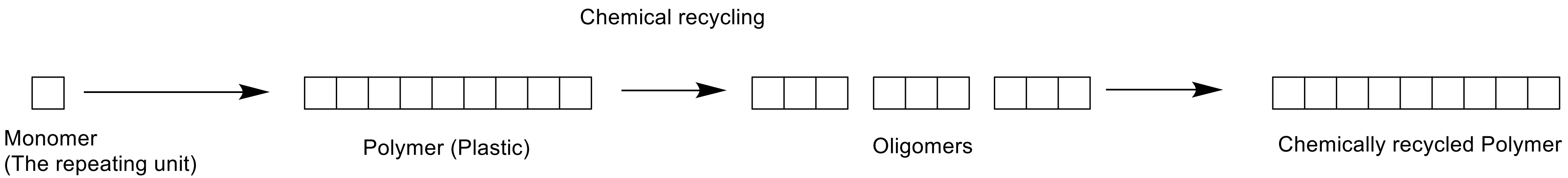
Arlene Karidi, Oct. 5th, 2020

Ademola et. al. Current developments in chemical recycling of post-consumer polyethylene terephthalate wastes for new materials production: A review,
Journal of Cleaner Production,
Volume 225, 2019, Pages 1052-1064, ISSN 0959-6526,
https://doi.org/10.1016/j.jclepro.2019.04.019.

Huang S, Wang H, Ahmad W, Ahmad A, Ivanovich Vatin N, Mohamed AM, Deifalla AF, Mehmood I. Plastic Waste Management Strategies and Their Environmental Aspects: A Scientometric Analysis and Comprehensive Review. Int J Environ Res Public Health. 2022 Apr 10;19(8):4556. doi: 10.3390/ijerph19084556. PMID: 35457426; PMCID: PMC9024989.

Chemical Recycling?

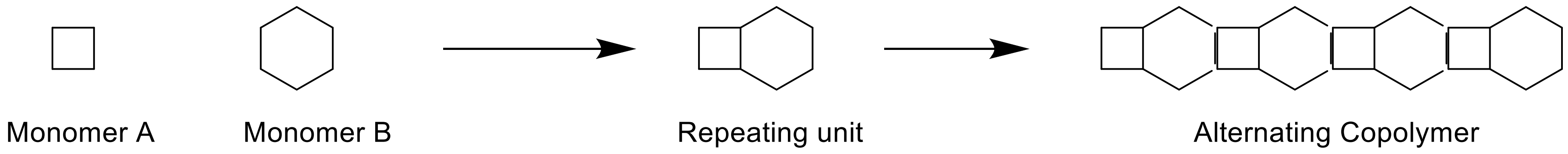
- **Chemical Recycling:** An advanced form of recycling where the polymer (plastic) is chemically broken down into its monomeric or oligomeric forms and repurposed
- **Polymer**: A molecular structure consisting of many repeating units
- **Oligomer:** A molecular structure consisting of few repeating units
- **Monomer:** A molecule that can bond to other identical molecules to form a polymer

