

MODULE 3 SYNTHETIC DYES AND FIBRES

Unit 1	Synthetic Fibres
Unit 2	Polymer Fibres
Unit 3	Polyesters and Polyamide Fibres
Unit 4	Polyurethanes, Cellulose and Polyacrylonitrile
Unit 5	Aramids, Poly (methyl methacrylate) and Polycarbonate

UNIT 1 SYNTHETIC FIBRES

CONTENTS

1.0	Introduction
2.0	Objectives
3.0	How to Study this Unit
4.0	Main Content
4.1	Definition of Synthetic Fibres and Synthetic Dyes
4.2	Kinds of Synthetic Fibres
4.3	Properties and Application of Synthetic Fibres
4.4	Kinds of Synthetic Dyes
4.5	Dyes for Man- Made Fibres
5.0	Conclusion
6.0	Summary
7.0	Tutor -Marked Assignment
8.0	References/Further Reading

1.0 INTRODUCTION

Synthetic or man-made fibres generally come from synthetic materials such as petrochemicals. But some types of synthetic fibres are manufactured from natural cellulose, including rayon, modal, and the more recently developed Lyocell. Cellulose-based fibres are of two types, regenerated or pure cellulose such as from the cupro-ammonium process and modified cellulose- the cellulose acetates.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- define synthetic dyes and fibres
- differentiate between synthetic dye and fibre
- identify each kind of synthetic dye and fibre
- identify the properties and applications of synthetic dye and fibre

3.0 HOW TO STUDY THIS UNIT

1. You are expected to read carefully, through this unit at least twice before attempting to answer the self-assessment questions or the tutor marked assignments.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers.
3. Share your difficulties with your course mates, facilitators and by consulting other relevant materials particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

4.0 MAIN CONTENT

4.1 Definition of Synthetic Fibres

Synthetic fibres are a subset of man-made fibres, which are based on synthetic chemicals (often from petrochemical sources) rather than arising from natural materials by a purely physical process.

While, Synthetic dyes are man-made dyes that impart better properties upon the dyed materials.

4.2 Kinds of Fibres

- (a) Cellulose fibres are a subset of man-made fibres, regenerated from natural cellulose. The cellulose comes from various sources. Modal is made from beech trees, bamboo fiber is a cellulose fiber made from bamboo, soy silk is made from soybeans, seacell is made from seaweed, etc.
- (b) Mineral fibres:
 - Fiberglass made from specific glass, and optical fiber, made from purified natural quartz, are also man-made fibres that come from natural raw materials.
 - Metallic fibres can be drawn from ductile metals such as copper, gold or silver and extruded or deposited from more brittle ones, such as nickel, aluminum or iron.
 - Carbon fibres are often based on carbonised polymers, but the end product is pure carbon.

(c) Polymer fibres

Polymer fibres are a subset of man-made fibres, which are based on synthetic chemicals (often from petrochemical sources) rather than arising from natural materials by a purely physical process. These fibres are made from:

- polyamide nylon,
- PET or PBT polyester
- phenol-formaldehyde (PF)
- polyvinyl alcohol fiber (PVA)
- polyvinyl chloride fiber (PVC)
- polyolefins (PP and PE)
- acrylic polyesters, pure polyester PAN fibres are used to make carbon fiber by roasting them in a low oxygen environment. Traditional acrylic fiber is used more often as a synthetic replacement for wool. Carbon fibres and PF fibres are noted as two resin-based fibres that are not thermoplastic, most others can be melted.
- aromatic polyamids (aramids) such as Twaron, Kevlar and Nomex thermally degrade at high temperatures and do not melt. These fibres have strong bonding between polymer chains
- polyethylene (PE), eventually with extremely long chains / HMPE (e.g. Dyneema or Spectra).
- elastomers can even be used, e.g. spandex although urethane fibres are starting to replace spandex technology.
- polyurethane fiber

(d) **Microfibres:** Micro fibres in textiles refer to sub-denier fiber (such as polyester). Denier and Detex are two measurements of fiber yield based on weight and length. If the fiber density is known you also have a fiber diameter, otherwise it is simpler to measure diameters in micrometers. Microfibres in technical fibres refer to ultra finefibres (glass or meltblown thermoplastics) often used in filtration. Newer fiber designs include extruding fiber that splits into multiple finer fibres. Most synthetic fibres are round in cross-section, but special designs can be hollow, oval, star-shaped or trilobal. The latter design provides more optically reflective properties. Synthetic textile fibres are often crimped to provide bulk in a woven, non woven or knitted structure. Fiber surfaces can also be dull or bright. Dull surfaces reflect more light while bright tends to transmit light and make the fiber more transparent.

SELF ASSESSMENT EXERCISE 1

Mention two kinds of synthetic fibres

4.3 Properties and Applications of Synthetic Fibres

Table 1.1: Application of Synthetic Fibres

Polymer family and type	Common Names & Trade Names	Deniers (gm/9,000 m)	Tensile Strength (gm/denier)	Elongation at Break (%)	Initial Modulus (gm/denier)	Apparel and Home-Furnishing Applications	Industrial Applications
Polyamides							
Polycaprolactam (textile fibre)	nylon 6 (textile)	1.5-5	4.5-6.8	23-43	25-35	hosiery, lingerie, sports garments, soft-sided luggage, upholstery	no significant applications
Polyhexamethylenedipamide (textile fibre)	nylon 6,6 (textile)	1.5-5	4.5-6.8	23-43	25-35	hosiery, lingerie, sports garments, soft-sided luggage, upholstery	no significant applications
Polycaprolactam (industrial fibre)	nylon 6 (industrial)	1.5-5	8.5-9.5	12-17	33-46	no significant applications	tyres, ropes, seat belts, parachutes, fishing lines and nets, hoses
Polyhexamethylenedipamide (industrial fibre)	nylon 6,6 (industrial)	1.5-5	8.5-9.5	12-17	33-46	no significant applications	tyres, ropes, seat belts, parachutes, fishing lines and nets, hoses
Aramids							
Poly- <i>p</i> -phenyleneterephthalamide	Kevlar, Twaron, Technora	1.0-1.5	25-30	3-6	500-1,000	no significant applications	radial tyre belts, bulletproof vests, reinforcement for boat hulls and aircraft panels
Poly- <i>m</i> -phenyleneis	Nomex, Conex	2-5	3-6	2-30	130-150	no significant	filter bags for hot stack

oph-thalamide						applications	gases, flame-resistant clothing
Polyesters							
Poethyleneterephthalate	Dacron, Terylene, Trevira	1.5-5	4.7-6.0	35-50	25-50	permanent-press clothing, fibre fill insulation, carpets	sewing thread, seat belts, tyre yarns, non-woven fabrics
Polyacrylonitrile							
Acrylic (>85%) acrylonitrile	Acrilan, Creslan, Courtelle	2-8	2.5-4.5	27-48	25-63	substitute for wool-- <i>e.g.</i> , in sweaters, hosiery, blankets	filters, battery separators, substitute for asbestos in cement
Modacrylic(35-85%) acrylonitrile	Verel, SEF	2-8	2.5-4.5	27-48	22-56	flame-resistant clothing-- <i>e.g.</i> , artificial fur, children's sleepwear	flame-resistant awnings, tents, boat covers
Polyolefins							
Polypropylene	Herculon, Marvess	2-10	5-9	15-30	29-45	upholstery, carpets, carpet backing	ropes, nets, disposable non-woven fabrics
Polyethylene							
Regular		2-10	2-4	20-40	--	no significant applications	cordage, webbing
High-Modulus	Dyneema, Spectra	--	30-35	2.7-3.5	1,370-2,016	no significant applications	reinforcement for boat hulls, bulletproof vests
Polyurethane	spandex, Lycra	2.5-20	0.6-1.5	400-600	--	stretch fabrics-- <i>e.g.</i> , for sportswear, swimsuits	no significant applications

4.4 Kinds of Synthetic Dyes

There are various kinds of synthetic dyes that impart colours on dyed materials. These are:

- a. **Acid Dyes:** They come in a wide variety of colours, it is fairly fast to light and to washing. It is named acid dyes because they work best when applied in an acid bath. It is mainly used on nylon, silk and wool.
- b. **Azoic (or Naphthol) Dyes:** This type of dyes is extremely fast to light, it is commonly used to dye a material red, orange or maroon. It is mainly used in cotton.
- c. **Basic Dyes:** This type of dye is just fair when it comes to fastness to light and to washing, however this type can create a brilliant colour. It is mainly used on natural and acrylic fibres, it is also sometimes used for wool and silk. This dye is also used to colour paper. **Acetic acid** is usually added to the dyebath to help in the quick penetration of the dye onto the fiber.
- d. **Chrome (or Mordant) Dyes:** This type of dye is fairly fast to light and to washing, it is especially useful for black and navy shades. The choice of mordant is very important as different mordants can alter the final colour significantly, it is important to know also that many mordants, particularly those in the hard metal category can be hazardous to health, which is why caution should be followed when using it. It is mainly used for wool and silk.
- e. **Mordant** is a chemical that is mixed with the dye and the fiber, the modern mordants are dichromates and chromium complexes, that is why it is also called chrome dye.
- f. **Developed (or Diazo) Dyes** are used to treat certain dyed fabrics to improve their fastness to light and to washing and also to change fabric's colour. The treatments are used primarily on cotton. Diazotizing is the treatment which involves the use of chemical called a developer. It is mainly used on cotton.
- g. **Direct Dyes** this type is one of the easiest to use and has a wide range of colours, it is not fast to washing, but its fastness is often improved by more treatment. It is mainly used on cotton, rayon leather, wool, silk and nylon. It is also used as pH indicators and as biological stains.
- h. **Disperse (or Acetate) Dyes** this dyes is finely ground in the presence of dispersing agent, its dyeing rate is greatly influenced by the dispersing agent used during the grinding. Disperse dyes were developed because other dyes would not work with acetate it is also used on different manmade fibres, including acrylic, acetate, and polyester fibres.

- i. **Reactive (or Fiber-reactive) Dyes:** these types of dye have a good fastness to light and to washing. Reactive dyes create strong chemical bonds with the material being dyed which makes it the most permanent of dyes. This dye is by far the best choice for dyeing cotton, nylon, wool and other cellulose fibres at home or in the art studio.
- j. **Sulphur Dyes:** these dyes are especially fast to washing and the best for material that is washed frequently. Sulphur dyes are colourless (upon application), but upon exposure to air they are oxidized and turn into their respective colours. They come mainly in dark, dull colours and used on cotton, linen and rayon.
- k. **Vat Dyes:** This type is superior compared to the other dye when it comes to its fastness to light and to washing. Vat dyes like sulphur dyes must be oxidized before their real colour comes out. This dye is mainly used for cotton, linen, wool and silk. The indigo colour of blue jeans is vat dye.

