POLYMERS AND PLASTICS

TECHNIQUES REQUIRED : Reflux apparatus, extraction, vacuum filtration, yield calculation

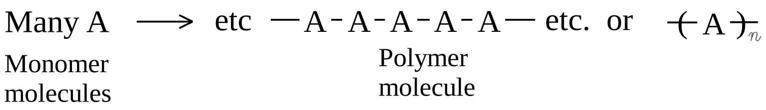
OTHER DOCUMENTS Experimental procedure, Report template (Word)

INTRODUCTION

Chemically, plastics are chainlike molecules of high molecular weight, called polymers and are built up from simpler chemicals, the individual links, called monomers. A different monomer or combination of monomers is used to manufacture each different type or family of polymers. There are many polymers around us that are so familiar we take them for granted. Examples of man-made polymers are Teflon, nylon, Dacron, polyethylene, polyester, Orlon, epoxy, vinyl, polyurethane, silicones, Lucite, and boat resin. Examples of natural polymers are starch and cellulose (from glucose), rubber (from isoprene) and proteins (from amino acids). Certainly, polymers have had and continue to have a great influence on our society. As these materials have been created, problems have arisen concerning their use. Many are not biodegradable, they contribute a significant volume to the garbage we create and the raw materials for their manufacture are a finite resource. Plastic recycling is an important process for reducing waste and recovering potentially valuable raw materials, for example, it has been possible to buy fleece clothing made from recycled materials for many years.

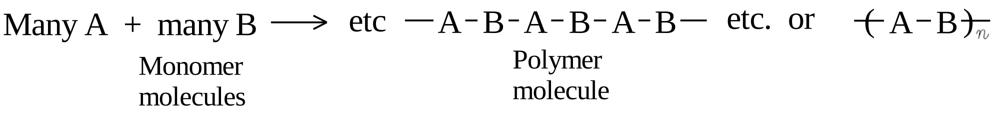
CHEMICAL STRUCTURES OF POLYMERS

Basically a polymer is made up of many repeating molecular units formed by sequential addition of monomer molecules to one another. Many monomer molecules of A, say 1,000 to 1,000,000, can be linked to form a gigantic polymeric molecule:



$$\underset{\text{Monomer molecules}}{\text{Many A}} \longrightarrow \text{etc} \underset{\text{Polymer molecule}}{-\text{A}-\text{A}-\text{A}-\text{A}-\text{A}-} \text{etc. or } \left(\text{A}\right)_n$$

Monomers that are different can also be linked, to form a polymer with an alternating structure. This type of polymer is called a copolymer.

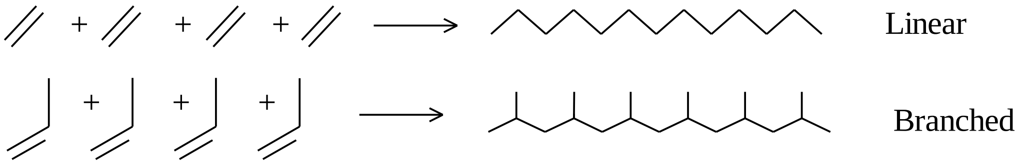


$$\underset{\text{Monomer molecules}}{\text{Many A} + \text{many B}} \longrightarrow \text{etc} \underset{\text{Polymer molecule}}{-\text{A}-\text{B}-\text{A}-\text{B}-\text{A}-\text{B}-} \text{etc. or } \left(\text{A}-\text{B}\right)_n$$

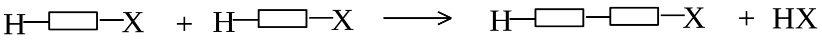
TYPES OF POLYMERS

For convenience, chemists classify polymers in several main groups, depending on method of synthesis.

