



# YALE NATIONAL INITIATIVE

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## Materials for the Future

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### Overview

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This unit is designed for 10<sup>th</sup> grade gifted students who are taking their first Chemistry class. I teach at an urban school which offers separate classes for identified gifted students. These students have the option of taking a course at the gifted level; students who find math and science difficult often opt to take it at the regular level. The teachers of these classes have flexibility about curriculum and determine how to offer enrichment. This unit will be a culmination of the work covered throughout the year and is designed to allow students to be both creative and apply the principles of bonding, intermolecular forces, states of matter and solubility. At the end of this unit, the students will be asked to design a "new" material that will serve a purpose that they have chosen. They will determine the properties that this material will need to serve the function the students have in mind. In light of the needed properties, the students will then determine appropriate molecular sub-units and structure. Needless to say, they will be expected to justify their designs.

### Rationale

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In High School chemistry, we spend much time on the structure of the atom, the arrangement of electrons around the nucleus and the position of the atom on the periodic table. We do indeed look at bonding and maybe get into the shape of a molecule and how that might influence the properties of a substance. I would argue that a typical beginning high school chemistry student will have the impression that chemistry is all about individual atoms and less about the molecules themselves and the arrangement of said molecules. Phillip Ball in the opening chapter of "Stories of the Invisible: A guided Tour of Molecules" states that "molecules are the smallest units of meaning in chemistry."<sup>1</sup> He makes the analogy that atoms are like letters and that molecules are like words, where longer words are more subtle and the order of the letters (atoms) are important. He suggests that we can invent new molecules (words) that can replace whole sentences and tell new stories.<sup>1</sup> A molecule is the fundamental piece of matter. Certainly by changing some atoms in large molecules we can subtly change the properties of that substance, and so, knowledge of the atomic structure is important but more secondary.

Roald Hoffmann suggests that chemistry is the science of molecules and their transformations. Some molecules are just waiting to be discovered, whereas many more molecules are waiting to be made in the laboratory. Nearly ten million new compounds have been made by man. <sup>2</sup> They are not found naturally. Primo Levi in "The Monkey Wrench" likens a chemist to an engineer who just builds and dismantles very tiny constructions. <sup>3</sup> Yaron, Leinhardt and Karabinos in their paper identifying critical resources for thinking in Chemistry, suggest that chemists analyze matter to determine its composition, they synthesize and design new combinations for particular purposes and that they explain actions and reactions of molecules at the atomic and macroscopic level. This movement from levels of scale makes chemistry a difficult topic to master. Their analysis of recent chemistry findings and Nobel prizes showed an emphasis on synthesizing or design activities, analytic activities and explanation activities. <sup>4</sup> The activity of designing and synthesizing refers to the construction of new materials for desired properties. We can now make synthetic skin, blood and bone. We can make an information highway from glass. We can make materials that repair themselves, that swell and flex like muscles, that repel any ink or paint, that capture the energy of the sun. <sup>1</sup> We are now in a position to design a material for a specific application.

This unit is designed for students to make observations at the macro-level and then link molecular structure at the nano-level to the properties. Most of Chemistry 1 involves very small molecules and so the basic properties of these individual molecules will be used as building units for bigger molecules. It is not unreasonable to expect Chemistry 1 students to link small molecules with weak intermolecular forces to gaseous behavior, long stringy molecules to more fluid behavior and small polar molecules to strong crystalline structures. Some consideration will be given to assembly and the relationship to both overall structure and the nature of sub units. Analogies will be made with the macro-level. For example the strong fibers of the body such as skin and nails are made from keratin which consists of proteins twisted together like a piece of twine or strong rope. Looking at various ropes/string and what makes them strong will help students understand the assembly process at the molecular level. If students understand that bonds are strong attraction between atoms and that intermolecular forces are also attractive forces that are just weaker, then they should be able to understand at a simplified level what is necessary to bring about some of the desired properties.

Again Roald Hoffmann suggests that the synthesis of molecules puts chemistry very close to the arts and represents a highly creative activity. <sup>2</sup> Since I teach gifted students, I want to show them the opportunities to be creative in the scientific world. They always seem to relish these opportunities to design something new and should be encouraged to develop this type of thinking. Whenever a teacher is able to show how what has been learned can be applied to the 'real world', then the learning seems to be both deeper and richer. So with this unit, I would like students to think of a material that they think would be useful or even fanciful, and then determine the required properties of this material at the macro-level and then translate these properties to molecular structural requirements. As mentioned above this may only entail designing the necessary sub-units without actually designing an assembly process.

The design of the material and sub units would be the culminating activity for the unit.

