

# CHEMICAL ENGINEERING 445/545 POLYMER LABORATORY

## *POLYMER SYNTHESIS LABORATORY SESSION*

### **Introduction:**

There will be three separate synthesis experiments in this laboratory session. Each of the experiments is relatively short, and some preparation can be done simultaneously by different members of the group. *Try to work efficiently and conserve space.*

### **REMEMBER TO FOLLOW GOOD LABORATORY PRACTICE -- SAFETY FIRST!**

- Always wear safety goggles and conduct synthesis experiments in the hood.
- Read each of the Material Safety Data Sheets (MSDS) for the chemicals you will be using (these are available in the lab).
- Wear protective apparel (gloves, etc.) as needed.
- If you have questions about a procedure, contact Dr. Rochefort or the Lab TA.

### **Polymer Synthesis Experiments in Laboratory Session I**

**Experiment #1a: Polystyrene Synthesis**

**Experiment #1b: Polyurethane Foam Production**

**Experiment #1c: Polyamide Synthesis (Nylon 6,6) -- "Nylon Rope" Trick**

The Laboratory Manual (such as it is) provides you with some introductory material on the various polymerization techniques to be studied, as well as information on polymer synthesis and structure in general (B. Shakhshiri, *Chemical Demonstrations*, Vol. 1, (1983); D. L. Pavia et. al., *Introduction to Organic Laboratory Techniques: A microscale approach* (1990)). This material, along with the textbook and other information you may find in your literature searches, should provide you with the information necessary to complete the *background section of your lab reports*.

## **EXPERIMENT #1a Polystyrene Polymerization**

We will follow the procedure outlined by Flynn and Smith in, "A Safe and Novel Polymerization of Styrene." (*J. Chem. Education*, **68** (12), 1038 (1991)). This procedure uses a common skin care product, OXY-10, which contains 10% benzoyl peroxide as the active ingredient in the cream, as the initiator for the polymerization reaction. The benzoyl peroxide initiator in pure form is extremely flammable and may detonate, so the substitution of the cream product makes the experiment much safer. The only disadvantage is the cream residue in the final polystyrene product (should be clear because it is an amorphous polymer), but this can be removed by subsequent dissolution in a solvent and precipitation (if so desired).

As indicated in the Flynn and Smith article, the procedure outlined in Shakhshiri and Dirreen (*Chemical Demonstrations*, Vol. 1, **Experiment 3.11**, p. 241 (1983)) will be followed, with the substitution of OXY-10 for the pure benzoyl peroxide initiator.

**FOLLOW THE PROCEDURE OUTLINED IN EXP. 3-11, substituting OXY-10 for pure benzoyl peroxide.**

The weight of OXY-10 to use for your polystyrene polymerization will be supplied to you by Dr. Rochefort. **Why is this important, or does it even matter?**

# Polystyrene Polymerization

## REFERENCES

Flynn, Brendan R. and Wayne L. Smith. "A Safe and Novel Polymerization of Styrene," *Journal of Chemical Education*, p. 1038 (December 1991).

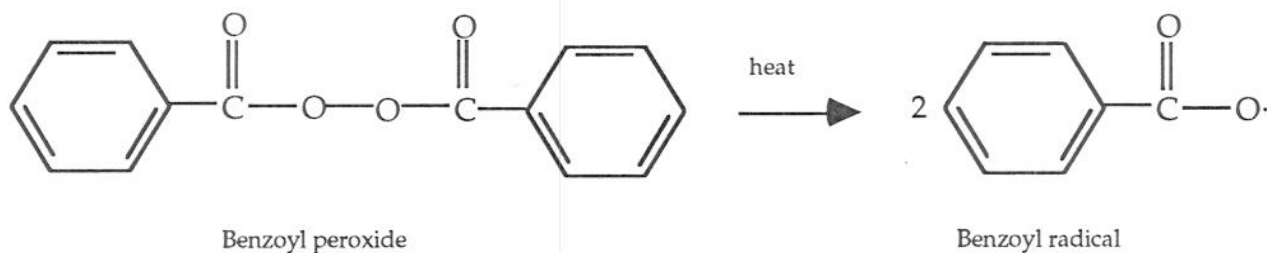
Pavia, Donald L., Lampman, Kriz, and Engel. **Introduction to Organic Laboratory Techniques: A Microscale Approach**, p. 394, *Saunders College Publishing*, Harcourt, Brace and Jovanovich, Fort Worth (1990)

Shakhashiri, B.Z. and G. E. Dirreen, **Chemical Demonstrations: Vol. 1**, p. 241, University of Wisconsin Press (1983).

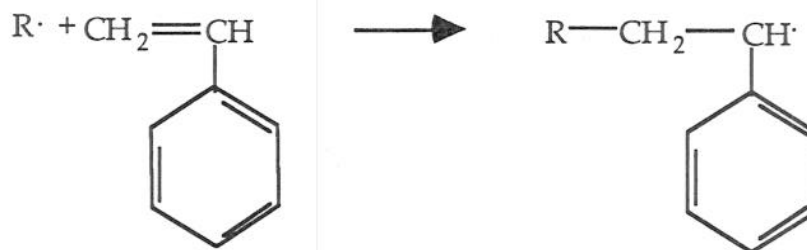
## OVERVIEW

Polystyrene is one of the major commercial plastics widely used in appliances, toys, food containers, packaging, etc. It is a good electrical insulator. Many copolymers of styrene with other monomers have been investigated, and some, such as styrene-acrylonitrile copolymers, are commercially important.

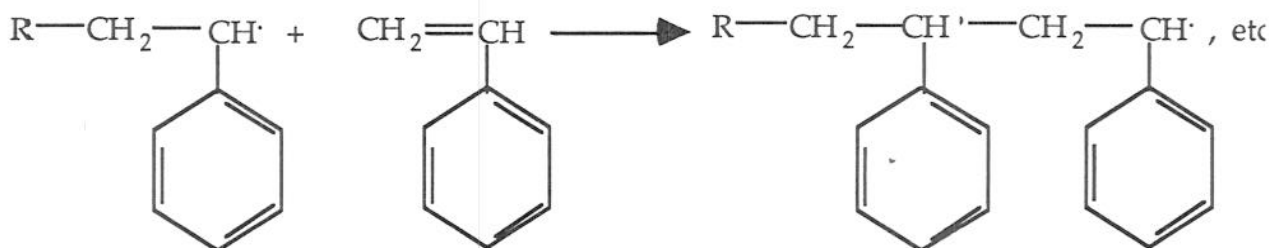
An addition polymer, polystyrene, can be prepared by reaction brought about by free-radical, cationic, or anionic catalysts, the first of these being the most common. In this experiment, polystyrene is prepared by free-radical-catalyzed polymerization. The reaction is initiated by a free-radical source. At 80 to 90 °C the benzoyl peroxide decomposes with homolytic cleavage of the oxygen-oxygen bond:



If an unsaturated monomer is present, the catalyst radical adds to it, initiating a chain reaction by producing a new free radical. If we let R stand for the catalyst radical, the reaction with styrene can be represented as,



The chain continues to grow:



The chain can be terminated by causing two radicals to combine (either both polymer radicals or one polymer radical and one initiator radical) or by causing a hydrogen atom to be abstracted from another molecule.