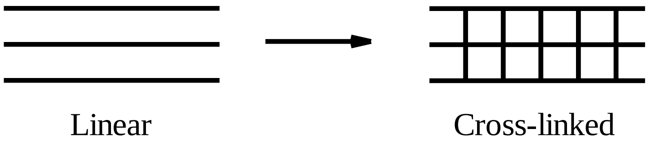
1. **Addition polymers** are formed by a reaction in which monomer units simply add to one another to form a long-chain (generally linear or branched) polymer. The monomers usually contain carbon-carbon double bonds (whose characteristic reactions are addition reactions). Common examples of addition polymers are polyethylene and Teflon. The process can be represented as follows:



2. **Condensation polymers** are formed by reaction of bi- or polyfunctional molecules, with the elimination of some small molecule (such as water, ammonia, or hydrogen chloride) as a by-product. Common examples of condensation polymers are nylon, Dacron, and polyurethane. The process can be represented as follows:



3. **Cross-linked polymers** are formed when long chains are linked in one gigantic, 3-dimensional structure with tremendous rigidity. Addition and condensation polymers can exist with a cross-linked network, depending on the monomers used in the synthesis. Familiar examples of cross-linked polymers are Bakelite, rubber, and casting (boat) resin. The process can be represented as follows:



Industrialists, engineers and technologists often classify polymers in other categories based on their properties.

1. **Thermoplastics** are materials that can be softened (melted) by heat and re-formed (molded) into another shape. Weaker, noncovalent bonds are broken during the heating. Technically, thermoplastics are the materials we call plastics. Both addition and condensation polymers can be so classified. Familiar examples include polyethylene (addition polymer) and nylon (condensation polymer).

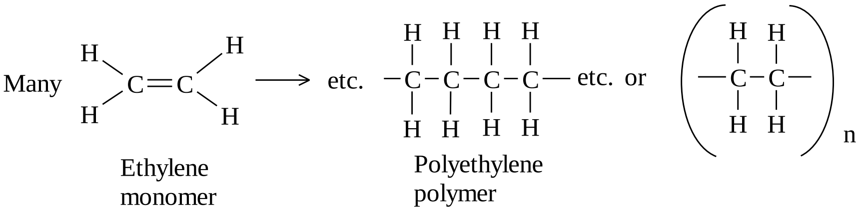
2. **Thermoset plastics** are materials that melt initially but on further heating become permanently hardened. They cannot be softened and remolded without destruction of the polymer because

covalent bonds are broken. Chemically, thermoset plastics are cross-linked polymers. Bakelite is an example of a thermoset plastic.

Polymers can also be classified in other ways; for example, based on their uses, many varieties of rubber are often referred to as elastomers, Dacron is a fiber, and polyvinyl acetate is an adhesive. The chemical based classification will be used in this essay.

ADDITION POLYMERS

Most of the polymers made are of the addition type. The monomers generally contain a carbon-carbon double bond. The most important example of an addition polymer is the well-known polyethylene, for which the monomer is ethylene. Countless numbers of ethylene molecules are linked in long-chain polymeric molecules by breaking the pi bond and creating two new single bonds between the monomer units. The number of recurring units may be large or small, depending on the polymerisation conditions.



This reaction can be promoted by heat, pressure, and a chemical catalyst. The molecules produced in a typical reaction vary in the number of carbon atoms in their chains. In other words, a mixture of polymers of varying length is produced, rather than a pure compound.

Polyethylenes, with linear structures, can pack together easily and are referred to as high-density polyethylenes. They are fairly rigid materials. Low-density polyethylenes consist of branched-chain molecules, with some cross-linking in the chains. They are more flexible than the high-density polyethylenes. The reaction conditions and the catalysts that produce polyethylenes of low and high density are quite different. The monomer, however, is the same in each case. Another example of an addition polymer is polypropylene. In this case, the monomer is propylene. The polymer that results has a branched methyl on alternate carbon atoms of the chain.