The first activity of the year for my Chemistry 1 class is an examination of several substances that are similar and the students are asked to distinguish between them. They compare three metals- one is malleable, one has a very low density and one is stiff. They compare three liquids- one has an odor, one is more viscous. Three plastics are compared and again they vary in ability to be stretched, flexibility and transparency. Finally the interaction of water with three white powders is studied. One dissolves in water, one repels water and one

absorbs the water. So I start the year with the idea that chemistry is about why different substances have different properties. An early unit in my Chemistry 1 course is an exploration of the properties of solids, liquids and gases. The students then relate these properties to the arrangement of the particles of matter. At this point, we refer to particles and really do not distinguish between atoms or molecules but rather establish the particulate nature of matter. At this early stage, students are able to recognize that if water is a liquid at room temperature and that carbon dioxide is a gas, then there must be a stronger attraction between the water particles than the carbon dioxide particles. The subsequent units that follow include atomic structure, basic bonding, nomenclature, moles, stoichiometry, etc. The fourth quarter begins with a second unit on bonding when Lewis structures, VSEPR and intermolecular forces are discussed. From there, we study the solution process and look at the impact polarity has on solubility. I would see this unit coming after the solubility unit, almost at the end of the year and tying together the opening units. Now, the students have the tools to see the connections.

The unit would begin by looking at plastics and their varying properties and relating these differences to molecular structure. Since nanotechnology is very hot now and some exciting work is being done at a local college, the University of Pittsburgh, nanotubes and some other nanomolecules will be studied. These series of examples will give students an opportunity to see the connection between the properties and molecular structure so that they can then give free rein to their imaginations.

While we will not be focusing on actual production methods for these molecules, I would like to discuss the responsibility of making products that are not detrimental to the environment. While plastics are materials that we use everyday in large quantities, they have filled our landfills and even broken down to give toxic substances. I would like

students to realize, that rather than looking at recycling as a tool at the end of product use, material design should look at eliminating waste and having end products be biodegradable. The principles of green chemistry will also be part of the unit.

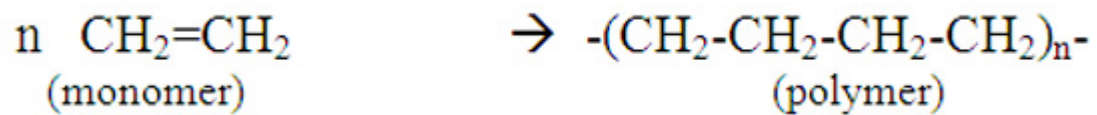
## Background

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### Polymers

Polymers are very long chained molecules made up of repeating units called monomers. There may be up to 1,000 units for one polymer strand. Recognition that polymeric macromolecules make up many important natural materials was followed by the creation of synthetic analogs having a variety of properties. Applications of these materials as fibers, flexible films, adhesives, resistant paints and tough light solids are part of our everyday lives. <sup>5</sup> I will study the structure of various polymers and relate the variation in properties to the differences in structure.

A chemical polymer-forming reaction will cause one molecule to add on to another and so continue, until a very long strand has formed. Ethylene (ethene) is the monomer for the corresponding polymer called high density polyethylene (HDPE).



Unlike simpler pure compounds, most polymers are not composed of identical molecules. The HDPE molecule for example are all long carbon chains, but may vary by thousands of monomer units with a range of molecular masses from  $2 \times 10^5$  to  $3 \times 10^6$ .<sup>5</sup> Some other addition polymers are our most common plastics (Table 1).

Table 1.<sup>5</sup>

name	formula	monomer	properties	uses
Polyethylene Low density (LDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	Soft, waxy solid	Film wrap, plastic bags
Polyethylene High density (HDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	Rigid, translucent solid	Electrical insulation, bottles, toys
Polypropylene (PP) different grades	$-(CH_2-CH(CH_3))_n-$	propylene $CH_2=CH(CH_3)$	Atactic: soft, elastic solid isotactic: hard, strong solid	Similar to LDPE Carpet, upholstery
Poly(vinyl chloride) PVC	$-(CH_2-CHCl)_n-$	vinyl chloride $CH_2=CHCl$	Strong, rigid solid	Pipes, siding, flooring
Poly(vinylidene chloride) (Saran A)	$-(CH_2-CCl_2)_n-$	vinylidene chloride $CH_2=CCl_2$	Dense, high melting solid	Seat covers, films
Polystyrene (PS)	$-(CH_2-CH(C_6H_5))_n-$	styrene $CH_2=CHC_6H_5$	Hard, rigid, clear, solid soluble in organic solvents	Toys, cabinets, packaging (foamed)
Polyacrylonitrile (PAN, orlon, acrilan)	$-(CH_2-CHCN)_n-$	acrylonitrile $CH_2=CHCN$	High melting solid soluble in organic solvents	Rugs, blankets, clothing
Polytetrafluoroethylene (PFTE, Teflon)	$-(CF_2-CF_2)_n-$	tetrafluoroethylene $CF_2=CF_2$	Resistant, smooth solid	Non-stick surfaces, electrical insulation
Poly(methylacrylate) (PMMA, Lucite, plexiglass)	$-(CH_2-CHOCOCH_3)_n-$	Methyl methacrylate $CH_2=C(CH_3)CO_2CH_3$	Hard, transparent solid	Lighting covers, signs, skylights
Poly(vinyl acetate (PVAc)	$-(CH_2-CHOCOCH_3)_n-$	vinyl acetate $CH_2=CHOCOCH_3$	Soft, sticky solid	Latex paints, adhesives
Cis-polyisoprene Natural rubber	$-(CH_2-CH=C(CH_3)-CH_2)_n-$	Isoprene $CH_2=CH-C(CH_3)=CH_2$	Soft, sticky solid	Requires vulcanization for practical use
Polychloroprene(cis + trans) Neoprene	$-(CH_2-CH=CCl-CH_2)_n-$	Chloroprene $CH_2=CH-CCl=CH_2$	Tough, rubbery solid	Synthetic rubber, oil resistant