In this experiment, the initiator to be used is *benzoyl peroxide*. **In the interest of safety**, a common skin care product, *OXY-10*, which contains *10% benzoyl peroxide* as the active ingredient in the cream (check to label to be certain), will be used as the initiator for the polymerization reaction. The benzoyl peroxide initiator in pure form is extremely flammable and may *detonate upon exposure to air*, so the substitution of the cream product makes the experiment much safer. The only disadvantage is the cream residue in the final polystyrene product (it should be clear because it is an amorphous polymer), but this can be removed by subsequent dissolution in a solvent and precipitation (if so desired).

## EXPERIMENT

**NOTE: Perform this experiment in a hood and wear gloves and safety goggles.**

- a) To remove the inhibitor from the styrene, place 20 ml of styrene in a small beaker and add 2-3 g of alumina. Stir the mixture well to form a slurry. Filter the mixture either through filter paper supported in a small funnel or through a syringe with a filter attached.
- b) Place <sup>10 15</sup>20 ml of styrene in a test tube. Add a known weight (see below) of OXY-10 to the styrene, stopper and shake the tube vigorously.
- c) Heat the test tube in a water bath (approximately 80°C) in the hood. **Keep the stopper loosely in the test tube, taking care to remove it often in order to prevent the stopper from becoming a projectile as a result of pressure in the test tube.**
- d) In 30 to 45 minutes, the contents of the test tube will become noticeably more viscous. Pour the syrupy liquid into an aluminum weighing pan. Hardening may take a day or more at room temperature. Alternatively, the styrene can be placed in an oven at approximately 100 °C. The styrene should harden in an hour or two.

**NOTE:** The weight of OXY-10 to use for your polystyrene polymerization will be supplied to you by Dr. Rochefort. **Why is this important, or does it even matter?**

### **Removal of the cream from your polystyrene sample.**

If time permits, the creamy residue in your PS sample can be removed by dissolving the sample in a good solvent for PS (toluene) and filtering the solution to remove the creamy residue. This will need to be done before your PS sample can be *characterized by dilute solution viscometry* in a future experiment.

**SAVE YOUR POLYSTYRENE SAMPLE FOR A FUTURE EXPERIMENT.**

## Freezing Point Depression In a Bottle of Soda

Submitted by  
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Checked by  
**Mel Mosher**  
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The ravenous consumption of soda by today's students makes soda an interesting model with which to demonstrate the effect of solute concentration on the freezing point of an aqueous solution.

The use of pressure by the bottling company to maintain a high CO<sub>2</sub> concentration makes it possible to decrease this concentration rapidly simply by unscrewing the cap. As a result, a soda actually has two separate freezing points; one before the cap is removed, and one, which is higher, after the cap is removed and the concentration of CO<sub>2</sub> has decreased. A soda, therefore, when cooled to the proper temperature, will remain fluid as long as the seal remains unbroken. When the cap is unscrewed, however, ice immediately forms near the mouth of the bottle and quickly migrates down through the beverage.

### Experimental

Although any carbonated beverage will work for this demonstration, the simplest system is soda water. "Syfo" brand seltzer is USP pure carbonated water and works exceptionally well. A 10-ounce bottle of Syfo seltzer was cooled to 0 °C in an ice bath. One hour before the demonstration, the bottle was transferred to a salted ice bath<sup>1</sup> and maintained at -8 °C.<sup>2</sup>

For the demonstration, remove the bottle, showing that although it has been cooled far below the freezing point of pure water, the solution remains fluid. Gently invert the bottle a few times and, holding upright, open over a sink. **Do not shake vigorously.**

- **Caution:** Gloves and goggles should be worn, and the bottle should be opened behind a demonstration shield, because of the danger involved with dealing with compressed gas in a glass container, especially when temperature changes occur.

As the gas escapes, the concentration decreases and the freezing point is raised; the water freezes instantly. The rapidness of the ice formation causes the crystals to be very small and therefore, white in appearance. Consequently, the ice formation can be made readily visible by opening the bottle in front of a black or dark-colored background.

A thermometer will show that the ice/water mixture formed has risen in temperature to equilibrate at its new freezing point just below 0 °C.

### Safety

As mentioned above, gloves and goggles should be worn and the bottle should be opened behind a demonstration shield. Excessive agitation of the solution is unnecessary, and extreme agitation can lead to premature freezing. If

<sup>1</sup> Instructions for the preparation of cold temperature baths can be found in Gordon, A. J.; Ford, R. A. *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*; Wiley: New York, 1972; p 452.

<sup>2</sup> The colder the carbonated water, the more rapid and complete the subsequent ice formation will be. Excessively low temperatures are to be avoided, however, as the solution freezes at approximately -10 °C, often breaking the bottle and ruining the demonstration.

the solution begins to freeze prematurely, open the bottle immediately to relieve any excess pressure. The low temperature bath should be covered with a towel in case the bottle should freeze and break in the bath.

**Acknowledgment:** The author wishes to convey his appreciation to the National Science Foundation (Grant Number MDR-87-51183) for their support of this project.

## A Safe and Novel Polymerization of Styrene

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Checked by:  
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ChE 445/545  
LAB  
Procedure

The benzoyl peroxide initiated polymerization of styrene is frequently used as a laboratory exercise<sup>1</sup> or as a demonstration<sup>2</sup> to introduce students to the synthesis of addition polymers. All procedures, however, carefully describe the hazards of using this peroxide initiator, which is flammable and may detonate.<sup>1,2</sup> These warnings and the associated problems of storage and disposal of benzoyl peroxide may deter some instructors from using this procedure. We have avoided these hazards by using the initiator as contained in commercially available acne medications such as OXY-10, which contains 10% benzoyl peroxide.<sup>3</sup>

Following the procedure of Shakhashiri and Dirreen,<sup>2</sup> 25 mL of styrene, which contained inhibitor, was placed in a small beaker and 3 g of alumina added. After stirring, the slurry was filtered and the inhibitor-free styrene transferred to a test tube.

To the test tube containing styrene was added a generous dollop (~ 1 tsp) of OXY-10 skin cream and the tube was stoppered and shaken vigorously. The stopper was removed and the test tube heated in a water bath. Within 30 min, the contents became noticeably more viscous, and after heating for 45 min, polymer filaments could be drawn using a stirring rod. The syrupy liquid was then poured onto a watch glass. After cooling, the polystyrene resembles a brittle glass, which can be lifted from the watch glass with a spatula.

- All operations were carried out in a hood. Plastic gloves and safety goggles were worn throughout. The polymer and the test tube may be discarded in the waste container.

