

Cross-Linked Polymers



Center for Nanotechnology Education



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Based on a work at www.nano-link.or

Cross-Linked Polymers

Abstract

This module allows students to investigate forces and interactions at the molecular scale by mixing different liquids with a cross-linked polymer. The polymer (sodium polyacrylate) is similar to the structure found in cellulose and collagen. The interactions are dependent upon the charge distribution of the liquid molecules as well as temperature. Liquids with non-uniform charge distribution will interact with (attach to) the atoms in the polymer and if the strength of attraction between the liquid and the atom is stronger than the forces holding the atom in the polymer structure then the atomic structure of the system is changed and therefore changes in the material properties can be observed. By observing the different results with different liquids, students can compare and contrast interactions between different fluids and the polymer. The students, by observing the interactions that different fluids have with the polymer can infer the nanoscale interactions between the atoms within the polymer and the fluid molecules.

Outcomes

After completing this module, students will gain an appreciation and understanding of how different molecules have different charge densities or charge configurations and how those differences result in different interactions with the polymer. The polymer/fluid system will have different physical attributes dependent upon the fluid.

Prerequisites

- Concept of atoms and molecules and how they are related
- Understanding that physical properties are related to the atomic arrangement

Science Concepts

- Electrostatic interactions
- Polymers
- Molecular charge distribution (uniform and non-uniform)

Nanoscience Concepts

- Forces that act at the nanometer scale lead to observable macroscopic phenomena

Background Information

Polymers

Some polymers, such as rubber and cellulose, occur naturally and may be formed by plants or fungi. Synthetic polymers are created by engineering the combination of hydrogen and carbon atoms and the arrangement of the chains they form. A polymer molecule is a long chain of covalent-bonded atoms and secondary bonds that hold groups of polymer chains together to form the polymeric material. Polymers are primarily produced from petroleum or natural gas raw products, but the use of organic substances as polymer feed stocks is growing. Polymers are very useful materials because their structures can be altered and tailored to produce materials 1) with a range of mechanical properties 2) in a wide spectrum of colors and 3) with different transparent properties. For example, the advanced material known as Kevlar is a synthetic polymer that can be used in bullet-proof vests, strong/lightweight frames, and underwater cables that are 20 times stronger than steel.

Polymer Structure

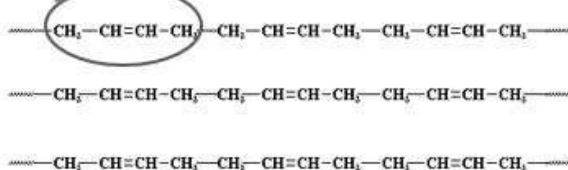
Terms

- Mer– The repeating chemical unit in a polymer chain
- Monomer – A single mer unit (n=1)
- Polymer – Many mer-units along a chain (n=10³ or more)
- Degree of Polymerization – The average number of mer-units in a chain.

A mer in a polymer of rubber

Mer: a group of atoms

Polymer: A group of repeating "mers"



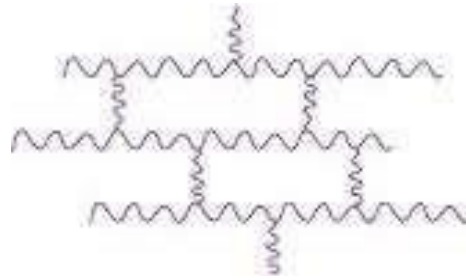
Monomers

A polymer is composed of many simple molecules that are repeating structural units called monomers. A single polymer molecule may consist of hundreds to a million monomers and may have a linear, branched, or network structure. Covalent bonds hold the atoms in the polymer molecules together and secondary bonds then hold groups of polymer chains together to form the polymeric material. Copolymers are polymers composed of two or more different types of monomers.

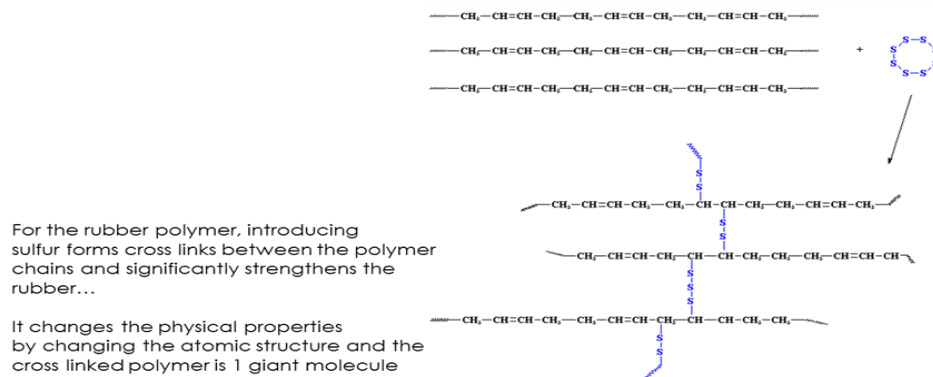
Cross-linked Polymers

The polymer (a variant of sodium polyacrylate) used in this activity is called a cross-linked

polymer because it has shorter chains of atoms that serve as connectors between the longer polymer chains.