### Properties of Macromolecules

A comparison of properties of polyethylene (both LDPE & HDPE) shows that even though they are comprised of the same monomer the properties are not the same. HDPE is a rigid translucent solid which softens on heating above 100 °C and can be fashioned into various forms including films. It is not easily stretched and deformed as is LDPE. Both HDPE and LDPE are insoluble in water. LDPE is a soft translucent solid which deforms badly above 75 °C. Films made from LDPE stretch easily and are commonly used for wrapping. To account for these differences, the nature of the aggregate macromolecular structure, or morphology, of each substance needs to be considered. Polymer molecules are very large and so they tend to pack together in a non-uniform fashion, with ordered crystalline regions mixed together in with disordered or amorphous

domains. In some cases, the entire solid may be amorphous, composed entirely of tangled macromolecular chains. Crystallinity occurs when linear polymer chains are structurally oriented in a uniform three dimensional matrix. Increased crystallinity or order is associated with an increase in rigidity, tensile strength and opacity (due to light scattering). Amorphous polymers are usually less rigid, weaker and more easily deformed. They are often transparent. Three factors that influence the degree of crystallinity are: Chain length, chain branching, and inter-chain bonding. <sup>5</sup>

The importance of the first two factors can explain the differences in properties between LPE and HDPE. HDPE is made up of very long unbranched hydrocarbon chains. These pack together easily in crystalline domains that alternate with amorphous segments, and the resulting material, while relatively strong and stiff, retains a degree of flexibility. In contrast, LDPE is composed of smaller and more highly branched chains which will not easily adopt crystalline structures. This material is, therefore, softer, weaker and less dense and more easily deformed than HDPE. As a rule, mechanical properties such as ductility, tensile strength, and hardness rise and eventually level off with increasing chain length. <sup>5</sup>

Inter-chain bonding is what vulcanization does to rubber to stiffen it and make it a useful material. Natural rubber is an amorphous polymer and so is soft and liable to lose all usefulness at high temperatures. The chains of rubber molecules become cross-linked by adding sulfur to the chains and sulfur to sulfur bonds hold the polymer chains together. The degree of crosslinking determines the hardness and strength. At 2-3% crosslinking, a useful soft rubber forms that no longer suffers from the stickiness and brittleness problems on heating and cooling. At 25-35 % crosslinking, a rigid hard rubber product is formed. <sup>6</sup>

On heating and cooling most polymers undergo thermal transitions that are related to their morphology. These are defined as  $T_m$  the melt transition which is the temperature at which crystalline domains lose their structure or melt.  $T_m$  is an indication of the degree of crystallinity.  $T_g$  is the temperature below which amorphous domains lose their structural mobility of the polymer chains and become rigid glasses. It is often interpreted as the temperature above which significant portions of polymer chains are able to slide past each other. The introduction of relatively large and stiff substituents (such as benzene rings) will interfere with this chain movement and so lead to a higher  $T_g$  value. Polystyrene has benzene attached to the ethylene monomer and has a higher  $T_g$  value than those of other polyethylenes. Elastomers are amorphous polymers that have the ability to stretch and then return to their original shape above  $T_g$ . This property is important in applications such as gaskets and O-rings, so the development of synthetic elastomers that can function under harsh or demanding conditions remains a practical goal. At temperatures below  $T_g$ , elastomers become rigid glassy solids and lose all elasticity. A tragic example of this caused the space shuttle Challenger accident. The heat- and chemical-resistant O-rings used to seal sections of the solid booster rockets had an unfortunately high  $T_g$  value near  $0^\circ\text{C}$ . The temperature was low that morning and below the  $T_g$  allowing hot rocket gases to escape the seals. Thermoplastic polymers may be shaped or pressed into molds above  $T_g$ . Even after cooling, the hardened polymer will lose its shape if once again heated above  $T_g$ . Whereas, thermosets are polymers which once formed cannot be reshaped by heating. <sup>5</sup>

### **Another level of complexity**

Symmetrical monomers such as ethylene and tetrafluoroethylene can join together in only one way. Monosubstituted monomers can join together in two organized ways or one random manner. The orientation of the substituted group (Z) is what varies and it can be above or below the plane defined by the carbon chain.

One version has Z on one side of the plane – called isotactic. The other symmetric version has Z alternating from one side to the other of the chain in a regular manner – syndiotactic. The other option is to have Z randomly arranged about the chain – atactic. <sup>6</sup> Many common and useful polymers, such as polystyrene, polyacrylonitrile, polyvinyl chloride, and propylene are atactic as normally prepared, but catalysts may control the process and produce just one of any three forms. The properties of a given polymer will vary considerably with its tacticity. Atactic polypropylene is useless as a solid construction material and is used mainly as an adhesive. In contrast, isotactic polypropylene molecules will line up in straight chains and so have a much higher melting point and better crystalline properties. <sup>5</sup>