The use of this commercial product as a reactant leads to a discussion of the other listed ingredients and their probable functions: citric acid and sodium citrate as a buffer and antioxidant, propylene glycol as a moisturizer, sodium lauryl sulfate as a detergent, and methyl- and propylparaben (methyl and propyl esters of *p*-hydroxybenzoic acid) as antimicrobial agents.<sup>4</sup> The students are intrigued by the practical uses of these chemicals and are stimulated to read the labels of other commercial products.

<sup>1</sup> Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. *Introduction to Organic Laboratory Techniques: A Microscale Approach*; Saunders: Orlando, FL, 1990; pp 394-396.

<sup>2</sup> Shakhashiri, B. Z.; Dirreen, G. E. in *Chemical Demonstrations*; Shakhashiri, B. Z., Ed.; University of Wisconsin Press, Vol 1, 1983; p 241.

<sup>3</sup> OXY-10 is the trade name of the acne pimple medication manufactured by Norcliff-Thayer Inc., Tarrytown, NY. Other brands also contain benzoyl peroxide but were not used.

<sup>4</sup> Sax, N.I.; Lewis, R. L. *Hawley's Condensed Chemical Dictionary*, 11th ed., Van Nostrand: New York, 1987.

## 3.11

Shakhashiki and Dirksen  
Chemical Demonstrations, Vol. 1, 1983  
University of Wisconsin Press

### Polystyrene

Clear, liquid styrene is mixed with an initiator, benzoyl peroxide, and the mixture is then heated in a boiling water bath. The styrene slowly polymerizes to form a transparent solid.

#### MATERIALS

20 ml styrene,  $C_6H_5CH=CH_2$   
3 g alumina,  $Al_2O_3$   
0.5 g benzoyl peroxide,  $(C_6H_5CO)_2O_2$   
gloves, plastic or rubber  
2 800-ml beakers  
stirring rod  
11-cm filter paper  
60-mm funnel  
test tube, 16 mm  $\times$  150 mm, with stopper  
hot plate

#### PROCEDURE

Perform this demonstration in a hood and wear gloves.

To remove the inhibitor from the styrene, place 20 ml of styrene in a small beaker and add 2–3 g of alumina. Stir the mixture well to form a slurry. Filter the mixture through filter paper supported in a small funnel.

Place the styrene in a test tube. Add 0.5 g of benzoyl peroxide <sup>OXY-10</sup> stopper and shake the tube well to dissolve the initiator. Remove the stopper and heat the tube in a boiling water bath for 10–20 minutes. The styrene will become viscous with heating.

If you prefer a mold other than the test tube, check the viscosity periodically during the heating period. When the styrene is still liquid enough to pour, transfer it to another mold to harden. Hardening may take a day or more. Alternatively, if the mold and styrene are placed in an oven at approximately 100°C, the styrene should harden in an hour or two.

You can embed objects in the polystyrene matrix or make castings by keeping the temperature of the mixture at approximately 50°C for several days [1].

#### HAZARDS

The demonstration should be performed in a hood. Plastic or rubber gloves should be worn.

Styrene is flammable, and it is irritating to the eyes and mucous membranes. In high concentrations, it can be narcotic.

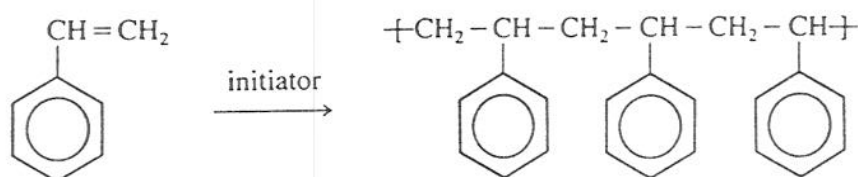
Benzoyl peroxide (dibenzoyl peroxide) is highly flammable and shock sensitive. It should not be stored in screw-capped bottles, because the friction produced by opening the bottle could cause an explosion.

## DISPOSAL

Although the polymer will ignite in a direct flame, it is otherwise inert and should be discarded in a waste container.

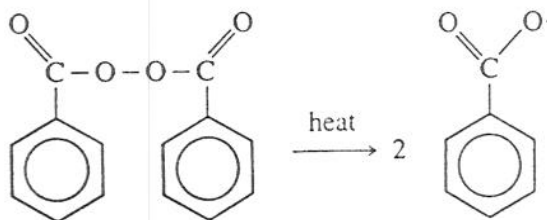
## DISCUSSION

Free radical polymerization of styrene can be carried out by bulk, solution, suspension, or emulsion techniques. The reaction equation can be represented as:



The arrangement of styrene in the polymer is considered to be "head-to-tail."

The initiator, benzoyl peroxide, is cleaved by heat into two benzoyl radicals:



Polystyrene is one of the major commercial plastics widely used in appliances, toys, food containers, packaging, etc. It is a good electrical insulator. Many copolymers of styrene with other monomers have been investigated, and some, such as styrene-acrylonitrile copolymers, are commercially important [2].

## REFERENCES

1. Sorenson, W. R.; Campbell, T. W. "Preparative Methods of Polymer Chemistry," 2nd ed.; Interscience Publishers, John Wiley and Sons: New York, 1968; pp 218-19.
2. Saunders, K. J. "Organic Polymer Chemistry"; Chapman & Hall Ltd.: London, 1973; Ch. 3.



## **EXPERIMENT #1b Polyurethane Foam Production**

The procedure to be followed is outlined in Pavia, "Introduction to Laboratory Techniques", Procedure 48D Polyurethane Foam, a copy of which is supplied.

The recipe for the magical *mixture A* is given on the bottom of p. 398. This will be made up as a "co-operative" effort by all groups in the lab with the assistance of the lab TA (Kim Renton). This is typical *batch processing* as commonly practiced by Chemical Engineers.

**NOTE: The questions which appear on p. 398 pertain to all the polymerization experiments conducted in the synthesis lab session, and should be answered as part of the laboratory report.**

## **EXPERIMENT #1c Condensation Polymerization of Nylon 6,6 Nylon "Rope Trick"**

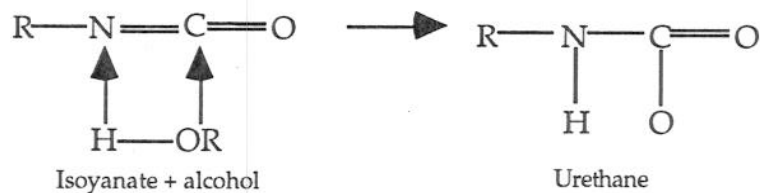
The procedure to be followed is outlined in the section titled **Condensation Polymerization of Nylon 6,6** and headed with *ChE 445/545 Polymer Lab*. It is essentially identical to the experiment in Pavia, "Introduction to Laboratory Techniques", Procedure 48B Polyamide (Nylon), which is also included for reference and background. A procedure for the production of Nylon 6,10 taken from Shakhshiri (*Chemical Demonstrations*, Vol. 1, Experiment 3.1, p. 213 (1983)) is also included for reference only. We will not do the Nylon 6,10 experiment, but it is a useful exercise to examine the synthesis to see how other forms of Nylon can be manufactured using the same interfacial polymerization technique.

