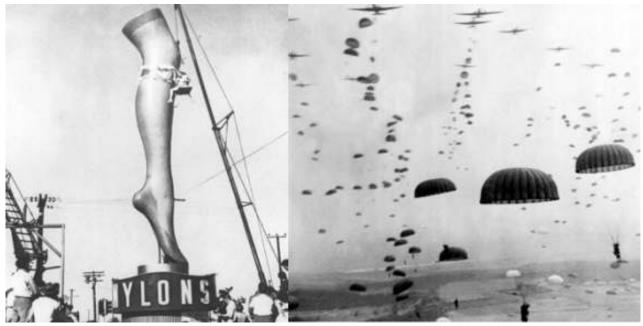
Unit - Chemistry of Garments: Synthetic (man-made) Fibres

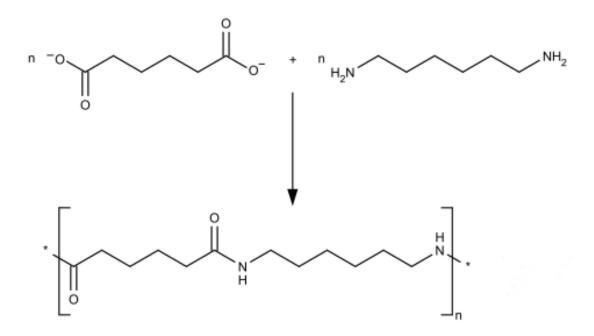
Acrylic, Aramid (Twaron, Kevlar, Technora, Nomex), Microfiber, Modacrylic, Nylon, Olefin Polyester, Polyethylene (Dyneema, Spectra), Spandex, Vinylon, Vinyon, Zylon

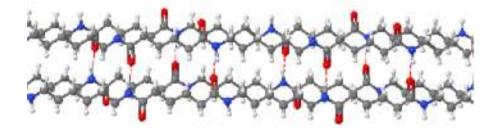
Nylon (Polyamide)

Nylon is a thermoplastic silky material, commercially first used in a <u>nylon-bristled toothbrush (1938)</u>, followed more famously by women's stockings ("nylons") in the 1940's. The name may have been derived from *'no-run'* to emphasise the durability of the stockings produced from it.



Introduction of Nylon in the 1940's, stockings and parachutes.





Preparation and structure of Nylon 6 6

Nylon was the first synthetic fibre to be made. Nylon-66 and Nylon-6 are the two important synthetic fibres belonging to the polyamide group. The numerical suffixes specify the number of carbons donated by the monomers; the diamine first and the diacid second. The most common variant is Nylon 6-6 which refers to the fact that the diamine (hexamethylene diamine, IUPAC name: hexane-1,6-diamine) and the diacid (adipic acid, IUPAC name: hexanedioic acid) each donate 6 carbons to the polymer chain. The Nylon salt so formed on polymerization gives polyhexamethylene adipamide.

Crystallinity

Note that the molecular graphic images on these pages suggest a high degree of regular crystallinity which is generally not the case.

When applied to polymers, the term crystalline has a somewhat ambiguous usage. In some cases, the term crystalline finds identical usage to that used in conventional crystallography. For example, the structure of a crystalline protein or polynucleotide, such as a sample prepared for x-ray crystallography, may be defined in terms of a conventional unit cell composed of one or more polymer molecules with cell dimensions of hundreds of angstroms or more.

A synthetic polymer may be loosely described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline.

The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers.

Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions. Thus for many polymers, reduced crystallinity may also be associated with increased transparency.

<u>Nylon 6 or polycaprolactam</u> is a polymer developed at IG Farben to reproduce the properties of nylon 6,6 without violating the patent on its production. Unlike most other nylons, nylon 6 is not a condensation polymer, but instead is formed by ring-opening polymerization of caprolactam (with 6 C's in the ring, hence the name).