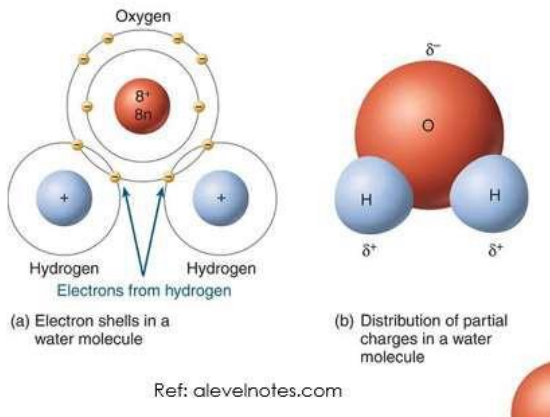
This structure is similar to that of cellulose and collagen. It is also the structure of strengthened rubber. The polymer chains found in natural rubber are very flexible and become fluid like when heated. It was discovered that when sulfur was introduced to natural rubber that the sulfur created links between the long polymer chains in the rubber and significantly improved the response to temperature. Hence the rubber used in tires is a cross-linked polymer.



The bonds between the atoms both in the polymer itself as well as the bonds in the shorter cross links have specific strengths. When a material, such as a liquid in the case of this activity, is introduced to the polymer, changes in the polymer can occur if the force of attraction between the fluid and the atoms in the cross link system is stronger than the bonds between the atoms in the cross link polymer system.

For this activity, the initial fluid introduced or added to the dry cross link polymer is water.

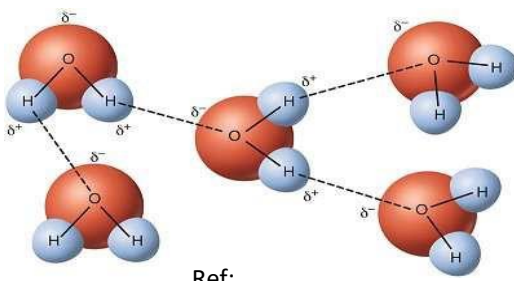
Water is a natural dipole molecule, having a region of the molecule that is negatively charged most of the time and regions that are positively charged most of the time. Since opposites attract and likes repel, this dipole nature of water creates bonds between the individual water molecules – forming what are called hydrogen bonds. Water molecules tend to be triangular in shape and the negative portion of the molecule is located around the oxygen molecule (the top point of the triangle) and the positive regions are located near the hydrogen atoms (the bottom two points of the triangle).



When water is introduced into the cross-linked polymer system – bonds will form between the charged portions of the water molecules and atoms within the cross link polymer structure. If the bond between the water molecule and the atom is stronger than the bond holding the atom within the polymer structure then bonds will be broken and that atom will be displaced from the cross link structure. Atoms have then been rearranged and the physical properties of system (polymer) have been changed. (See Power Point slides)

In this activity, different fluids can be added to the dry cross link polymer, with significantly different results. The different results are dependent on the charge distribution of the fluid molecules. Molecules which are similar to water in the sense that they are dipole or multi pole molecules and have a non-uniform charge distribution will interact with the polymer in a manner similar to the water. Other fluids, with molecules that have a more uniform charge distribution, will have less of an interaction response.

Finally, temperature can have a dramatic effect, especially with hot and cold water. Within a system of water molecules, many of the charged portions of the water molecules are bonded to other water molecules via the hydrogen bonds.



When the water is heated up, thermally induced vibrations are introduced into the water system. At a certain temperature the thermally introduced vibrations will be stronger than the hydrogen bonds between the water molecules and the hydrogen bonds will be broken. More of the water molecules will have more of the charged regions available to interact with the atoms in the polymer.

Taking the same amount of polymer in 2 petri dishes and adding the same amount of water – one hot and one cold – will result in a drastic difference in the time it takes for the polymer to expand.