4.5 Dyes for Man- Made Fibres

The first man-made fibre to achieve commercial significance was viscose rayon, in the early 1900s. This is chemically similar to cotton (in other words it is a cellulosic fibre) and so the dyes already available for cotton were used on viscose rayon. At the time these were mainly direct, vat, azoic and sulphur dyes, but since the 1960s fibre-reactive dyes have come to be widely used on all cellulosic fibres. In the 1930s, when acetate rayon appeared, the existing dyes were not very suitable, with the notable exception of the natural dye logwood black, which was already being used on silk and wool. A new class of dyes eventually to be called disperse dyes, was developed which allowed a full range of shades to be successfully applied to acetate rayon.

In the 1940s and 1950s the truly synthetic fibres, such as the polyamides (nylon), polyesters and acrylics, began to appear commercially. Disperse dyes proved to be particularly suitable for polyester and so the importance of this class of dye increased enormously. Because both fibres and dyes have been modified since then, polyamides are now dyed mainly with acid dyes, and acrylics mainly with modified basic dyes.

Over the last twenty to thirty years, developments in dye chemistry have enabled the man-made fibre to be dyed with better fastness to light and washing, and in an ever increasing range of colours.

5.0 CONCLUSION

It could be seen that synthetic or man-made fibres generally come from synthetic materials such as petrochemicals. Like fibres, synthetic dyes are also man made from various materials such as inorganic and metallic compounds. Synthetic fibres have wide application especially in clothing industry and other products being used in our day to day activities. Dyes also contribute to aesthetics by imparting various colours depending on convenience.

6.0 SUMMARY

In this unit, we have learnt that:

- polymer fibres are a subset of man-made fibres, which are based on synthetic chemicals (often from petrochemical sources) rather than arising from natural materials by a purely physical process
- microfibrillar technical fibres refer to ultra finefibres (glass or melt blown thermoplastics) often used in filtration
- reactive dye is by far the best choice for dyeing cotton, nylon, wool and other cellulose fibres at home or in the art studio
- disperse dyes proved to be particularly suitable for polyester, and the different kinds of synthetic dyes and fibres
- the application of synthetic dyes and fibres.

7.0 TUTOR-MARKED ASSIGNMENT

- i. What are polymer fibres
- ii. In a tabular form, mention three of the polymer fibres and their application
- iii. Write short notes on the following
 - a. cellulose fibre
 - b. sulphur dye

8.0 REFERENCES/FURTHER READING

Synthetic Fibres: Nylon, Polyesters, Acrylic and Polyolefins; Edited by J.E McIntyre.

Woodhead Textiles Series No. 36, Woodhead Publishing Limited, 2009.

UNIT 2 POLYMER FIBRES

CONTENTS

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
 - 3.1 Definition of Polymer Fibres
 - 3.2 Kinds of Synthetic Polymers
 - 3.3 Polyethylene
 - 3.4 Polypropylene
 - 3.5 Poly (vinyl) chloride PVC
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor- Marked Assignment
- 7.0 References/Further Reading

1.0 INTRODUCTION

Polymer fibres are a subset of man-made fibres, which are based on synthetic chemicals (often from petrochemical sources) rather than arising from natural materials by a purely physical process. It is important to point out that fibres are always made of polymers which are arranged into crystals. They have to be able to pack into a regular arrangement in order to line up as fibres. (In fact, fibres are really a kind of crystal, a really long kind of crystal.). A polymeric fibre is a polymer whose chains are stretched out straight (or close to straight) and lined up next to each other, all along the same axis.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- define polymeric fibre
- identify the kind of polymeric synthetic fibres
- explain the production and applications of polymers made from olefins

3.0 HOW TO STUDY THIS UNIT

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4.0 MAIN CONTENT

4.1 Definition of Polymer Fibres

Polymer fibres are a subset of man-made fibres, which are based on synthetic chemicals (often from petrochemical sources) rather than arising from natural materials by a purely physical process.

4.2 Kinds of Synthetic Polymers

(i) Olefins

Olefin includes the varieties of polyethylene, polystyrene and polypropylene. A very light fibre, Olefin particularly resembles wool; it is soil resistant and is a good heat insulator. Herculon and Vectra are trade names.

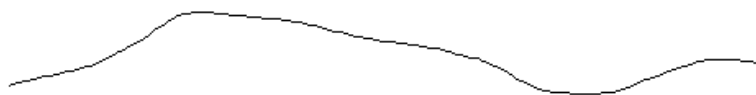
(ii) Acrylics

Acrylics are made from petroleum. They have wool like fibres. It is not as strong as polyester/nylon but it is soft and warm to handle. It washes and dry clean well. It is very resistant to UV light but sensitive to heat. It is moth proof. Modacrylics are also named because they have been chemically modified to offer good flame resistance. They do not wrinkle or crease easily. It can shrink with hot heat. Trade names include (unmodified) Acrilian, Orlon, Verel, Sef, Zefran, and Dynel (which also comes modified).

(iii) Polyesters

Polyester is a petroleum/oil byproduct. It is very strong and easy to wash. It dries quickly and has good shape retention. It is shrink and crease resistant. It is resistant to sunlight, perspiration and moths and has a low absorbency. A light fibre resembling wool or silk, polyester is often blended with natural fibres. It is an ideal fibre for sheeting when mixed with cotton. Dacron, Fortrel, and Kodel are trade names. Dacron is used as a substitute for the base in cushions and upholstery.

polyethylene is much stronger than branched polyethylene, but branched polyethylene is cheaper and easier to make.



A molecule of linear polyethylene, or HDPE

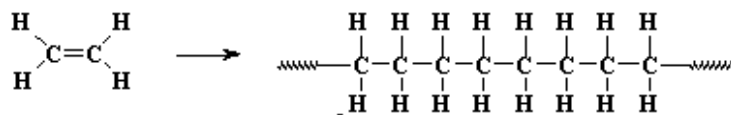


A molecule of branched polyethylene, or LDPE

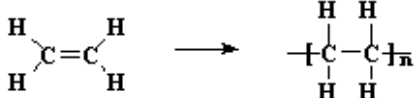
Linear polyethylene is normally produced with molecular weights in the range of 200,000 to 500,000, but it can be made even higher. Polyethylene with molecular weights of three to six million is referred to as ultra-high molecular weight polyethylene, or UHMWPE. UHMWPE can be used to make fibres which are so strong and are used in bullet proof vests. Large sheets of it can be used instead of ice for skating rinks.

Polyethylene is vinyl polymer, made from the monomer ethylene. Branched polyethylene is often made by free radical vinyl polymerisation. Linear polyethylene is made by a more complicated procedure called Ziegler-Natta polymerisation. UHMWPE is made using metallocene catalysis polymerisation.

But Ziegler-Natta polymerisation can be used to make LDPE, too. By copolymerising ethylene monomer with a alkyl-branched comonomer such as one gets a copolymer which has short hydrocarbon branches. Copolymers like this are called *linear low-density polyethylene*, or LLDPE. BP produces LLDPE using a co-monomer with the catchy name 4-methyl-1-pentene, and sells it under the trade name Innovex. LLDPE is often used to make things like plastic films.

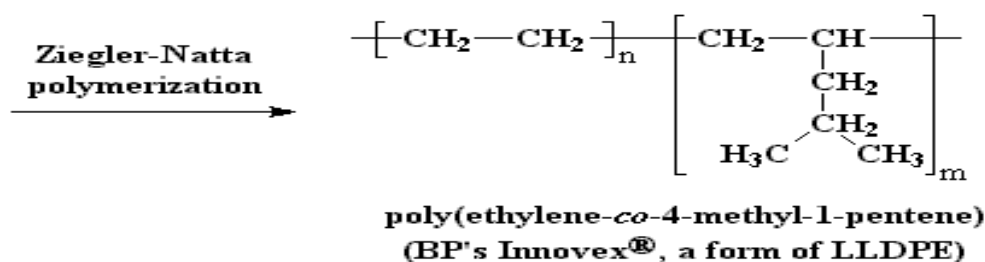
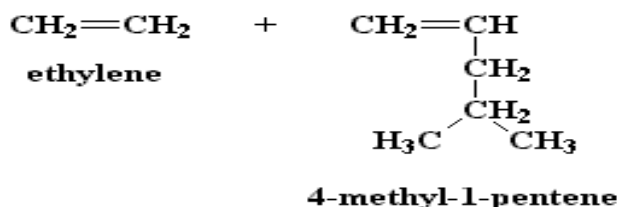
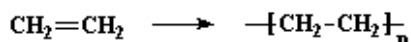


This can get tedious to draw, so we often use shorthand like this.



(Note: A line drawn between two atoms represents a pair of electrons shared by those atoms, which constitutes a chemical bond. Two lines represent two pairs of shared electrons, a double bond.)

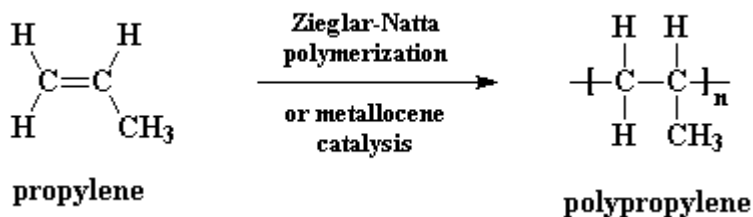
And when we're feeling really lazy we just draw it like this:



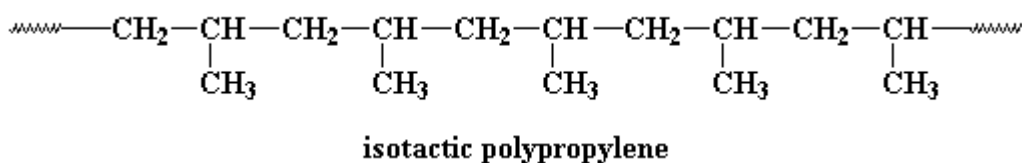
4.4 Polypropylene

Polypropylene is one of those rather versatile polymers. It serves double duty, both as plastic and fibre. As a plastic it is used to make things like dishwasher-safe food containers. It can do this because it is stable to heat below 160°C. Polyethylene, a more common plastic, will anneal at around 100°C, which means that polyethylene dishes will warp in the dishwasher. As a fibre, polypropylene is used to make indoor-outdoor carpeting, the kind that you always find around swimming pools and miniature golf courses. It works well for outdoor carpet because it is easy to make coloured polypropylene, and because polypropylene does not absorb water, like nylon.

