Chemical Data

- Kevlar is made during a condensation reaction making hydrochloric acid as a by product.
- The production of Kevlar is extremely expensive due to the costs implicated with storing concentrated sulphuric acid.
- Kevlar when spun, has a relative density of 1.44 and has a tensile to weight ration of 5:1

- Kevlar is rarely used outdoors unprotected from sunlight as it suffers from ultra violet light degradation.
- Kevlar is very heat resistant and decomposes above 675K without melting.



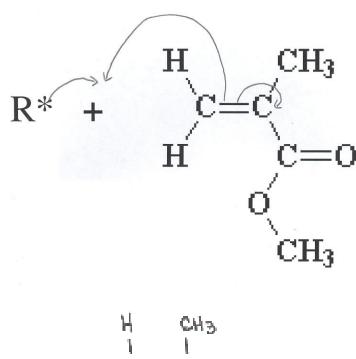
Good for its function

- Kevlar's physical hardness and tensile strength both make it very suitable for its function, in bulletproof vests, for example.
- Its hydrogen bonds give strength to the material, creating quite strong intermolecular bonds between kevlar molecules, giving it its strength and durability.

Polymethyl Methacrylate

 PMMA is manufactured from Methyl methacrylate by addition poylmerisation (Free Radical Polymerization).

• Step 1: Free radical (R*) plus methyl methacrylate



$$\longrightarrow \begin{array}{c} R - C - C^* \\ C + C - C^* \end{array}$$

Step 2 : Polymerization - MMA radical plus MMA :repeated many, many times

Step 3: Termination – occurs when two radicals join

$$(R)-CH_{2}C + \cdot CCH_{2}-(R) \longrightarrow (R)-CH_{2}C-CCH_{2}-(R)$$

$$X \qquad X \qquad X \qquad X \qquad X$$

Disproportination

Combination

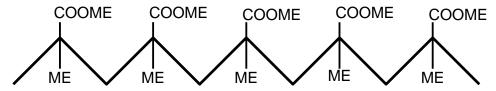
$$(R)-CH_{\epsilon}C \cdot + \cdot CCH_{\epsilon}-(R) \longrightarrow (R)-CH_{\epsilon}C-H + C=CH-(R)$$

Catalysts

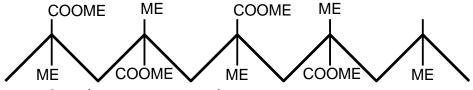
- Multiple catalysts can be used in production of PMMA. Some of these are:
 - Butyl Lithium
 - Highly active catalysts based on group 4 metallocenes
 - An aluminum system supported by salen ligands

Why Use Different Catalysts?

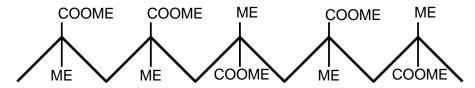
- Different catalysts result in different versions of the polymer
 - Variation is due to the placement of the ester (R-O-R) and methyl (CH₃) groups along the polymer backbone
- Isotactic similar groups on same side of chain



Syndiotactic – two groups alternate



Atatactic – displays no regular pattern



Every other carbon in the chain is a steriocenter

Properties of PMMA

- Lighter than glass (density is about half that of glass)
- Shatter proof
- Softer and easier to scratch than glass (scratch resistant coatings may be applied)
- Transmits more light than glass (92% of visible light)
- Does not filter UV light (may be coated with UV film)
- More transparent than glass, so windows can be made thicker

Current uses for PMMA

 Include many uses similar to those for which it was first developed but include many things never imagined by the inventors! A partial list of the uses for PMMA includes: Safety glass such as Plexiglass and Lucite – uses range from windows for aquariums and under-water restaurants to safety shields at hockey rinks to skylights in your home to simple paperweights