How can different structures result for the same monomers? The formation of addition polymers must be initiated by some kind of radical - an atom or molecule lacking a complete electron shell and looking to form a bond by sharing an electron with another atom. Once the reaction starts and proceeds for some time, the reaction chamber will become crowded with many different free radicals which may combine with other monomers or with another free radical. This combination of two radical chains stops the continued building of a chain. This chain though may combine with another radical fragment and so branched molecules form. If the reactions proceed unchecked, a mixture of branch lengths and branching will occur. Catalysts can be used to control the level of branching and, hence, the properties. <sup>5</sup>

The synthesis of macromolecules composed of more than one monomeric repeating unit has been explored as a means of fine tuning or increasing the properties of the resulting material. These are called copolymers. The molecules form blocks and different blocks are covalently bonded together. These can be combined in symmetric patterns, randomly or in blocks depending on the properties sought. One of the most commercially important block copolymer consists of blocks of polybutadiene sandwiched between two blocks of polystyrene. The polystyrene units aggregate into clusters linked together via polybutadiene chains. The clusters are stiff, like polystyrene itself; but the polybutadiene chains are flexible, and the material behaves like a rubbery elastomer. Unlike rubber, this polymer can be molded and is used to make the soles of sneakers. <sup>6</sup>

Nylon is an example of a condensation polymer where an ester linkage joins the monomers. With these polymers, there is more opportunity for hydrogen bonding intermolecular attractions and, hence, tougher materials. Polyester, spandex and Kevlar are other examples of condensation polymers. <sup>7</sup>

### **Natural versus Synthetic Polymers**

The reactions to form synthetic polymers are difficult to control and often do not lead to the consistent structures needed to provide given properties. Natural polymers on the other hand are self-assembled, can be coded by DNA, and have a complexity of structure that the synthetic processes can never achieve. <sup>1</sup>

The body creates a variety of different materials: skin which is elastic yet resistant to penetration by water and other fluids, nails which are much tougher and more brittle, and hair which is extremely difficult to break. The basis of these is proteins. Proteins are condensation polymers using a combination of twenty-two possible amino acids, where the acids used and the order of combination being determined by DNA. When the type of amino acid is varied and the order changed, then a very different protein is formed with a very different shape and properties. The proteins can be woven into strong fibers, cross-linked or entangled; they form the stiff matrix of horn and claw or elastic sheets. Their construction is encoded in our genes. <sup>1</sup>

The most abundant structural protein in the human body, comprising about one quarter of our total protein mass is collagen. This is a relatively simple protein whose chainlike molecules contain mainly glycine and

proline. Collagen shows the major difference between natural protein-based structural materials compared with most synthetic polymer-based plastics. Both are composed of long chains of molecules but, in the natural materials, the chains gather together in complex arrangements, forming thicker groups like ropes woven together, like string woven from thread. Each collagen molecular chain crumples up into a helix. Three of these twist around each other to form a rope-like microfibril. These microfibrils aggregate together in various ways. For example, they can gather together in a staggered arrangement to form thick strands called banded fibrils. These constitute the connective tissue between cells. They hold our flesh together. In the eye's cornea, the fibrils are packed close together in a very orderly pattern. These fibrils are too small to scatter light and so the material is virtually transparent. Collagen has a fibrous structure at the molecular and microscopic level but the body organizes them into other shapes depending on the need. <sup>1</sup>

A spider silk is a fiber stronger than steel. This silk can be spun into almost invisible threads which can withstand the impact of flying insects. These impressive properties are a consequence of the way its protein chains are organized. In silk, the basic organized structural element is not a coil but a sheet. Neighboring chains sit side by side in aligned ranks and each chain is linked to those on either side via hydrogen bonding, which zip the chains together in beta sheets. The orderly, relatively rigid sheets can stack on top of one another to create tiny, three-dimensional protein crystallites. These crystallites are microscopic and become dispersed in the tangled, flexible protein matrix and form a copolymer. So, the silk has both strength and flexibility. <sup>1</sup>

Silk fibers are insoluble in water- otherwise they would dissolve in rain or dew. The spider spins the threads from a solution of protein molecules in water, thereby achieving the remarkable feat of changing a soluble substance into an insoluble one. This change in solubility is a result of a change in the way that the chains are organized. The spider manufactures silk protein in its silk gland, at which point it is still soluble. This solution passes from the gland towards the spinneret. During this stage the silk solution loses water and becomes more concentrated. The proteins rather than being hydrogen bonded to the water now become cross-linked to each other. By the time the silk leaves the spinneret most of the water has been squeezed out and the proteins have formed beta sheets. The molecules in these crystalline regions are so closely packed together that it is difficult for the water molecules to penetrate, and so, the silk fibers are essentially solid and insoluble. <sup>6</sup>

For the spider, its DNA contains the blueprint for making the polymer silk. Biotechnology is a means to use nature's controlled building of the molecule into sophisticated structures. To produce a fiber stronger than steel on a larger scale than a spider's web, the spider gene has been inserted into goats and the hope is to duplicate the extrusion process of the spinneret to make a silk from the goat's milk. The responsible gene can also be spliced into the DNA of host bacteria - *Escherichia coli* - and then the bacteria proceed to translate the synthetic genes into polypeptides. At the moment, these processes are too expensive to replace the commercial processes of the giant plastics industry. <sup>1</sup>

Besides control and enhanced structure, natural polymers are biodegradable and do not leave their imprint on the environment. Plastics on the other hand have filled our landfills and even created toxic waste. Most of us separate out our plastics on trash day and assume that they will be recycled. Plastic recycling mainly comprises re-use but normally as lower grade plastic. Much recycled plastic is used to make shopping bags and at some point we should not need as many. In the life of a plastic, there becomes a time where the recycled plastic no longer has a use and so once again will need to be added to a landfill or burned. We are slowly learning that when we design new materials that we need to look at what happens to them after their useful lifetime. Re-use will only go so far and better planning would have the molecules broken down to safely



enter the environment. See appendix 2 for the principles of green Chemistry.