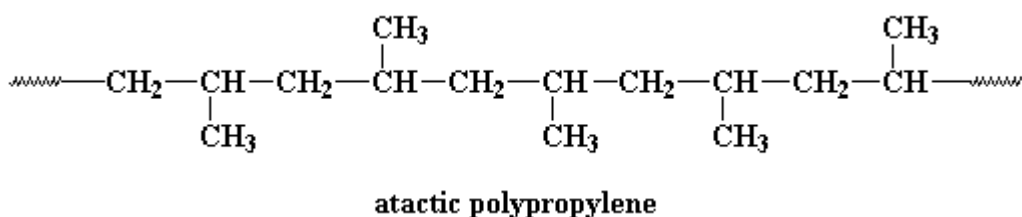
Structurally, it's a vinyl polymer, and is similar to polyethylene, only that on every other carbon atom in the backbone chain has a methyl group attached to it. Polypropylene can be made from the monomer propylene by Ziegler-Natta polymerisation and by metallocene catalysis polymerisation.



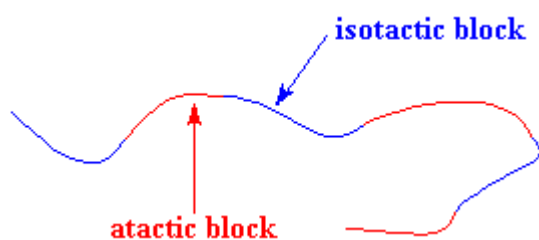
Research is being conducted on using metallocene catalysis polymerization to synthesise polypropylene. Metallocene catalysis polymerisation can do some pretty amazing things for polypropylene. Polypropylene can be made with different tacticities. Most polypropylene we use is *isotactic*. This means that all the methyl groups are on the same side of the chain, like this:



But sometimes we use *atactic* polypropylene. *Atactic* means that the methyl groups are placed randomly on both sides of the chain like this:



However, by using special metallocene catalysts, it is believed that we can make polymers that contain blocks of isotactic polypropylene and blocks of atactic polypropylene in the same polymer chain, as is shown in the picture:



This polymer is rubbery, and makes a good elastomer. This is because the isotactic blocks will form crystals by themselves. But because the isotactic blocks are joined to the atactic blocks, the little hard clumps of crystalline isotactic polypropylene are tied together by soft rubbery tethers of atactic polypropylene. Indeed atactic polypropylene would be rubbery without help from the isotactic blocks, but it will not be very strong. The hard isotactic blocks hold the rubbery isotactic material together, to give the material more strength. Most kinds of rubber have to be crosslinked to give them strength, but not polypropylene elastomers.

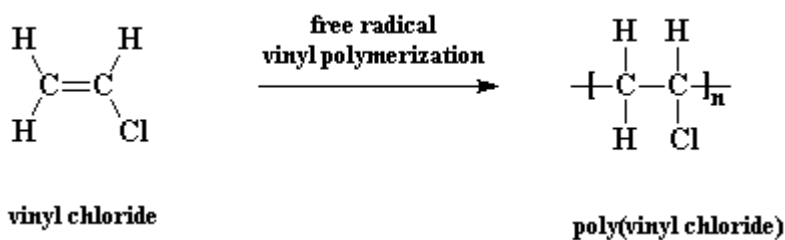
Elastomeric polypropylene, as this copolymer is called, is a kind of thermoplastic elastomer. However, until the research is completed, this type of polypropylene will not be commercially available.

4.5 Poly (vinyl chloride) PVC

Poly (vinyl chloride) is the plastic known at the hardware store as PVC. This is the PVC from which pipes are made, and PVC pipe is everywhere. The plumbing in modern day structures is probably PVC pipe. PVC pipe is what rural high schools with small budgets use to make goal posts for their football fields. But there's more to PVC than just pipe. The "vinyl" siding used on houses is made of poly(vinyl chloride). Inside the house, PVC is used to make linoleum for the floor. In the seventies, PVC was often used to make vinyl car tops.

PVC is useful because it resists two things that are opposite of each other: fire and water. Because of its water resistance it is used to make raincoats and shower curtains, and of course, water pipes. It has flame resistance, too, because it contains chlorine. When you try to burn PVC, chlorine atoms are released, and chlorine atoms inhibit combustion.

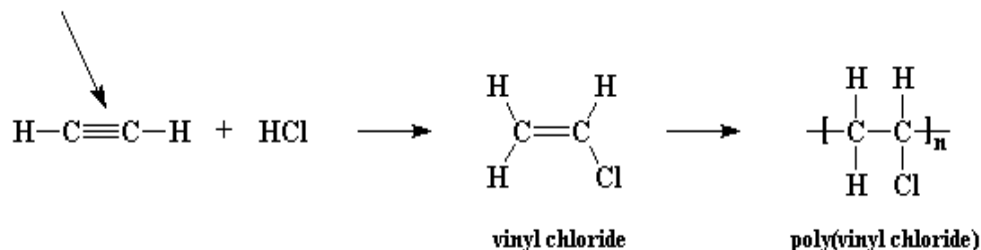
Structurally, PVC is a vinyl polymer. It is similar to polyethylene, but on every other carbon in the backbone chain, one of the hydrogen atoms is replaced with a chlorine atom. It is produced by the free radical polymerization of vinyl chloride.



PVC was one of those odd discoveries that actually had to be made twice. It seems around a hundred years ago, a few German entrepreneurs

decided they were going to make loads of cash lighting people's homes with lamps fueled by acetylene gas. Would you believe it?, right about the time they had produced tons of acetylene to sell to everyone who was going to buy their lamps, new efficient electric generators were developed which made the price of electric lighting drop so low that the acetylene lamp business was finished. That left a lot of acetylene lying around.

leftover acetylene from the
acetylene lamp fiasco



So in 1912 one German chemist, Fritz Klatte decided to do something with it, and reacted some acetylene with hydrochloric acid (HCl). Now, this reaction will produce vinyl chloride, but at that time no one knew what to do with it, so he put it on the shelf, where it polymerized over time. Not knowing what to do with the PVC he had just invented, he told his bosses at his company, Greisheim Electron, who had the material patented in Germany. They never figured out a use for PVC, and in 1925 their patent expired. However, in 1926 the very next year, an American chemist; Waldo Semon was working at B.F. Goodrich when he independently invented PVC. But unlike the earlier chemists, it dawned on him that this new material would make a perfect shower curtain. He and his bosses at B.F. Goodrich patented PVC in the United States. Tons of new uses for this wonderful waterproof material followed, and PVC was a smash hit the second time around.

SELF ASSESSMENT EXERCISE 2

- i. Propose a simple equation for the production low density polyethylene
- ii. Differentiate between polyethylene and polypropylene.

5.0 CONCLUSION

Polymer fibres are a subset of man-made fibres, which are based on synthetic chemicals. Two or more fibres can be combined in one yarn to maximize the strength and minimize the weaknesses of each. For example, natural and artificial fibres can be combined to retain the texture and appearance of the natural yarn. Olefins, polyesters, polyamide etc are common examples of synthetic fibres of importance.

6.0 SUMMARY

In this unit, we have learnt that:

- It is well known that fibres are always made of polymers which are arranged into crystals
- Polyethylene is probably the polymer you see most in daily life. Polyethylene is the most popular plastic in the world. This is the polymer from which grocery bags, shampoo bottles, children's toys, and even bullet proof vests are made
- Polypropylene is one of those rather versatile polymers out there. It serves double duty, both as plastic and fibre
- Poly (vinyl chloride) is the plastic known at the hardware store as PVC. It is used in the manufacture of pipes.

7.0 TUTOR-MARKED ASSIGNMENT

- i. What is Ziegler-Natta polymerisation?
- ii. With relevant examples explain the concept 'Fibres are known to be polymers'

8.0 REFERENCES/FURTHER READING

Burke, J. (1978). *Connections*. Boston: Little, Brown and Co.

Fenichell, S. (1996). *Plastic: The Making of a Synthetic Century*. New York: HarperCollins

UNIT 3 POLYMERS AND POLYAMIDE FIBRES

CONTENTS

- 1.0 Introduction
- 2.0 Objectives
- 3.0 How to Study this Unit
- 4.0 Main Content
 - 4.1 Definition of Nylons and Polyesters
 - 4.2 Nylons
 - 4.3 Polyesters
- 5.0 Conclusion
- 6.0 Summary
- 7.0 Tutor- Marked Assignment
- 8.0 Reference/Further Reading

1.0 INTRODUCTION

Nylon's first real success came with its use in women's stockings, in about 1940. They were a big hit, but they became hard to get, because a year later the United States entered World War II, and nylon was needed to make war materials, like parachutes and ropes. However, polyesters can be both plastics and fibres.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- identify materials made of polyester and polyamide fibres
- explain the chemical principles involved in the production of polyester and polyamide fibres
- describe the applications of polyester and polyamide fibres

3.0 HOW TO STUDY THIS UNIT

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4.0 MAIN CONTENT

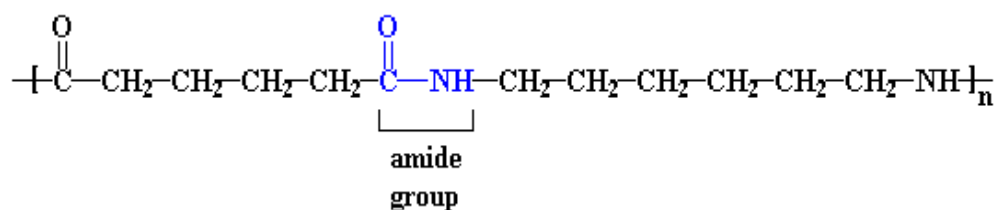
4.1 Definitions of Nylon and Polyester

Nylons are also called polyamides, because of the characteristic amide groups in the backbone chain.

Polyesters are the polymers, in the form of fibres, which were used back in the seventies to make wonderful disco clothing.

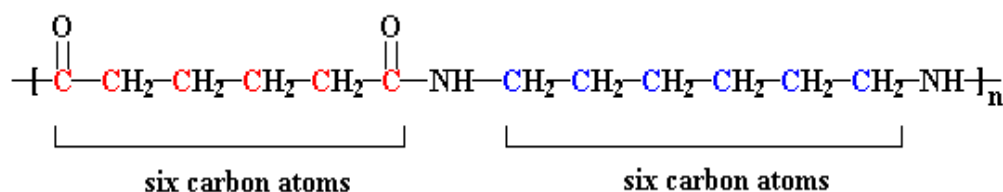
4.2 Nylons

Nylons are one of the most common polymers used as a fibre. Nylon is found in clothing all the time, but also in other places, in the form of a thermoplastic.