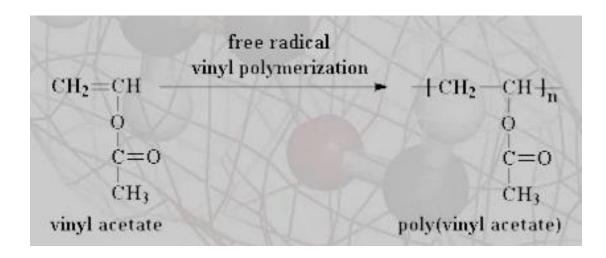
Medical Uses

- Used as bone cement for use in arthroplastic procedures of the hip, knee, and other joints for the fixation of polymer or metallic prosthetic implants to living bone
- Used in Pacemakers

What are characteristics of biomedical polymers?

Polyvinyl acetate (PVAc)

- Poly(vinyl acetate) was discovered in Germany in 1912 by Fritz Klatte.
- The monomer, vinyl acetate, was first produced on an industrial scale by addition of acetic acid to acetylene with a mercury(I) salt but it is now primarily made by palladium catalyzed oxidative addition of acetic acid to ethylene.
- Polyvinyl acetate is prepared by polymerization of vinyl acetate monomer (free radical vinyl polymerization of the monomer vinyl acetate).



PROPAGATION

$$R - H_2C - \dot{c}H + n(H_3C = cH) \rightarrow R(H_3C - cH) + hc - \dot{c}H$$

$$C = cH_3 \qquad cH_4 \qquad cH_4$$

PERMINATION

PROPERTIES

- ✓ Under alkaline conditions, boron compounds such as boric acid or borax cause the polymer to cross-link.
- ✓ A number of microorganisms can degrade polyvinyl acetate(fungi and algae).
- ✓ Sets by the removal of water due to evaporation or absorption into a substrate.
- ✓ Have good weather resistance
- ✓ Withstand water, grease, oil, and petroleum fuels degradation.
- √ good biodegradation resistance
- ✓ poor resistance to creep under load.
- ✓ Softens at 30-45C
- ✓ Soluble in benzene, chloroform, methanol, acetone, butyl acetate
- ✓ Insoluble in ligroin, diethyl ether, butanol, turpentine, water, oils
- √ Can absorb 3-5% water when immersed for 16 hours at 60 C.
- ✓ Burns with a dark yellow flame that smells of acetic acid.
- √ Combustible.

Uses

- · PVA water-based emulsions have been used as latex house paints.
- Making commonly used household white glues.
- · Making wood glue.
- · Makin paper glue.
- · Adhesives.
- · Glues for porous material.
- · Used as a primer for drywall and other substrates.
- · As a mortar additive.

PolyLactic acid (Bio-Degradable Polymer)

Condensation mechanism- Removal of water molecule

Polylactic acid, **PLA** is a <u>thermoplastic polyester</u> with backbone formula $(C_3H_4O_2)_n$ or $[-C(CH_3)HC(=O)O-]_n$, formally obtained by <u>condensation</u> of <u>lactic acid</u> $C(CH_3)(OH)HCOOH$ with loss of water. It can also be prepared by ring-opening polymerization of <u>lactide</u> $[-C(CH_3)HC(=O)O-]_2$, the cyclic dimer of the basic repeating unit.

The degree of crystallinity, and hence many important properties, is largely controlled by the ratio of D to L enantiomers used.

PLA has become a popular material due to it being economically produced from <u>renewable resources</u>. The monomer is typically made from fermented plant starch such as from <u>corn</u>, <u>cassava</u>, <u>sugarcane</u> or <u>sugar beet pulp</u>.

In 2010, PLA had the second highest consumption volume of any bioplastic of the world. Its widespread application has been hindered by numerous physical and processing shortcomings. PLA is the most widely used plastic filament material in 3D printing.

Properties-

PLA polymers range from amorphous glassy polymer to semi-crystalline and highly crystalline polymer with a glass transition 60–65 °C, a melting temperature 130-180 °C, and a Young's modulus 2.7–16 GPa.

Heat-resistant PLA can withstand temperatures of 110 °C.