γ form gives pleated sheets of Nylon 6 from caprolactam DOI: 10.1002/pol.1965.100030132

Although Nylon thread looks delicate, it is in fact as strong as steel. It has only one-seventh the weight of a steel wire of the same diameter and hence its tensile strength per unit weight is superior to that of steel. Because of its great strength, it is used in making hosiery, textiles, ropes, upholstery, tooth brush bristles, paint brushes, fishing lines and nets, tennis racquets, sewing thread, syringes, spectacle frames, zip fasteners and vehicle tyres blended with rubber. Synthetic grass, which has been used on tennis courts is made from Nylon. Nylon also improves the utility of wool fabrics and in mouldable form, it is used for making bearings and gears, which are self-lubricating.

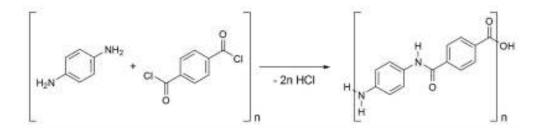


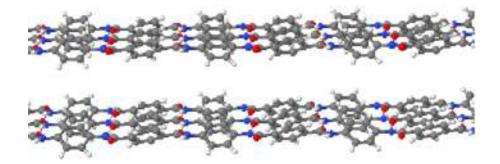
Preparation of thread of Nylon 6 10 in the Physical Chemistry Laboratory

Kevlar

Poly-paraphenylene terephthalamide - better known by the Trademark, Kevlar - was patented by DuPont in 1962. A research group at DuPont, began searching for a new lightweight strong fiber as a substitute to use in the manufacturing of light but strong tyres having recognised that gasoline resources were limited. The polymers they had been working with prior to that time were poly-p-phenylene-terephthalate and polybenzamide, which formed liquid crystals while in solution, something unique to those polymers at the time.

In recalling the critical experiment, the discoverer, <u>Stephanie Kwolek</u>, reported that the solution was "cloudy, opalescent upon being stirred, and of low viscosity" and usually was thrown away. However, Kwolek persuaded the technician who ran the "spinneret", to test her solution, and was amazed to find that the fibre formed did not readily break, unlike nylon. Her supervisor and her laboratory director understood the significance of her discovery and within a few years (1971) modern Kevlar was introduced.





Kevlar, a poly aromatic amide Structure based on: Northolt, M.G., Eur. Polym. J. 1974, 10, 799. <u>doi:10.1016/0014-3057(74)90131-1</u>

Kevlar's structure consists of relatively rigid molecules which tend to form mostly planar sheet-like structures similar to silk protein. It has a high strength/lightweight combination that makes it the perfect solution for a variety of applications:

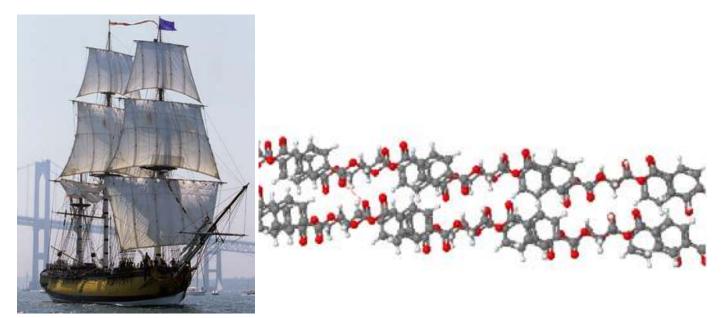
- Kevlar K-29 in industrial applications, such as cables, asbestos replacement, brake linings, and body/vehicle armour.
- Kevlar K49 high modulus used in cable and rope products.
- Kevlar K100 coloured version of Kevlar
- Kevlar K119 higher-elongation, flexible and more fatigue resistant.
- Kevlar K129 higher tenacity for ballistic applications.
- Kevlar AP has 15% higher tenacity than K-29.
- Kevlar XP lighter weight resin and KM2 plus fibre combination.
- Kevlar KM2 enhanced ballistic resistance for armour applications

Some of the characteristics that make Kevlar useful in protective applications:

- Bullet resistant
- Fragment resistant
- Excellent thermal properties
- Lightweight
- Flexible
- Excellent dimensional stability
- Comfortable
- High strength
- Cut resistant
- Chemical resistance
- Puncture resistant
- Slash resistant
- Flame resistant, self-extinguishing

Polyesters

Polyester is made under a range of brand names including: Dacron (USA), Diolen, Fortel, Kodel, Tergal, Terlenka, Terylene (UK), Tetoron, Trevira (Germany) and Vycron.



