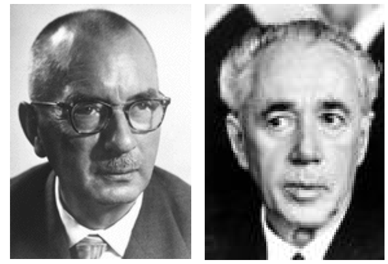
Experiment 31

POLYMER EXPERIMENTS

Fig. 31-1



Karl Ziegler and Giulio Natta shared the Nobel Prize in Cheimstry in 1963 for their contributions to polymer chemistry. http://nobelprize.org/chemistry/laureates/1963/

Text Topics

This experiment is intended to promote interest in polymer chemistry and presents a glimpse of the very broad and important field of polymer chemistry.

Comments

In **Part D**, the solution of seaweed in sodium carbonate should be allowed to stand for a couple of hours. It might be best to do this in one lab period and continue with its use in the next lab period. For **Part E**, please bring a thin, transparent piece of plastic to the laboratory. This could be a piece from a roll of food wrap, a freezer bag, an oven bag, a packaged food or candy wrapper or the top of a microwaveable package.

Discussion

In the 1967 classic movie, *The Graduate*, the following conversation was heard between the main character, Benjamin Braddock (portrayed by Dustin Hoffman, a 29 year-old playing a 21 year-old in his film debut), the guests and a family friend, Mr. McGuire, at Ben's college graduation party:

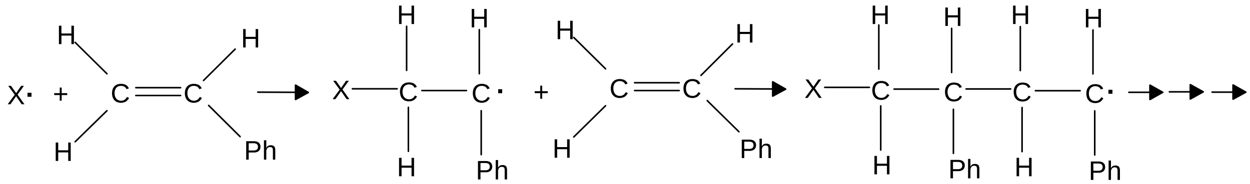
Guests: We're all so proud of you, proud, proud, proud, proud, proud, proud, proud. What are you going to do now?
Ben: I was going to go upstairs for a minute.
Guests: I meant with your future, your life.
Ben: Well, that's a little hard to say.
Mr. McGuire: I just want to say one word to you - just one word.
Ben: Yes sir.
Mr. McGuire: Are you listening?
Ben: Yes I am.
Mr. McGuire: 'Plastics.'
Ben: Exactly how do you mean?
Mr. McGuire: There's a great future in plastics. Think about it. Will you think about it?
Ben: Yes I will.
Mr. McGuire: Shh! Enough said. That's a deal.

Mr. McGuire correctly predicted and, if anything, understated the impact plastics would have on our lives. The synthesis of improved plastics engages a significant percentage of all research chemists. Many additional chemists work on the characterization of natural polymers such as DNA, RNA and proteins. From the paper of this book, the plastic of your pen and computer, the fibers of your clothes to your hair and skin, polymers make up a significant amount of the structural material surrounding us. Find a bunch of paper clips and connect them together to make a chain. You have just constructed a model of a polymer. The linking of molecules (or monomers) with chemical bonds end to end hundreds of times results in the formation of a polymer. The structural material of plants, cellulose, is a polymer of the sugar, glucose. The structural material of animals, protein, is a polymer made from amino acids.

Today's experiment will give you a brief excursion into the field of polymers including the cross linking of two polymers and the use of infrared spectroscopy to characterize a plastic.

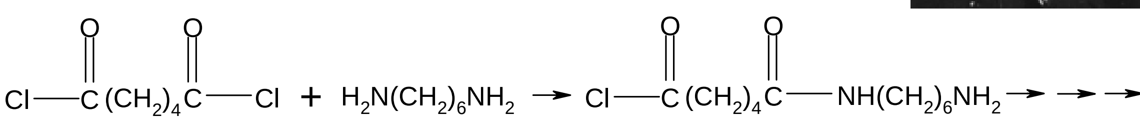
There are two common classes of polymers. Polystyrene, polyethylene, polyvinylchloride and teflon are all examples of addition polymers. For example, styrene can be polymerized by a free radical initiator (a source of a chemical having an unpaired electron). The free radical adds to the styrene creating a new free radical which then adds to another styrene and the process continues until several hundred styrenes have been linked to form a chain. ***Experiment 11*** included some experiments with the polymerization of styrene.

free radical initiator X–X → 2 X•, Ph = phenyl (benzene ring)



Polyesters and nylon belong to another class called condensation polymers. Nylon 66 can be made in the laboratory by reacting adipoyl chloride with 1,6-diaminohexane. Notice that after one molecule of each reacts, the two ends are still reactive and the left end will react with another 1,6-diaminohexane while the right reacts with adipoyl chloride. The process can continue hundreds of times. Your instructor should demonstrate this reaction.