Several technologies such as <u>annealing</u>, adding <u>nucleating</u> agents, forming composites with fibers or <u>nano-particles</u>, chain extending and introducing crosslink structures have been used to enhance the mechanical properties of PLA polymers. Polylactic acid can be processed like most thermoplastics into <u>fiber</u> and film.

The high surface energy of PLA results in good printability, making it widely used in 3D printing. PLA is used as a feedstock material in desktop <u>fused filament fabrication</u> by <u>3D printers</u>, such as <u>RepRap</u> printers. PLA objects can be fabricated by 3D printing, casting, <u>injection moulding</u>, <u>extrusion</u>, machining, and solvent welding.

PLA is soluble in a range of organic solvents like ethyl acetate. PLA is also soluble in hot <u>benzene</u>, <u>tetrahydrofuran</u>, and <u>dioxane</u>.

PLA can be <u>solvent welded</u> using <u>dichloromethane</u>. <u>Acetone</u> also softens the surface of PLA, making it sticky without dissolving it, for welding to another PLA surface.

Applications-

PLA is used in <u>disposable tableware</u>, <u>cutlery</u>, housings for kitchen appliances and electronics such as laptops and handheld devices, and microwavable trays. (However, PLA is not suitable for microwavable containers because of its low glass transition temperature.

It is used for compost bags, food packaging and loose-fill packaging material that is cast, injection molded, or spun.

In the form of a film, it shrinks upon heating, allowing it to be used in <u>shrink</u> tunnels.

In the form of fibers, it is used for monofilament fishing line and netting. In the form of <u>non-woven fabrics</u>, it is used for <u>upholstery</u>, disposable garments, <u>awnings</u>, feminine hygiene products, and <u>diapers</u>.

PLA has applications in engineering plastics, where the stereocomplex is blended with a rubber-like polymer such as <u>ABS</u>. Such blends have good form stability and visual transparency, making them useful in low-end packaging applications.

PLA is used for automotive parts such as floor mats, panels, and covers.

PLA is used for vegetation and weed prevention. It is used for sandbags, planting pots, binding tape and ropes.

Applications in the field of Medicine-

PLA can degrade into innocuous lactic acid, so it is used as medical implants in the form of anchors, screws, plates, pins, rods, and mesh.

It breaks down inside the body within 6 months to 2 years. This gradual degradation is desirable for a support structure, because it gradually transfers the load to the body (e.g. to the bone) as that area heals. PLA has high strength characteristics.

Thanks to its bio-compatibility and biodegradability, PLA has also found ample interest as a polymeric scaffold for drug delivery purposes.

The composite blend of various PLA with tricalcium phosphate (TCP) is used as scaffolds for bone engineering.

Poly-L-lactic acid (PLLA) is the main ingredient in <u>Sculptra</u>, a facial volume enhancer used for treating <u>lipoatrophy</u> of the cheeks.

PLLA is used to stimulate collagen synthesis in fibroblasts via foreign body reaction in the presence of macrophages. Macrophages act as a stimulant in secretion of cytokines and mediators such as <u>TGF-β</u>, which stimulate the fibroblast to secrete collagen into the surrounding tissue. Therefore, PLLA has potential applications in the dermatological studies

Degradation-

PLA is degraded abiotically by three mechanisms: [42]

- 1. Hydrolysis: The ester groups of the main chain are cleaved, thus reducing molecular weight.
- 2.Thermal degradation: A complex phenomenon leading to the appearance of different compounds such as lighter molecules and linear and cyclic oligomers with different *Mw*, and lactide.
- 3.Photodegradation: UV radiation induces degradation. This is a factor mainly where PLA is exposed to sunlight in its applications in <u>plasticulture</u>, packaging containers and films.

PLA is effectively digested in hotter industrial composts, usually degrading best at temperatures of over 60°C.

PLA samples of various molecular weights were degraded into methylactate (a green solvent) by using a metal complex catalyst.

