MAKING NYLON

THE HISTORY OF NYLON

In 1924, shortly after completing his doctorate at the University of Illinois, Wallace Hume Carothers (1896-1937) was recruited by the DuPont Company to investigate the chemistry of an acetylene polymer that the company hoped would lead to the development of a synthetic rubber. In 1930 one of Carother's assistants, Arnold M Collins, isolated a new liquid compound known as chloroprene. This polymer spontaneously polymerized to produce a rubber-like solid, chemically similar to natural rubber. This product, later known as Neoprene, became the first

commercially successful specialty rubber.

Shortly after this discovery, Carother's group went on to create a strong, elastic synthetic fiber while attempting to produce super-polymers of high molecular weight by reacting glycols and dibasic acids with strong acids under reduced pressure in a molecular still. The polymers resulting from this work were known as polyesters. Since they had very low melting points and

high solubility in dry cleaning solvents they were not commercially viable.

After many attempts to work around the problems surrounding polyesters, this team of scientists from DuPont went on to use amines rather than glycols to produce polyamides rather than polyesters. Polyamides are synthetic proteins which prove to be much more stable than

polyesters since polyesters are structurally similar to natural fats and oils.

This group went on to later discover an amazing polyamide fiber, a material with a structure similar to silk, called nylon 6-6 in 1931. DuPont decided to commercialize nylon by creating stockings in 1939. Other applications of nylon followed in the years to come, particularly during World War II when nylon was used to make parachutes and other items needed by the military. The very first nylon product was a toothbrush with nylon bristles.

NYLON STRUCTURE

Many types of nylon are commercially available. The most popular in Nylon 6-6, followed by Nylon 6, then Nylon 6-12, Nylon 11 and Nylon 12. Nylon 6-6 is the

strongest of the nylons. Nylon 6 has improved creep resistance over Nylon 6-6 but has a lower modulus, Nylon 6 absorbs moisture more rapidly but has improved processability. Compared to Nylon 6-6 it can be molded at about 27 degrees Celsius lower with less mold shrinkage because it is less crystalline. Nylon 11 is a low water absorbing nylon, has good chemical resistance and has the ability to accept a high loading of fillers, but has little heat resistance and a very high cost in comparison to other nylons.

Nylon absorbs more moisture from the air than most polymers. This affects its processability, dimensional stability and physical properties. Moisture acts as a plasticizer, reducing tensile strength and stiffness and increasing elongation. Although water absorption reduces many of nylon's properties, it significantly increases its impact strength and general energy absorbing characteristics.

Glass reinforced nylon is a polyamide that has had glass fibers filled into it. These fibers increase the polymers stiffness and heat deflection but reduce its elongation and impact strength. By introducing a material to increase toughness in the glass filled polymer, DuPont has been able to improve these weakened characteristics.

Carbon fiber-reinforced nylons excel over their base resin and glass-reinforced nylons with improved tensile and flexural strengths. Nylon 6-6 has up to 36,000 psi tensile and 50,000 psi flexural strength, lower expansion, better dimensional stability, and improved thermal and electrical conductivities. Nylon 6-6 has static dissipative characteristics when reinforced with carbon fiber. Because of their high modulus, good wear resistance and static electricity discharge characteristics, carbon fiber-reinforced nylons have potential for replacement of die cast metals, such as those found in moving textile machines.

THE CHEMISTRY OF NYLON AND OTHER FIBERS

Nylons are the most common polymers used as a fiber. A polymeric fiber is a polymer whose chains are stretched out straight, or close to straight, and lined up next to each other long the same axis, similar to what you see below:
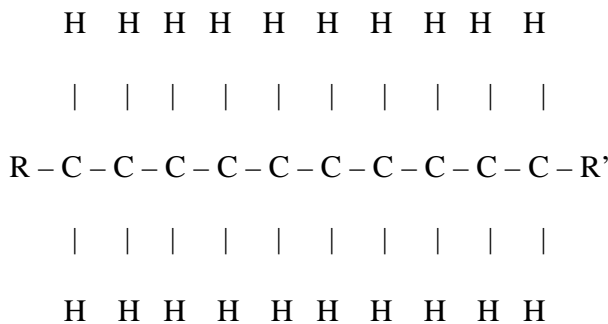
_____   _____