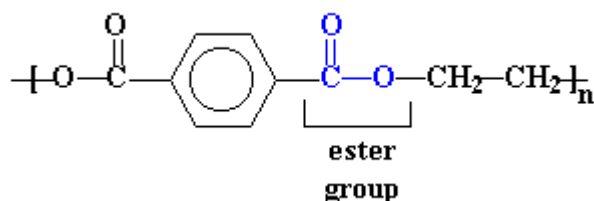


Nylons are also called polyamides, because of the characteristic amide groups in the backbone chain. Proteins, such as the silk nylon, are also polyamides. These amide groups are very polar, and can hydrogen bond with each other. Because of this, and because the nylon backbone is so regular and symmetrical, nylons are often crystalline and make very good fibres.

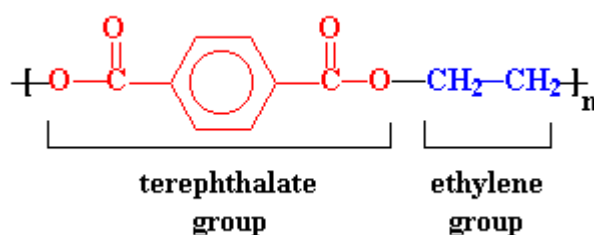
The nylon below is called nylon 6,6, because each repeat unit of the polymer chain has two stretches of carbon atoms, each being six carbon atoms long. Other nylons can have different numbers of carbon atoms in these stretches.



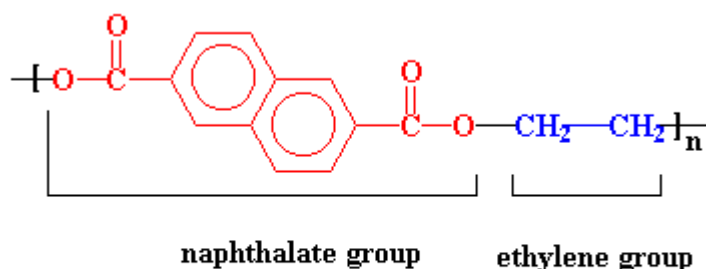
polyester film made by DuPont called Mylar. The balloons are made of a sandwich, composed of Mylar and aluminum foil. Materials like this, made of two kinds of material, are called composites. Polyesters have hydrocarbon backbones which contain ester linkages, hence the name.



The structure is called poly (ethylene terephthalate), or PET for short, because it is made up of ethylene groups and terephthalate groups.



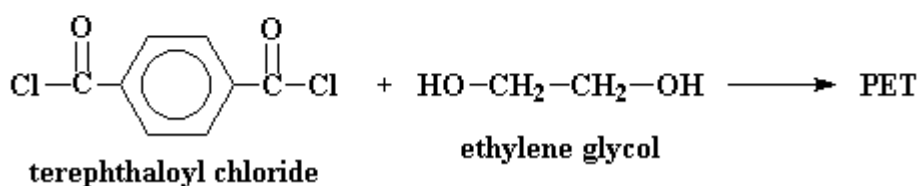
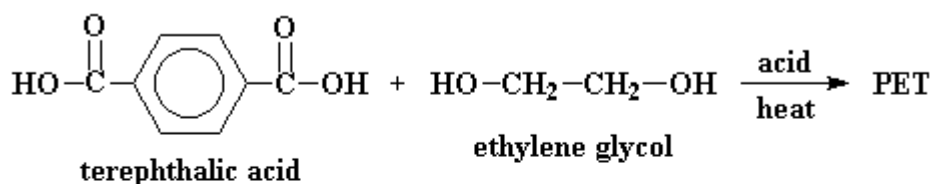
The ester groups in the polyester chain are polar, with the carbonyl oxygen atom having a somewhat negative charge and the carbonyl carbon atom having a somewhat positive charge. The positive and negative charges of different ester groups are attracted to each other.



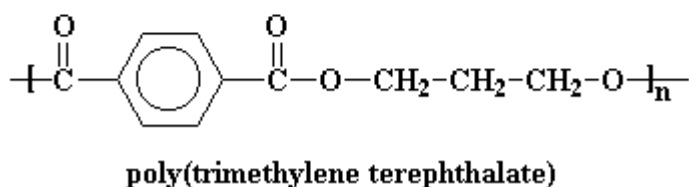
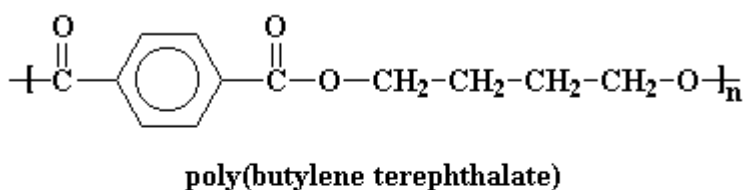
**Poly(ethylene naphthalate), the polymer
that bestows upon us the plastic jelly jar.**

This allows the ester groups of nearby chains to line up with each other in crystal form, which is why they can form strong fibres. The inventor who first discovered how to make bottles from PET was Nathaniel Wyeth.

There is a new kind of polyester that is been used for jelly jars and burnable bottles. It is poly (ethylene naphthalate), or PEN. In the big industrial plants where polyester is produced, it is normal to start off with a compound called dimethyl terephthalate. This is reacted with



There are two more polyesters in the market that are related to PET. There is poly(butylene terephthalate) (PBT) and poly(trimethylene terephthalate) (PTT). They are usually used for the same type of things as PET, but in some cases these perform better.



SELF ASSESSMENT EXERCISE

- i. Differentiate between a nylon and a polyester
- ii. What are the main chemical functional groups in both nylon and polyester?

5.0 CONCLUSION

Polyesters can be both plastics and fibres while nylon is mainly made up of fibres. They both contained repeating units of the corresponding monomeric unit. Nylons are also called polyamides, because of the characteristic amide groups in the backbone chain. There are different kinds of these products which have impacted positively to human life.

6.0 SUMMARY

In this unit, we have learnt that:

- nylons are some of the most common polymers used as fibre. Nylon is found in clothing all the time, but also in other places, in the form of a thermoplastic
- nylons are also called polyamides, because of the characteristic amide groups in the backbone chain
- polyesters are the polymers, in the form of fibres
- the commonly used forms of polyesters are: poly (ethylene terephthalate), or PET, poly (ethylene naphthalate), or PEN
- there are two more polyesters in the market that are related to PET. They are poly (butylene terephthalate) (PBT) and poly (trimethylene terephthalate) PTT. They are usually used for the same type of things as PET, but in some cases these perform better.

7.0 TUTOR-MARKED ASSIGNMENT

- i. Differentiate between PET and PEN
- ii. Propose a simple laboratory procedure for the manufacturing of nylon 6.

8.0 REFERENCE/FURTHER READING

Synthetic Fibres: Nylon, Polyester, Acrylic, Polyolefin: Edited by J E McIntyre, Woodhead Textiles Series No. 36, Woodhead Publishing Limited (2009).

UNIT 4 POLYURETHANES, CELLULOSE AND POLYACRYLONITRILE

CONTENTS

- 1.0 Introduction
- 2.0 Objectives
- 3.0 How to Study this Unit
- 4.0 Main Content
 - 4.1 Definition of Polyurethane, Cellulose and Polyacrylonitrile
 - 4.2 Polyurethanes
 - 4.2.1 Spandex
 - 4.3 Cellulose
 - 4.4 Polyacrylonitrile
 - 4.5 Polymers and Applications
- 5.0 Conclusion
- 6.0 Summary
- 7.0 Tutor- Marked Assignment
- 8.0 Reference/Further Reading

1.0 INTRODUCTION

If you are sitting on a padded chair right now, the cushion is more than likely made of polyurethane foam. Cellulose is one of many polymers found in nature. Wood, paper, and cotton all contain cellulose. Cellulose is an excellent fibre.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- identify the substances making up a polyurethanes
- define cellulose and its compositions
- discuss the nature, properties and uses of polyacrylonitrile.

3.0 HOW TO STUDY THIS UNIT

1. You are expected to read carefully, through this unit at least twice before attempting to answer the self-assessment questions or the tutor marked assignments.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers.
3. Share your difficulties with your course mates, facilitators and by

consulting other relevant materials particularly the internet.

- Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

4.0 MAIN CONTENT

4.1 Definition of Polyurethane, Cellulose and Polyacrylonitrile

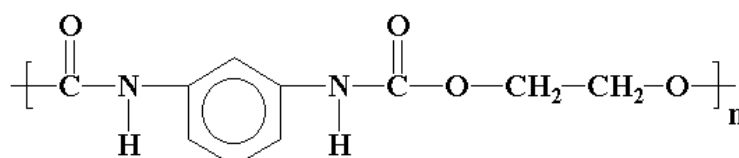
Polyurethanes are the most well-known polymers used to make foams. Polyurethanes are more than foam.

Cellulose is made of repeat units of the monomer glucose.

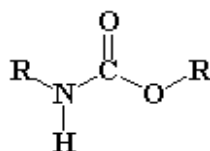
Polyacrylonitrile is a vinyl polymer, and a derivative of the acrylate family of polymers.

4.2 Polyurethanes

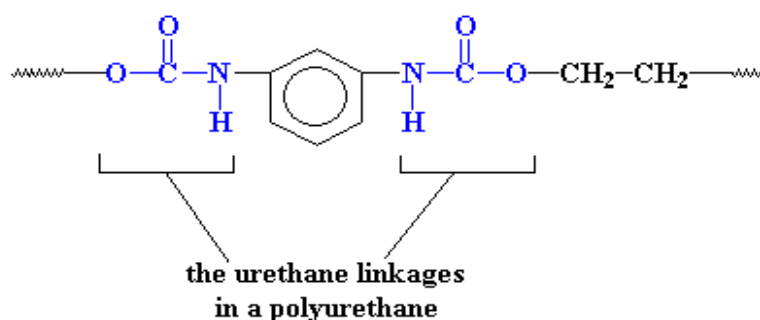
Polyurethanes are the single most versatile family of polymers there is. Polyurethanes can be elastomers, and they can be paints. They can be fibres, and they can be adhesives. A wonderful bizarre polyurethane is spandex. Of course, polyurethanes are called polyurethanes because in their backbones they have a *urethane* linkage.