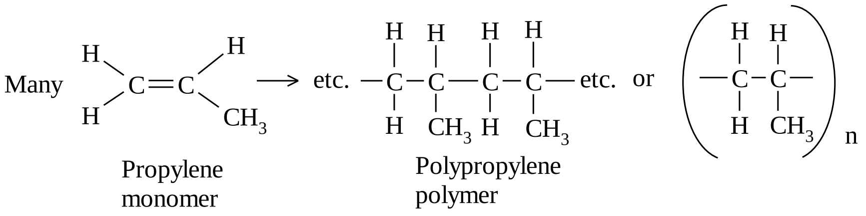
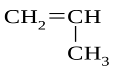
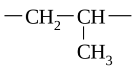
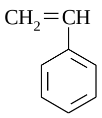
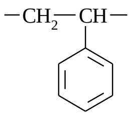
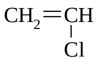
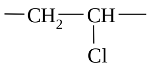
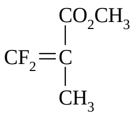
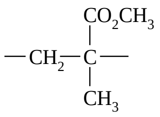
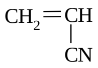
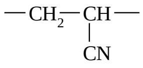
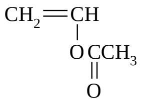
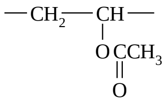
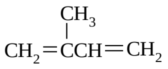
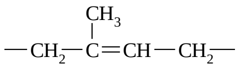
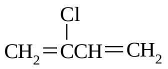
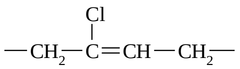
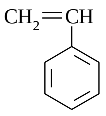
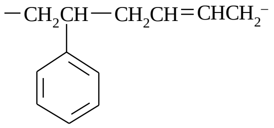


TABLE 1. ADDITION POLYMERS

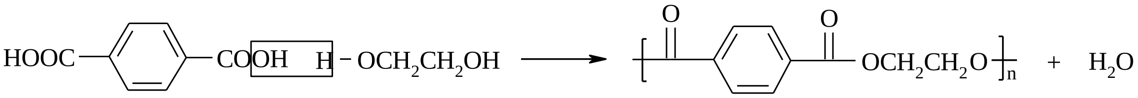
EXAMPLE	MONOMER(S)	POLYMER	USE
Polyethylene	$CH_2{=}CH_2$	$-CH_2-CH_2-$	Most common and important polymer. Bags, insulation for wires, squeeze bottles
Polypropylene	 $CH_2{=}CH(CH_3)$	 $-CH_2-CH(CH_3)-$	Fibers, indoor-outdoor carpets, bottles
Polystyrene			Styrofoam, inexpensive household goods, inexpensive molded objects
Polyvinyl chloride (PVC)	 $CH_2{=}CH(Cl)$	 $-CH_2-CH(Cl)-$	Synthetic leather, clear bottles, floor covering, phonograph records, water pipe
Polytetrafluoroethylene (Teflon)	$CF_2{=}CF_2$	$-CF_2-CF_2-$	Nonstick surfaces, chemically resistant films
Polymethyl methacrylate (Lucite, Plexiglas)	 $CF_2{=}C(CO_2CH_3)(CH_3)$	 $-CH_2-C(CO_2CH_3)(CH_3)-$	Unbreakable "glass", latex paints
Polyacrylonitrile (Orlon, Acrilan, Creslan)	 $CH_2{=}CH(CN)$	 $-CH_2-CH(CN)-$	Fiber used in sweaters, blankets, carpets
Polyvinyl acetate (PVA)	 $CH_2{=}CH(OCCH_3)$, $C{=}O$	 $-CH_2-CH(OCCH_3)-$, $C{=}O$	Adhesives, latex paints, chewing gum, textile coatings
Natural rubber	 $CH_2{=}C(CH_3)CH{=}CH_2$	 $-CH_2-C(CH_3){=}CH-CH_2-$	The polymer is cross-linked with sulfur (vulcanization)
Polychloroprene (Neoprene rubber)	 $CH_2{=}C(Cl)CH{=}CH_2$	 $-CH_2-C(Cl){=}CH-CH_2-$	Cross-linked with ZnO, resistant to oil, gasoline
Styrene butadiene rubber (SBR)	 $CH_2{=}CHCH{=}CH_2$		Cross-linked with peroxides. Most common rubber. Used for tires. 25% styrene. 75% butadiene

Several common addition polymers are shown in Table 1. Some of their principal uses are also listed. The last three entries in the table all have a carbon-carbon double bond remaining after the polymer is formed. These bonds activate or participate in a further reaction to form cross-linked polymers called elastomers; this term is almost synonymous with *rubber*, since they designate materials with common characteristics.