Tall ship replica Surprise, with polyethylene terephthalate (PET) sails from 125,000 recycled soft-drink bottles.

The polyester PET is based on the petroleum products ethylene glycol and terephthalic acid and is called <u>polyethylene terephthalate</u>. The fibres are linear, long stretched filamentous molecules. Polyester-cotton blends are popular for making fabrics, which are used in winter-suits, shirts, pullovers, socks, carpets, parachute cloth, ropes, wire insulators, and blankets. Polyesters contribute several properties to blends, such as wash- and-wear quality, wrinkle-free texture. Rayon is made from cellulose, cuprammonium and viscose, it is very cheap and can easily be blended with other materials as well. Terylene is blended with cotton to produce what is known as terycot, which is crease resistant and comfortable as cotton.

PET Recycling



Identification code used on bottles to allow for recycling of PET

PET has a resin identification code of 1. While most thermoplastics can, in principle, be recycled, PET bottle

recycling is more practical than many other plastic applications. The primary reason is that plastic carbonated soft drink bottles and water bottles are almost exclusively PET.

The first drink bottles manufactured with PET had round bottoms and a second plastic (black polyethylene) as a cup on the bottom to provide a base. This was because the sharp bend needed to make a flat base weakened the plastic. Current designs mould a bottom with five, or more convolutions all of which have rounded edges and this eliminates the need for a second plastic and means that during the recycling process there is no need to separate the plastics.

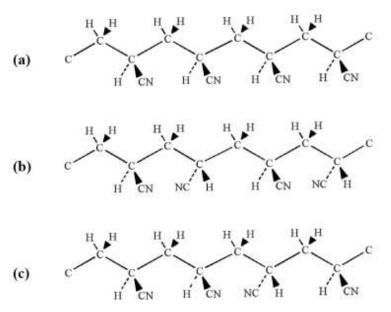
According to the <u>PCI Group</u>, in 2009 approximately 5.8 million tons of recycled PET were collected worldwide. From this 4.7 million tons of flake were obtained. 3.4 million tons were used to produce fibre, 0.5 million tons to produce bottles, 0.5 million tons to produce APET sheet for thermoforming, 0.2 million tons to produce strapping tape and 0.1 million tons for miscellaneous applications.

Acrylic Fibres (polyacrylonitrile, PAN)

Polyacrylonitrile is known by a number of brand names, including: Acrilan, Creslan, Orlon and Zefran (all of which have 10% to 14% of other monomers added to improve dyeing), Verel (which is 40% to 50% vinyl chloride), Dynel (more than 50% vinyl chloride) as well as Belson, Casmilon, Courtelle, Crylor, Darvan, Teklan and Vonnel. PAN thus represents a whole family of fibres, which can be prepared by the polymerization of acrylonitrile. Mixing ammonia, propylene and oxygen to obtain liquid acrylic nitrile, which upon polymerization is converted to polyacrylyonitrile, a synthetic resin powder. As a textile material polyacrylonitrile is lighter than wool, soft and warm. It can be washed and drip-dried. It is used as a cheaper substitute of wool for making warm clothes. Orlon is used in making coats, pullovers, carpets, and blankets.

Russian Journal of Applied Chemistry, Volume 79, Number 8, 1378-1380, DOI: 10.1134/S1070427206080349

Polyacrylonitrile (PAN) is one of the most important and widely industrially used polymers. It serves to obtain various polymeric materials with unique properties (thermal stability, strength, electrical conductivity, hydrophilicity, etc.). This is determined by specific structural features of the PAN molecule, whose quantitative and qualitative parameters depend on preparation techniques and methods of its modification. Various methods of acrylonitrile polymerization can he used to obtain polymers with predominance of 3D structures of atactic, isotactic, and syndiotactic types. Stereoisomers of this kind possess various properties and differently behave in forming and under thermal treatment. The "wet" method is for the most part used in the industry to form PAN fibers, and, therefore, the spatial orientation of polymer chains of PAN in solution is important. As a rule, spinning solutions of PAN arc oriented by mechanical treatment in fibre forming on a technological line.