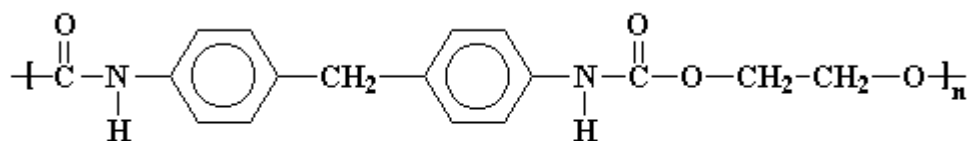
The structure above shows simple polyurethane, but polyurethane can be any polymer containing the urethane linkage in its backbone chain.



a urethane

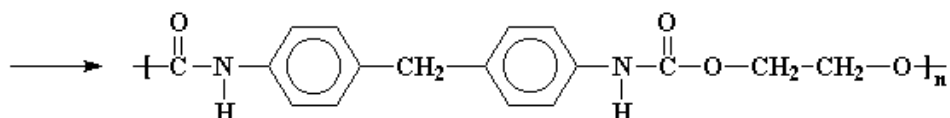
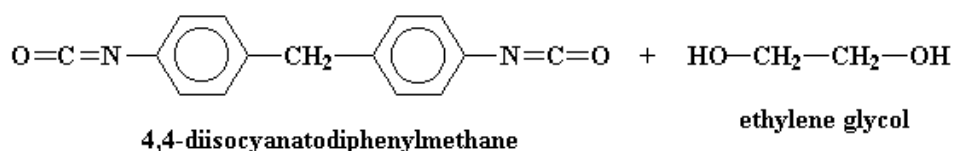


More sophisticated polyurethanes are possible, for example

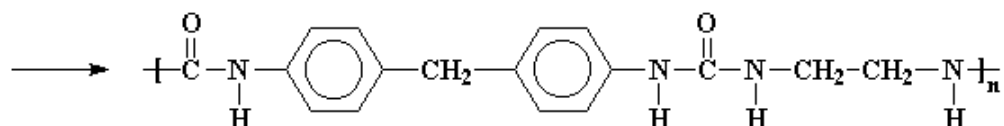
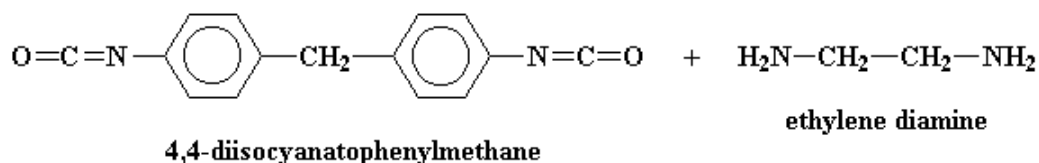


a more sophisticated polyurethane

Polyurethanes are made by reacting diisocyanates with di-alcohols;



Sometimes, the dialcohol is replaced with a diamine, and the polymer we get is a polyurea, because it contains a urea linkage, rather than a urethane linkage. But these are usually called polyurethanes, because they probably would not sell well with a name like polyurea.

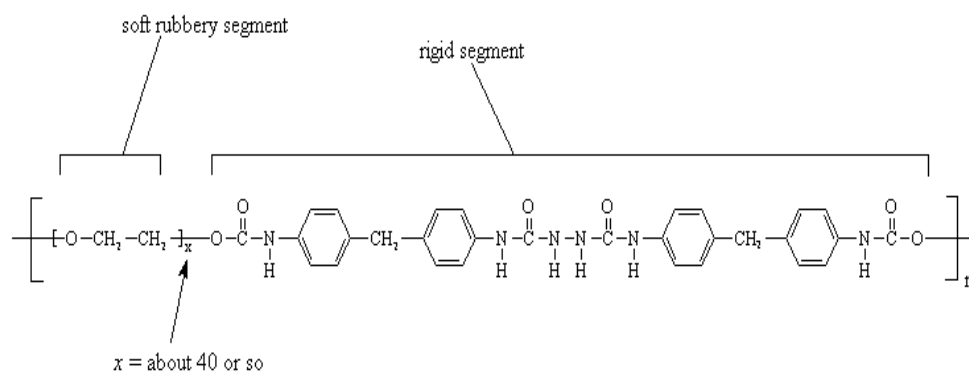


a polyurea

Polyurethanes can hydrogen bond very well and thus can be very crystalline. For this reason they are often used to make block copolymers with soft rubbery polymers. These block copolymers have properties of thermoplastic elastomers.

4.2.1 Spandex

One unusual polyurethane thermoplastic elastomer is spandex, which DuPont sells under the trade name Lycra. It has both urea and urethane linkages in its backbone. What gives spandex its special properties is the fact that it has hard and soft blocks in its repeat structure. The short polymeric chain of a polyglycol, usually about forty or so repeats units long, is soft and rubbery. The rest of the repeat unit, the stretch with the urethane linkages, the urea linkages, and the aromatic groups, is extremely rigid. This section is stiff enough that the rigid sections from different chains clump together and align to form fibres. Of course, they are unusual fibres, as the fibrous domains formed by the stiff blocks are linked together by the rubbery soft sections. The result is a fibre that acts like an elastomer! This allows us to make fabric that stretches for exercise clothing and the like.



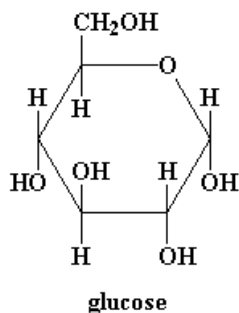
Spandex has a complicated structure, with both urea and urethane linkages in the backbone chain.

SELF ASSESSMENT EXERCISE 1

- i. What are polyurethanes?
- ii. Mention two uses of the polyurethanes

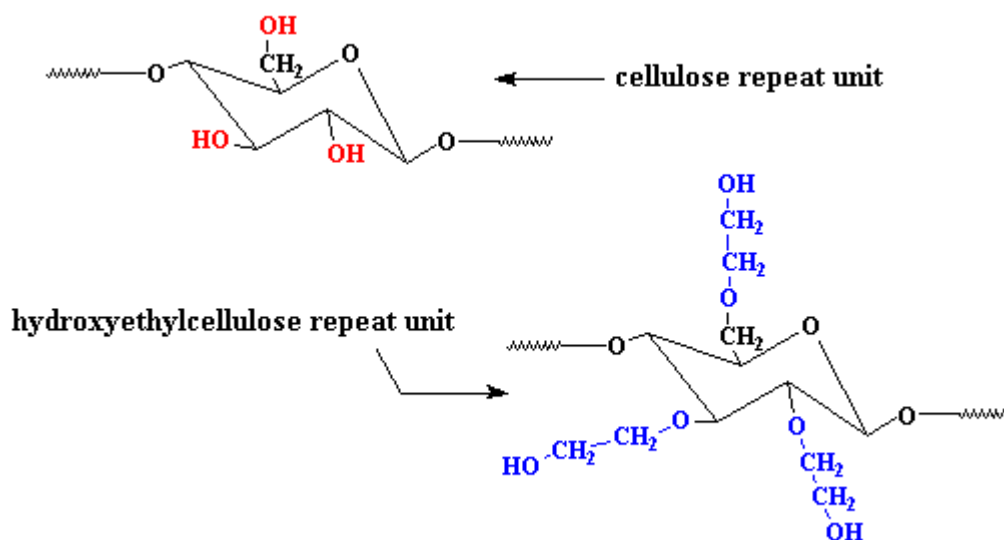
4.3 Cellulose

Cellulose is one of many polymers found in nature. Wood, paper, and cotton all contain cellulose. Cellulose is an excellent fibre. Wood, cotton, and hemp rope are all made of fibrous cellulose. Cellulose is made of repeat units of the monomeric glucose. This is the same glucose which the body metabolizes in order to live, but you cannot digest it in the form of cellulose. Because cellulose is built out of a sugar monomer, it is called a polysaccharide



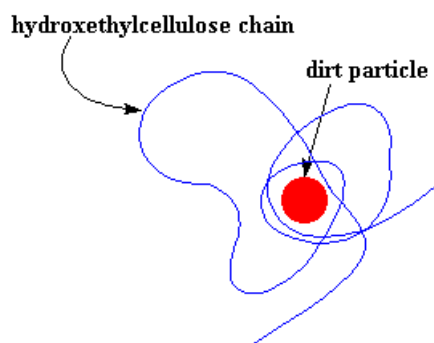
Cellulose has an important place in the story of polymers because it was used to make some of the first synthetic polymers, like cellulose nitrate, cellulose acetate, and rayon.

Another cellulose derivative is hydroxyethylcellulose. It differs from plain old regular cellulose in that some or all of the hydroxyl groups of the glucose repeat unit have been replaced with hydroxyethyl ether groups



These hydroxyethyl groups get in the way when the polymer tries to crystallize. Because it cannot crystallize, hydroxyethylcellulose is soluble in water. In addition to being a great laxative, it's used to thicken shampoos as well. It also makes the soap in the shampoo less foamy, and helps the shampoo clean better by forming *colloids* around dirt particles.

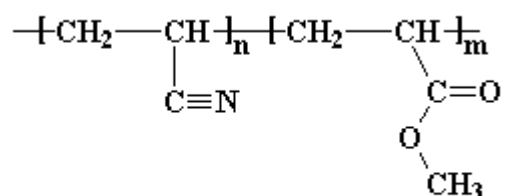
The hydroxyethylcellulose chain wraps around a particle of dirt, so it stays in suspension in water.



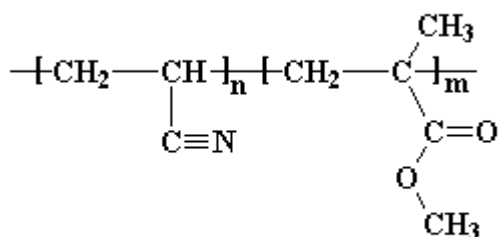
Normally, particles of dirt are insoluble in water. But a chain of hydroxyethylcellulose can wrap itself around a dirt particle. This mass can be thought of as a snack cake, with the polymer chain as the cake and the dirt as the creamy filling. This snack cake is soluble in water, so by wrapping around the dirt like this, the hydroxyethylcellulose tricks the water into accepting the dirt. In this way, the dirt gets washed away instead of being deposited back onto your hair.

4.4 Polyacrylonitrile

Polyacrylonitrile is used for very few products an average consumer would be familiar with, except to make another polymer, carbon fibre. Homopolymers of polyacrylonitrile have been used as fibres in hot gas filtration systems, outdoor awnings, sails for yachts, and even fibre reinforced concrete. But mostly copolymers containing polyacrylonitrile are used as fibres to make knitted clothing, like socks and sweaters, as well as outdoor products like tents. If the label of some piece of clothing says "acrylic", then it is made out of some copolymer of polyacrylonitrile. Usually they are copolymers of acrylonitrile and methyl acrylate, or acrylonitrile and methyl methacrylate:

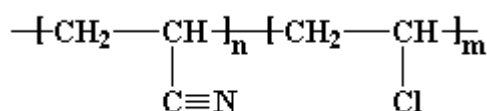


poly(acrylonitrile-*co*-methyl acrylate)



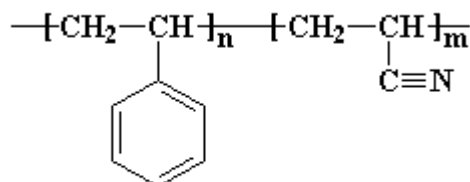
poly(acrylonitrile-*co*-methyl methacrylate)

Also, sometimes we make copolymers of acrylonitrile and vinyl chloride. These copolymers are flame-retardant, and the fibres made from them are called *modacrylic* fibres.