CONDENSATION POLYMERS

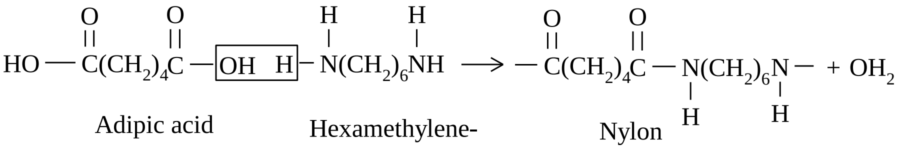
Condensation polymers, for which the monomers contain more than one type of functional group, are more complex than addition polymers. In addition, most condensation polymers are copolymers made from more than one type of monomer. You will recall that addition polymers, in contrast, are all prepared from substituted ethylene molecules. The single functional group in each case is one or more double bonds, and a single type of monomer is generally used.

Dacron, or polyethyleneterephthalate (PET) is a polyester, can be prepared by causing a dicarboxylic acid to react with a bifunctional alcohol (a diol):



Terephthalic acid Ethylene glycol Dacron or PET

Nylon 6-6, a polyamide, can be prepared industrially by causing a dicarboxylic acid to react with a bifunctional amine:

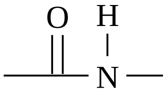


$$\mathrm{HO-\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-\boxed{OH\ \ H}-\overset{H}{\overset{|}{N}}(CH_2)_6\overset{H}{\overset{|}{N}}H \longrightarrow -\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}(CH_2)_6\underset{H}{\underset{|}{N}}- + OH_2}$$

Adipic acid Hexamethylene-diamine Nylon

Notice, in each case, that a small molecule, water, is eliminated as a product of the reaction. Several other condensation polymers are listed in Table 2. Linear (or branched) chain polymers as well as cross-linked polymers are produced in condensation reactions.

The nylon structure contains the amide linkage at regular intervals,

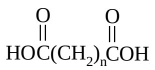
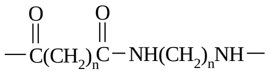
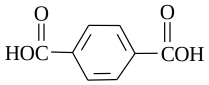
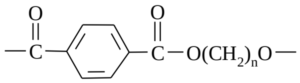
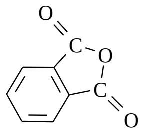
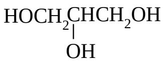
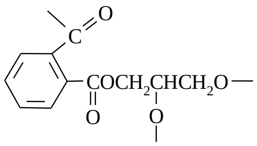
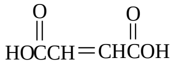
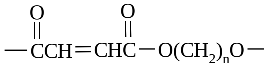
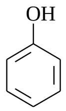
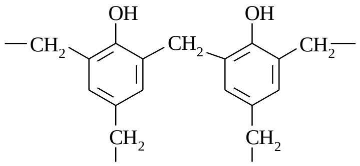
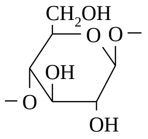
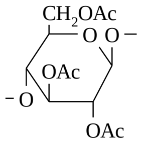
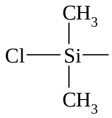
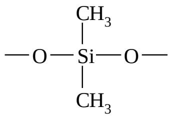
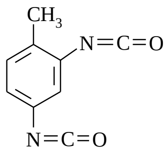
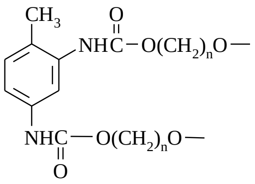


$$\mathrm{-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-}$$

This type of linkage is extremely important in nature because of its presence in proteins and polypeptides. Proteins are gigantic polymeric substances made up of monomer units of amino acids. They are linked by the peptide (amide) bond.

Other important natural condensation polymers are starch and cellulose. They are polymeric materials made up of the sugar monomer glucose. Another important natural condensation polymer is the DNA molecule. A DNA molecule is made up of the sugar deoxyribose linked with phosphates to form the backbone of the molecule.