## Carbon and Nanotubes

Technology is such that we can build molecules atom by atom and isolate these molecules or very few clusters of molecules. It seems appropriate to look at some examples of this, as this is the new materials science. Elemental carbon is an example of how structure explains properties. Diamond is one of the hardest materials known. This is due to all carbon atoms being bonded to four other carbons and forming a network with a tetrahedral shape around each carbon. Since each atom is bonded in this highly symmetrical shaped pattern, the resulting structure is very strong. In graphite, the carbon atoms, though, are arranged in sheets of co-joined hexagons where each carbon atom is bonded to three other carbons – two single bonds and one double bond. These sheets then experience weak London intermolecular forces between them. The layers can easily slide past one another and so graphite flakes easily. Buckyballs or Fullerenes are nanometer sized and one of these, C<sub>60</sub>, contains sixty carbon atoms arranged like the vertices for the sections of a soccer ball.<sup>8</sup>

Graphene is a single layer of graphite that displays incredible properties of electron conductivity, strength and stiffness. Three million sheets of graphene are equivalent to 1mm. Graphene's electrons move one hundred to one thousand times faster than those of silicon. Therefore, there is potential to replace silicon and provide even smaller computer chips with even faster computing.<sup>9</sup> The ability to conduct electrons means that it would be very useful for applications where quick energy surges are needed, such as in electric cars or stabilizing energy grids. Graphene has a breaking strength two hundred times greater than that of steel. A sheet of graphene, as thick as a piece of cellophane, would support the weight of a car. If paper was as stiff as graphene, you could hold a one hundred yard long sheet of it at one end without it breaking or bending.<sup>10</sup> Small flakes of graphene can be mixed with other materials to form composite materials which can be used to build stronger and lighter products. Sheets of graphene can be folded in several ways to form tubes which are used in many applications. Different folds give different properties and the challenge of nano-science is finding a way to control the type of tube produced. Nanotubes are used in flat screen televisions, high electrical conductivity applications, storing hydrogen for fuel cells, artificial muscles, sensors, transistors and the delivery of drugs. Nanotubes have been mixed with nylon to form very small components. The carbon nanotubes have excellent thermal conductivity properties that cause the material to cool slowly and evenly, allowing for better molding characteristics of the nano-composite. The slowing of the process allows the composite molecules to fill the tiny micron-sized mold. As of now, graphene and nanotubes cannot be produced either cheaply or on a large scale, but the potential is there.<sup>11</sup>

Professor Alexander Star at the University of Pittsburgh is conducting research using nanotubes in novel applications such as the production of chemical and biological sensors, energy conversion devices (fuel cells) and nanocapsules for drug delivery. As one-dimensional structures electrons are confined to the exterior of the nanotube, making them extremely sensitive to perturbations in the local environment. Carbon nanotubes decorated with metal nanoparticles exhibit unique selectivity for absorbing gas molecules, with the potential for detecting nitrogen gas and warning asthma patients before an attack or detecting oxygen levels in mines. He has also developed nitrogen-doped nanocups which show good catalytic properties for the Oxygen Reduction Reaction, which makes them attractive substitutes for metals such as Pt or Ru in fuel cell cathodes. Dr Star's group has been able to form nanocapsules with the potential to be used as incredibly specific drug delivery systems. Currently, it is known that carbon nanotubes can cause negative effects such as inflammation, oxidative stress and cell death. His group has shown a natural biodegradation of single-walled carbon nanotubes through enzymatic catalysis. I have seen a presentation by Dr. Star and he is available to

give a talk to my class about his interesting research. <sup>12</sup>

## **Molecules Used in Demonstrations/Labs**

Sodium polyacrylate can absorb almost eight hundred times its mass in water. It is used in diapers and to regulate water around plants in agriculture. Sodium polyacrylate is obtained by the co-polymerization of sodium acrylate and acrylic acid, in the presence of a cross-linking agent. The two monomers form a random copolymer, with sodium acrylate and acrylic acid repeating units randomly distributed within a typical polymer molecule. The cross-linking agent is a reactive molecule that can 'insert' itself into two or more growing polymer chains as the polymerization reaction continues. This serves to tie together several polymer chains into a large, three dimensional, polymer network. Extensive cross-linking makes the polymer insoluble in water and creates a membrane-like barrier on the surface of the polymer that allows water to flow inside. The presence of the  $\text{-CO}_2^-$  groups in the polymer structure means that there is also a high concentration of sodium ions within the polymer network. This creates a concentration imbalance or gradient when the polymer is added to water. Osmosis occurs and the water molecules diffuse across the membrane to equilibrate the sodium ion concentration inside and outside the polymer. Once inside the polymer network, the water molecules form hydrogen bonds with the ionic  $\text{-CO}_2^-$  groups, creating a thick viscous, translucent gel. The amount of water that can be absorbed by the polymer depends on the ratio of  $\text{-CO}_2^-$  and  $\text{-CO}_2\text{H}$ , the amount of or extent of cross-linking, and the concentration of sodium ions. When sodium ions are added to this gel, then the flow of water is reversed out of the polymer network and a slurry forms. <sup>7</sup>