_____   _____   _____

  _____   _____   _____
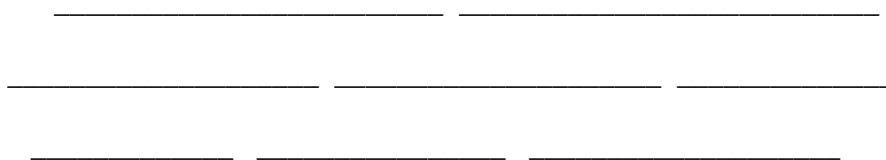
Polymers that are arranged in fibers this can be spun into threads and used in textiles. Most of the clothes that we wear and the carpets and ropes that we use are made out of

polymeric fibers. Fibers are always made of polymers that are arranged into crystals. The have to be able to be packed into a regular arrangement in order to line up into fibers. Examples of polymers that may be drawn into fibers include the following: polyethylene, polyacrylonitrile, cellulose and polyurethanes, and nylon.

POLYETHYLENE   --[--CH2—CH2--]-- n

Polyethylene is the most popular plastic in the world. It is the **polymer** used to make grocery bags, shampoo bottles, children's toys, and even bullet proof vests. This extremely versatile **polymer** has a very simple structure. It is the simplest of all commercial polymers. One molecule of polyethylene is nothing more than a long chain of carbon atoms, with two hydrogens attached to each carbon (see figure below).

```
    H   H   H   H   H   H   H   H   H   H

    |   |   |   |   |   |   |   |   |   |

R – C – C – C – C – C – C – C – C – C – C – R'

    |   |   |   |   |   |   |   |   |   |

    H   H   H   H   H   H   H   H   H   H
```

Sometimes the structure of polyethylene is more complicated. For example long chains of polyethylene may replace some of the hydrogens, to form branched or low density polyethylene (LDPE). When no branching is present, the molecule is called linear polyethylene, or HDPE. Linear polyethylene is much stronger than branched polyethylene, but branched polyethylene is cheaper and easier to make.

Linear polyethylene is normally produced with molecular weights in the range of 200,000 to 500,000, or even higher. Polyethylene with molecular weights of 3 to 6 million is referred to as ultra high molecular weight polyethylene, or UHMWPE. It can be used to make fibers so strong that they have been able to be used in bullet proof vests. Large sheets of it can be used instead of ice for ice skating rinks.

Polyethylene is a vinyl **polymer**, made from the monomer ethylene. Branched polyethylene is often made by free radical vinyl polymerization. Linear is made by a more complicated procedure known as Ziegler-Natta polymerization. This method can also be used to synthesize LDPE. UHMWPE is made using metallocene catalysis polymerization.

By copolymerizing the ethylene monomer with an alkyl-branched comonomer a copolymer with short hydrocarbon branches is formed. Such copolymers are called

linear low-density polyethylene, or LLDPE, and are often used to make plastic films.

POLYACRYLONITRILE

http://www.pslc.ws/macrog/pan.htm

Polyacrylonitrile is used for very few products an average consumer would be familiar with. It is commonly used to make carbon fibers. Homopolymers of polyacrylonitrile can be used as fibers in hot gas filtration systems, outdoor awnings, sails for boats, and reinforcement for concrete. Copolymers containing polyacrylonitrile are often used as fibers to make knitted clothing, such as socks and sweaters. If the label on clothing reads "acrylic" then it is made up of a copolymer of polyacrylonitrile such as acrylonitrile and methyl acrylate, or acrylonitrile and methyl methacrylate.

Sometimes copolymers are made from acrylonitrile and vinyl chloride. These copolymers are flame-retardant. Fibers made from them are known as modacrylic fibers. Below is the structure of vinyl chloride:

H   H

 \   /

   C=C

 /   \

H   Cl
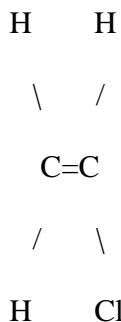
When vinyl chloride undergoes free radical vinyl polymerization poly vinyl chloride (PVC) is produced. PVC is plastic from which pipes, linoleum floors and vinyl top cars are made. PVC is useful because it is fire and ==water==-resistant. Its ==water== resistance makes it useful for shower curtains and ==water== pipes. It is flame resistant because it contains chlorine. When burned, PVC releases chlorine atoms, which prevent combustion.