Tacticity arrangements for tetrad fragments of PAN a) isotactic b) syndiotactic c) atactic

Tacticity is a term used to describe the structures of polymers.

Isotactic polymers are composed of **isotactic macromolecules** (IUPAC definition). In isotactic macromolecules all the substituents are located on the same side of the macromolecular backbone. Isotactic polymers are usually semicrystalline and often form a helix configuration.

In **syndiotactic or syntactic macromolecules** the substituents have alternate positions along the chain. The macromolecule consists 100% of racemo diads.

In **atactic macromolecules** the substituents are placed randomly along the chain. Due to their random nature atactic polymers are usually amorphous.

In **eutactic macromolecules**, substituents may occupy any specific (but potentially complex) sequence of positions along the chain. Isotactic and syndiotactic polymers are therefore instances of the more general class of eutactic polymers.



A syndiotactic fragment of polyacrylonitrile (PAN)

Heat treatment of PAN leads initially to the formation of fused pyridine rings and eventually to <u>carbon fibre</u>. This has been used to reinforce substances, such as epoxy resins, where lightness but great strength is required for example in the turbine blades of jet engines.

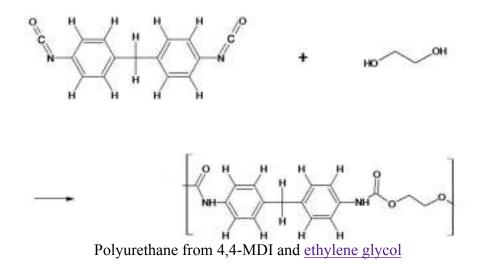
Polyolefins

Polyethylene and polypropylene are the lightest fibres and are generally used in blankets, upholstery, carpets and apparel. They are difficult to dye given that there are no functional groups to react with. Polypropylene is also a substitute for sisal in rope making and in synthetic grass. (Question: What is the material used at the Mona Hockey Field or the Mona track?).



polypropylene

<u>Polyurethane</u> See as well the <u>GB Kauffman J. Chem. Educ. article on polyurethanes</u>



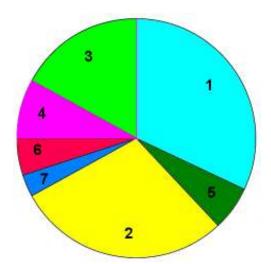
<u>Methylene diphenyl diisocyanate (MDI)</u>, is an aromatic diisocyanate that exists as three isomers, 2,2'-MDI, 2,4'-MDI, and 4,4'-MDI with the 4,4' isomer (InChI:UPMLOUAZCHDJJD-UHFFFAOYSA-N), being the most widely used. MDI reacts with polyols in the manufacture of polyurethane. Total world production of MDI and polymeric MDI is over 2 million tonnes per year (Mt/a) and it accounted for over 60% of the

isocyanate global market in the year 2000.

MDI is the least hazardous of the commonly available isocyanates but that does not imply that it is benign. Its very low vapour pressure reduces its hazards during handling and this has led to it being used as a replacement to the other major isocyanate TDI.

<u>2,4-toluene diisocyanate (TDI)</u> is the second most used aromatic diisocyanate and it is largely produced for preparing polyurethanes. It exists in two isomers, 2,4-TDI (InChIKey: DVKJHBMWWAPEIU-UHFFFAOYSA-N) and 2,6-TDI (InChIKey: RUELTTOHQODFPA-UHFFFAOYSA-N). 2,4-TDI is produced in the pure state, but is often marketed as 80/20 and 65/35 mixtures of the 2,4 and 2,6 isomers respectively. It is a highly produced diisocyanate, accounting for 34.1% of the global isocyanate market in 2000, second only to methylene diphenyl diisocyanate (MDI). All major producers of TDI are members of the International Isocyanate Institute, whose aim is the promotion of the safe handling of isocyanates (in particular (MDI and TDI) in the workplace, community and environment.