Wallace Hume Carothers (1896—1937)discovered nylon in 1934
http://www.chemheritage.org/EducationalServices/chemach/pop/whc.html

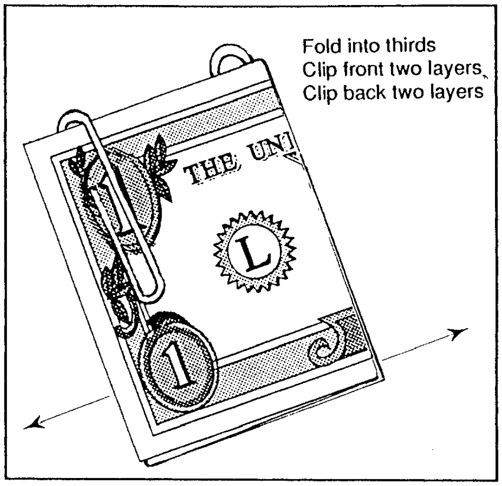


One way of changing the properties of a polymer is to chemically connect adjacent strands. This process is called crosslinking and is the topic of two parts of today's experiment. In one case, the crosslinking of the polymer polyvinyl alcohol, will result in a fluid with unusual properties that you should investigate.

Procedure

A. Polymer models. Link together at least 8 paper clips and explain the analogy to a polymer. Make another chain of at least 8 paper clips and lay the two chains down side by side. Link the two chains together with single paper clips at two different sites. How does this "cross linking" affect the behavior of the chains when they are moved? In *Part C* of this experiment, you will cross link a couple of real polymers.

Catalysts are often needed to cause polymerizations to occur. To model the use of a catalyst, fold a dollar bill into thirds like a fan. Place two paper clips on the dollar bill as illustrated in *Figure 31-2* with one paper clip clipping the first two thirds and the second clipping the last two thirds. Grab the two ends of the dollar bill with your left and right hands and quickly pull in opposite directions. Explain how the dollar bill in this "magic trick" serves as a model for a catalyst and comment on the quality of the analogy. (Thanks go to Dr. Alan McCormack of California State University at San Diego for sharing this analogy with me.)



B. Demonstrations.

It is recommended that the instructor perform these experiments as demonstrations as some of the chemicals are potential irritants and/or corrosive. This also minimizes the amount of waste disposal necessary.

1. Nylon synthesis

   a. Prepare a solution containing 0.5 M NaOH and 0.5 M 1,6-diaminohexane. Add about 2 mL of the solution to a watch glass or evaporating dish.
   b. Put a small loop in the end of a 4 inch piece of copper wire.
   c. Add about 4 mL of 0.25 M adipoyl chloride in cyclohexane to the watch glass, insert the loop into the solution and slowly pull a nylon string out of the solution.

2. Disappearing polystyrene.

Pour about 100 mL of acetone into a 600 mL beaker. Have students line up and have each one add a handful of polystyrene peanuts to the beaker. Stir between each addition.

C. Preparation of slime by use of cross linking.

A 4% borax solution (sodium borate decahydrate - $Na_2B_4O_7 \cdot 10H_2O$ - 20 Mule Team Borax works fine) should be available in the laboratory.

Slime 1. Prepare 50 mL of 4% polyvinyl alcohol by adding about 2 grams of polyvinyl alcohol to 50 mL of water in a 400 mL beaker. Stir and then microwave until dissolution is complete. Add 5 mL of the borax solution to the polymer solution and stir for several minutes. Try the following experiments with your *slime 1*:

a. Pull the *slime 1* slowly and record your observations.
b. Pull the *slime 1* quickly and record your observations.
c. Mount a funnel in a ring on a ring-stand. Put some *slime 1* into the funnel and push it through the funnel. Record your observations as the *slime 1* comes out of the funnel.
d. Try some other safe experiments, describe them, and record your observations.

Slime 2. Add 20 mL of water to 20 grams of Elmer's glue. Add 20 mL of borax solution and stir. Try some safe experiments with your *slime 2.*

D. Preparation of plastic worms by use of cross linking.

A 2 percent (w/w) aqueous solution of sodium alginate and a 1% (w/w) calcium chloride are needed for this experiment. Sodium alginate can be purchased or extracted from seaweed.

