CHEM3020: POLYMER CHEMISTRY

Unit-5: Preparation, structure, properties and application of polymers

Polyamides and related polymers. Phenol formaldehyde resins (Bakelite, Novalac), Polyurethanes, Teflon

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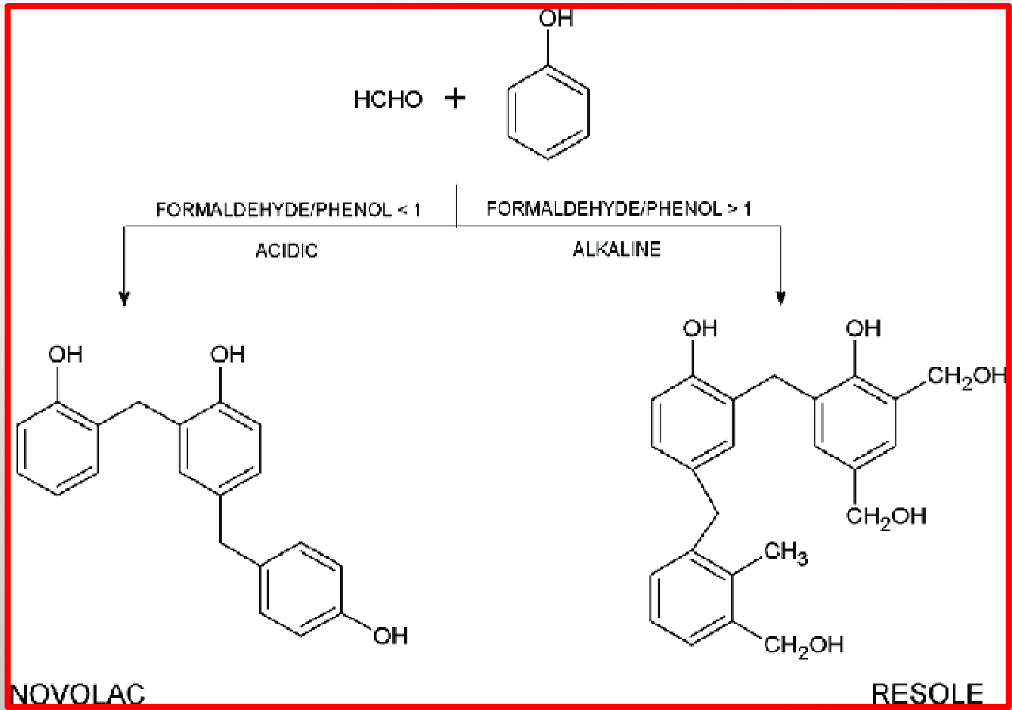
Phenol - formaldehyde polymer (Bakelite and related polymers)

Phenol - formaldehyde polymer: Phenol - formaldehyde polymers are the oldest synthetic polymers. These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst. The reaction starts with the initial formation of *o*-and/or *p*-hydroxymethyl phenol derivatives, which further react with phenol to form compounds having rings joined to each other through –CH_2 groups. The initial product could be a linear product.

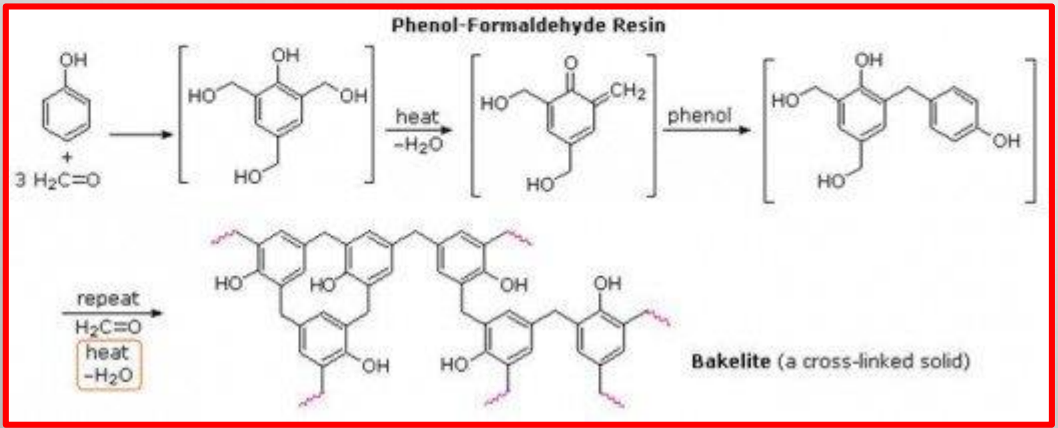
Base-catalyzed phenol formaldehyde resins are made with formaldehyde to phenol ratio of around 1.5. Such resins are sometimes called resols, and are found in varied industrial products.

