Addition Polymerization

Preparation of Polymers

Introduction

Use this interactive classroom activity to teach students about the steps involved in the preparation of addition polymers via free-radical chain reactions.

Concepts

- Polymers
- Chain reaction
- Addition reactions
- Free-radical initiators

Materials

Student volunteers, 7 or more

Safety Precautions

This activity is considered nonhazardous.

Procedure

1. Select six or more student volunteers who will act as *alkene* monomers—molecules with at least one carbon-carbon double bond. The simplest alkene monomer is ethylene, $H_2C{=}CH_2$, which is used to make polyethylene. The main uses of polyethylene are in packaging materials.
2. Have the students pair up and hold hands—the partners should grasp one hand as in a handshake, and hold their other hands together above them (see Figure 1).

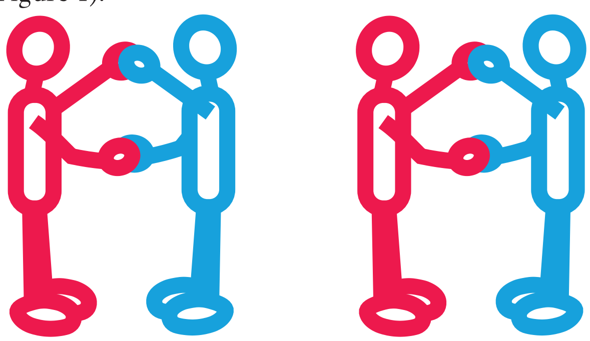


Figure 1. Holding hands to represent carbon-carbon double bonds.

3. Discuss the nature of the sigma and pi bonds making up a carbon-carbon double bond. The students, representing carbon atoms, are held together by a "handshake" bond corresponding to the strong sigma-bond component of a double bond. The electrons in the sigma bond are localized along the bond axis linking the two atoms. The hands held together over the students' heads represent the weaker pi-bond component of the double bond. The electrons in the pi-bond are not as strongly held as the sigma electrons, because the electron density is above and below the atoms, rather than directly between them. Pi bonds are formed by overlap of p-orbitals which are perpendicular to the bond axis. Because pi bonds are weaker than sigma bonds, less energy is required to break pi bonds. They should be easy to break!
4. Have the student alkene monomers line up next to each other.
5. Select a volunteer to act as a *free radical*, that is, an atom with an unpaired electron. Holding one hand out over his head to represent the unpaired electron, the free radical approaches the carbon atom in the first alkene and reacts with it by "pulling" the p-electron out of the pi-bond. The double bond in the first alkene is broken as the free radical becomes joined to the carbon atom via a new sigma bond.

6. What happens to the former p-electron in the second carbon atom? It is now “free” or unpaired as well—a new free radical has been formed!
7. The new free radical is also very reactive. It desperately wants to “join hands” with another electron to form a bond. Fortunately, the neighboring alkene molecule is an easy target. The second carbon atom grabs the upper hand of the next alkene, breaking its pi-bond, forming a new sigma bond, and releasing another new free radical in the process.
8. A *chain reaction* ensues as the new free radical repeats step 7 with the third alkene in the chain. This chain reaction may continue as long as there are neighboring alkenes with which to react.
9. Ask students to predict how long the polymer chain will grow. Is there any way to stop the reaction? Start a second chain reaction with a new free radical initiator and a new group of alkenes. Let the free-radical end of one chain join hands and thus combine with the free-radical end of a second chain. The chain reaction stops, because there is no longer a new free-radical being generated.

Disposal

None required.