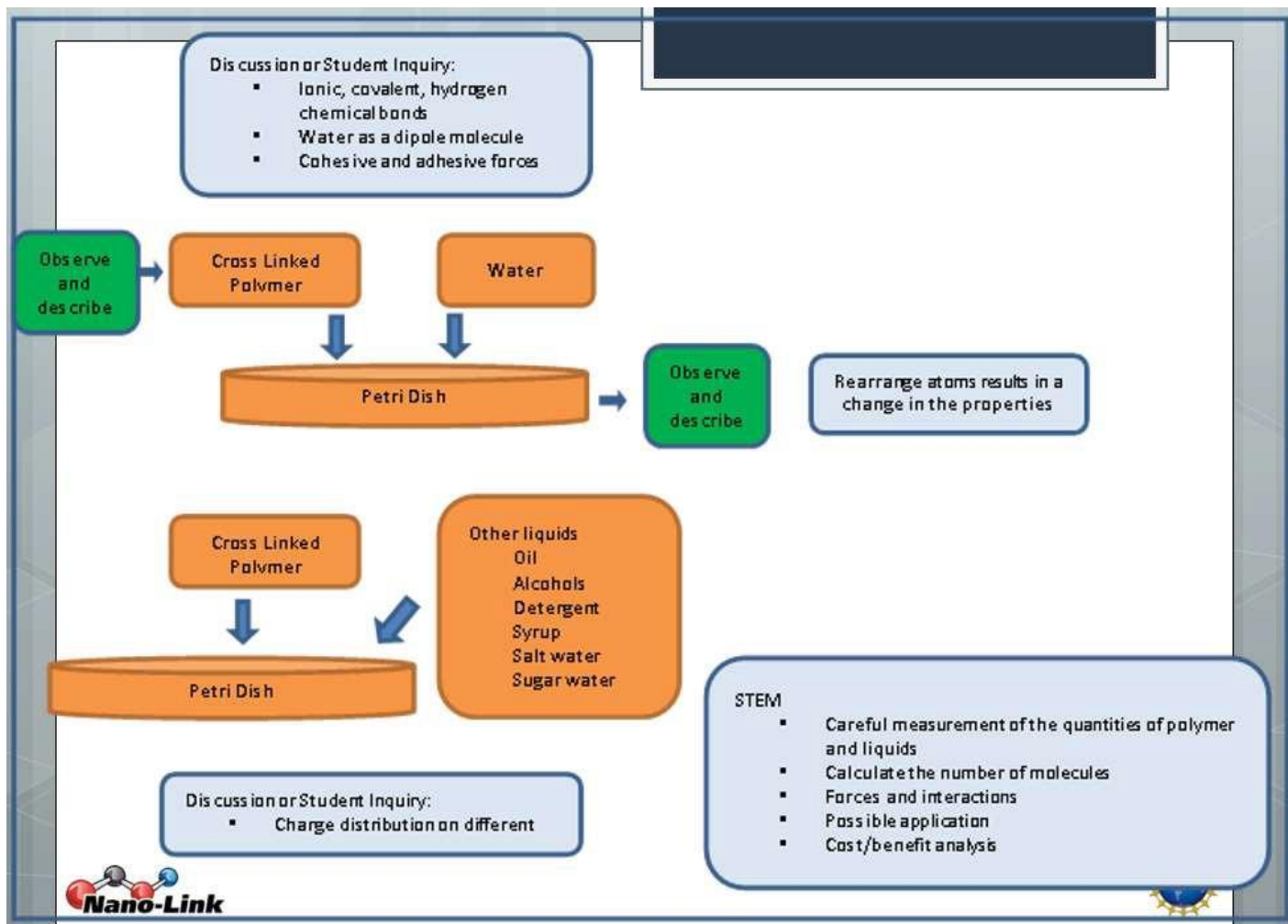
Current and Future Applications

The current applications of cross-linked polymers are widespread and diverse. Any room you are sitting in is likely to have many types of cross-linked polymers present, from the paints and varnishes on the walls to the polyester threads in your clothes to the synthetic rubber on the soles of your shoes.

Future applications of sodium polyacrylate will no doubt build on its ability to absorb large amounts of water.

Learning Activity: Cross-linked Polymers

Activity Flow Chart



Video of Activity

www.youtube.com/watch?v=bhQv57PbkQM

Cross-Linked Polymers

Background

A polymer is a material that contains many chemically bonded parts or units which themselves are bonded together to form a solid. The word polymer literally means "many parts." Polymers occur naturally in the form of starch, cellulose, and chitin (the hard part of shell fish). Synthetic polymers include all types of plastics.