PLA can also be degraded by some bacteria, such as <u>Amycolatopsis</u> and <u>Saccharothrix</u>. A purified protease from <u>Amycolatopsis</u> sp., <u>PLA depolymerase</u>, can also degrade PLA. Enzymes such as <u>pronase</u> and most effectively <u>proteinase</u> <u>K from <u>Tritirachium album</u> degrade PLA.</u>

Four possible end-of-life scenarios are the most common:

Recycling: which can be either chemical or mechanical. Currently, the SPI <u>resin</u> <u>identification code</u> 7 ("others") is applicable for PLA.

Composting: PLA is biodegradable under industrial composting conditions, starting with chemical hydrolysis process, followed by microbial digestion, to ultimately degrade the PLA. Under industrial composting conditions (58 °C), PLA can partly (about half) decompose into water and carbon dioxide in 60 days, after which the remainder decomposes much more slowly.

Incineration: PLA can be <u>incinerated</u> without producing chlorine-containing chemicals or heavy metals because it contains only <u>carbon</u>, <u>oxygen</u>, and <u>hydrogen</u> atoms. Since it does not contain chlorine it does not produce <u>dioxins</u> during incineration.

Landfill: the least preferable option is landfilling because PLA degrades very slowly in ambient temperatures, often as slowly as other plastics.

PolyDimethylsiloxane (Inorganic Polymer)

$$H_{3}C \xrightarrow{Si} + 2 H_{2}O \xrightarrow{H_{3}} + 2 HCI$$

$$H_{3}C \xrightarrow{CH_{3}} + 2 HCI$$

$$H_{3}C \xrightarrow{CH_{3}} + 2 HCI$$

$$H_{4}C \xrightarrow{CH_{3}} + 1 HCI$$

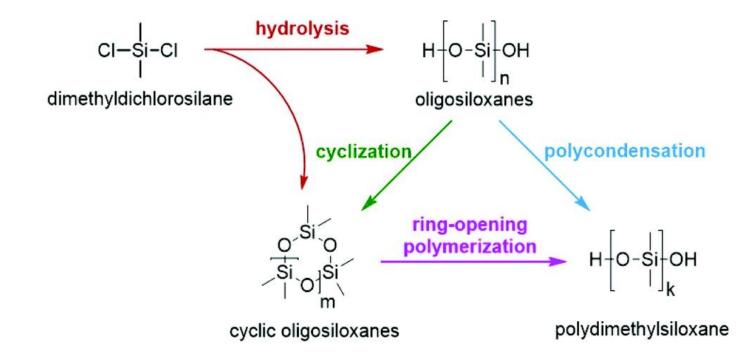
$$H_{5}C \xrightarrow{CH_{3}} + 1 HCI$$

$$H_{5}C \xrightarrow{CH_{3}} + 1 HCI$$

$$H_{7}C \xrightarrow{CH_{3}} + 1 HCI$$

$$H_{7}C \xrightarrow{CH_{3}} + 1 HCI$$

$$H_{7}C \xrightarrow{CH_{3}} + 1 HCI$$



Polydimethylsiloxane (**PDMS**), also known as **dimethylpolysiloxane** or **dimethicone**, belongs to a group of polymeric <u>organosilicon</u> compounds that are commonly referred to as <u>silicones</u>.

It can be prepared by polycondensation.

Well-defined PDMS with a low polydispersity index and high homogeneity is produced by controlled anionic ring-opening polymerization of hexamethylcyclotrisiloxane. Using this methodology it is possible to synthesize linear block copolymers, heteroarm star-shaped block copolymers and many other macromolecular architectures.

PDMS is the most widely used <u>silicon</u>-based <u>organic</u> <u>polymer</u>, as its versatility and properties lead to many applications.

It is particularly known for its unusual <u>rheological</u> (or flow) properties. PDMS is optically clear and, in general, inert, non-<u>toxic</u>, and non-<u>flammable</u>.

Properties-

PDMS is viscoelastic.

this unique polymer is relatively easy to tune.