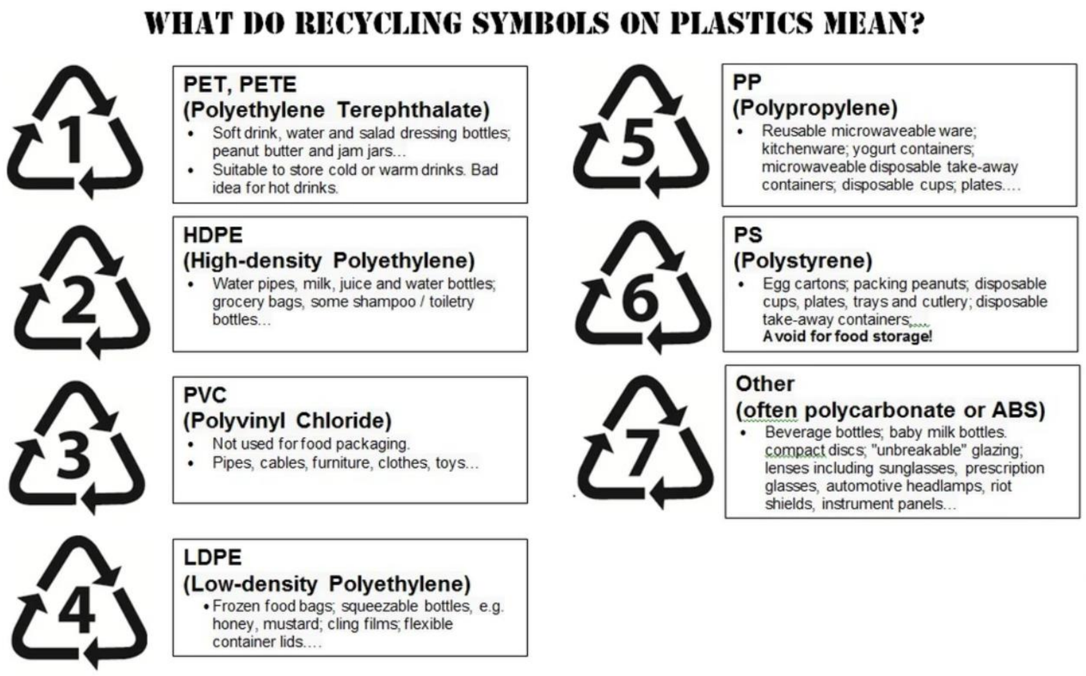


Copolymers and the chemical structure of PET

- **Poly(ethylene terephthalate) (PET)**: A copolymer made up ethylene glycol and terephthalic acid. It is commonly known as water bottle plastics and designated recycling code #1

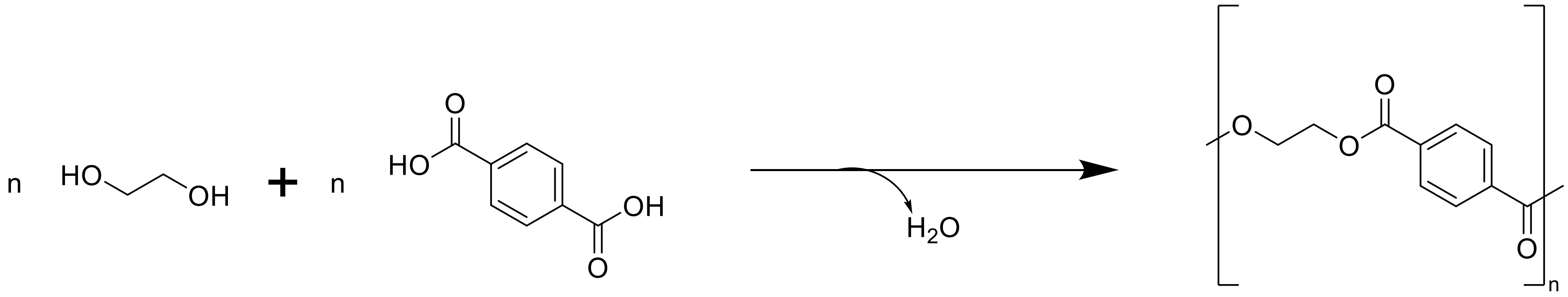
- **Copolymer**: A polymer made up of two (or more) different types of monomers





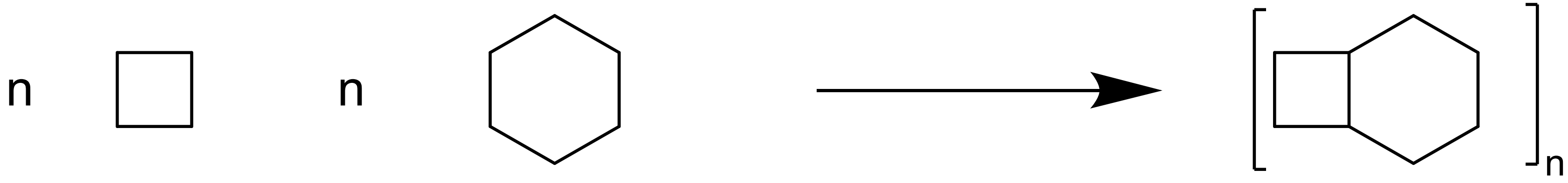
Amenpackaging.com (10/10/22)
Hebrongoesgreen.com/recycling-symbols (10/10/22)