In this lab you will explore the properties of a special cross-linked polymer called sodium polyacrylate. This polymer is similar to cellulose; it has a "zigzag" molecular chain structure which gives it elastic properties, while the cross-linking between the zigzag chains helps maintain a rigid structure.

Materials

- Petri dish
- Water
- Optional: Other liquids such as alcohols, detergent, oil, salt water, sugar water, hydrogen peroxide etc.
- Cross-linked polymer (sodium polyacrylate)
- Pipette

Procedure

1. Place a small amount of the polymer in a Petri dish. Feel it. Observe and describe its physical properties.
2. Using a plastic transfer pipette, add some water to the polymer.
3. Observe and describe what happens. Feel the newly formed material – How have the physical properties changed?
4. List other liquids that could be tested. Based on what happened with water, what is your hypothesis for what will happen when one of the other liquids is added to the polymer? ("I know __. If __, then I think __ because __.")
5. Make a data table or other organizational format to record the resulting physical description of liquids mixed with the polymer. It can include labeled drawings.
6. Add water observations to the table.
7. Repeat steps 1-4 for each additional liquid tested. Record results in the data table.



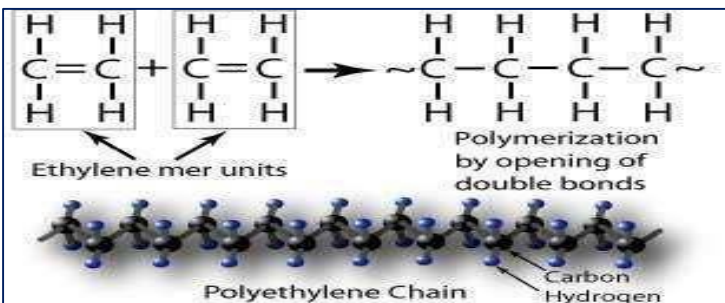
Discussion Questions

1. What are some of the forces that act on all matter?
2. Which of these are most important at the nanoscale?
3. What are polymers? Describe their molecular structure.
4. Draw or describe the molecular structure of sodium polyacrylate.
5. How does the structure of a cross-linked polymer affect its function?
6. What was observed when water was added to sodium polyacrylate?
7. Draw and label the molecular interaction of water with the polymer.
8. Summarize the evidence in your results. Compare the polymer's physical changes when mixed with different liquids.
9. What science concepts explain why the polymer changed?
10. Explain your observation of the polymer mixtures in terms of forces and interactions at the nanoscale.

Extension: How could this technology be used to design a new product or solve a problem?
What are ways it is currently being used?

Additional Background

Polymer Chains



The ability of molecules to form long chains is vital to producing polymers. Consider the material polyethylene, which is made from the monomer ethylene, C_2H_4 . Ethylene is a gas that has a two carbon atoms in the chain and each of the two carbon atoms share two valence electrons with the other. If two molecules of ethylene are brought together, one of the carbon bonds in each molecule can be broken and the two molecules can be joined with a carbon-carbon bond. After the two monomers are joined, there are still two free valence electrons at each end of the chain for joining other monomers or polymer chains. The process can continue linking more monomers and polymers together, until it is stopped by the addition of another chemical called a terminator, which fills the available bond at each end of the molecule. This is called a linear polymer..

The polymer chain is often shown in two dimensions, but it should be noted that they have a three dimensional structure. Each carbon-carbon bond is at 109° to the next and, therefore, the carbon backbone extends through space like a twisted chain of Tinker Toys. When stress is applied, these chains stretch and the elongation of polymers can be thousands of times greater than it is in crystalline structures like silica or iron.

The length of the polymer chain is very important. As the number of carbon atoms in the chain is increased beyond several hundred, the material will pass through the liquid state and become a waxy solid. When the number of carbon atoms in the chain is over 1,000, the solid material polyethylene, with its characteristics of strength, flexibility and toughness, is obtained. The change in state occurs because as the length of the molecules increases, the total binding forces between molecules also increases.

Forces at Different Scales

Over many centuries we have discovered, studied and quantified a multitude of forces or energies – this broad area of phenomena impacts the interaction of all matter. For a long time we were only able to observe the manifestation of these forces at the macro scale.

Compass needles moving under the influence of magnetic force, apples falling from trees due to gravity, and dust particles sticking to surfaces due to electrostatic force, are all examples of forces at work. As our tools (both experimental hardware and mathematical) improved, we



have been able to observe more and more interactions at smaller scales.

From a physics standpoint there are four fundamental forces: electromagnetism, gravitation, the weak force (which governs certain types of radioactive decay), and the strong force (which holds together the atomic nucleus). All of these forces are field forces as opposed to contact forces. With field forces objects do not have to be in direct contact to experience the force. From introductory physics we are also aware of forces such as friction (static and kinetic) as well as the forces that can be exerted by springs. These types of forces are contact forces.