PDMS can easily be integrated into a variety of microfluidic and microelectromechanical systems.

the cross-linked cured version of PDMS resembles rubber in a solidified form.

PDMS has a low elastic modulus.

The <u>shear modulus</u> of PDMS varies in the range of 100 kPa to 3 MPa. The <u>loss</u> tangent is very low (tan $\delta \ll 0.001$).

PDMS is hydrophobic.

Solid PDMS samples will not allow aqueous solvents to infiltrate and swell the material.

most organic solvents will diffuse into the material and cause it to swell.

<u>Diisopropylamine</u> swells PDMS to the greatest extent; solvents such as <u>chloroform</u>, <u>ether</u>, and <u>THF</u> swell the material to a large extent. Solvents such as <u>acetone</u>, <u>1-propanol</u>, and <u>pyridine</u> swell the material to a small extent. Alcohols and polar solvents such as <u>methanol</u>, <u>glycerol</u> and water do not swell the material appreciably.

Applications-

PDMS is a common <u>surfactant</u> and is a component of <u>defoamers</u>. PDMS, in a modified form, is used as an <u>herbicide</u> <u>penetrant</u> and is a critical ingredient in water-repelling coatings, such as Rain-X.

Dimethicone is used in the active silicone fluid in automotive viscous limited slip differentials and couplings.

PDMS is commonly used as a stamp resin in the procedure of <u>soft</u> <u>lithography</u>, for flow delivery in <u>microfluidics</u> chips.

it possesses superior optical properties, allowing for minimal background and autofluorescence during for fluorescent imaging. researchers can utilize various surface chemistry techniques of PDMS for different functions creating unique lab-on-a-chip devices for rapid parallel testing.

PDMS is being used in the making of synthetic <u>gecko adhesion</u> dry adhesive materials.

Medicine and cosmetics

Used in <u>over-the-counter drugs</u> as an <u>antifoaming</u> <u>agent</u> and <u>carminative</u>. [25][26] It has also been at least proposed for use in contact lenses.

Silicone <u>implants</u> used for body enhancement are made out of a PDMS elastomer shell

PDMS is useful as a lice or flea treatment because of its ability to trap insects. It also works as a moisturizer that is lighter and more breathable than typical oils.

PDMS compounds such as amodimethicone, are effective conditioners and act as surfactants.

Used in contact lenses.

PDMS is added to many cooking oils as an antifoaming agent to prevent oil splatter during the cooking process. As a result of this, PDMS can be found in trace quantities in many fast food items such as McDonald's Chicken McNuggets, french fries, hash browns, milkshakes and smoothiesand Wendy's french fries.

Polymers In Medicine

Cellophane
PGA, PLA, PLGA
Polydimethylsiloxane
Polyethylene and PMMA
Polytetrafluoroethylene
Polyurethane

What are they?

Substances other than food or drugs contained in therapeutic or diagnostic systems that are in contact with tissue or biological fluids.

Why use Biomaterials?

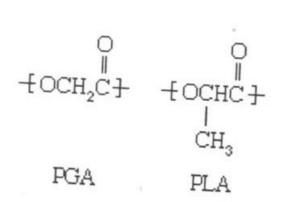
Improve patient's quality of life by replacing a defective body part with a substitute.

Physicians were limited to use off-the shelf supplies.

Novel biodegradable polymers and modified natural substances.