TABLE 2. CONDENSATION POLYMERS

EXAMPLE	MONOMERS	POLYMER	USE
Polyamides (Nylon)	 $HO\overset{O}{\overset{\Vert}{C}}(CH_2)_n\overset{O}{\overset{\Vert}{C}}OH$ $H_2N(CH_2)_nNH_2$	 $-\overset{O}{\overset{\Vert}{C}}(CH_2)_n\overset{O}{\overset{\Vert}{C}}-NH(CH_2)_nNH-$	Fibers, molded objects
Polyesters (Dacron, Mylar, Fortrel)	 $HO(CH_2)_nOH$		Linear polyesters Fibers, recording tape
Polyesters (Glyptal resin)	  $HOCH_2\underset{OH}{\underset{\vert}{C}}HCH_2OH$		Cross-linked polyester Paints
Polyesters (Casting resin)	 $HO\overset{O}{\overset{\Vert}{C}}CH=CH\overset{O}{\overset{\Vert}{C}}OH$ $HO(CH_2)_nOH$	 $-\overset{O}{\overset{\Vert}{C}}CH=CH\overset{O}{\overset{\Vert}{C}}-O(CH_2)_nO-$	Cross-linked with styrene and peroxide. Fiberglass boat resin
Phenol-formaldehyde resin (Bakelite)	 $CH_2=O$		Mixed with fillers. Molded electrical goods, adhesives, laminates, varnishes
Cellulose acetate*	 CH_3COOH		Photographic film
Silicones	 $Cl-\overset{CH_3}{\underset{CH_3}{Si}}-Cl$ H_2O	 $-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-$	Water-repellent coatings, temperature-resistant fluids and rubbers (CH_3SiCl_3 cross-links in water)
Polyurethanes	 $HO(CH_2)_nOH$		Rigid and flexible foams, fibers

* Cellulose, a polymer of glucose, is used as the monomer.

PROBLEMS WITH PLASTICS

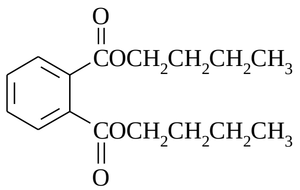
Plastics waste is one of the biggest global challenges as they pollute the highest mountains, the deepest oceans and within living organisms. Global plastic production has doubled since 2000, reaching 400,000,000 metric tons in 2021. With an average lifespan of 10 years, plastics can then take 500 years to compose depending on structure and disposal method. The current estimate is that 350,000,000 metric tons of waste are generated annually[1] with less than 10% actually being recycled. The majority is either consigned to a landfill or incinerated generating other pollutants with 25% being "mismanaged" (e.g. illegal dumping) or creating litter.

We should all be aware of the problems of plastics including disposal problems, health hazards, littering problems, fire hazards, and energy shortages associated with their manufacture and use and make reasonable and responsible choices on how and when we use them and how we dispose of them.

Plasticizers and Health Hazards

Certain types of plastics such as polyvinyl chloride (PVC) are mixed with plasticizers that soften the plastic so that it is more pliable. If plasticizers were not added, the plastic would be hard and brittle. Some of the plasticizers used in vinyl plastics are phthalate esters. The structure of a phthalate ester is shown over. These esters are volatile compounds of low molecular weight. Part of the new car "smell" comes from the odor of these esters as they evaporate from the vinyl upholstery. The vapor often condenses on the windshield as an oily, insoluble film. After some time, the vinyl material may lose enough plasticizer to cause it to crack. Phthalate esters may constitute a health hazard. Sometimes vinyl containers incorporating phthalate plasticizers are used to store blood. The esters are leached from blood bags made of PVC and may be partly responsible for shock lung, a condition that sometimes leads to death during a blood transfusion. The long-term effects of these plasticizers are, however, not known.

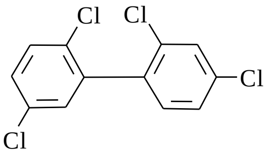
Recently, a rare and fatal form of liver cancer (angiosarcoma) was discovered among small numbers of workers in chemical companies making polyvinyl chloride. The monomer used in making PVC is vinyl chloride, a gas. The structure is shown in Table 1. Currently, industry is required to eliminate this health hazard by reducing or eliminating vinyl chloride from the atmosphere.