Chemical Structure of PET



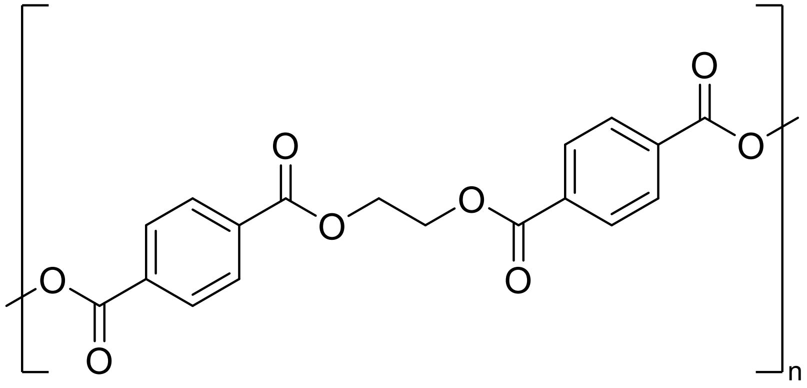
Ethylene Glycol Terephthalic Acid

An Alternating Copolymer!



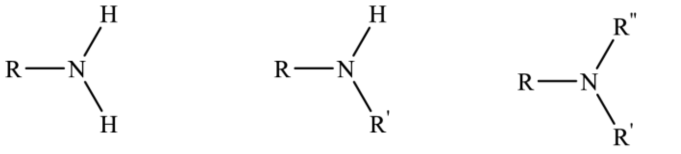
Monomer A Monomer B Repeating unit

Chemical Recycling: How to break PET into oligomers/monomeric units?

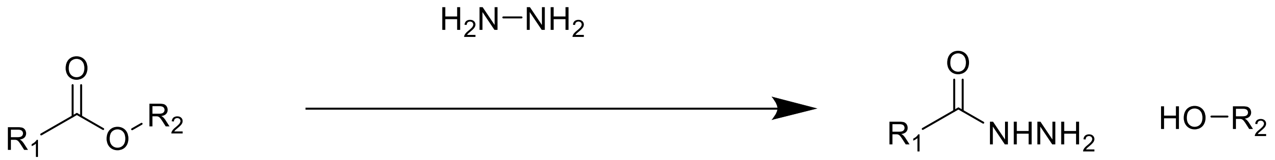


We propose the depolymerization of PET by aminolysis

- Aminolysis
  - Breaking a chemical bond with an amine
- The proposed scheme demonstrates the bond cleavage by a strongly nucleophilic amine



Primary amine   Secondary amine   Tertiary amine



R_1= Abbreviation for Carbon atom

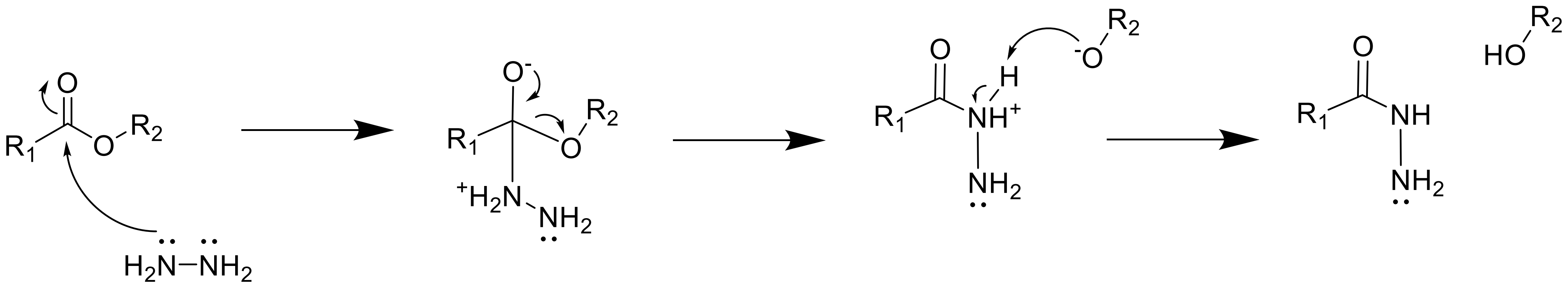
R_2= Abbreviation for a seperate Carbon atom

What's an amine?