SAN, polystyrene-co-acrylonitrile, is a simple random copolymer of styrene and acrylonitrile used in plastics. ABS, acrylonitrile-co-butadiene-co-styrene, is also used in plastics and is made by polymerizing styrene and acrylonitrile in the presence of

polybutadiene. ABS contains a polybutadiene chain with SAN chains grafted onto it. ABS is very strong and lightweight. It can be used to make automobile body parts. It makes automobiles lighter so that they use less fuel.

ABS is a stronger plastic than polystyrene because it contains nitrile groups that are very polar and attracted to each other.

CELLULOSE

http://www.pslc.ws/macrogcss/cell.html

Cellulose is one of the many polymers found in nature. Materials containing cellulose include wood, paper and cotton. It is made up of repeated units of the glucose monomer. Cellulose was used to make some of the first synthetic polymers such as cellulose nitrate, cellulose acetate and rayon.

A cellulose derivative known as hydroxy-ethyl-cellulose is commonly used as a shampoo thickener. It makes shampoo less foamy and helps it to clean better by forming colloids around dirt particles. Normally dirt particles are insoluble in water but a chain of this cellulose derivative wraps itself around the dirt particle, increasing its solubility in water.

POLYURETHANE

http:// www.elmhurst.edu/˜chm/vchembook/402condensepolymers.html

Polyurethanes are most well known for making foams. (SEE POLYURETHANE FOAM LAB)

Polyurethanes are the single most versatile family of polymers. They can be elastomers and also found in paints. They can also be found in fibers, adhesives and spandex. Polyurethanes are polymers containing a urethane linkage in its backbone. They are commonly made by reacting diisocyanates with di-alcohols.

This reaction is discussed in detail in the "Polyurethane Foam" lab experiment.

Polyurethanes can hydrogen bond very well. As a result they can be quite crystalline in structure. As a result they are often used to make block copolymers with soft rubbery polymers. These block copolymers have properties of thermoplastic elastomers.

Spandex is a polyurethane thermoplastic elastomer that has a urea and urethane linkage in its backbone. This **polymer**'s structure is unique because it has both hard and soft blocks in its repeating structure. Its short chain of polyglycol is soft and rubbery and the remaining chain, made up of urethane linkages, urea linkages and aromatic groups, is extremely rigid. The result is a structure that acts as an elastomer used to make fabric that stretches for clothing such as exercise wear.

NYLON

Nylon is often found in clothing but it can also be found in other substances, in the form of thermoplastics. Plastics are pliable, meaning they can be shaped and molded easily. When they are heated they become more pliable and even melt when they get too hot. Hot plastics are known as thermoplastics.

Nylons are known as polyamides because their backbones contain amine groups. These amide groups are extremely polar and hydrogen bond with each other. The backbone of nylon is regular and symmetrical so nylon is often crystalline and makes very good fibers.

Nylon is named by the number of carbon atoms in the repeating units of the **polymer** chain. For example the following structure is named Nylon 6-6 because each repeating unit in the **polymer** chain are six carbon atoms long:

```
     O                    O

     ||                   ||

--[-C-CH2-CH2-CH2-CH2-C-NH-CH2-CH2-CH2-CH2-CH2-CH2-NH--]—n
```
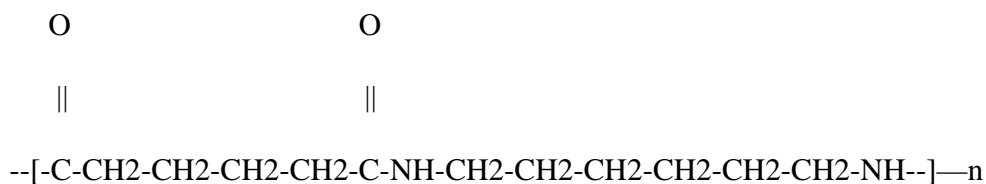
Nylon 6-6

MAKING NYLON 6-6

Nylon is made by reactions known as step-growth polymerization and condensation polymerization. Both of these reactions will be discussed later on in this paper. Nylons are made from diacids, such as adipic acid, and diamines, such as hexamethylene diamine. The synthesis of nylon does not require a catlyst, but the reaction is

automatically catalyzed from acids such as the adipic acid.