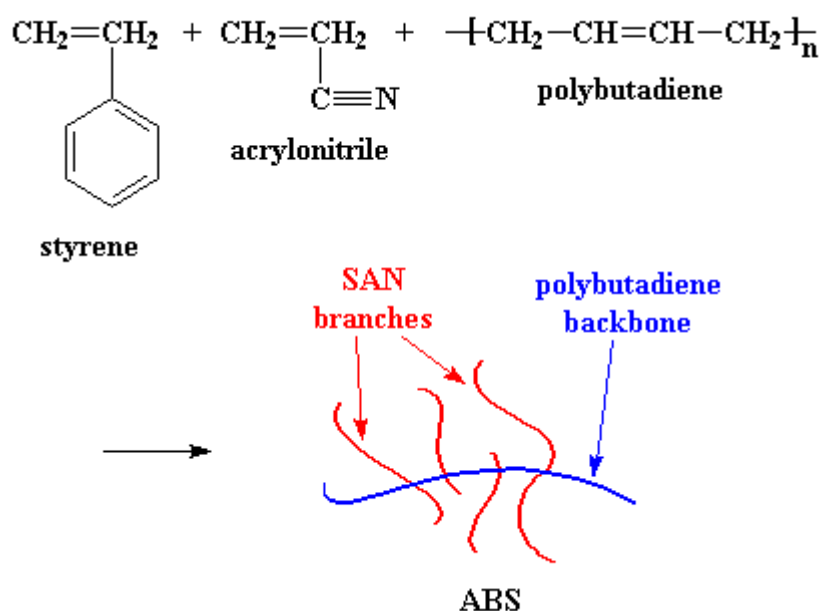
poly(acrylonitrile-*co*-vinyl chloride)

But the slew of copolymers of acrylonitrile does not end there as well. Poly(styrene-*co*-acrylonitrile) (SAN) and poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS), are used as plastics.



SAN

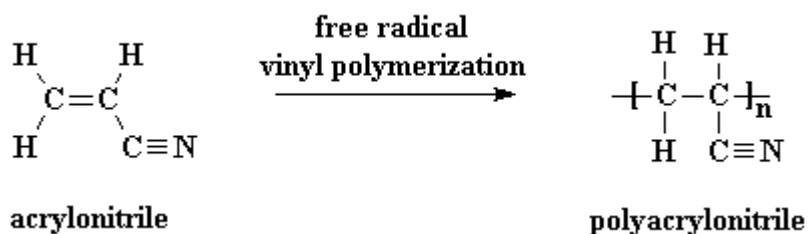
SAN is a simple random copolymer of styrene and acrylonitrile. But ABS is more complicated. It's made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. Polybutadiene has carbon-carbon double bonds in it, which can polymerize, too. So we end up with a polybutadiene chain with SAN chains grafted onto it.



ABS is very strong and lightweight. It is strong enough to be used to make automobile body parts. Using plastics like ABS makes automobiles lighter, so they use less fuel, and therefore they pollute less.

ABS is a stronger plastic than polystyrene because of the nitrile groups of its acrylonitrile units. The nitrile groups are very polar, so they are attracted to each other. This allows opposite charges on the nitrile groups to stabilize each other. This strong attraction holds ABS chains together tightly, making the material stronger. Also the rubbery polybutadiene makes ABS tougher than polystyrene.

Polyacrylonitrile is a vinyl polymer, and a derivative of the acrylate family of polymers. It is made from the monomer acrylonitrile by free radical vinyl polymerization.



4.5 Polymers an Application

Table 4.1: Plastics and Fibre Polymers

Polymers used as plastics	Polymers used as fibres
Polypropylene	Polypropylene
Polyesters	Polyesters
Polystyrene	Polyethylene
Polycarbonate	Kevlar and Nomex
PVC	Polyacrylonitrile
Polyethylene	Cellulose
Poly(methyl methacrylate)	Polyurethanes

SELF ASSESSMENT EXERCISE 2

- i. What are the chemical constituents of cellulose and polyarylonitrile
- ii. Differentiate between Spandex and ABS

5.0 CONCLUSION

Polyurethanes can be fibres, and they can be adhesives. These block copolymers have properties of thermoplastic elastomers. Cellulose is one of many polymers found in nature. Wood, paper, and cotton all contain cellulose. Cellulose is an excellent fibre. Cellulose has an important place in the story of polymers because it was used to make some of the first synthetic polymers, like cellulose nitrate, cellulose acetate, and rayon.

Polyacrylonitrile is a vinyl polymer, and a derivative of the acrylate family of polymers. It is made from the monomer acrylonitrile by free radical vinyl polymerization. SAN is a simple random copolymer of styrene and acrylonitrile. But ABS is more complicated. It is made by polymerizing styrene and acrylonitrile in the presence of polybutadiene.

6.0 SUMMARY

In this unit, we have learnt that:

- polyurethanes are the most well known polymers used to make foams
- cellulose is made of repeat units of the monomer glucose
- polyacrylonitrile is a vinyl polymer, and a derivative of the acrylate family of polymers

- poly (styrene-*co*-acrylonitrile) (SAN) and poly(acrylonitrile-*co*-butadiene-*co*--styrene) (ABS), are copolymers of polyacrylonitrile which are used as plastics.

7.0 TUTOR-MARKED ASSIGNMENT

- Write short notes on the following:
(a) Polyurea (b) SAN (c) ABS
- What are the functions of hydroxyethylcellulose

8.0 REFERENCE/FURTHER READING

Synthetic Fibres: Nylon, Polyesters, Acrylic and Polyolefins; Edited by J.E McIntyre, Woodhead Textiles Series No. 36, Woodhead Publishing Limited, 2009.

UNIT 5 ARAMIDS, POLY(METHYLMETHACRYLATE) AND POLYCARBONATE

CONTENTS

- 1.0 Introduction
- 2.0 Objectives
- 3.0 How to Study this Unit
- 4.0 Main Content
 - 4.1 Definition of Aramids, Poly (methyl methacrylate) and Polycarbonate
 - 4.2 Aramids
 - 4.3 Poly (methyl methacrylate), PMMA
 - 4.4 Polycarbonate
- 5.0 Conclusion
- 6.0 Summary
- 7.0 Tutor-Marked Assignment
- 8.0 Reference/Further Reading

1.0 INTRODUCTION

The diverse nature of polymers allow for diverse applicable usage of the materials produced from them.

2.0 OBJECTIVES

By the end of this unit, you should be able to state:

- the meaning of aramids, Kevlar and Nomex
- the meaning of poly (methyl methacrylate) and Polycarbonate
- the chemical structures of these polymers and their uses.

3.0 HOW TO STUDY THIS UNIT

1. You are expected to read carefully, through this unit at least twice before attempting to answer the self-assessment questions or the tutor marked assignments.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers.
3. Share your difficulties with your course mates, facilitators and by consulting other relevant materials particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

4.0 MAIN CONTENT

4.1 Definitions of Aramids, Poly (methyl methacrylate) and Polycarbonate

Aramids are a family of nylons, including Nomex[®] and Kevlar[®].

Poly (methyl methacrylate), which lazy scientists call PMMA, is a clear plastic, used as a shatterproof replacement for glass.

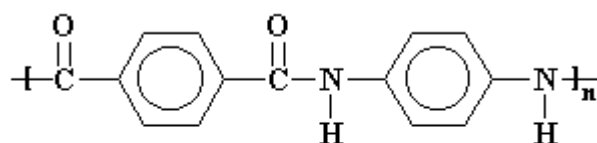
Polycarbonate, or specifically polycarbonate of bisphenol A, is a clear plastic used to make shatterproof windows, lightweight eyeglass lenses

4.2 Aramids

Aramids are a family of nylons, including Nomex and Kevlar. Aramids are used in the form of fibers. They form into even better fibers than non-aromatic polyamides, like nylon 6,6.

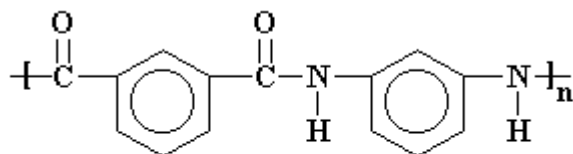
Kevlar is used to make things like bullet proof vests and puncture resistant bicycle tyres. It is also possible to produce bullet proof bicycle tyres from Kevlar if one felt the need. Blends of Nomex and Kevlar are used to make fireproof clothing. Nomex is what keeps the monster truck and tractor drivers from burning to death should their fire-breathing rigs breathe a little too much fire. Polymers play another part in the monster truck show in the form of elastomers from which those giant tires are made. Nomex-Kevlar blends also protect fire fighters.

Kevlar is a polyamide, in which all the amide groups are separated by *para*-phenylene groups, that is, the amide groups attach to the phenyl rings opposite to each other, at carbons 1 and 4.



In Kevlar the aromatic groups are all linked into the backbone chain through the 1 and 4 positions. This is called *para*- linkage.

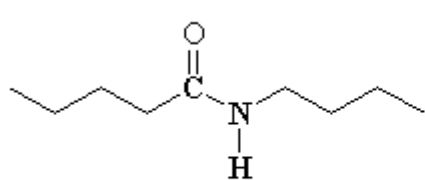
Nomex, on the other hand, has *meta*-phenylene groups, that is, the amide groups are attached to the phenyl ring at the 1 and 3 positions.



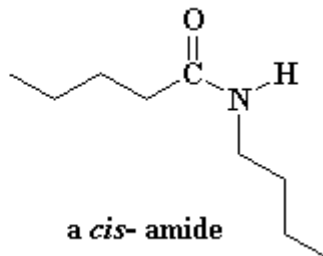
In Nomex the aromatic groups are all linked into the backbone chain through the 1 and 3 positions. This is called *meta*-linkage.

Kevlar is a very crystalline polymer. It took a long time to figure out how to make anything useful out of Kevlar because it would not dissolve in anything. So processing it as a solution was out. It would not melt below 500 °C, so melting it down was out, too. Then a scientist named Stephanie Kwolek came up with a brilliant plan.

Aramids are used in the form of fibers. They form into even better fibers than non-aromatic polyamides, like nylon 6,6. They have the ability to adopt two different shapes, or *conformations*. The two shapes below are the same compound, in two different conformations. The one on the left is called the *trans* conformation, and the one on the right is the *cis*-conformation.