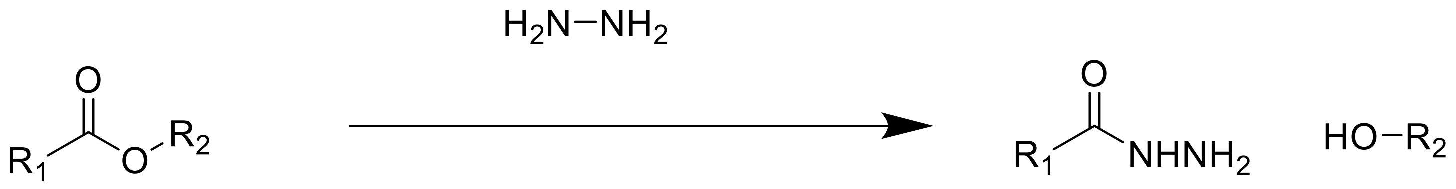
And

How many lone pairs are on the nitrogen? (formal charges)

Mechanism of Bond Cleavage

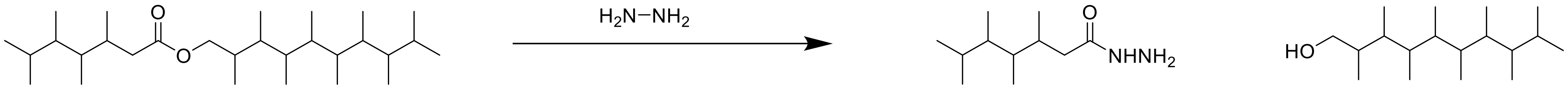


Chemical Recycling: How to break PET into oligomers/monomeric units?



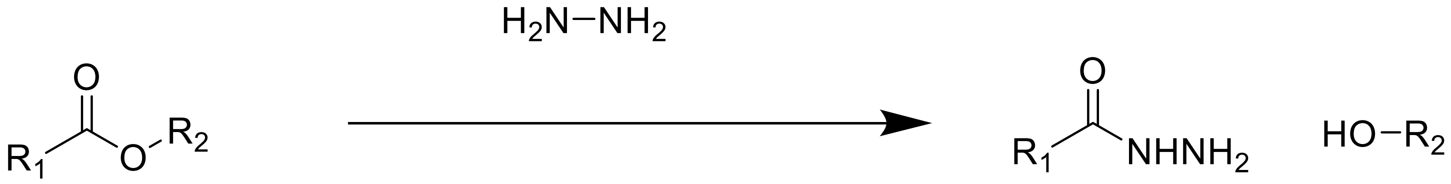
R_1= Abbreviation for Carbon atom
R_2= Abbreviation for a seperate Carbon atom