**Note: Answer the questions posed at the end of the procedure section in the lab report.**

# Polyurethane Foam Production

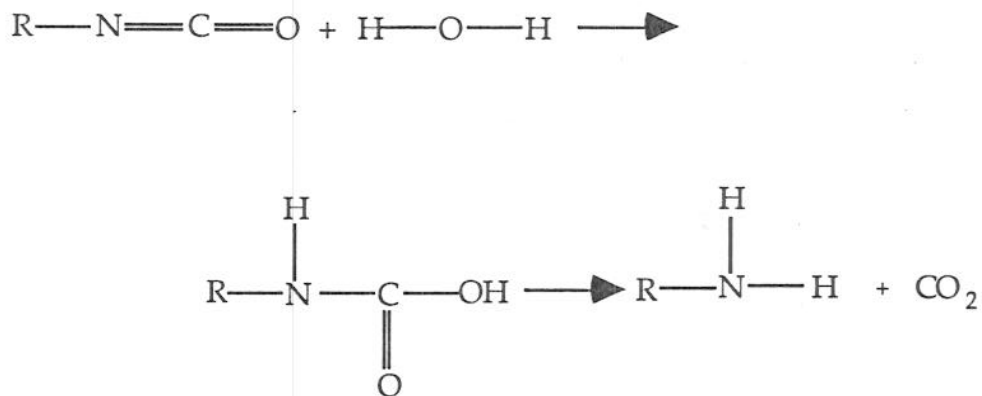
## OVERVIEW

A cross-linked polymer, polyurethane foam, is prepared in this experiment from a diisocyanate and a triol. The main reaction is the addition of the alcohol across the  $-N=C-$  bond of an isocyanate:



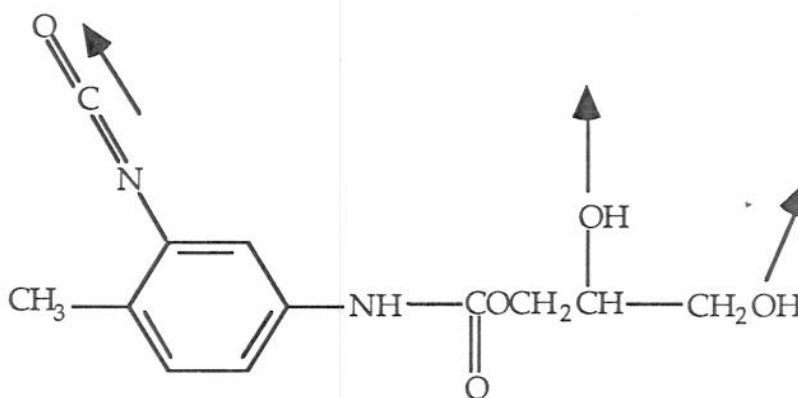
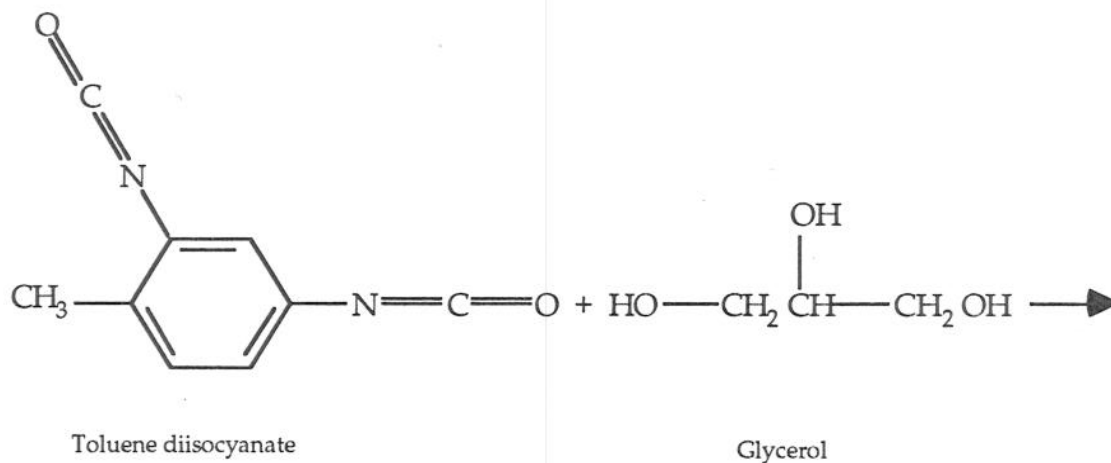
With a diisocyanate and a triol, the reaction can proceed in three directions, leading to a large molecule that is rigidly held into a three-dimensional structure.

The foaming is caused by the evolution of carbon dioxide, much as in the baking of bread. In baking, carbon dioxide is evolved by the fermentation of sugars with yeast, which causes the bread to rise. In the present preparation, the carbon dioxide is produced by the small amount of water present, which decomposes a small amount of the isocyanate:



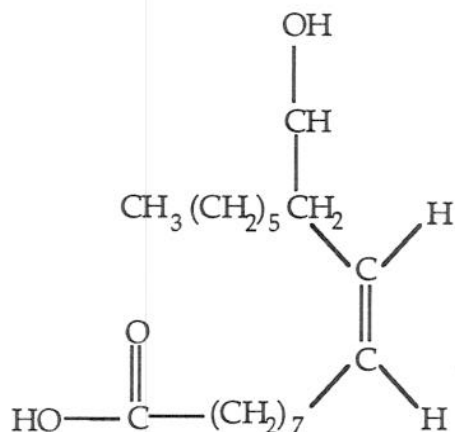
The evolution of carbon dioxide bubbles creates pores in the viscous mixture as the foam sets into a rigid mass. Thus, the foam has excellent buoyant properties. The cell size and structure of the foams are controlled by adding silicone oil.

The structure of the polymer is as follows:



The polymer can grow in all the indicated directions.

Castor oil, a triol, can also react in the same way. It is a triglyceride (fat) of ricinoleic acid.



In the present experiment, glycerol, castor oil, small amounts of water, silicone oil (a foaming agent) and stannous octoate (a catalyst) are mixed together. The toluene diisocyanate (TDI) is added to this mixture. The mixture is stirred and foaming begins. Commercial foams are not usually prepared from these simple materials. A polymeric diol or triol is generally used instead of glycerol and castor oil.

## EXPERIMENT

**Caution:** Toluene diisocyanate (TDI) is toxic. It will irritate the skin and eyes. Avoid breathing the vapor. It may cause an allergic respiratory response. Work in a hood or in an area with adequate ventilation. Keep the container tightly closed when it is not in use (TDI reacts with moisture in the air). After handling TDI, wash your hands thoroughly.