Dibutyl phthalate

$CH_2{=}CHCl$

Vinyl chloride



A polychlorinated biphenyl (PCB)

Other types of plasticizers once used were the polychlorinated biphenyls (PCB). These compounds and DDT have similar physiological effects, and they are even more persistent in the environment! The PCBs are actually a mixture of compounds that have had the hydrogens on the basic hydrocarbon structure, biphenyl, replaced with chlorines (from one to ten hydrogens can be replaced). One typical PCB that may be present in a plasticizer mixture is shown. PCBs are no longer being sold except for use in closed systems, where they cannot leak into the environment.

Disposal Problems

What do we do with all our waste? One of the most popular methods is to bury our garbage in landfills. However, as we run out of good places to bury our garbage, incineration appears to be an attractive method for solving the solid waste problem. It is currently estimated that about 300,000,000,000 kg of plastics are discarded globally per year with the United States being the highest per capita and it's growing at about 9% per year. About 50% is single use and less than 10% of US waste plastic is actually recycled. About 80% of this plastic currently ends up in landfill sites, and so plastics account for about 25% of the volume of landfill refuse. Microplastics are also found virtually everywhere on earth and are a cause for significant environmental concern due to their toxicity.

One option to reduce landfill waste would be to combust the plastics that burn readily. The new high-temperature incinerators are extremely efficient and can be operated with very little air pollution. It should also be possible to burn our garbage and generate electrical power from it, albeit with the unacceptable production of carbon dioxide, a critical greenhouse gas in climate change.

Ideally, we should either recycle all our wastes or just not produce the waste in the first place. Plastic waste consists of about 55% polyethylene and polypropylene, 20% polystyrene, and 11% PVC. All these polymers are thermoplastics and can be recycled. They can be resoftened and remolded into new goods. Unfortunately, thermosetting plastics (cross-linked polymers) cannot be remelted. They decompose on high-temperature heating. Thus, thermosetting plastics should not be used for "disposable" purposes. Alternative techniques to simple reforming are depolymerisation. This allows us to recover the monomers for purification and potential repolymerisation. The depolymerisation of PET (a polyester found in soft drink bottles) will be carried out as part of this experiment. Polyester clothing can be recycled and reused in new polyester product and polyester clothing can be made from recycled PET. In order to recycle plastics effectively, we must sort the materials according to the various types. This requires will power as well as knowledge about the plastics that we are discarding. Neither requirement is easily effected. Even in areas where plastic is collected for recycling, all is not what is seems as some is not actually recycled and it may often to transported long distances where it *may* be recycled.

Littering Problems

Plastics, if they are well made, will not corrode or rust, and they last almost indefinitely. Unfortunately, these desirable properties also lead to a problem when plastics are buried in a landfill or thrown on the landscape - they do not decompose. Currently, research is being undertaken to discover plastics that are biodegradable or photodegradable, so that either microorganisms or light from the sun can decompose our litter and garbage. Some success has been achieved. Recently, an increasing number of jurisdictions have started to ban the use of single use plastics.

Fire Hazards

Numerous injuries are caused by clothing made of polymers, especially children's clothing. Many of these organic fibers burn readily. To combat this problem, chemists have developed flame-retardant fabrics, especially for children's sleepwear.

Toxic gases are sometimes liberated when plastics burn. For example, hydrogen chloride is generated when PVC is burned, and hydrogen cyanide when polyacrylonitriles are burned. This presents a problem associated with fires involving these polymers.

Energy Shortage

The demand for energy has increased at an alarming rate, leading to an on going energy crisis. The production of polymers requires petroleum as a raw material and as a source of energy to conduct manufacturing. Unfortunately, fossil fuels are a nonrenewable resource, and as their availability decreases, we shall have an even greater problem. On the other hand, natural substances, such as cotton are renewable resources; perhaps for some uses they would actually be better and less costly than the synthesized polymers. There are many plastics, however, that are superior to natural materials. Surely the answer lies in using ***and reusing*** plastics wisely when other alternatives are not available.