When two molecules of adipic acid react, one of the molecules donates a proton to a carbonyl of oxygen of the other. When this oxygen is protonated, the carbonyl oxygen becomes vulnerable to attack by the nitrogen atom of the diamine, because it posses a positive charge. One of the electron pairs of the carbonyl double bond shifts entirely to the oxygen, leaving the nitrogen positively charged.

A further movement of electrons is observed as electrons move from the hydrogen oxygen bond back to the oxygen. This frees a proton and regenerates the acid catalyst. The carbonyl oxygen then shares the electrons that it has just gained with the carbon atoms, to reform the carbonyl double bond. Ultimately, after the severing of the bond between the oxygen of the hydroxyl group and the carbon, a ==water== molecule splits off of the molecule to generate an amide-containing dimmer.

The dimmer that is formed can react with other dimmers to make a tetramer or even a pentamer. They can then react to form larger molecules known as oligomers. Eventually these oligomers will be large enough to be called polymers such as Nylon 6-6. Remember that ==water== molecules are produced as a by-product so it is best if this reaction is carried out in a vacuum. Otherwise the reaction will be driven in the reverse direction, according to LeChatalier's principle.

Towards the end of the polymerization, despite the fact that there are few acid groups left to act as catalysts, the reaction continues. Amine is capable of reacting with the unprotonated carboxylic acids to make a high molecular weight ==polymer== such as Nylon 6-6.

Nylons can also be made from a diamine, such as adipoyl chloride, and a diacid chloride, such as hexamethylene diamine. The mechanism of this reaction is the same but it needs a small amount of acid to catalyze it. Hydrochloric acid is produced as a by-product instead of ==water==.

CHAIN GROWTH AND STEP GROWTH POLYMERIZATION

During the process of chain growth polymerization, monomers become part of a larger ==polymer== one at a time. The process of step growth polymerization is more complex. In the beginning of the process two monomers react to form a dimer, then a trimer and so on

until it forms a large oligomer, or ==**polymer**==. These two processes are quite different from addition polymerization. During an addition polymerization, only monomers can react with growing chains. Two growing chains are unable to join together the way that they can in a step growth polymerization.

ADDITION AND CONDENSATION POLYMERIZATIONS

An addition polymerization is a polymerization in which the entire monomer molecule becomes part of the ==**polymer**==. An example of this type of polymerization is the synthesis of polyethylene by ethylene. Both structures contain exactly two carbon atoms and four hydrogen atoms.

A condensation polymerization takes place when part of the monomer molecule is kicked out of the structure as the ==**polymer**== is formed. This piece becomes a by-product such as ==**water**== or hydrochloric acid. An example of this type of polymerization is the synthesis of Nylon 6-6. When Nylon 6-6 is synthesized from adipoyl chloride and hexamethylene diamine, the chlorine atoms from the adipoyl chloride and the hydrogen atoms from the amine are released as the by-product HCl.

COMPARING NYLON 6 TO NYLON 6-6

Below is a list of some of the chemical and physical properties of Nylon 6 and Nylon 6-6.

NYLON 6

Applications: Commonly used in Fibers and Thermoplastics

Monomer: Caprolactam

Type of Polymerization: Ring Opening Polymerization **

Morphology: Highly Crystalline

Melting Point: 215° C

Glass Transition Temperature: 40° C

NYLON 6-6

Applications: Commonly used in Fibers and Thermoplastics

Monomers: Adidpic Acid and Hexamethylene Diamine

Polymerization: Acid Catalyzed Condensation Polymerization

Morphology: Highly Crystalline

Melting Point: 280° C

Glass Transition Temperature: 50° C

** Ring Opening Polymerization is a polymerization in which cyclic monomers are converted in to a polymer that does not contain rings.

<u>NYLON SALT</u>

Nylon 6-6 is synthesized by the reaction of adipic acid and hexamthylene diamine, which acts as a base. Just as in other neutralization reactions, a salt is formed. When Carothers and his team began synthesizing nylon they used this nylon salt, which is synthesized in an exact 1:1 mixture of the acid and base, to make future nylon. This proved to be more efficient than just mixing the acid and base together since they would need to be mixed in specific ratios to ensure a high molecular weight of at least 10,000. Nylon salt can be purified into a crystalline solid and then be heated to temperatures above 285 degrees Celsius to react and become a nylon polymer.