Now imagine each “R” represents a large chain

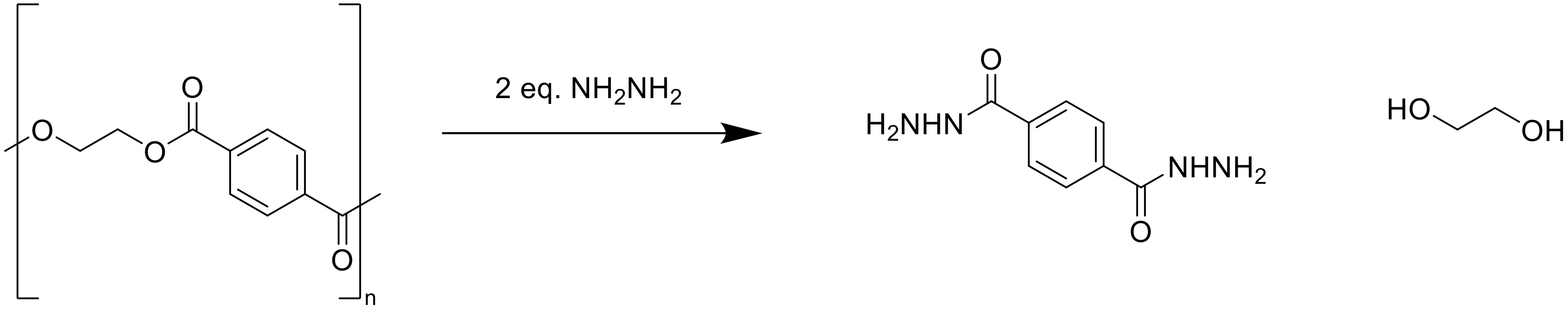


Just cleaved a large molecule into two smaller fragments

Same idea in PET Chemical recycling

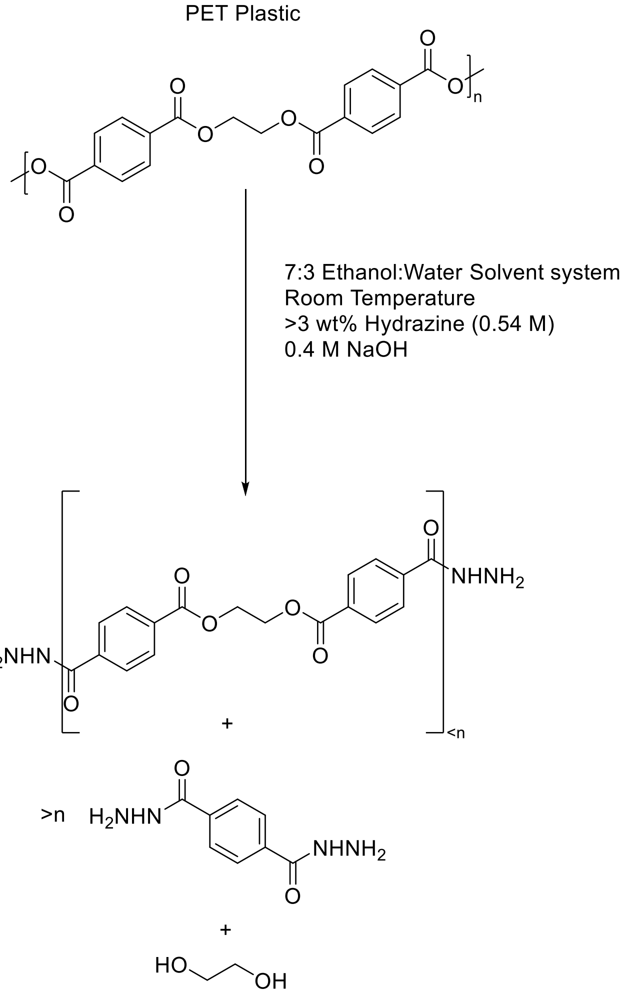


R_1= Abbreviation for Carbon atom
R_2= Abbreviation for a seperate Carbon atom



In each repeating unit of PET there are two ester bonds. That means each repeating unit needs two eq. of hydrazine to cleave in the way above.

Experiment PART 1: Chemically recycle PET



Procedure

- Students should be in groups of 4-6
- Each group should be given/bring a PET water bottle to class
- Groups are to use scissors to start cutting their plastic bottle
- Groups may go to coffee grinding stations to further shred plastic
- Shredded plastic should be smaller than 2 in.
- Groups should prepare up to 1.5 g of shredded plastic

Procedure

- After weighing out your plastic the demo team will distribute stock solution to media bottles in the fume hood
- Come to the fume hood with your group and media bottle
- Reactor components
  - 100 mL per group
    - 30% water 70% ethanol
    - 0.84 M hydrazine
    - 0.4 M NaOH
  - Equipment
    - Stir bar and Plate
    - Fume hood