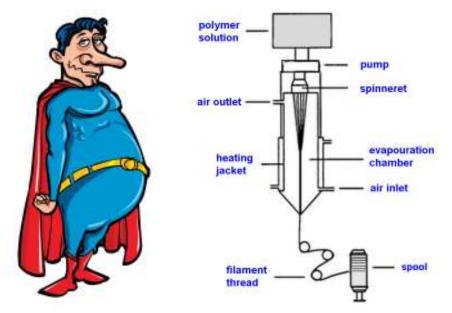
A Google preview of the 2003 book <u>MDI and TDI: Safety, Health and the Environment: A Source Book and</u> <u>Practical Guide</u> is available from the Wiley website.



1998 Regional production figures for polyurethane 1) USA and Canada 32%, 2) Western Europe 29%, 3) Asia Pacific excluding Japan 17% 4) Japan 7%, 5) Latin America 6%, 6) Rest of the World 5%, 7) Eastern Europe 3%.

Spandex

Spandex is a polyurethane-polyurea copolymer that was co-invented in 1959 by chemists C. L. Sandquist and Joseph Shivers of DuPont. Spandex when blended with wool, cotton, nylon, linen or silk develops properties of stretch and recovery, thus making the blended fabrics useful for furniture upholstery, light weight garments and swimsuits.



Every superhero has a right to wear Spandex, schematic of the dry-spinning process.

Spandex fibers are produced in four different ways: melt extrusion, reaction spinning, solution dry spinning, and solution wet spinning. All of these methods include the initial step of reacting monomers to produce a prepolymer. Once the prepolymer is formed, it is reacted further in various ways and drawn out to make the fibers. The solution dry spinning method accounts for over 94.5% of the world's spandex fibers.

Solution dry spinning

Step 1: The first step is to mix a macro glycol with a diisocyanate monomer in the reaction vessel to produce the prepolymer. A typical ratio of glycol to diisocyanate is 1:2.

Step 2: The prepolymer is further reacted with an equal amount of diamine in what is known as a *chain extension reaction*. The resulting solution is diluted with a solvent to produce the spinning solution. The solvent helps make the solution thinner and more easily handled so it can be pumped into the fibre production cell.

Step 3: The spinning solution is pumped into a cylindrical spinning cell where it is cured and converted into fibres. In this cell, the polymer solution is forced through a metal plate called a spinneret. This causes the solution to be aligned in strands of liquid polymer. As the strands pass through the cell, they are heated in the presence of nitrogen and a solvent gas. This process causes the liquid polymer to react chemically and form solid strands.

Step 4: As the fibres exit the cell, an amount of solid strands are bundled together to produce the desired thickness. Each fibre of spandex is made up of many smaller individual fibres that adhere to one another due to the natural stickiness of their surface.

Step 5: The resulting fibres are then treated with a finishing agent which can be magnesium stearate or another polymer. This treatment prevents the fibres' sticking together and aids in textile manufacture. The fibres are then transferred through a series of rollers onto a spool.

Step 6: When the spools are filled with fibre, they are put into the final packaging and shipped to the textile manufacturers.

Polylactate fibres

It has been reported that <u>a team of South Korean scientists</u> have produced the polymers used for everyday plastics through bioengineering, rather than through the use of fossil fuel-based chemicals. This technique may allow for the production of environmentally-friendly plastic that is biodegradable and low in toxicity. For a review on <u>polylactate fibres</u> see the article by Jim Lunt and Associates as well as <u>other articles on</u> <u>polymers</u>

Non-woven Fabrics

Most non-woven fabrics are made like paper by sticking layers of fibres together with a liquid adhesive. These fabrics are commonly used in making hats, bra and shoulder padding, inner-lining of suits, disposable nappy liners, duvet filling, furniture upholstery, vacuum cleaner bags and car carpets.

Assignment

The examples provided above are largely based on the same monomeric reagent polymerising to give homopolymers. Polymers that are formed containing a mixture of repeat units are known as copolymers.

- Choose any copolymer
- Describe the applications that it is suitable for
- Describe its structure, for example alternating, random or block coplymer
- Identify where it is produced and by which company
- Obtain an estimate of the production figures worldwide
- What environmental issues surround its use and disposal?

Acknowledgements.

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Continue to Dyeing Fibres or return to CHEM2402 course outline.



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