Extraction method. To extract alginic acid from seaweed (see Reference for possible source), dry and grind 4 g of seaweed. Add the ground seaweed to 100 mL of 2% (w/w) sodium carbonate and stir. The mixture should be allowed to stand a couple of hours (it might be best to add the solid to the sodium carbonate at the end of a lab period and then continue with the procedure the next lab period). Filter the solution using muslin cloth. To the filtrate, add 150 mL of 0.2 M HCl and stir. Filter to obtain a solid that is presumably alginic acid. As with most procedures, it is highly advisable to provide evidence that the intended product has been collected. As alginic acid is a polymer, there are very few simple measurements that can provide evidence. However, the *Part E* includes a method for determining the infrared spectrum of a polymer. The ir of alginic acid is available online for comparison purposes. Take an ir of alginic acid and compare the spectrum to the literature spectrum. Now add 2% sodium carbonate to convert the alginic acid to sodium alginate. Add an equal volume of 95% ethanol, filter to collect the sodium alginate and allow to dry at room temperature at least overnight before determining the percent recovery. However, the sodium alginate can be used wet to prepare plastic worms as it is dissolved in water at the start of the procedure. Weigh the sodium alginate and determine the percent recovery from seaweed.

Preparation of plastic worms. Prepare 25 mL of a 2% (w/w) aqueous solution of sodium alginate and 25 mL of 1% (w/w) calcium chloride solution. If colored worms are desired, add a few drops of food coloring to the sodium alginate solution. Add about 5 mL of the calcium chloride solution to a very small beaker or a large test tube. Using a dropper, squirt a few mL of the sodium alginate solution into the calcium solution. Curl the end of a 4 inch piece of copper wire and dip the wire into the solution and attempt to pull out the worms. Record your observations and think about how the calcium ions cross link the alginate polymers.

Additional experiments - work with other students and use sodium alginate with different ionic solutions paying particular attention to the oxidation state of the cation and the success of worm formation.

E. Polymer identification using infrared spectroscopy.

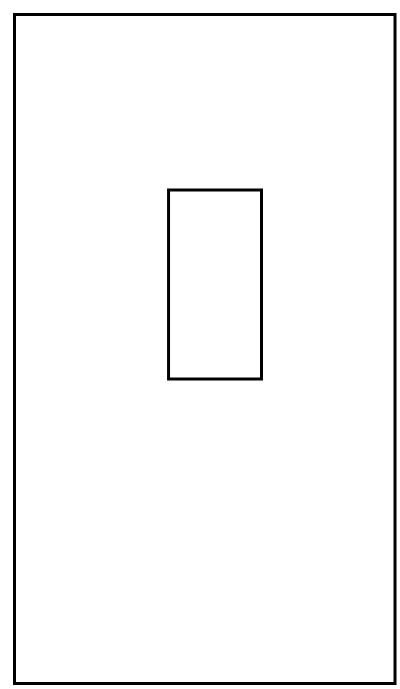
As indicated in the *Comments* section at the beginning of this experiment, you will need a thin, transparent piece of plastic from a roll of food wrap, freezer bag, oven bag or the wrapper from a packaged food or candy or the top of a microwaveable package.

1. Using cellophane tape, fasten a small piece of your plastic over a 1 inch by 0.5 inch hole appropriately placed in a business sized card (2 inches by 3.5 inches) so that the hole, when placed in your ir instrument is in the ir beam. Record the ir spectrum

2. On a milligram (or better) balance, weigh a second piece of your plastic that is about the same size as that used above. Using tongs dip the plastic carefully into a beaker in the hood containing methylene chloride for several seconds. This may take several tries with new plastic pieces until you get a piece you can attach to a second card as in Part 1 above. After the plastic piece has dried, weigh the piece before attaching it to the card, tape it to the card and record the ir spectrum.

The list below contains most of the plastics that are used as wrapping materials. Infrared spectra for comparison purposes for most of these plastics (except polypropylene and polyvinylidine chloride) can be found online at one or more of the sites listed below. From the difference in the mass before and after methylene chloride immersion, determine the approximate percentage of additives in the plastic. Using the spectrum obtained after washing, try to determine the identity of the plastic by comparing the spectrum to literature spectra. Try running the washed sample as a background spectrum and then running the original. The result should be the spectrum of the additives. Try to deduce the identity of the additive(s).

cellulose acetate
polyethylene
poly(ethylene terephthalate)
poly(methylmethacrylate)
polypropylene
polystyrene
polyvinyl acetate
polyvinyl alcohol
polyvinyl chloride
poly(vinylidine chloride)



References

General polymer references:
http://pslc.ws/macrog/index.htm
http://www.chemheritage.org/EducationalServices/Polymers+People/PREFACE.html
http://matse1.mse.uiuc.edu/polymers/polymers.html
http://agpa.uakron.edu/p16/

Possible source of seaweed - http://seafarms.com/html/products.html ($50/450 g)