**Mixture A:** 350 g castor oil  
100 g glycerol  
50 drops stannous octoate (stannous 2-ethylhexanoate)  
50 drops Dow-Corning 200 silicone oil (estimate because very viscous)  
150 drops of water  
Cap the bottle and shake. **Allow to stand no more than 12 hours before use.**

Pour 8.5 mL of **mixture A** (stir well before using) into a waxed soft-drink cup. Then add 5 mL of toluene diisocyanate (tolylene-2-4-diisocyanate). *Stir the mixture rapidly and thoroughly with a stirring rod until the mixture is smooth and creamy.* The mixture should become warm and should begin to evolve bubbles of carbon dioxide after about one minute. When the gas begins to evolve, immediately stop stirring (foaming will be spontaneous). **Do not breathe the vapors.** Place the mixture in the hood. After the foaming has ceased, allow the material to cool and set thoroughly. The polyurethane is initially sticky, but after several hours it will become firm. If time permits, you can make another foam with different structure by altering the "recipe".

## QUESTION

1) Explain the mechanism of foam formation. How would you change the formulation to change the structural properties of the foam (i.e., make a more (less) rigid foam)?

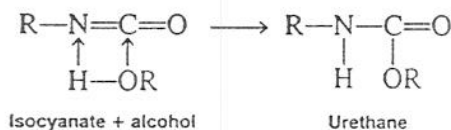
After the reaction subsides, put the beaker of styrene back on the hot plate and continue heating it until the liquid becomes very syrupy. With a stirring rod, draw out a long filament of material from the beaker. If this filament can be cleanly snapped after a few seconds of cooling, the polystyrene is ready to be poured. If the filament does not break, continue heating the mixture and repeat the above process until the filament breaks easily. Pour the syrupy liquid on a watch glass. After being cooled, the polystyrene can be lifted from the glass surface by gentle prying with a spatula.

PAVIA et al. "Intro. to Laboratory Techniques" (1990)

## Procedure 48D

### Polyurethane Foam

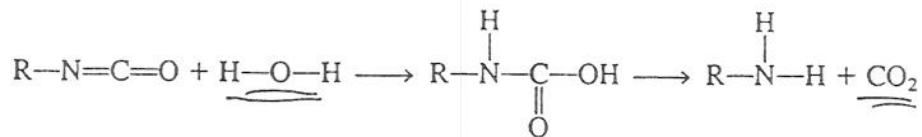
A cross-linked polymer, polyurethane foam, is prepared in this experiment from a diisocyanate and a triol. The main reaction is the addition of the alcohol across the  $\text{--N=C--}$  bond of an isocyanate:



With a diisocyanate and a triol, the reaction can proceed in three directions, leading to a large molecule that is rigidly held into a three-dimensional structure.

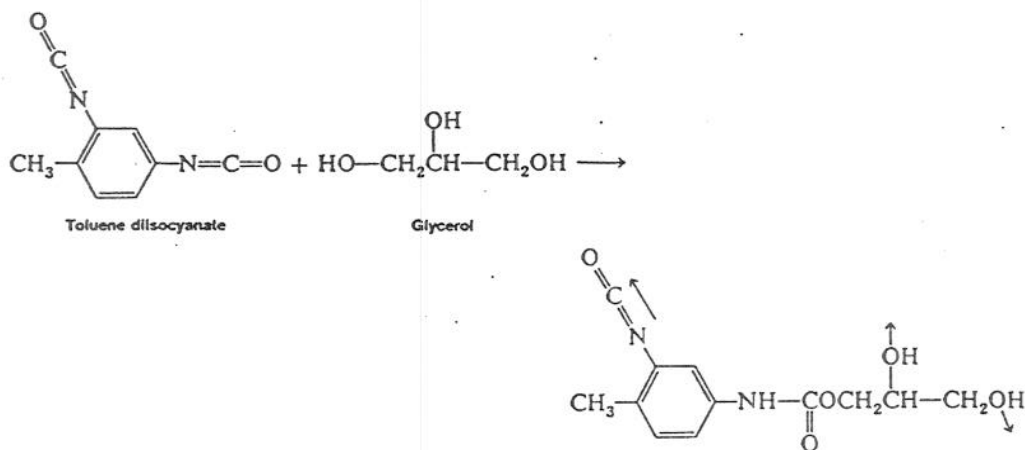
The foaming is caused by the evolution of carbon dioxide, much as in the baking of bread. In baking, carbon dioxide is evolved by the fermentation of sugars with yeast, which causes the bread to rise. In the present preparation, the carbon dioxide is produced by the small amount of water present, which decomposes a small amount of the isocyanate:

$\text{CO}_2$  produced  
from  $\text{H}_2\text{O}$   
present



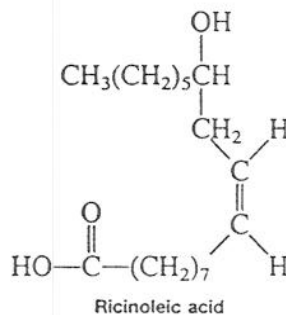
The evolution of carbon dioxide bubbles creates pores in the viscous mixture as the foam sets into a rigid mass. Thus, the foam has excellent buoyant properties. The cell size and structure of the foams are controlled by adding silicone oil.

The structure of the polymer is as follows:



The polymer can grow in all the indicated directions.

Castor oil, a triol, can also react in the same way. It is a triglyceride (fat) of ricinoleic acid (see the essay, "Fats and Oils," p 166):



*Silicone oil  
(foaming agent)*

In the present experiment, glycerol, castor oil, small amounts of water, silicone oil (a foaming agent) and stannous octoate (a catalyst) are mixed together. The diisocyanate (TDI) is added to this mixture. The mixture is stirred and foaming begins. Commercial foams are not usually prepared from these simple materials. A polymeric diol or triol is generally used instead of glycerol and castor oil.

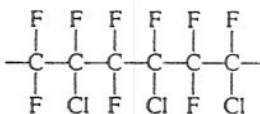
## PROCEDURE

**CAUTION:** Toluene diisocyanate (TDI) is toxic. It will irritate the skin and eyes. Avoid breathing the vapor. It may cause an allergic respiratory response. Work in a hood or in an area with adequate ventilation. Keep the container tightly closed when it is not in use (TDI reacts with moisture in the air). After handling TDI, wash your hands thoroughly.

Pour 8.5 mL of mixture A (shake well before using) into a waxed soft-drink cup.<sup>1</sup> Then add 5 mL of toluene diisocyanate (tolylene-2,4-diisocyanate). Stir the mixture rapidly and thoroughly with a stirring rod until the mixture is smooth and creamy. The mixture should become warm and should begin to evolve bubbles of carbon dioxide after about one minute. When the gas begins to evolve, immediately stop stirring (foaming will be spontaneous). Do not breathe the vapors. Place the mixture in the hood. After the foaming has ceased, allow the material to cool and set thoroughly. The polyurethane is initially sticky, but after several hours it will become firm. The paper container can then be removed. The material will shrink noticeably on standing.