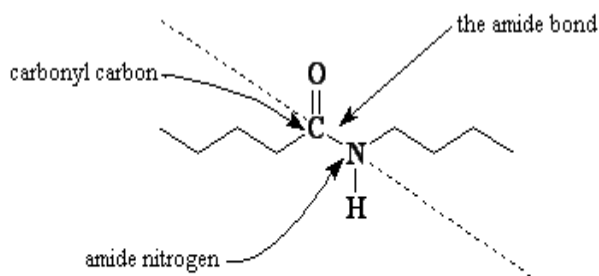


a *trans*-amide

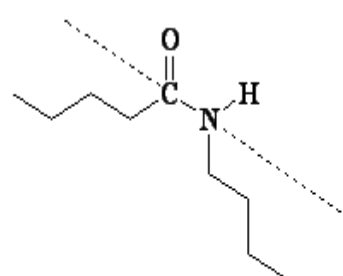


a *cis*-amide

In Latin, *trans* means "on the other side". So when the hydrocarbon groups of the amide are on opposite sides of the *amide bond*, the bond between the carbonyl oxygen and the amide nitrogen, it's called a *trans*-amide. Likewise, *cis* in Latin means "on the same side", and when both hydrocarbon groups are on the same side of the amide bond, we call it a *cis*-amide.



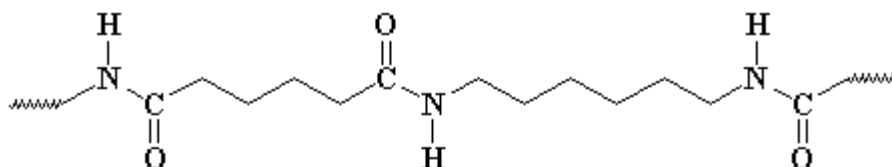
In the *trans* amide, the hydrocarbon groups are on opposite sides of the amide bond



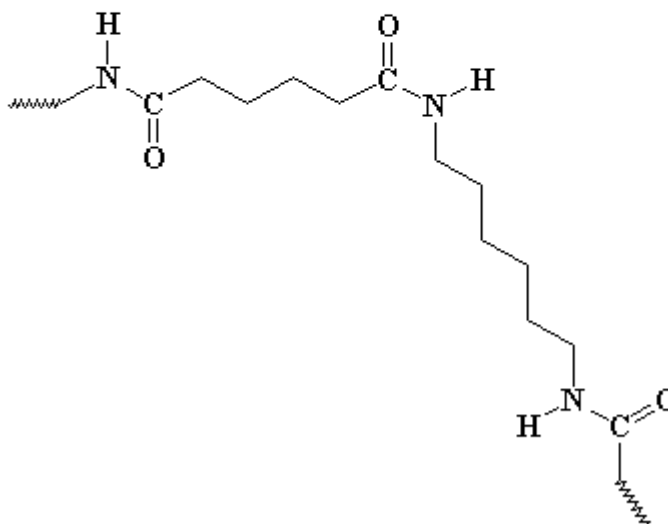
In the *cis* amide, both hydrocarbon groups are on the same side of the amide bond.

The same amide molecule can twist back and forth between the *cis*- and *trans*- conformations, given a little bit of energy.

The same *cis*- and *trans*-conformations exist in polyamides, too. When all the amide groups in a polyamide, like nylon 6,6 for example, are in the *trans* conformation, the polymer is fully stretched out in a straight line. This is exactly what we want for fibers, because long, straight, fully extended chains pack more perfectly into the crystalline form that makes up the fiber. But sadly, there is always at least some amide linkages in the *cis*-conformation. So nylon 6,6 chains never become fully extended.

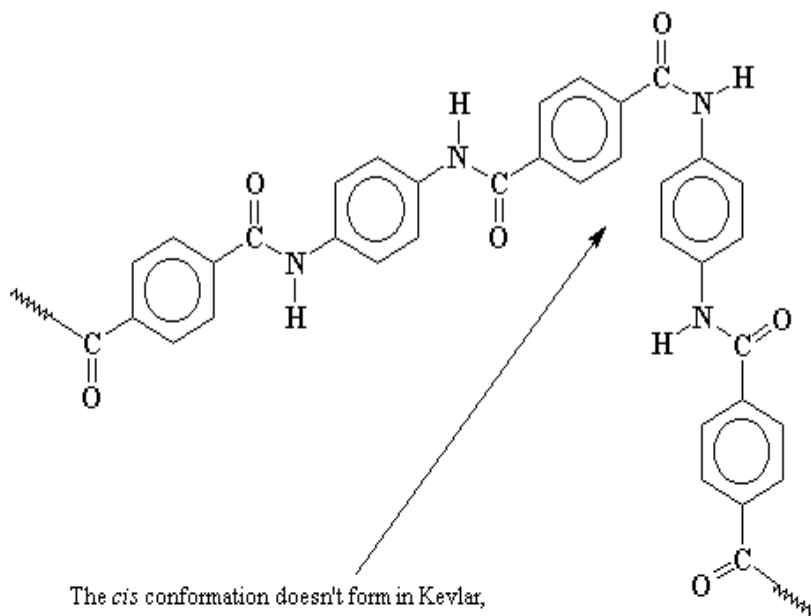


Nylon 6,6 can stretch into fibers easily when all the amide groups are in the *trans* conformation...



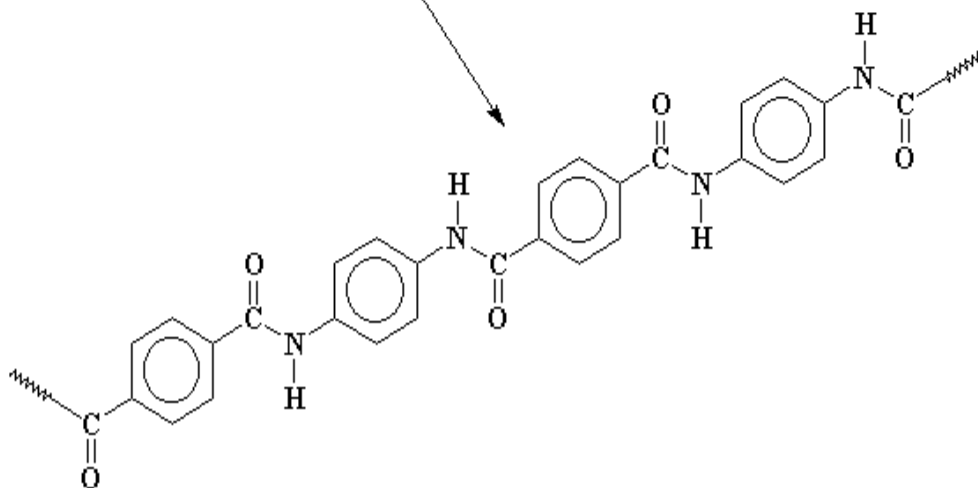
...but one *cis* linkage causes a kink which messes everything up!

But Kevlar[®] is different. When it tries to twist into the *cis*-conformation, the hydrogens on the big aromatic groups get in the way! The *cis* conformation puts the hydrogens just a little closer to each other than they want to be. So Kevlar[®] stays nearly fully in the *trans*-conformation. So Kevlar[®] can fully extend to form beautiful fibers.

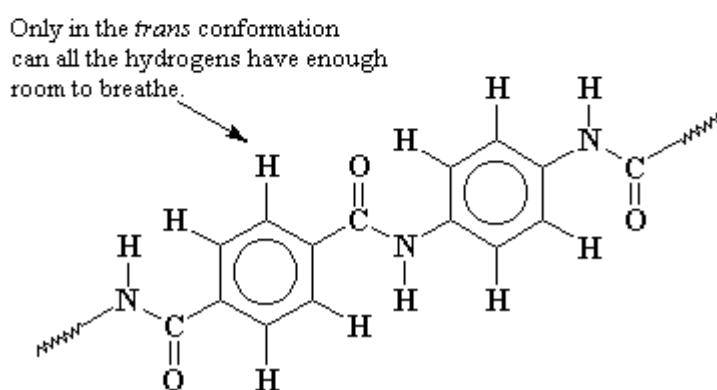
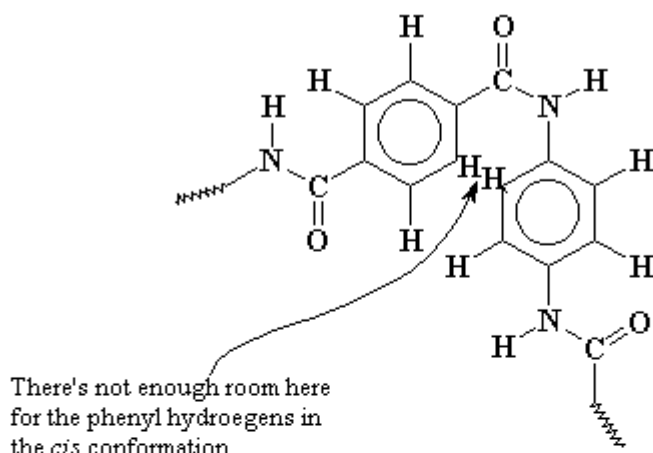


The *cis* conformation doesn't form in Kevlar, because it's too sterically hindered. These big aromatic rings just get in the way!

So we're left with a nearly all *trans* polyamide, which stretches out fully extended to form beautiful fibers.



When Kevlar[®] tries to form the *cis*-conformation, there's not enough room for the phenyl hydrogens. So only the *trans*-conformation is usually found.



SELF ASSESSMENT EXERCISE 1

- i. Distinguish chemically between Kevlar and Nomex
- ii. Mention two uses of each of the aramids.

4.3 Poly (methyl methacrylate), PMMA

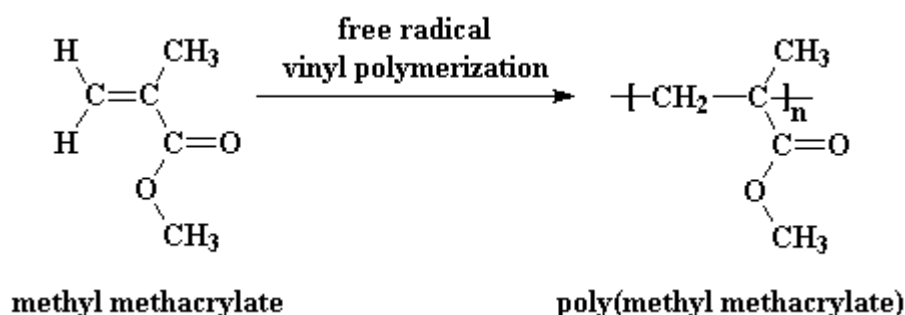
Poly (methyl methacrylate), or PMMA, is a clear plastic, used as a shatterproof replacement for glass. The barrier at the ice rink which keeps hockey pucks from flying in the faces of fans is made of PMMA. The chemical company Rohm and Haas makes windows out of it and calls it Plexiglas. Ineos Acrylics also makes it and calls it Lucite. Lucite is used to make the surfaces of hot tubs, sinks, and the ever popular one piece bathtub and shower units, among other things.