In 1934 Wesley R. Peterson, a chemist who had been using this method, was creating polymers that were of a molecular weight that was too high. If the molecular weight of nylon is too high it can not be spun into yarn. Peterson added acetic acid to the reaction in an attempt to address this problem. A growing chain of nylon polymer has either an amine group or an acid group on the end of it. If acetic acid reacts with the amine end group, the result is a chain with and unreactive group on the end. The chain will be unable to grow anymore so the acetic acid, added in at a specific ratio, acts as a limiting reagent that limits the molecular weight.

ARAMIDS

Aramids belong to a family of nylons that are used to make things such as bullet- proof vests and puncture resistant bicycle tires. These nylons include polymers such as Kevlar→ and Nomex→. Blends of these two polymers are used to make fireproof clothing.

Kevlar→ is a polyamide. The amide groups in its structure are attached to the phenyl rings on carbons opposite to each other. This is known as a "para" structure.

It is a crystalline polymer that is quite insoluble and has an extremely high melting point. Kevlar→ is a useful polymer in fibers because if it attempts to twist into a cis-conformation, the hydrogens on the aromatic groups keep the trans-structure.

Nomex has meta phenylene groups, meaning the amide groups are attached to the phenyl ring at the 1 and 3 positions.

ACKNOWLEDGEMENTS

http://www.dupont.com/industrial-polymers/plastics/functions/mod_pa.html

http://www.jefallbright.net/node/2628

http://www.chemsoc.org/timeline/pages/1935_nylon.html

http://www.madsci.org/posts/archives/dec96/848371367.Ch.r.html

http://www.matse1.mse.uiuc.edu/~tw/polymers/c.html

http://www.polymerprocessing.com/polymersPA6.html

http://www.chemicalheritage.org/EducationalServices/faces/teacher/poly/activity/nylon6a.html

http://www.rtpcompany.com/info/guide/descriptions/0200C.html

http://www.pslc.ws/macrogcss/nysyn.html

http://www.chemheritage.org/EducationalServices/nylon/chem/chem.html

SUNY Stony Brook GARCIA MRSEC Program

The Nylon Rope Trick

The interfacial polymerization method to prepare polyamides involves the reaction of a diacid dichloride with a diamine between two immiscible liquids as the reaction zone (with or without stirring). The method is very useful where the reactants are sensitive to high temperature and where the **polymer** degrades before the melting point is reached as in melt polymerization techniques (Ref: P. W. Morgan and S. L. Kwolek, *J. Chem. Ed.* **36**, 182 (1959)).

Safety Precautions

Before the experiment is carried, one must read the material safety data sheets (MSDS) for all the chemicals used as well as for the products.

Materials

- Sebacoyl chloride (reagent grade or freshly distilled).
- Tetrachloroethylene (reagent grade or freshly distilled).
- Hexamethylenediamine (reagent grade or freshly distilled).
- 50% aqueous ethanol.

Procedure

- Add a solution of 3.0 mL (0.014 mol) of sebacoyl chloride dissolved in 100 mL of anhydrous tetrachloroethylene as received to a tall-form beaker.
- Carefully pour a solution of 4.4 g (0.038 mol) of hexamethylenediamine dissolved in 50 ml of water over this acid chloride solution.
- Grasp the polyamide film that begins to form at the interface of these two solutions with tweezers or a glass rod and slowly pull it out of the beaker in a continuous fashion. Stop the process when one of the reactants becomes depleted.
- Wash the resulting "rope"-like polymer with 50% aqueous ethanol or acetone and dry it.

Results and Discussion

When a solution of a fast reacting diacid chloride in a waster-immiscible solvent is brought into contact with an aqueous solution of an aliphatic diamine, a film of high polymer forms at once where the two solutions meet. The film is very thin but strongly coherent. The film can be pulled out of the interface and is immediately and continuously replaced to form a long endless cord of polyamide. The process is like pulling a string of silk handkerchiefs out of a top hat. From clear solutions comes a cord of white polymer. When the pulling is stopped nothing appears to happen; when pulling is resumed, more polymer follows. This can be repeated over a period of many hours. The removal of film can be continued by hand.