### QUESTIONS

1. Ethylene dichloride,  $\text{ClCH}_2\text{CH}_2\text{Cl}$ , and sodium polysulfide,  $\text{Na}_2\text{S}_4$ , react to form a chemically resistant rubber, Thiokol A. Write the structure of the rubber.
2. Vinylidene chloride,  $\text{CH}_2=\text{CCl}_2$ , is polymerized with vinyl chloride to make Saran. Write a structure that includes at least two units for the copolymer formed.
3. Isobutylene,  $\text{CH}_2=\text{C}(\text{CH}_3)_2$ , is used to prepare cold-flow rubber. Write a structure for the addition polymer formed from this alkene.
4. Kel-F is an addition polymer with the following partial structure. What is the monomer used to prepare it?

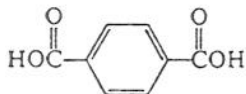


5. Maleic anhydride reacts with ethylene glycol to produce an alkyd resin. Write the structure of the condensation polymer produced.



Maleic anhydride

6. Kodel is a condensation polymer made from terephthalic acid and 1,4-cyclohexanedimethanol. Write the structure of the resulting polymer.



Terephthalic acid



1,4-Cyclohexanedimethanol

Mixture A.

<sup>1</sup>Mixture A is prepared as follows: Place 350 g of castor oil, 100 g of glycerol, 50 drops of stannous octoate (stannous 2-ethylhexanoate), 50 drops of Dow-Corning 200 silicone oil (this is estimated since it is difficult to measure), and 150 drops of water in a bottle. Cap the bottle and shake it thoroughly. Allow this mixture to stand no more than 12 hours before use.

## Condensation Polymerization of Nylon 6,6 The Nylon "Rope Trick"

### References:

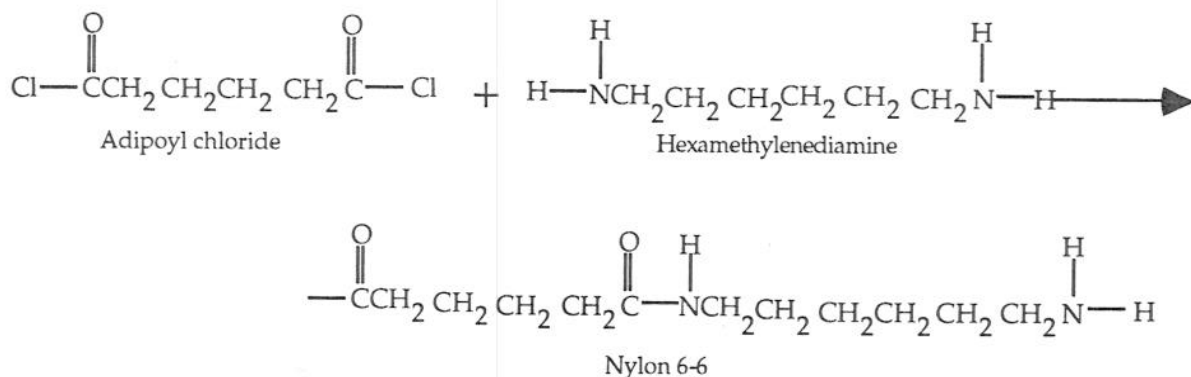
Pavia, Donald L., Lampman, Kriz, Engel. **Introduction to Organic Laboratory Techniques: A Microscale Approach**; Saunders College Publishing, Harcourt, Brace Jovanovich, Fort Worth, 1990; p. 393-394.

Shakhashiri, B.Z. and G. E. Dirreen, **Chemical Demonstrations; Vol. 1**, University of Wisconsin Press, 1983; p. 241.

### OVERVIEW

The word "nylon" is used to represent synthetic polyamides. The various nylons are described by a numbering system that indicates the number of carbon atoms in the monomer chains. Nylons from diamines and dibasic acids are designated by two numbers, the first representing the diamine and the second the dibasic acid.

Reaction of a dicarboxylic acid, or one of its derivatives, with a diamine leads to a linear polyamide through a condensation reaction. Commercially, nylon 6-6 (so called because each monomer has six carbons) is made from adipic acid and hexamethylenediamine.



In this experiment, you use the acid chloride instead of adipic acid. The acid chloride is dissolved in cyclohexane and this is added carefully to hexamethylenediamine dissolved in water. These liquids do not mix and two layers will form. The nylon can then be drawn out continuously to form a long strand. Imagine how many molecules have been linked in this long strand. It is a fantastic number!



## EXPERIMENT

The procedure to be followed is outlined is essentially identical to the experiment in Pavia, "Introduction to Laboratory Techniques", Procedure 48B Polyamide (Nylon), which is also included for reference and background. A procedure for the production of Nylon 6,10 taken from Shakhshiri (*Chemical Demonstrations*, Vol. 1, Experiment 3.1, p. 213 (1983)) is also included for reference only. We will not do the Nylon 6,10 experiment, but it is a useful exercise to examine the synthesis to see how other forms of Nylon can be manufactured using the same interfacial polymerization technique.