Seaweed information and struture of alginic acid.
http://www.seaweed.ie/uses_general/alginates.php
http://en.wikipedia.org/wiki/Alginic_acid
http://www.fao.org/docrep/006/y4765e/y4765e07.htm
http://www.cybercolloids.net/information/technical-articles/introduction-alginate
http://www1.lsbu.ac.uk/water/hyalg.html
http://www.fao.org/docrep/x5822e/x5822e04.htm
http://www.kimica-alginate.com/alginate/chemical_structure.html

Extraction of alginic acid from seaweed.
N. Saleem Basha
http://www.academia.edu/1044502/Preliminary_Investigation_on_Sodium_Alginate_Extracted_from_Sargassum_Subrepandum_of_Red_Sea_of_Eritrea_as_Tablet_Binder

Preparation and properties of plastic worms.
Mock, E.; Lyman-Holt, A.; Rochefort, S.
http://engineering.oregonstate.edu/momentum/k12/feb05/M!_GelBeads_final021405.pdf
Criswell, B. *J. Chem. Educ.*, **2006**, *83*, 574-576.
Bowles, R. D.; Saroka, J. M.; Archer, S. D.; Bonassar, L. J. *J. Chem. Educ.*, **2012**, *89*, 1308-1311.
Friedli, A. C.; Schlager, I. R. *J. Chem. Educ.*, 2005, *82*, 1017-1020.
Waldman, A. s.; Schechinger, L.; Govindarajoo, G.; Nowick, J. S.; Pignolet, L. H. *J. Chem. Educ.*, **1998**, *75*, 1430-1431.
http://psaalgae.org/website/resources/Alginate_Gel.html

Infrared spectra are available online at:
NIMC site - http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng
PSLC site - http://pslc.uwsp.edu/
NIST site - http://webbook.nist.gov/chemistry/

References for the infrared of polymers section:
Webb, J.; Rasmussen; M., Selinger, B. *J. Chem. Educ.*, **1977**, *54*, p. 303.
Brandup, J.; Sederberg, D.,
http://www.chem.purdue.edu/teacher/table_of_contents/Infrared%20Spectroscopy/IRFILMS.pdf
Wirth, J. J.; Christie, S.; Beebe, Jr., T. P. *FTIR Determination of Polymers and Plasticizers*
http://www.udel.edu/chem/beebe/Chem438/Lab%205%20FTIR%20of%20polymers%20and%20a%20plasticizer.pdf
Bowen, H. J. M. *J. Chem Educ.*, **1990**, *67*, 75-77.
Hodgson, S. C.; Bigger, S. W. *J. Chem. Educ.*, **2001**, *78*, pp. 555-556 and Supplemental Material online.

Prelaboratory Preparation - *Experiment 31*

Be sure to list all the goals of the experiment and to bring a piece of plastic film to the laboratory.

Observations and Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. How does "crosslinking" affect the movement of the model polymer chains?
3. Explain how this dollar-paper clip "magic trick" models a catalyst and comment on the quality of the analogy.
4. The 1,6-diaminohexane is on the bottom in the water phase and the adipoyl chloride is in the top phase in cyclohexane. Give and account for your observations as the copper loop was lifted from the mixture.
5. Report and explain your observations as the polystyrene peanuts are added to the acetone.
6. Write an equation for the polymerization of chloroethene (vinyl chloride - CH_2=CHCl) to polyvinylchloride assuming that a free radical initiator (X•) is present.
7. *Slime 1*
    a. Describe your observations when the *slime 1* was pulled slowly.
    b. Describe your observations when the *slime 1* was pulled quickly.
    c. Describe your observations on the funnel experiment.
8. *Slime 2*
    a. Describe your experiments and observations with *slime 2*.
9. Test the two types of slime in as many ways as you can think of. Report your tests and observations.
10. Alginic acid is a polymer of D-mannuronic acid and L-guluronic acid linked through the 1- and 4- positions. Draw the structures of D-mannose, L-gulose, D-mannuronic acid and L-guluronic acid and compare the structures of all four sugars. Draw an example of a 3 sugar strand of alginic acid.
11. Give your observations when the sodium alginate solution was added to calcium chloride. Explain your observations.
12. List some uses of sodium alginate. Check the label of a medical product called Gaviscon and comment on the reason for its ingredients.
13. What is the approximate percentage of additive(s) in your plastic?
14. Provide as much information about the identity of the plastic as you can. Did anyone else in the class have the same plastic?
15. Provide as much information about the identity of the plasticizer as you can.
16. Did the properties of the plastic change after the plasticizer was removed? Explain your answer?
17. Does color in the plastic affect this experiment? Explain your answer. Are there any interference patterns or fringes in the ir spectrum? For more information, see:

http://www.udel.edu/chem/beebe/Chem438/Lab%205%20FTIR%20of%20polymers%20and%20a%20plasticizer.pdf