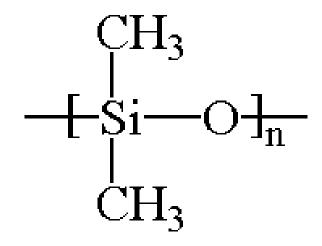
| | Applications of Biomaterials | | |
|--------------|------------------------------|------------------|-------------------|
| | | | |
| Polymer | Applications | Polymer | Applications |
| PDMS | Catheters, heart | Polytetrafluoroe | Heart valves |
| | Valves | thylene | Vascular grafts |
| | | | Nerve repair |
| Polyurethane | ventricular assist | Polyethylene | Catheters, hip |
| | Devices | | prostheses |
| | | Polymethylmetha | Fracture fixation |
| PGA, PLA, | Drug delivery, devices | crylate (PMMA) | |
| And PLGA | | | |
| | | Cellophane | Dialysis |
| | | | membranes |

Polylactic acid, Polyglycolic cid



- Amorphous forms used in drug delivery systems
- Crystalline forms good for scaffolding, or sutures; stents, plastic surgery, plates rods, pins, screws.
- Two essentials in scaffolding: high surface to volume ratio, highly porous
 - -Allows cells to easily proliferate for setup of pathways
 - -Setup of pathways for nutrients

Polydimethylsiloxane



- "Silicon"
- Lubricants and Foaming agents
- Pacemakers and Vaccine Delivery systems

- Used in treatment of prostate carcinoma
- Small biodegradable pellets (188 m)
 injected into area of body where needed;
 heart valves, blood filters, vascular tubing,
 artificial heart.
- Smaller doses, less toxic effects for patient

PMMA

- Thermoplastics, exhibit moderate to high tensile strength with moderate elongation
- Used for Hip replacement and Fracture Fixation
- Annual procedures approaching 5 Million
- Metal alternatives have corrosive problems



PMMA disc over femoral window during the molding process

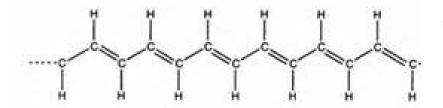


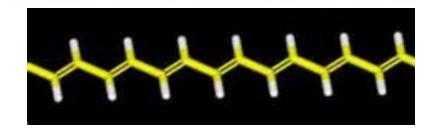
PMMA template after polymerization, showing molded plug

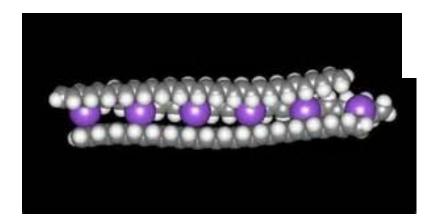
Conducting polymers

Intrinsically conducting polymers (ICPs) belong to a class of organic materials with unique electronic properties such as electric conductivity, electrochromism, and electroactivity. Conjugated electrons in the backbone of their macromolecules are responsible for these properties. Due to their high electrical properties, ICPs are intensively investigated for application in electronics, microelectronics, optoelectronics mainly for areas in aerospace and automobile industries. Among the most promising applications of the ICPs are corrosion protection, solid-state charge storage devices, electromagnetic screens, antistatic coatings and gas separation coatings. However, poor mechanical properties, environmental sensitivity, moderate stability of electrical properties with temperature significantly limit the industrial applicability of ICPs.

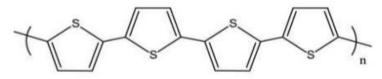
Polyacetylene



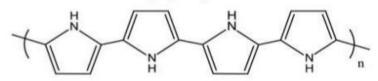




Few Common Conducting Polymers



polythiophene



polypyrrole

$$- \left(\begin{array}{c} \\ \\ \end{array} \right) - \left(\begin{array}{c} \\$$

polyaniline

(DCP) Doped conducting polymer

While the addition of a donor or an acceptor molecule to the polymer is called "doping", the reaction that takes place is actually a redox reaction. • The first step is the formation of a cation (or anion) radical, which is called a soliton or a polaron.

 $Pn \Leftrightarrow [Pn + A -]$ (reduction oxidation)

• As synthesized conductive polymers exhibit very low conductivities. It is not until an electron is removed from the valence band (p-doping) or added to the conduction band (n-doping, which is far less common) does a conducting polymer become highly conductive. • Doping (p or n) generates charge carriers which move in an electric field. Positive charges (holes) and negative charges (electrons) move to opposite electrodes. This movement of charge is what is actually responsible for electrical conductivity.