Procedure

- When the media bottle is filled with stock solution
  - Add plastic through the funnel
  - Must write the number of grams added
  - Do not open the media bottle outside of the fume hood
- Label your media bottle!
  - Group name and date: “AAAAA, ##/##/##”
  - Warnings: “Toxic, carcinogenic, 0.84 M hydrazine PET depolymerization reaction”
- Next time we meet we will do part 2!
  - Reaction may need as much as 72 hour to homogenize

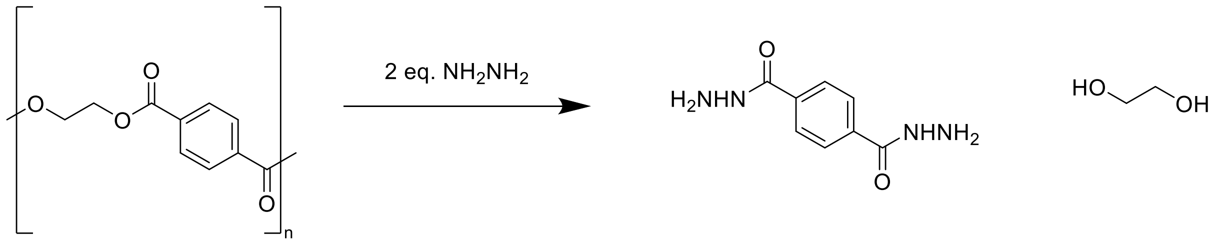
Work on Post-Lab 1 after the activity

PET Chemical Recycling Demo
Part 2

Y. Justin Lim, Brandon Wong, Katie Macfee, Alexa Cueva, Aaron Martinez, Cameron Paxton, Robin Barnes, Eric Kleinsasser, Travis Williams

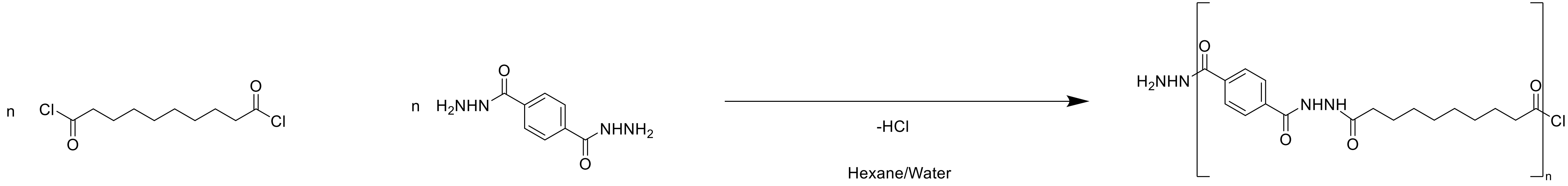
Part 2: Recycling the Chemicals

- Part 1 was about breaking down waste into chemicals we can use



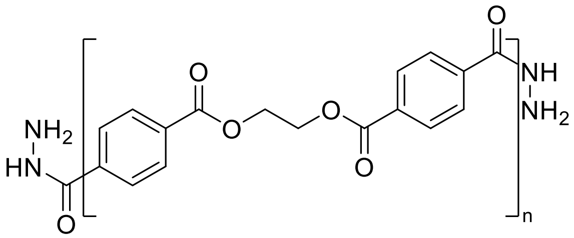
- What are these chemicals useful for?
  - Ethylene glycol is used as antifreeze
  - The hydrazide does not have any industrial use
    - However, we can use it to demonstrate polymerization

Part 2: Aramid Polymerization: Using the Hydrazides



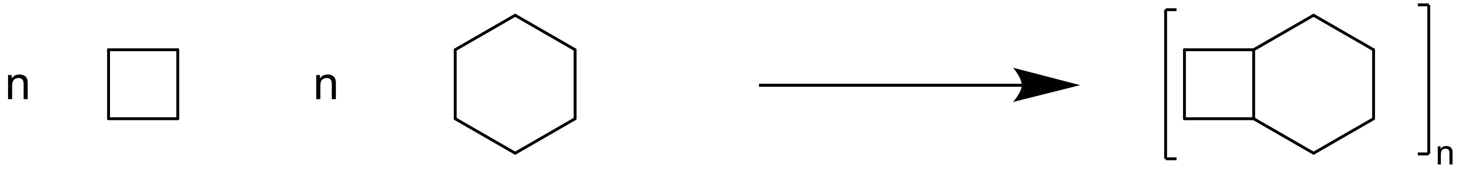
sebacoyl chloride

Hydrazide monomeric fragment



Hydrazide oligomeric fragment

Another type of copolymer!