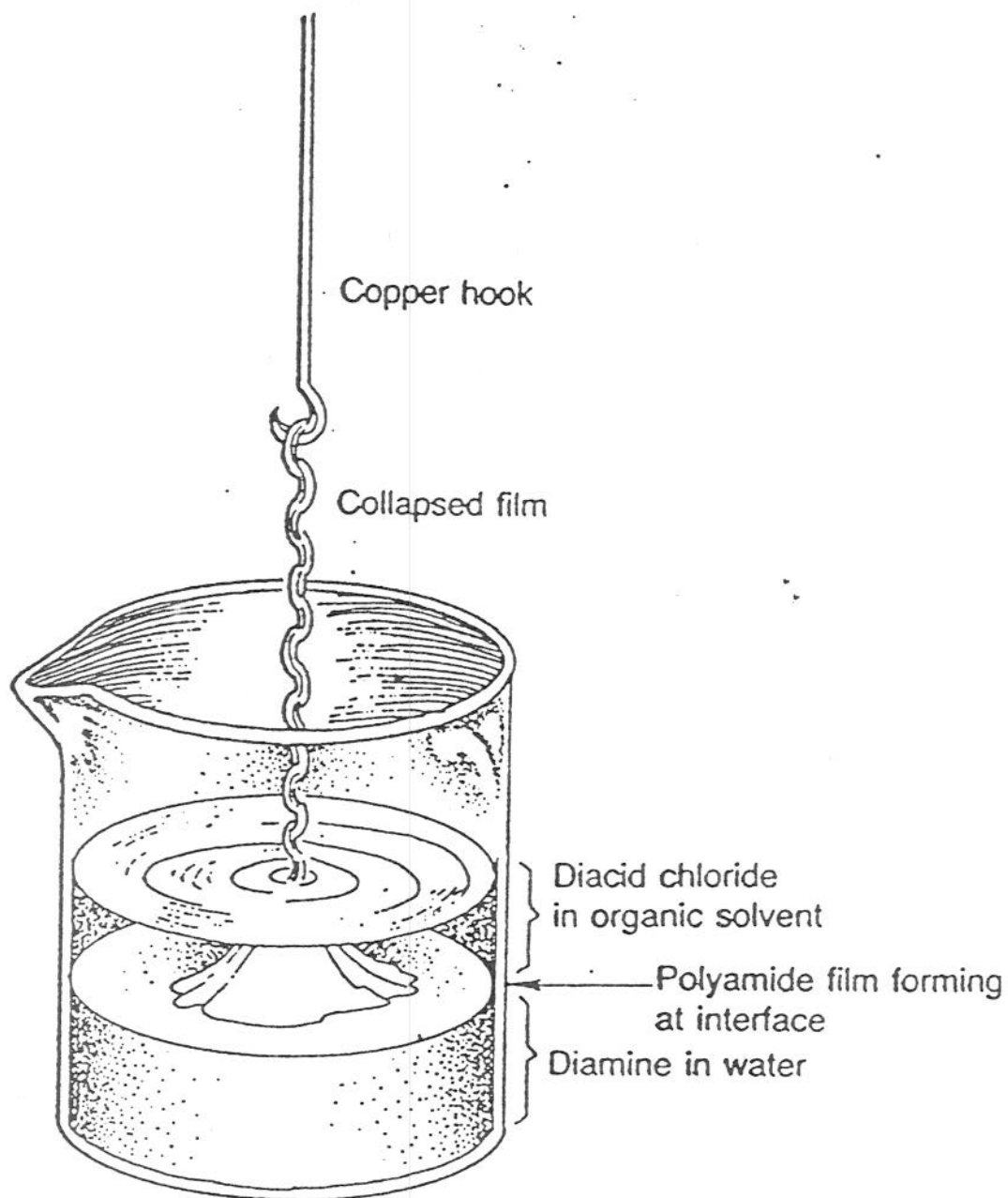
## PROCEDURE

- a) Pour 10 ml of a 5% aqueous solution of hexamethylenediamine (1,6-hexanediamine) into a 50 ml beaker.
- b) Add 10 drops of 20% sodium hydroxide solution.
- c) *Carefully* add 10 ml of a 5% solution of adipoyl chloride in cyclohexane to the solution by *pouring it down the wall* of the slightly tilted beaker. Two layers will form and there will be an immediate formation of a polymer film at the liquid-liquid interface.
- d) Using a copper-wire hook (a 6 in. piece of wire bent at the end or something similar), gently free the walls of the beaker from polymer strings. Then hook the mass at the center, and slowly raise the wire so that polyamide forms continuously, producing a "rope" that can be drawn out for many feet. Wind the rope around a glass stirring rod, taking care not to break the rope by pulling too quickly.
- e) Rinse the rope several times with water (make certain to squeeze it also to remove any fluid trapped inside the rope) and lay it on a paper towel to dry.
- f) With the piece of wire, vigorously stir the remainder of the two-phase system to form additional polymer. Decant the remaining liquid into a *waste container*.
- g) Remove the polymer using the copper wire, and wash it thoroughly as before. Allow the polymer to dry.
- h) After air-drying for some time, place all the polymer in an appropriate flat container (aluminum weighing pan or glass cover plate), spread it out, and place it in a vacuum oven at approximately 80°C overnight to remove the remaining water. **Weigh the polymer after drying.**

## QUESTIONS

- 1) **Calculate** the maximum amount of polymer that you **could** produce in this experiment.
- 2) Compare the calculated value to the amount actually produced. **What is your yield?**
- 3) Is cyclohexane a solvent for nylon 6,6. Is water?
- 4) What is the effect on the polymerization of *stirring* the solution at the end of the experiment?

# The Nylon "Rope Trick"

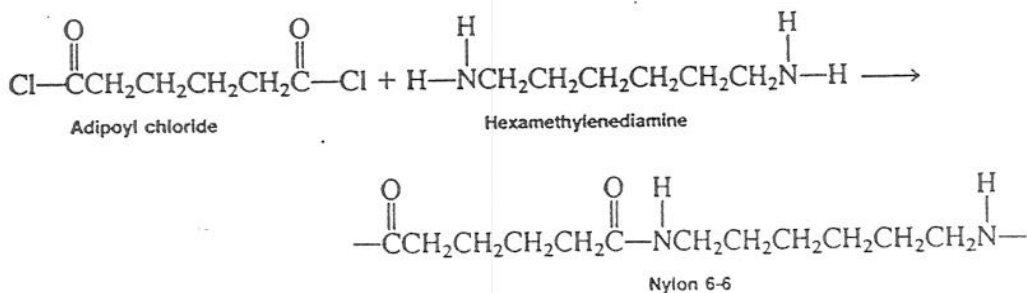


Preparation of nylon

# Procedure 48B

## Polyamide (Nylon)

Reaction of a dicarboxylic acid, or one of its derivatives, with a diamine leads to a linear polyamide through a condensation reaction. Commercially, nylon 6-6 (so called



because each monomer has six carbons) is made from adipic acid and hexamethylenediamine. In this experiment, you use the acid chloride instead of adipic acid. The acid chloride is dissolved in cyclohexane and this is added **carefully** to hexamethylenediamine dissolved in water. These liquids do not mix and two layers will form. It can then be drawn out continuously to form a long strand nylon. Imagine how many molecules have been linked in this long strand! It is a fantastic number.

### PROCEDURE

Pour 10 mL of a 5% aqueous solution of hexamethylenediamine (1,6-hexanediamine) into a 50-mL beaker. Add 10 drops of 20% sodium hydroxide solution. Carefully add 10 mL of a 5% solution of adipoyl chloride in cyclohexane to the solution by pouring it down the wall of the slightly tilted beaker. Two layers will form (see figure on page 394), and there will be an immediate formation of a polymer film at the liquid-liquid interface. Using a copper-wire hook (a 6-in. piece of wire bent at one end), gently free the walls of the beaker from polymer strings. Then hook the mass at the center, and slowly raise the wire so that polyamide forms continuously, producing a rope that can be drawn out for many feet. The strand can be broken by pulling it faster. Rinse the rope several times with water and lay it on a paper towel to dry. With the piece of wire, vigorously stir the remainder of the two-phase system to form additional polymer. Decant the liquid and wash the polymer thoroughly with water. Allow the polymer to dry. Do not discard the nylon in the sink. Use a waste container.