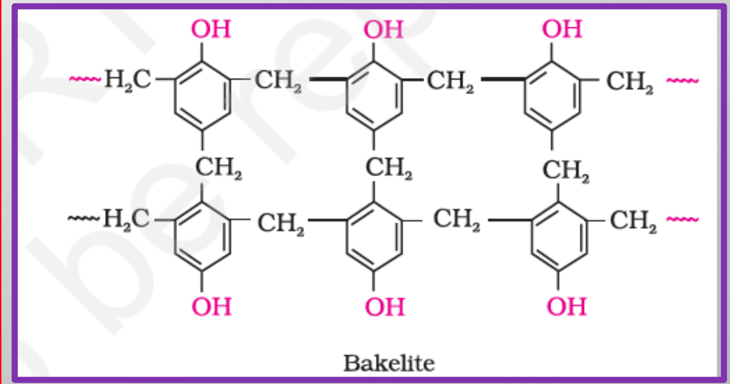


Novolaks (or novolacs)

Novolaks (or novolacs) are phenol-formaldehyde resins with a formaldehyde to phenol **molar ratio of less than one**. In place of phenol itself, they are often produced from cresols (methyl phenols) and the polymerization is completed by using acid-catalysis (sulfuric acid, oxalic acid, hydrochloric acid). The phenolic units are mainly linked by methylene and/or ether groups. The polymer obtained is thermoplastic and require to add hardener to form a thermoset. Hexamethylenetetramine is a hardener added to crosslink novolac and at a temperature greater than 90 °C, it forms methylene and dimethylene amino bridges.

Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called **bakelite**.



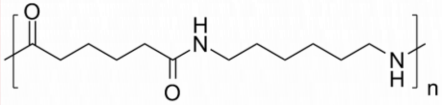


Application of Phenol - formaldehyde polymer

Phenol Formaldehyde resins were the first commercial synthetic resins (plastics). It has been widely used for the production of molded products including billiard balls, laboratory countertops, and coatings and adhesives.

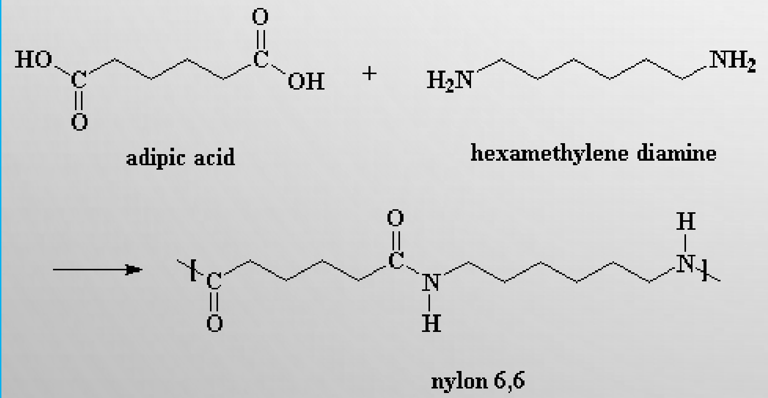
Novolacs have multiple uses as tire tackifier, high temperature resin, paints, binder for carbon bonded refractories and carbon brakes.

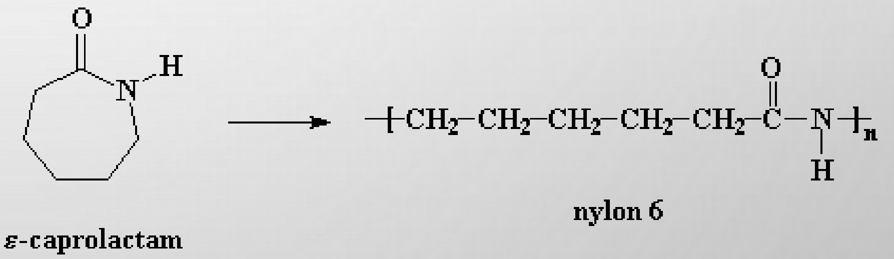
Bakelite is used for making combs, phonograph records, electrical switches and handles of various utensils.