Monomer A

Monomer B

Repeating unit

Part 2 Procedure

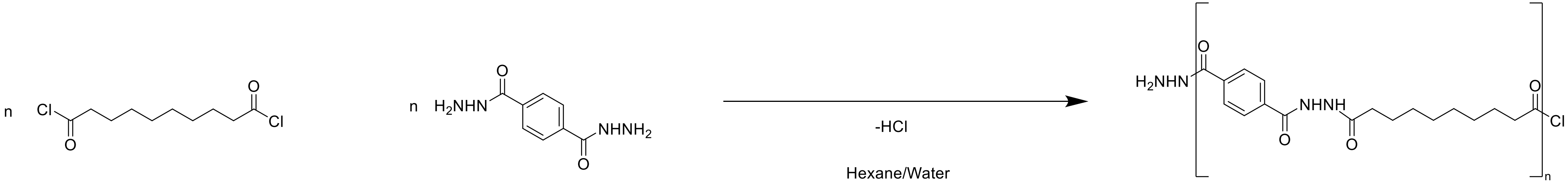
- Students must wear gloves, goggles, and lab coats
- Sebacoyl Chloride
  - Nasty chemical: Respiratory harm and skin irritant
- All unsealed bottles must be under the fume hood
- Without opening the bottle characterize how it changed since last week
  - Whiter? Dissolved plastic?

Part 2 Procedure

- Each group is then tasked with a molarity calculation question before they can continue the experiment under the fume hood
- For the sake of time one group will be called up first and finish the calculation after their activity
- Each group will be given a weight boat that will need to be labeled with the group name

Part 2 Procedure: Setting up 2 Reactions

- Pour 50 mL of the **Ethanol-based reaction** into a 150 mL beaker
- Pour 30 mL of 1.5 M **NaOH** into that beaker
  - Adjusts the pH of the solution to alkaline
  - Prevents deactivation of Hydrazide
  - Should turn clear
- Pour 50 mL of the 0.15 M **sebacoyl chloride** (in hexane) into a separate 150 mL beaker