PolySnow™ is a highly cross-linked formulation of sodium polyacrylate. The extra cross-linking means that PolySnow absorbs less water than sodium polyacrylate. PolySnow also does not form a typical gel when it absorbs water. The powder absorbs water to form white particles that look like snow. <sup>7</sup>

## **Sodium alginate**

Sodium alginate is a natural polymer obtained from kelp and seaweed. The polymer is a typical component of the cell wall in brown algae, comprising up to 40% of the dry weight of large species such as giant kelp. Worldwide, about 16 million pounds of sodium alginate are produced per year for use in the food, textile, medical, and pharmaceutical companies. <sup>7</sup>

Sodium alginate is a polysaccharide composed of thousands of oxidized sugar units joined together to form an ionic polymer. The repeating units are six-membered rings containing negatively charged  $\text{-CO}_2^-$  groups. An oxygen atom connects each ring. The presence of  $\text{-CO}_2^-$  side chains, as well as numerous  $\text{-OH}$  groups, make this polymer hydrophilic or 'water loving.' The polymer readily absorbs water and will swell up with contact with water to form a gel. The resulting gel is thick, viscous, and smooth. Sodium alginate is used as a thickening agent in many processed foods including ice-cream, yogurt, and artificial food snacks. The non-toxic food additive absorbs water, helps to emulsify oil and water components, and gives foods a smooth texture. <sup>7</sup> Replacing the sodium ions in sodium alginate with calcium ions gives an insoluble product, calcium alginate. Encapsulation of liquids or solids within a membrane is a convenient method to protect materials or allow their gradual release. Encapsulated or microencapsulated materials, such as pharmaceuticals, insecticides, toxic wastes, foods, inks, catalysts and bioartificial organs are common. Controlled pore size in or degradation of the membranes can result in timed release from minutes to months. The mild gelation of alginate solutions in the presence of calcium ions has allowed the entrapment of DNA, proteins, and cells in

cross-linked matrices without loss of biological activity. <sup>13</sup>

## Objectives

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The major objective for this unit is that students will be able to relate the structure and arrangement of the molecules to the properties of the material. Rather than looking at the actual details of each molecule, the primary focus will be on the size of the molecules, how they align, the forces holding them together, level of branching, level of cross-linking, and hydrophobic and hydrophilic centers. Another objective is that students will appreciate that the arrangement of the molecules in natural materials is more complex and has a greater hierarchy of arrangement. The production of these natural materials is also more precisely orchestrated, whereas, the production of synthetic products chemically is very difficult to control. In order to complete the final activity, students will need to be able to define the properties that might be used to describe a material and be able to describe how that property might be measured. Students will be able to describe the four different arrangements of elemental carbon and the properties associated with these forms. Size matters, so students should be able to create a relative scale to compare the size of an atom, a small molecule, a nanotube, a polymer and a protein. Finally, students should be able to analyze the material properties needed for a material to serve a specific purpose.

## Strategies and Activities

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Since this is a finale to my course, I will expect students to tie together much of what they have learned this year. Throughout the year, I use MACRO, NANO and SYMBOLIC as a means of looking at chemical principles from several angles. The main idea is that students connect what they can see with the atomic/molecular arrangement. The nano or atomic level should represent what can be seen (macro level). Finally, in the symbolic section students may draw a graph or give a chemical equation or other conventions used to represent processes. The students will be familiar with this system and I would like them to apply the Macro/Nano part when they link properties with structural arrangement. Since polymer chemistry is complex, much of the time I will have students matching pictures of structural arrangements with properties or sketching possible arrangements. They will not be giving a lot of detail about what is doing the crosslinking but using a more general approach to decide if there is crosslinking, branching, alignment, winding, etc.

Activity 1: I will start the unit with a demonstration which shows the absorption of water by sodium polyacrylate, the reaction of water to PolySnow™, the reaction of water to Magic Sand, and the formation of nylon. These demonstrations are all explained in Flinn Scientific LabTopic book on polymers. These demonstrations will serve to introduce the topic by discussing materials and the purposes that they serve. Sodium polyacrylate is used in diapers and to provide controlled water release to plants. Magic Sand, sand coated with a hydrophobic material, was designed to clean up oil spills. Nylon, we use everyday to provide strong but flexible fibers. The challenge of designing a cutting-edge material will be presented to the students, so that they will be thinking about their project and cueing into the topics that will be important.

Activity 2: After a basic description of a polymer and some possibilities of structure, the students will conduct a series of investigations of various plastics and their properties. The lab will be modeled on the "Structure and Properties of Polymers" found in the Flinn Polymer book (there will be some modifications, some of which may be described in other sections of the book). This is an activity stations lab, where students move from station to station.