EXPERIMENT

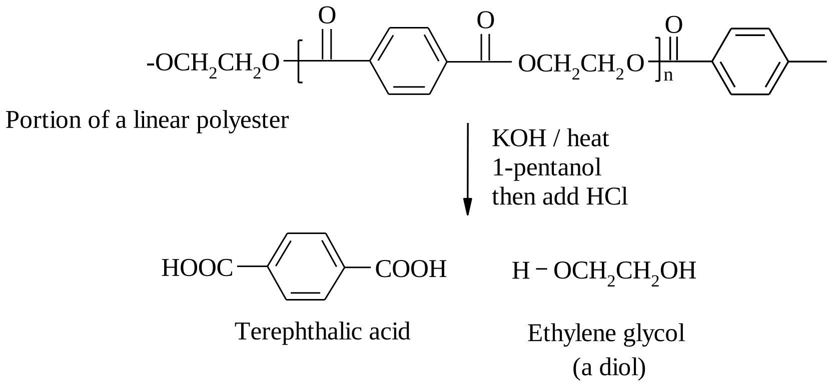
There are two parts to this experiment. In the first part, a polyester will be "recycled" from a PETE soft drink bottle by depolymerisation using a base promoted saponification using a reflux apparatus to isolate and recover one of the raw monomers. Since the plastic is a polyester, it undergoes the reactions that are characteristic of esters[2] and in this case, it is ester hydrolysis under basic conditions[3].

The second part is a short demonstration of the synthesis of the polyamide nylon. Nylon is an amide and the nylon synthesis is an example of one of the common ways to make an amide in the laboratory setting by the reaction of an acyl halide with an amine[4].

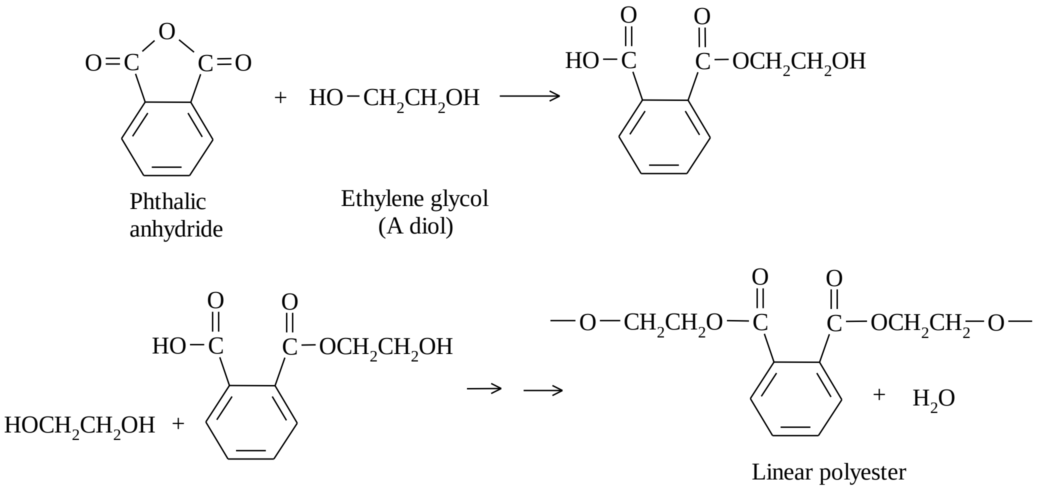
These polymers represent some of the most important commercial plastics.