Our discussion can also be expanded to include interactions, forces and energy that are associated with vibration, rotation, Brownian motion, and chemical bonding at both the atomic and molecular scale. A more comprehensive list of forces might include

- Gravity
- Electromagnetic force
- The strong and weak nuclear forces
- Chemical bonding forces: ionic, covalent, metallic
- The force which causes Brownian motion
- Van der Waals and London (close range) forces
- Friction
- Elastic (“spring-type”) forces
- Casimir force

These different forces and interactions will have a different priority ranking at different size scales. At the level of atoms and molecules, the most important force is electromagnetism. This force dominates the interaction between atoms as they bond with other atoms to form molecules, and is thus responsible for nearly everything we call “chemistry”. Chemical bonding will have an impact at the nanoscale. Whether two atoms may be brought and held together by covalent or ionic bonds will impact the stability, organization, and the crystal structure of a material. The same is true for molecular bonding, where the electromagnetic force gives rise to interactions that go by the names of dipole/dipole, induced dipole/induced dipole, van der Waals force, London force, and so on.

One thing that is absolutely critical in the discussion of forces and interactions at all size scales is that ALL of these forces or interactions are present ALL of the time independent of the size scale we are observing. Gravity does not “go away” at the nanoscale nor do polymer vibrations cease to occur at the macro scale. All of these interactions are occurring all of the time – the difference is in the PRIORITY which impacts our awareness of and ability to measure the force. We will find that at different size scales the ranking or priority in terms of interaction importance will change.

When we are looking at objects in the nanoscale range, we are looking at a different priority of the list of forces; for example, gravity is not a big deal at the nanoscale. But we are also asking students to look at forces that are much less familiar than the classical forces that they may have learned about in introductory science classes.



Contributors

- Deb Newberry and Billie Copley of Dakota County Technical College
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Multimedia Resources

Videos

- *Sodium polyacrylate demonstration*. Retrieved at www.youtube.com/watch?v=Vais8pL0w8U&feature=player_embedded

Articles

- American Chemistry Council. (2014). *History of Polymers and Plastics for Students*. Retrieved at <http://plastics.americanchemistry.com/Education-Resources/Hands-on-Plastics/Introduction-to-Plastics-Science-Teaching-Resources/History-of-Polymer-and-Plastics-for-Students.html>
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Alignment to the Next Generation Science Standards

Table 1 clarifies the nature of the alignments by Scientific and Engineering Practice (Practice), Disciplinary Core Idea (DCI), and Crosscutting Concept as related to a Performance Expectation.

TABLE 1. ALIGNED PRACTICES, DISCIPLINARY CORE IDEAS, AND CROSSCUTTING CONCEPTS		
PRACTICE	DCI	CROSSCUTTING CONCEPT
<p><i>HS. Obtaining, evaluating, and communicating information:</i> Communicate scientific and technical information (e.g. about the process of development and the design and performance of a proposed process or system) in multiple formats</p> <p><i>Partial alignment in student materials</i></p>	<p><i>HS-PS2.B: Types of interactions:</i> Attraction and repulsion between electric charges at the atomic scale explain the structure, properties, and transformations of matter, as well as the contact forces between material objects.</p> <p><i>Strong in student materials</i></p>	<p><i>HS. Structure and function:</i> Investigating or designing new systems or structures requires a detailed examination of the properties of different materials, the structures of different components, and connections of components to reveal its function and/or solve a problem.</p> <p><i>Partial alignment in student materials</i></p>

Alignment to Common Core State Standards: English Language Arts/Literacy & Mathematics

Alignments in Table 2 were made to the Anchor Standards, unless a more specific version of the standard was a closer fit to the skills in the module.

TABLE 2. ALIGNED COMMON CORE STANDARDS FOR ENGLISH LANGUAGE ARTS & LITERACY
<p>CCR.L.6: Acquire and use accurately a range of general academic and domain-specific words and phrases sufficient for reading, writing, speaking, and listening at the college and career readiness level; demonstrate independence in gathering vocabulary knowledge when encountering an unknown term important to comprehension or expression.</p> <p><i>Partial in teacher and student materials</i></p>
<p>RST.11–12.3: Follow precisely a complex multistep procedure when carrying out experiments, taking measurements, or performing technical tasks; analyze the specific results based on explanations in the text.</p> <p><i>Partial in student materials</i></p>

No alignments to mathematics were found.