(i) Oxidation process (p-doping):

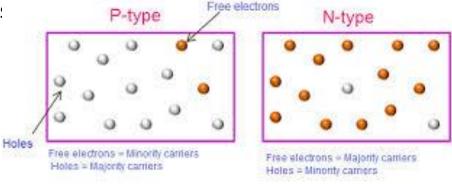
$$(C_2H_2)_n$$
 + FeCl₃ \rightarrow $(C_2H_2^+)_n$.FeCl₄ + FeCl₂
Polyacetylene lewis acid +vely charged backbone $2(C_2H_2)_n$ + $3I_2$ \rightarrow $2[(C_2H_2^+)_nI_3^-]$

(i) Reduction process (n-doping):

$$(C_2H_2)_n + C_{10}H_7NH_2$$
 \rightarrow $[(C_2H_2^-)_nNH^+] + C_{10}H_8$
Polyacetylene Naphthylamine reduction -vly charged backbone naphthalene

The above reactions are most likely to occur saturated polym electrons, as they can be very easily removed from the polymeric chains to form polyion therefore, these are the

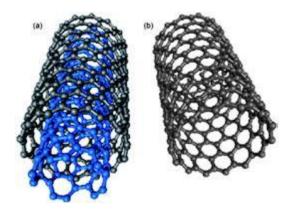
types of polymers, which as:



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• *ECP*

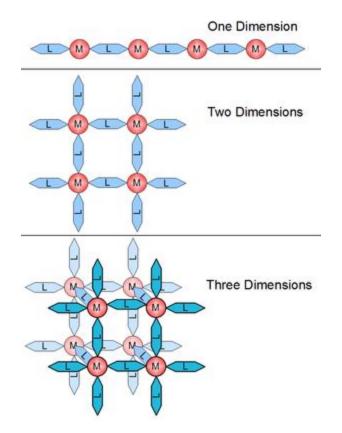
> One type of extrinsically conducting polymer consists of a matrix of poly(ethene) with a percentage of conducting carbon black (a form of powdered graphite) incorporated (filled) in it. If the carbon black particles are close enough to be in contact with one another, the material conducts. If the particles are not in contact, it is an insulator. This means that the degree of electrical conduction depends on temperature. At high temperature, the poly(ethene) matrix expands and pulls the particles of carbon black away from each other, decreasing the conductivity. At lower temperatures the poly(ethene) contracts, the carbon black particles are closer and the material conducts well. This temperature dependence of conductivity leads to the use of this material in self-regulating heater cable and PolySwitch* re-settable circuit protection devices.



- Another type includes the blends Extrinsically conductive polymers can involve a blend of conductive and nonconductive polymers.
 - Co-ordinate Conjugate Polymers (CCP)-
 - A coordination polymer is an inorganic or organometallic polymer structure containing metal cation centers linked by organic ligands. More formally a coordination polymer is a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions.
 - It can also be described as a polymer whose repeat units are coordination complexes. Coordination polymers contain the subclass coordination networks that are coordination compounds extending, through repeating coordination entities, in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links, or a coordination compound extending through repeating coordination entities in 2 or 3 dimensions. A subclass of these are the metal-organic frameworks, or MOFs, that are coordination networks with organic ligands containing potential voids.

Coordination polymers are relevant to many fields such as <u>organic</u> and <u>inorganic chemistry</u>, <u>biochemistry</u>, <u>materials science</u>, <u>electrochemistry</u>, and pharmacology, having many potential applications. This interdisciplinary nature has led to extensive study in the past few decades.

Coordination polymers can be classified in a number of different ways according to their structure and composition. One important classification is referred to as <u>dimensionality</u>.



A structure can be determined to one-, two- or threebe dimensional, depending on the number of directions in space the extends in. A array dimensional structure extends in a straight line (along the x axis); a two-dimensional structure extends in a plane (two directions, x and y axes); and a three-dimensional structure extends in all three directions (x, y, and z axes). This is depicted in Figure