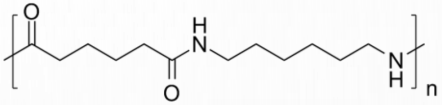
Polyamides-Nylon

Polyamides-Nylon: Nylon 66 (or 66-Nylon) is a condensation polymer formed by the condensation polymerization of Adipic acid (a dibasic acid) and hexamethylenediamine (a diamine). Nylon–6 is a polymer of caprolactum . The number refers to the total carbon atoms in the ring, which can vary from 5 to 12. Both Nylon–6 and Nylon–66 have similar properties and greatest commercial importance. The major difference in the physical properties of these two nylons is that the melting point of Nylon –66 is 40 – 45^0C higher than Nylon–6. Moreover, Nylon – 66 is harder, rigid and its abrasive – resistance is lower than that of Nylon–6.





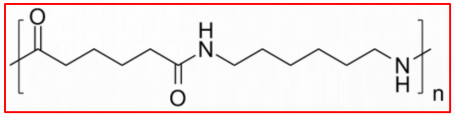
Polyamides-Nylon



Production of Nylon66: In the production of Nylon – 66, first, the amine and acid is mixed in an aqueous solution , with the pH adjusted at 7.8 to form Nylon salt. The salt is then concentrated under vacuum. It is thereafter charged to an autoclave where the rest of the water is removed. The temperature is gradually increased to 280^0C in the autoclave to complete the polymerization and the water of condensation is removed. The final product has a molecular weight of 12000–16000. It is extruded as ribbons onto chilling rolls. After filtration, the melt polymers are passed via a spinnerette (a small metal plate with fine holes) to produce nylon fibers. Upon cooling , these filaments harden and are wound on bobbins. In order to give the fibre desirable textile properties, the threads are stretched to about 4 times its original length.

Production of Nylon-6: Nylon–6 is manufactured by the step – wise condensation of caprolactum with no net water removal. The polymerization of caprolactam is carried out by adding water to open the ring and then removing the water again at higher temperature. The reaction can be performed in an autoclave or continuous reactor. Polycaprolactum is in equilibrium with about 10% of the monomer, hence the monomer must be removed by washing with water before the polymer can be spun.

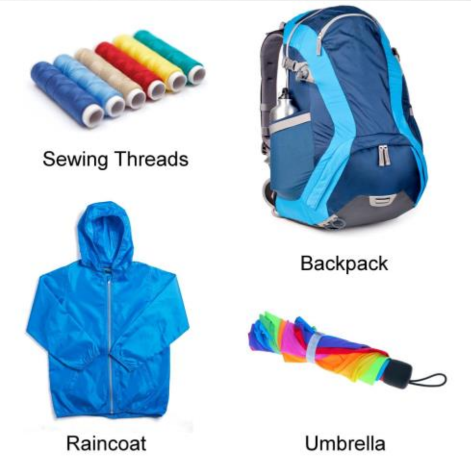
Properties and applications Nylon



Properties: Both as plastic and as fibers, the nylons are characterized by a good combination of high strength, elasticity, toughness, and abrasion resistance. Although mechanical properties not well maintained at higher temperature, but at lower temperature, toughness and flexibility retained very well. The electrical uses is restricted due to the presence of polar groups in the polymer chain.

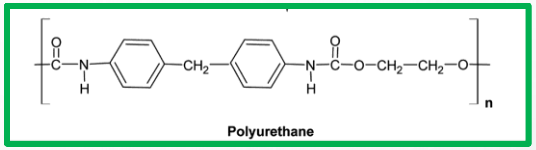
Both Nylon –6 and Nylon–66 have similar properties and can be used as thin films and fibers. Nylon 6 is used for the manufacture of tyre cords, fabrics and ropes.