When it comes to making windows, PMMA has another advantage over glass. PMMA is more transparent than glass. When glass windows are made too thick, they become difficult to see through. But PMMA windows can be made much thicker and they are still perfectly transparent. This makes PMMA a wonderful material for making large aquariums, whose windows must be thick in order to contain the high pressure due to millions of gallons of water. In fact, the largest single

window in the world, an observation window at California's Monterey Bay Aquarium, is made of one big piece of PMMA which is 54 feet long, 18 feet high, and 13 inches thick (16.6 m long, 5.5 m high, and 33 cm thick).

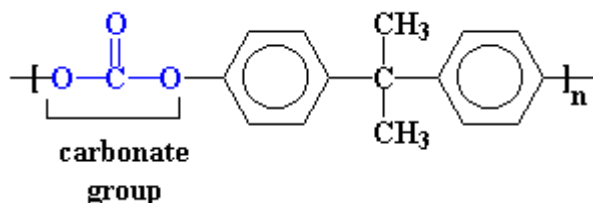
PMMA is also found in paint. Acrylic "latex" paints often contain PMMA suspended in water. PMMA does not dissolve in water, so dispersing PMMA in water requires another polymer to make water and PMMA compatible with each other. But PMMA is more than just plastic and paint. Often lubricating oils and hydraulic fluids tend to get really viscous and even gummy when they get really cold. This is a real pain when you are trying to operate heavy equipment in really cold weather. But when a little bit PMMA is dissolved in these oils and fluids, they do not get viscous in the cold, and machines can be operated down to $-100\text{ }^{\circ}\text{C}$ ($-150\text{ }^{\circ}\text{F}$), that is, presuming the rest of the machine can take that kind of cold!

PMMA is a vinyl polymer, made by free radical vinyl polymerization from the monomer methyl methacrylate.



4.4 Polycarbonate

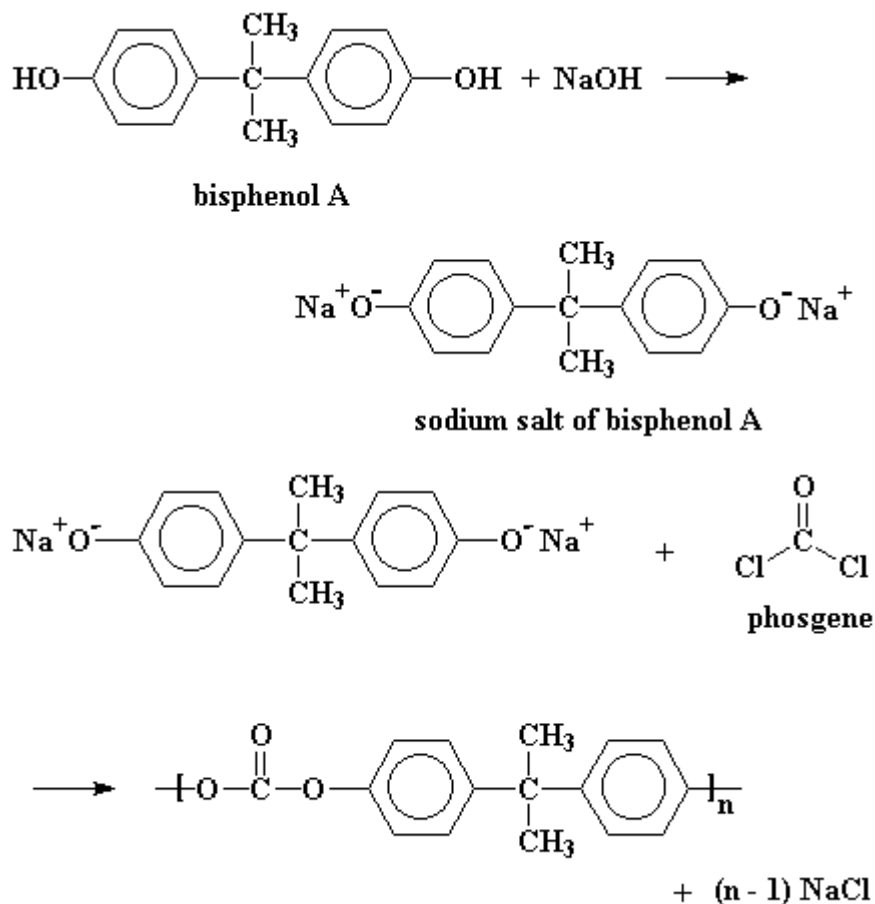
Polycarbonate, or specifically polycarbonate of bisphenol A, is a clear plastic used to make shatterproof windows, lightweight eyeglass lenses, and similar products. General Electric makes this stuff and sells it as Lexan.



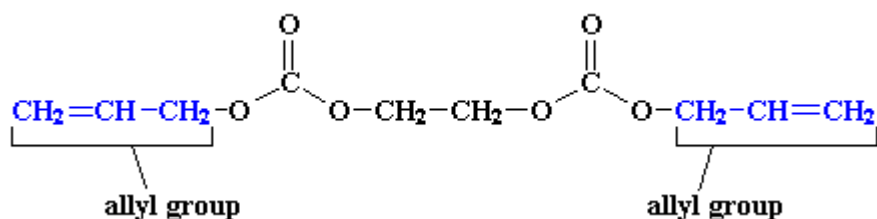
Polycarbonate gets its name from the carbonate groups in its backbone chain. It is known as polycarbonate of bisphenol A because it is made from bisphenol A and phosgene. This starts out with the reaction of

bisphenol A with sodium hydroxide to get the sodium salt of bisphenol A.

The sodium salt of bisphenol A is then reacted with phosgene, a right nasty compound which was a favorite chemical weapon in World War I, to produce the polycarbonate.



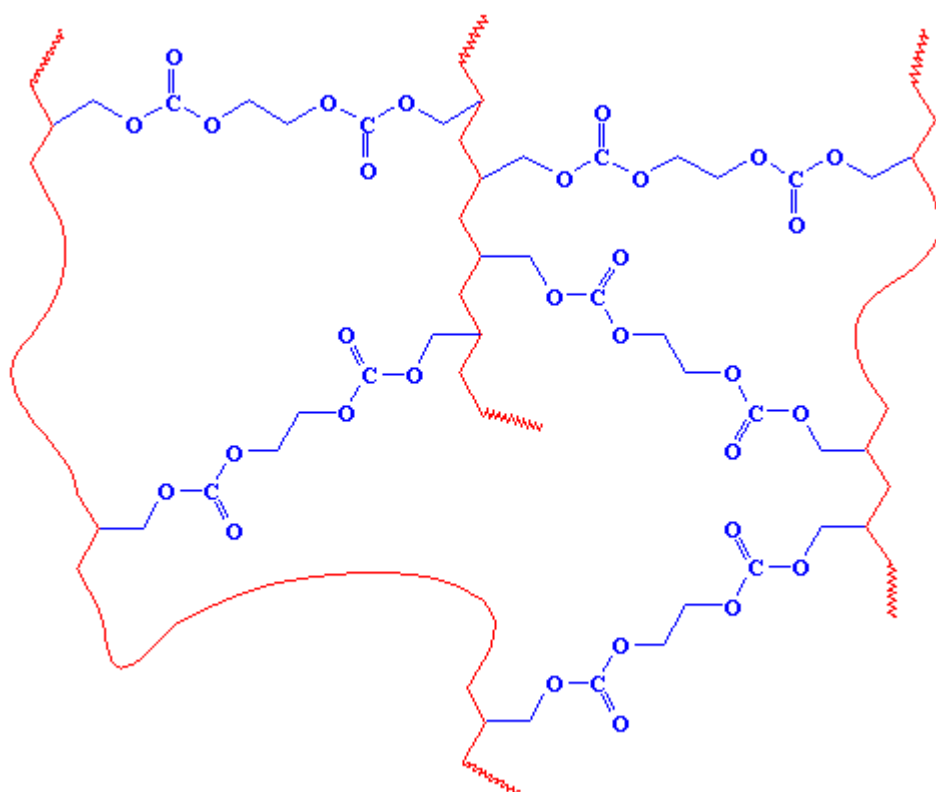
But there is another polycarbonate. This is the polycarbonate that is used to make ultra-light eyeglass lenses. For people with really bad eyesight, if the lenses were made out of glass, they would be so thick that they would be too heavy to wear. But this new polycarbonate changed all that. Not only is it a lot lighter than glass, but it has a much higher *refractive index*. That means it bends light more than glass.



It has two allyl groups on the ends. These allyl groups have carbon-carbon double bonds in them. This means they can polymerize by free

radical vinyl polymerization. Of course, there are two allyl groups on each monomer. The two allyl groups will become parts of different polymer chains. In this way, all the chains will become tied together to form a cross linked material. The carbonate-containing groups (shown in blue) form the cross links between the polymer chains (shown in red). This cross linking makes the material very strong, so it would not break nearly as easily as glass will. This is really important for kids' glasses!

There is a fundamental difference in the two types of polycarbonate described here. Polycarbonate of bisphenol A is a thermoplastic. This means it can be molded when it is hot. But the polycarbonate used in eyeglasses is a thermoset. Thermosets do not melt, and they can't be remolded. They are used to make things that need to be really strong and heat resistant.



SELF ASSESSMENT EXERCISE 2

- i. Propose a short equation for the preparation of poly (methyl methacrylate)
- ii. What are the striking features of a polycarbonate used in eyeglasses?

5.0 CONCLUSION

It has been clearly shown how new scientific discovery has brought an improvement into the nature and uses of polymers either as plastics or fibres.

6.0 SUMMARY

In this unit, we have learnt that:

- aramids are a family of nylons, including Nomex[®] and Kevlar[®]
- kevlar[®] is a polyamide, in which all the amide groups are separated by *para*-phenylene groups, that is, the amide groups attach to the phenyl rings opposite to each other, at carbons 1 and 4. Kevlar[®] stays nearly fully in the *trans*- conformation
- nomex[®], on the other hand, has *meta*-phenylene groups, that is, the amide groups are attached to the phenyl ring at the 1 and 3 positions
- poly (methyl methacrylate), or PMMA, is a clear plastic, used as a shatterproof replacement for glass
- there is a fundamental difference in the two types of polycarbonate described here. Polycarbonate of bisphenol A is a thermoplastic. But the polycarbonate used in eyeglasses is a thermoset.

7.0 TUTOR-MARKED ASSIGNMENT

- i. Distinguish between Kevlar and Nomex
- ii. Propose a simple laboratory step for the synthesis of polycarbonates
- iii. Mention four uses of each of the aramids.

8.0 REFERENCE/FURTHER READING

Synthetic Fibres: Nylon, Polyesters, Acrylic and Polyolefins; Edited by J.E McIntyre, Woodhead Textiles Series No. 36, Woodhead Publishing Limited, 2009.