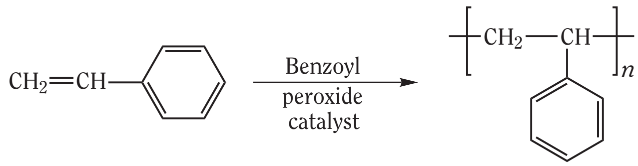
Tips

- Polymers are an indispensable part of life. Natural polymers include a wide range of biological molecules and materials, such as DNA, proteins, starch, cellulose, and wood. Synthetic polymers or plastics are incredibly useful modern materials. Examples of polymer “products” that could only be imagined more than 50 years ago include cell phones and computers, contact lenses and artificial joints, bike helmets and bulletproof vests. Have students research and prepare posters on the monomers, preparation, and uses of common addition polymers, including polyethylene, polypropylene, polystyrene, sodium polyacrylate, poly(methyl methacrylate), polytetrafluorethylene (Teflon®), polyvinyl chloride, and polyacrylonitrile (acrylic).
- Addition polymers are extremely large molecules. An interesting problem for students to solve is to estimate the number of alkene monomer units that make up a typical polymer molecule, such as polyethylene. High-density polyethylene or HDPE is a linear polymer with an average molecular weight (molar mass) of 500,000 g/mole. Assuming the basic or repeating structural unit in polyethylene is $–(CH_2–CH_2)_n–$, the value of *n* is 500,000/28, or about 18,000 ethylene molecules!
- For a collection of meaningful, easy-to-do laboratory activities that will help students understand the basic principles of polymer structure and function, see *Polymers*, Volume 21 in the *Flinn ChemTopic™ Labs* series (Catalog No. AP6988). The book has six experiments and five demonstrations that allow students to prepare a variety of common polymers, investigate their properties, and discover the fascinating uses and applications of these “giant” compounds.

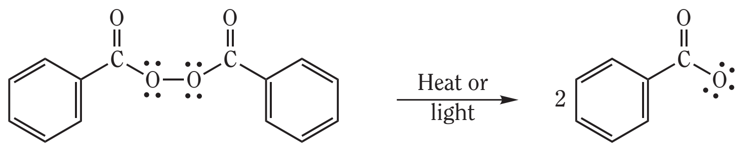
Discussion

Polymers are large, chain-like molecules composed of multiple repeating units of smaller molecules, called monomers, which have been joined together by a chemical reaction. All polymers can be classified into two main categories based on the nature of the chemical reaction by which they are made. *Addition polymers* are formed when organic compounds containing one or more C=C double bonds add to each other. Addition reactions typically require a catalyst to initiate the reaction, but once a reaction starts, it will continue as a chain reaction until thousands of monomer units have been added together. *Condensation polymers* are formed when two monomers with different functional groups combine to form a new functional group. Condensation reactions usually generate a simple by-product, such as H_2O or HCl, which is split off when two functional groups combine. Condensation polymers are formed in a step-wise process, so the resulting molecules are generally smaller than addition polymers.

Polystyrene, which is used to make rigid, clear plastics, is a common addition polymer. It is made by reacting styrene, $CH_2{=}CH{-}C_6H_5$, with dibenzoyl peroxide (Equation 1). Dibenzoyl peroxide is a free-radical catalyst—it breaks apart in the presence of heat or light to produce benzoyl radicals (Equation 2).



Styrene *Polystyrene* *Equation 1*



Benzoyl peroxide *Benzoyl radical* *Equation 2*

Free radicals contain unpaired electrons and are thus very reactive. There are three main steps in the addition reaction for the preparation of polystyrene (Figure 2, steps 1–3):

1. The benzoyl radical (abbreviated R.) attacks the C=C double bond in styrene to form a new free radical. This is called the *initiation step.*
2. The new free-radical intermediate adds to another styrene molecule, and a chain process begins. This *propagation step* will usually continue until thousands of styrene monomers have been added together.
3. If two free radicals combine, the chain reaction comes to an end. This is called *chain termination*.

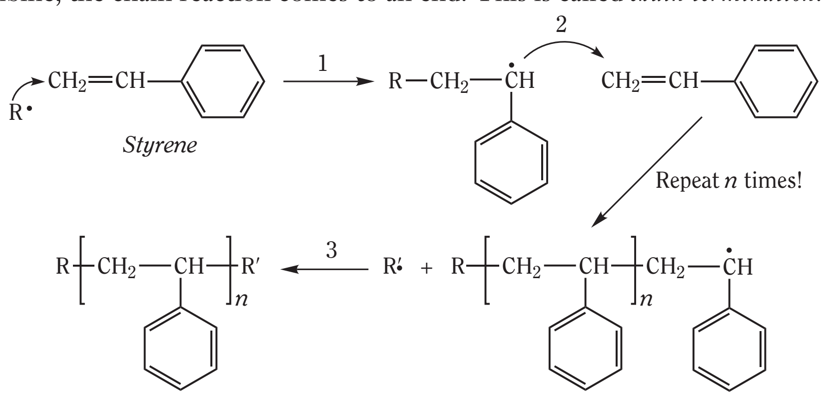


Figure 2. Free radical chain reaction for the preparation of polystyrene.

Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
Systems, order, and organization
Form and function
Content Standards: Grades 9–12
Content Standard A: Science as Inquiry
Content Standard B: Physical Science, structure and properties of matter, chemical reactions

Flinn Scientific—Teaching Chemistry™ eLearning Video Series

A video of the *Addition Polymerization* activity, presented by Annis Hapkiewicz, is available in *Preparation of Polymers*, part of the Flinn Scientific—Teaching Chemistry eLearning Video Series.