Station 1: They will take a hardened glue strip, made from Elmers glue that was left out for several days, and observe how the shape of the stick can be changed when it is immersed in warm water. This new shape can be retained by placing it in cold water. The glue strip is an example of an amorphous polymer. The temperature at which a polystyrene fork loses its shape will also be found.

Station 2: Compare what happens when polystyrene and polyethylene are exposed to polarized light. If the two filters are placed at right angles to each other, the polymer that is amorphous will appear dark while any semi-crystalline areas will appear as brightly colored areas. Students will observe the order within the CD case and the initial lack of order in a polystyrene baggie before it is stretched. The stretching will cause the chains to become straighter and some light or order will be observed.

Station 3: Students will compare bags made from LDPE (zip-type bag) and HDPE (grocery bags). They will take a pencil and insert it through a zip-bag partially filled with water and observe that there is no leakage. The pencil pushes the molecules together, and forms a temporary seal. Strips, cut lengthwise and widthwise, and compared in terms of stretch ability. The material will stretch more, in the direction that the molecules are lined up. Students will crack a polystyrene cup and notice how it cracks.

Station 4: Students will find the approximate density of HDPE, polystyrene, and PVC by adding pellets to solutions of water ( $d=1.0$  g/mL); 10% NaCl solution ( $d=1.06$  g/mL), 35% ethyl alcohol solution ( $d=0.94$  g/mL), corn oil ( $d=0.91$  g/mL), glycerin ( $d=1.25$  g/mL). The float and sink method will be used to give density ranges.

Station 5: Add weights to a rubber band and measure strain versus the stress.

Students will be asked to record their observations and then try to relate some of the properties to molecular arrangements. Small groups will try to come to agreement and develop a potential picture of what these materials look like at the nano scale, so that they can present their pictures. As groups present their conclusions, they will explain how they believe their pictures explain the properties observed. Other groups can challenge their assumptions. There may be some considerations that the groups have not raised and the teacher can challenge them with some other depictions. This whole class discussion will be followed by the teacher presenting some of the actual molecular arrangements of common plastics and comparing the student pictures and discussing the similarities and differences. The difficulty of getting a material where all the molecules are the same will be addressed by looking at the chain termination process and atactic and isotactic possibilities, so that students will understand the difficulty in controlling the production of these polymers. Plastics are hydrophobic, a property that is important for their many applications. The polymer, sodium polyacrylate, which was used in the opening demonstrations, will be further explained as described in the background. The chemical reaction of nylon will be used to explain a condensation polymer. Activity 3: Many students do not really know what we mean by a property and there generally is not a common understanding for the meaning of what we might mean by a property such as "strength". There are many interpretations for this and students need to determine how you might measure a particular property. As an example to challenge their thinking, snap a piece of chalk and then ask a student to stand on a board that is supported by four pieces of chalk. Ask students to then define what "strong" means. As a homework assignment, students will be given a list of properties such as, strength, flexibility, stretchability, permeability,

wearability, adhesion, rigidity, toughness, and they will provide a working definition for each property and decide how you could measure this property. Answers will be discussed until the class reaches a consensus. During this class, students will also be provided a list of properties and asked to match these with possible molecular arrangements.

Activity 4: Students will read Primo Levi's story "The Spider's Secret" for homework and the following night read the Scientific American article "Spider Webs and Silk" by Vollrath. In class, we will discuss the advantages of synthetic polymers versus natural polymers: the consistency of production, the greater complexity, and the environmental impact. The students will be shown the peptide linkage and we will renew their understanding of proteins from biology. In particular, we will discuss why proteins might form helices or pleat. Then as a class activity, students will read a description of a natural polymer such as collagen, keratin, spider silk and try to represent the arrangement using everyday items such as strings, ropes, Slinky's and LEGOS. They will then present these models to the class.

Activity 5: Watching the DVD "Making Stuff Stronger" will tie together many of the concepts presented. The concept of strength is explored. Some materials featured are spider silk, steel, Kevlar and bulletproof vests, nanotubes, composites, and using biotechnology to grow materials. The animations of molecular arrangements are good and the demonstrations of the strength and toughness are very impressive. In the course of discussing very strong materials, the program talks about nanotubes and this is an excellent segue into the remainder of the unit.

Activity 6: Nano molecules are often used to encapsulate drugs so that they can be delivered to the correct site. We cannot see molecules at the nano level but, to demonstrate this concept, sodium alginate containing food coloring is added drop wise to a calcium chloride solution. The periphery of the droplets is immediately cross-linked with  $\text{Ca}^{2+}$  ions to form spherical capsules. The dye will slowly leak out within a few minutes. The diffusion of the color demonstrates controlled release. This demonstration is described in the article cited in the bibliography. (Journal of Chem Ed. Vol. 82 No.7)

Carbon is a great example of the relationship between properties and molecular, or in this case, atomic arrangements. Carbon is also at the heart of much of the nano-technology. So using molecular models of diamond and graphite, students will once again be asked to link the correct model to its name. They will be asked to give written explanations to justify their choices. The teacher will then describe the discovery of buckyballs and graphene. Activity 7: Try to make some graphene using tape to pull a layer from a graphite pencil 'lead'. Then keep folding tape over the layer that was removed and try to remove several more layers. To further understand relative sizes and especially a nano scale, students choose an object to represent an atom and then find other everyday analogies to accurately give the relative size of graphene (thickness), nanotube (length), water molecule, polymer molecule, and protein.