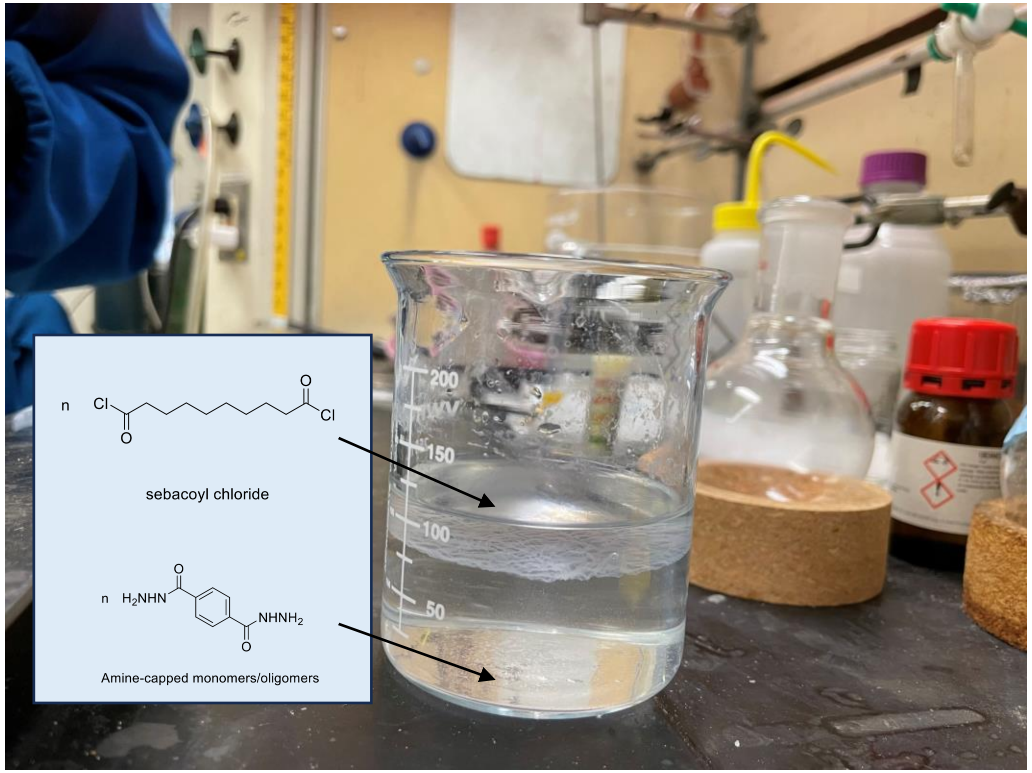
The Polymerization Technique

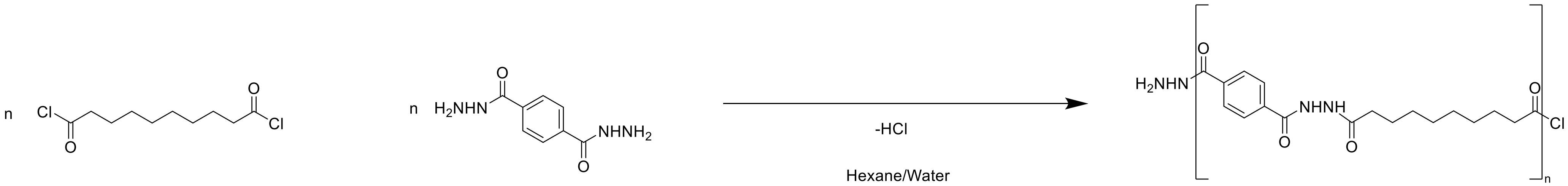
Interfacial polymerization: Polymerization at the interface between two immiscible phases.

The two solvents here are **water** and **hexane**.
Aqueous (Polar) and Organic (Non-polar) respectively.
Separate because of polarity.

Position dependent on density
Density of hexane: 0.659 g/mL
Density of Water: ###

Sebacoyl chloride is dissolved in hexane and the hydrazide products are dissolved in the water layer.





sebacoyl chloride

Hydrazide monomeric fragment

Part 2 Procedure: Polymerization

- Someone from the group will then carefully layer over 25 mL of the sebacoyl chloride over the aqueous solutions in the 150 mL beaker

Part 2 Procedure: 2 Polymerization Reactions

- Let the immiscible liquids sit for a minute
- Someone from the group should use a glass stir rod and puncture the interfacial layer
- Roll the stir rod until the polymer winds up on the stir rod. If it breaks, try scooping the polymer with a scoopula

Part 2 Procedure: Polymer characterization

- No one should be touching the polymer at any point (even with their gloves on)
- Wash polymer with water and acetone and place it on your group's weigh boat to dry
    - Inside the fume hood
- Complete any remaining calculations or the post-lab activity
- At the end of the class groups can look at their dried polymer

Entry Question

If I had a 50 mL solution of 0.4 M NaOH and mixed it with 30 mL of 1.5 M NaOH, what is the new concentration of NaOH in the 80 mL solution?

Hint: Solve for total number of moles of NaOH in the 80 mL solution

Assume MW of NaOH=40 Da

Da=g/mol

Safety

- Chemicals
  - Sebacoyl chloride
  - Hydrazine
  - Ethanol
  - NaOH
  - MSDS sheets present
- PPE
  - Lab goggles and gloves
  - Lab coats
  - Close toed shoes, long pants, hair tied back
- Storage of chemicals/reactor
  - Secondary containment
  - Under the fume hood

Work on Post-Lab 2 after the activity