# CHE 445/545 Polymer LAB

## Condensation Polymerization of Nylon 6-6

### Materials required:

- 4 pr safety glasses
- 2 pr neoprene gloves
- 1 50 ml beaker
- 1 10 ml graduated cylinder
- 1 eyedropper
- 1 6-in piece of copper wire
- 1 glass stirring rod
- 1 sheet of aluminum foil

### Chemicals required:

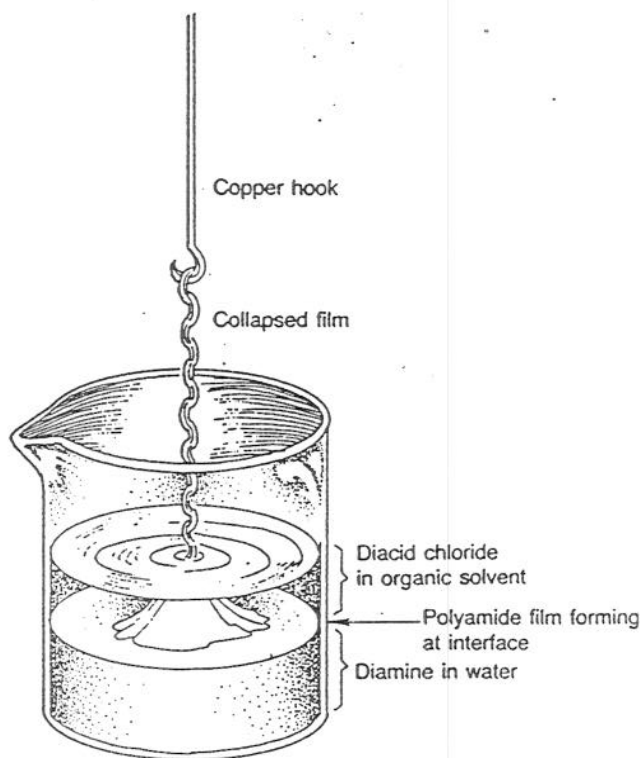
- 10 ml 5% aqueous solution of hexamethylenediamine (1,6-hexanediamine)
- 10 drops 20% sodium hydroxide solution
- 10 ml 5% of adipoyl chloride in cyclohexane

Procedure (adapted from Introduction to Organic Laboratory Techniques by Pavia, Lampman, and Kriz):

### SAFETY CONSIDERATIONS:

ALL THE REAGENTS USED ARE CORROSIVE, THE SOLVENTS ARE FLAMMABLE AND TOXIC. AVOID SKIN CONTACT OR INHALATION OF VAPORS. WEAR SAFETY GOGGLES AND GLOVES.

1. Pour 10 ml of the 5% aqueous solution of hexamethylenediamine into the 50-ml beaker. Add 10 drops of the 20% sodium hydroxide solution.
2. Using a glass rod to avoid mixing, slowly pour the 5% solution of adipoyl chloride in cyclohexane into the beaker. Two immiscible layers should form, and polymer should have formed immediately at the liquid-liquid interface. (See Figure 1.)



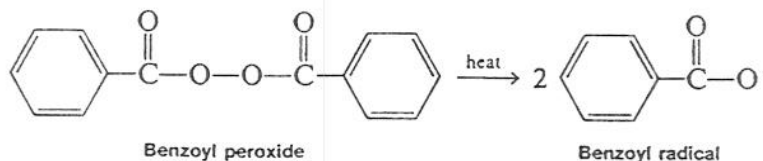
Preparation of nylon

## Procedure 48C

### Polystyrene

An addition polymer, polystyrene, is prepared in this experiment. Reaction can be brought about by free-radical, cationic, or anionic catalysts, the first of these being most common. In this experiment, polystyrene is prepared by free-radical-catalyzed polymerization.

The reaction is initiated by a free-radical source. The initiator will be benzoyl peroxide, a relatively unstable molecule, which at 80–90 °C decomposes with homolytic cleavage of the oxygen-oxygen bond:



## 3.1

B. Skakhashiri and Dirkeen  
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### Nylon 6-10

A film of nylon is formed at the interface between two immiscible liquids. When the film is lifted from the container, it is continually replaced forming a hollow thread of polymer. The continuous thread or "rope" of nylon can be wound on a windlass until one or the other of the two reactants is exhausted.

#### MATERIALS

50 ml 0.5M hexamethylenediamine (1,6-diaminohexane),  $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ , in 0.5M sodium hydroxide, NaOH (To prepare, dissolve 3.0 g of  $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$  plus 1.0 g NaOH in 50 ml distilled water. Hexamethylenediamine can be dispensed by placing the reagent bottle in hot water until sufficient solid has melted and can be decanted. The melting point is 39–40°C.)

50 ml 0.2M sebacoyl chloride,  $\text{ClCO}(\text{CH}_2)_8\text{COCl}$ , in hexane (To prepare, dissolve 1.5 ml to 2.0 ml sebacoyl chloride in 50 ml hexane.)

gloves, plastic or rubber

250-ml beaker or crystallizing dish

forceps

2 stirring rods or a small windlass

food-coloring dye (optional)

phenolphthalein (optional)

#### PROCEDURE

Wearing gloves, place the hexamethylenediamine solution in a 250-ml beaker or crystallizing dish. *Slowly* pour the sebacoyl chloride solution as a second layer on top of the diamine solution, taking care to minimize agitation at the interface. With forceps, grasp the polymer film that forms at the interface of the two solutions and pull it carefully from the center of the beaker. Wind the polymer thread on a stirring rod or a small windlass. Wash the polymer thoroughly with water or ethanol before handling.

Food coloring dyes or phenolphthalein can be added to the lower (aqueous) phase to enhance the visibility of the liquid interface. The upper phase can also be colored with dyes such as azobenzene [1], but observation of the polymer film at the interface is somewhat obscured. Some of the dye will be taken up with the polymer but can be removed by washing.

## HAZARDS

Hexamethylenediamine (1,6-diaminohexane) is irritating to the skin, eyes, and respiratory system. Sodium hydroxide is extremely caustic and can cause severe burns. Contact with the skin and eyes must be prevented.

Sebacoyl chloride is corrosive and irritating to the skin, eyes, and respiratory system. Hexane is extremely flammable. Hexane vapor can irritate the respiratory tract and, in high concentrations, can be narcotic.

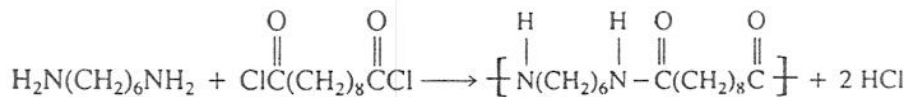
## DISPOSAL

Any remaining reactants should be mixed thoroughly to produce nylon. The solid nylon should be washed before being discarded in a solid waste container.

Any remaining liquid should be discarded in a solvent waste container or should be neutralized with either sodium bisulfate (if basic) or sodium carbonate (if acidic) and flushed down the drain with water.

## DISCUSSION

The word "nylon" is used to represent synthetic polyamides. The various nylons are described by a numbering system that indicates the number of carbon atoms in the monomer chains. Nylons from diamines and dibasic acids are designated by two numbers, the first representing the diamine and the second the dibasic acid [2]. Thus, 6-10 nylon is formed by the reaction of hexamethylenediamine and sebacic acid. In this demonstration the acid chloride, sebacoyl chloride, is used instead of sebacic acid. The equation is



The method of reaction used in this demonstration has been termed interfacial polycondensation. This method is useful because it is a low temperature process, it is rapid even at room temperature, and it does not depend on exact stoichiometry of reactants [3].

NOTE Many diamines and diacids or diacid chlorides can be reacted to make other condensation products that are described by the generic name "nylon." One such product is an important commercial polyamide, nylon 6-6, which can be prepared by substituting adipoyl chloride [4] for sebacoyl chloride in the procedure described here. The equation is