Activity 8: To demonstrate that the properties of materials change when only a few atoms or molecules are together, a colloid of gold is prepared. Colloidal gold consists of gold particles that range in size from 5-50 nm and are uniformly dispersed in water. The interaction of light on these particles is very different than when many more atoms are in one place. Whereas normal or 'bulk' gold is bright, shiny, metallic yellow, colloidal gold nanoparticles are red or blue, and not at all shiny. Depending on the size and shape of the particles, the color of the gold particles varies from red to purple. The optical properties of gold nanoparticles are not only unique, they are also useful, providing the basis for commercial products such as medical diagnostic kits for HIV detection, biosensors for DNA analysis, lasers, and optical filters. The colloid is primarily gold(III) ions stabilized by the citrate ions absorbed on the surface of the particles. Adsorption of the citrate ions gives the

gold particle an overall negative charge and this is the primary factor responsible for the formation of the stable colloid. This demonstration can be purchased from Flinn Scientific.

Activity 9: Again, watching the video "Making Stuff Smaller", will tie many of the concepts together. This episode shows 'machines' being replaced by materials that can perform the same function but take up minimal room. Some materials or devices discussed are graphene, materials which can be manipulated by magnets to deliver medicine, stained glass windows where artists knew that particle size of metals would influence the color of the glass, and encapsulated bee venom as a possible treatment of cancer.

Activity 10: Dr. Alex Star, located at the University of Pittsburgh, is developing many techniques to use nanotubes. He is an enthusiastic speaker and will be invited to discuss his research with the students. Students will be asked to prepare questions before the talk.

Students will then be asked to complete the final assignment. They will need to describe what the new material will accomplish. They will then need to list the required properties of the material in order to accomplish the final function. Using this list, they must describe the types of molecules involved, their molecular properties (such as polar, ionic, nonpolar), the types of intermolecular forces and their impact on molecular arrangement, and finally give a hierarchy for the final arrangement. An explanation will be needed to link the property to the molecular arrangement. Students will be evaluated on the thoroughness and accuracy of the possible properties, possible molecular arrangements and reasoning.

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All the books written by Philip Ball are very readable and have interesting literary references as well. This book discusses many molecules and their uses.

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This book focuses on cutting edge materials that have been identified as offering promise. The difficult part of producing these economically has not yet been pursued, so it is possible that we may never see these as products. This book provides more specifics on the molecular structures.

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Flinn ChemTopic™ Lab. #21 Polymers. Flinn Scientific is a chemical supply company that has produced a series of books providing labs and demos around specific topics. All descriptions describe in-depth how to conduct the labs and demonstrations, as well as the

chemistry behind them. P.O. Box 219, Batavia, IL 60510. 800-452-1261

Flinn Demonstration Kit. Ruby-Red Colloidal Gold: Nanotechnology Demonstration

Catalog # AP7117. P.O. Box 219, Batavia, IL 60510. 800-452-1261

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Making Stuff. NY Times science correspondent David Pogue hosts a four part series on NOVA about advances in material science. The DVD is available for purchase or can be found at [www.pbs.org/wgbh/nova/tech/making-stuff.html](http://www.pbs.org/wgbh/nova/tech/making-stuff.html). Making Stuff Stronger and Making Stuff Smaller are most appropriate for this unit.

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## Endnotes

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## Appendix 1

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### National Science Standards

1. Order-Order is the behavior of units of matter, objects, organisms, or events in the universe. The goal is to help students develop knowledge about factors influencing objects, organisms, systems, or events.
2. The physical properties of compounds reflect the nature of the interactions among its molecules. These interactions are determined by the structure of the molecule, including the constituent atoms and the distances and angles between them.
3. Carbon atoms can bond to one another in chains, rings, and branching networks to form a variety of structures, including synthetic polymers, oils, and the large molecules essential to life.
4. Creativity, imagination, and a good knowledge base are all required in the work of science and engineering.



## 5. Abilities of technological design

- a. Identify a problem or design an opportunity.
- b. Propose designs and choose between alternative solutions.
- c. Implement a proposed solution.
- d. Evaluate the solution and its consequences.
- e. Communicate the problem, process, and solution.

New science standards have been proposed to incorporate engineering concepts with basic science concepts. In other words, can students can apply their knowledge. This project is consistent with those goals.

## Appendix 2

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### The 12 Principles of Green Chemistry

- 1) It is better to prevent waste than treat or clean up waste.
- 2) Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- 3) Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- 4) Chemical products should be designed to preserve the efficacy of function while reducing toxicity.
- 5) The use of auxiliary substances (e.g. solvents, separation agents, etc. should be made unnecessary wherever possible and innocuous when used.
- 6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
- 7) A raw material or feedstock should be renewable rather than depleting, wherever technically and economically possible.
- 8) Unnecessary derivatization (blocking group, protection/de-protection and temporary modification of physical/chemical processes) should be avoided whenever possible.
- 9) Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- 10) Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
- 11) Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12) Substances and the form of a substance used in chemical processes should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

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