Nylon-66 is used in making sheets, bristles for brushes and in fiber for textile industry, carpets, rollers, slides and door latches



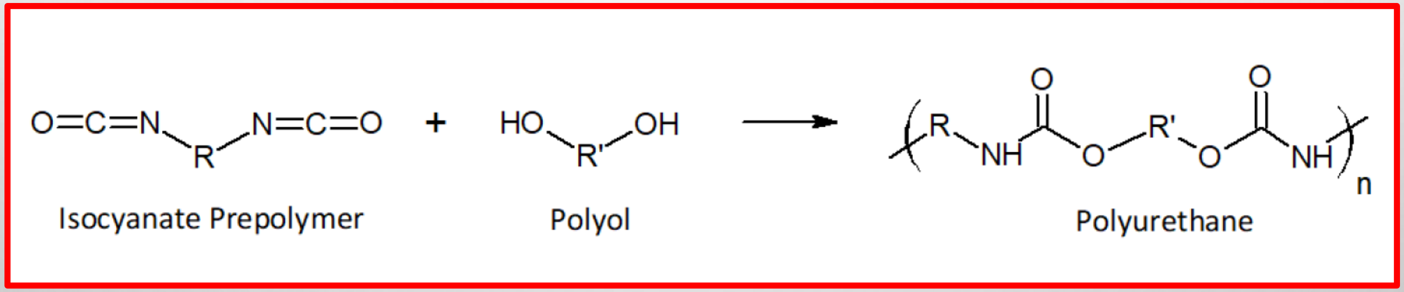
Polyurethane

Polyurethane is a polymer composed of organic units joined by carbamate (urethane) links. Most polyurethanes are thermosetting polymers that do not melt when heated.



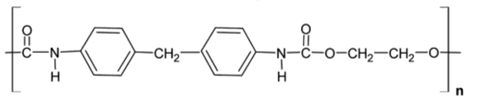
Polyurethane

Polyurethane polymers are typically formed by the reaction of a di- or triisocyanate and a polyol. Since polyurethanes contain two types of monomers, which polymerizes one after the other, they are classed as alternating copolymers.



Properties: In the production of urethane foams, excess isocyante groups react with water or carboxylic acid to produce carbon di oxide, blowing the foam. Urethane foam can be flexible or rigid depending on the type of crosslinking.

Applications of Polyurethanes

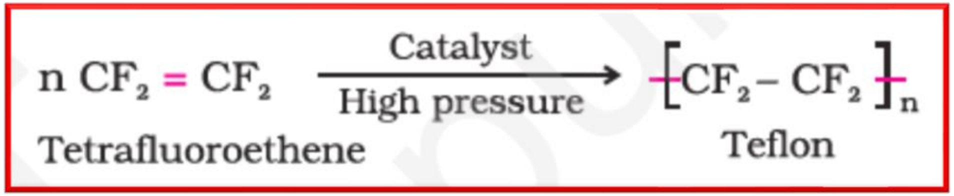


Polyurethane

The use of flexible urethanes foams for cushion for furniture's and automobiles were preferred over rubber foam because of better strength, low density and easier fabrications. Polyurethanes are also used in the manufacture of rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires. It is also used as high-performance adhesives, surface coatings and sealants.

Polytetrafluoroethylene (Teflon)

Polytetrafluoroethylene (Teflon): Teflon is manufactured by heating tetrafluoroethene with a free radical or persulphate catalyst at high pressures



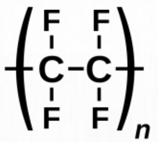
$$\underset{\text{Tetrafluoroethene}}{n\,CF_2=CF_2} \xrightarrow[\text{High pressure}]{\text{Catalyst}} \underset{\text{Teflon}}{\left[CF_2-CF_2\right]_n}$$

PTFE is produced by polymerization of tetrafluoroethylene with radical initiators at elevated temperature in presence of water..

$$n\ F_2C{=}CF_2 \rightarrow -(F_2C-CF_2)_n-$$

Tetrafluoroethylene can explosively decompose to tetrafluoromethane and carbon, hence redox initiators may also used for polymerization of tetrafluoroethylene. The process is typically initiated with persulfate (or hydrogen peroxide), which homolyzes to generate sulfate radicals:

$$[O_3SO-OSO_3]^{2-} \rightleftharpoons 2\ SO_4{}^{\bullet-}$$



$$\left(-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}- \right)_n$$

Polytetrafluoroethylene (Teflon)

Polytetrafluoroethylene is chemically inert and resistant to attack by corrosive reagents. It is hydrophobic in nature and possesses fairly high heat resistance. It is used in making oil seals and gaskets and is best known for its use in non–stick surface coated utensils (frying pans and other cookware).

References and suggestions for further reading:

1. Textbook of Polymer Science by Fred W. Billmeyer, Wiley
2. Polymer Chemistry by Charles E Carraher, Jr., Marcel Dekker, Inc.
3. Principle of Polymerization by George Odian, Wiley

THANK YOU