A. POLYESTERS

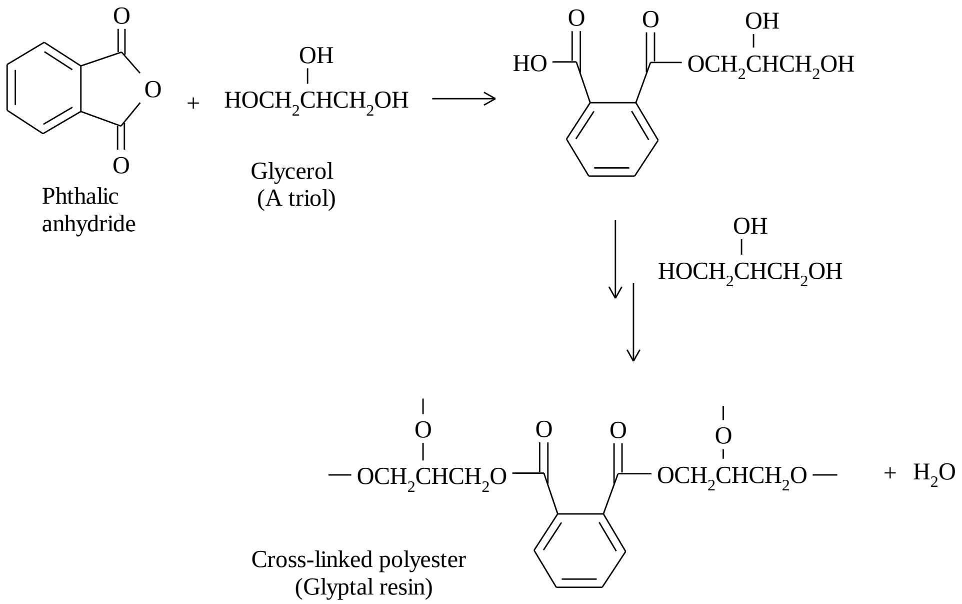
Polyesters are examples of condensation polymers. Polyethyleneterephthalate (PET), a linear polyester, will be depolymerised and the terephthalic acid recovered by the hydrolysis of the ester linkages in the polyester using potassium hydroxide in refluxing pentanol:



In principle it is possible to use the product to make other polymers or other chemicals. A linear polyester will be prepared as follows:



This linear polyester is isomeric with Dacron (which is prepared from terephthalic acid and ethylene glycol). Dacron and the linear polyester made in this experiment are both thermoplastics.

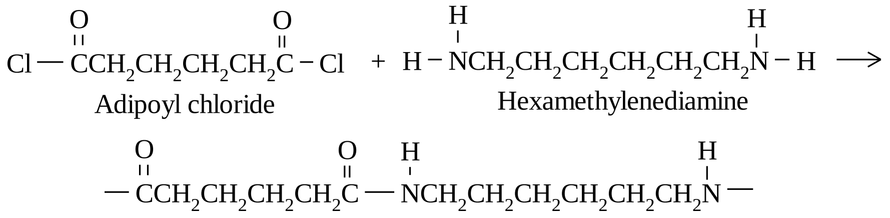


If more than two functional groups are present in one of the monomers, then the polymer chains can be linked to one another (cross-linked) to form a three-dimensional network. Such structures are usually more rigid than linear structures and are useful in making paints and coatings and are classified as thermosetting plastics. The polyester Glyptal preparation is shown above.

The reaction of phthalic anhydride with a diol (ethylene glycol) is described in the procedure. This linear polyester is compared with the cross-linked polyester (Glyptal) prepared from phthalic anhydride and a triol (glycerol).

B. POLYAMIDE (NYLON)

The reaction of a dicarboxylic acid (or one of its derivatives) with a diamine leads to a linear polyamide through a condensation reaction. Nylon and Kevlar, familiar for its strength and application in bullet-proof vests *etc*. are examples of polyamides. Commercially, nylon 6-6 (so called because each of the monomer units has 6 carbons) is made from adipic acid (1,6-hexandioic acid) and hexamethylenediamine (1,6-diaminohexane). In this experiment, the more reactive acid chloride is used instead of adipic acid to prepare nylon:



$$Cl-\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}-Cl \quad + \quad H-\overset{\overset{H}{|}}{N}CH_2CH_2CH_2CH_2CH_2CH_2\overset{\overset{H}{|}}{N}-H \longrightarrow$$

Adipoyl chloride

Hexamethylenediamine

$$-\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}CH_2CH_2CH_2CH_2CH_2CH_2\overset{\overset{H}{|}}{N}-$$

Nylon 6-6

The acid chloride is dissolved in cyclohexane and this is added **carefully** to hexamethylenediamine dissolved in water. Since these liquids do not mix, two layers will form. At the point of contact between the layers (the interface), the nylon forms. With care, the nylon can be drawn out continuously to form a long strand of nylon. Imagine how many molecules have been linked in this long strand! It is a fantastic number.

REFERENCES

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