Annexure I

FINAL REPORT OF THE WORK DONE IN THE THREE YEARS OF THE MAJOR RESEARCH PROJECT

Title: Synthesis and Characterization of Nanoporous Polymer and their Applications.

Ref. No. F No. : 42-314/2013(SR) Dated: 25 March 2013

A polymer is a large molecule (macromolecule) composed of repeating structural units typically connected by covalent chemical bonds. Polymers have played an important role from the beginning of life. Polymers like DNA, proteins, RNA and polysaccharides play a crucial role in animal and plants life. Polymeric materials have been used since early times, even though their exact nature was unknown. In the 1400s, Christopher Columbus found elasticity property playing with balls made from materials obtained from a tree. This was natural rubber which became an important product after Charles Goodyear who discovered that the addition of sulfur improved the properties. In 19th century, natural polymers were modified to meet the technical requirements. The excellent examples are nitrocellulose, cellophane and natural rubber (cis-polyisoprene). Goodyear in 1847 vulcanized the natural rubber with sulphur and develops useful products called tires for the cars.

The first synthetic polymer was invented by Baekeland in 20th centenary, by reacting phenol and formaldehyde resulting in black resin named Bakelite. In 1907 Leo Bakeland patented Bakelite, the first fully synthetic polymer. This hard plastic was used as an electrical insulator and paved the way for the more than 60,000 different synthetic plastics on the market today. Each year companies manufacture more than 30 million tons of plastics that are used in myriad of applications. We wear clothes containing polyester and nylon fibers, eat food packaged in polyethylene containers, drink water delivered through polyvinyl chloride pipes, walk on carpets made of polyolefin fibers, and sleep on mattresses made of polyurethane foam. The variety of applications of synthetic polymers is mind-boggling. Baekeland however, never realized in his life that he had made a polymer. Staudinger postulated the concept of polymer chains in 1920s, but scientific community did not accept his views. In 1930s the evidence for long chain molecules consisting of repeating unit became evident by the discovery of PE by ICI. Lack of supply of natural rubber during the

World War II form Asian countries to USA and Europe ignited the start of synthetic rubber industries. The synthetic polymer industries took off the ground in 1950s when Ziegler and Natta invented a catalyst for the synthesis of isotatic polypropylene and polyethylene.

In 1960s and 1970s the production of engineering polymers, such as polyethylene terephatalate (PET), polybutylene terephatalate (PBT), polycarbonate (PC), poly phenylene ether (PPE) catered the market with useful products. The control over the polymerization process was boosted by the new metallocene based catalyst system enabling the production of novel polymer structures such as syndiotactic-polystyrene (s-PS), syndiotactic-polypropylene (s-PP) and low density polyethylene (LDPE) matching the properties of elastomers. The 1980s can be considered as the decade of ‘High-Chem’ as huge research in industry and academic have been developed to search for ultimate performance for polymer as construction material. Today, polymers are commonly used in thousands of products as plastics, elastomers, coatings, and adhesives.

Polymers are organic compounds that have an extended p-orbital system through which electrons can move from one end of the polymer to the other. The most common are polyaniline and polypyrrole polyaniline films, which sandwiched around an ion-conducting film, are considered as material for artificial muscles for robots. Polypyrrole has been used for the development of micro muscles.

The enthusiasm of the polymer industries to develop new polymers became zero at the end of the century. The introduction of new polymers needs too many efforts in terms of production cost and marketing, that there would be no new polymers on the market the coming decades. In fact the polymers we use today have been invented in 1950s and 1960s. The focus is now on post-reactor modification rather than producing polymer in reactor from the monomers.

POLYMER TYPES

Traditionally, the industry has produced two main types of synthetic polymer – plastics and rubber. The distinction is that plastics are large and rigid materials at service temperatures while rubbers are flexible, low modulus materials which exhibit long-range elasticity [5]. Plastics are further subdivided into thermoplastics and thermosets, the latter type being materials where the long chains are linked together by crosslink’s, a feature they share with conventional vulcanized rubbers. As Figure 1 shows, however, the distinction in terms of stiffness has become blurred by the development of thermoplastic elastomers (TPEs). Moreover, all polymers, irrespective of their nature, can be reinforced by a very wide range of fillers to produce composite materials.

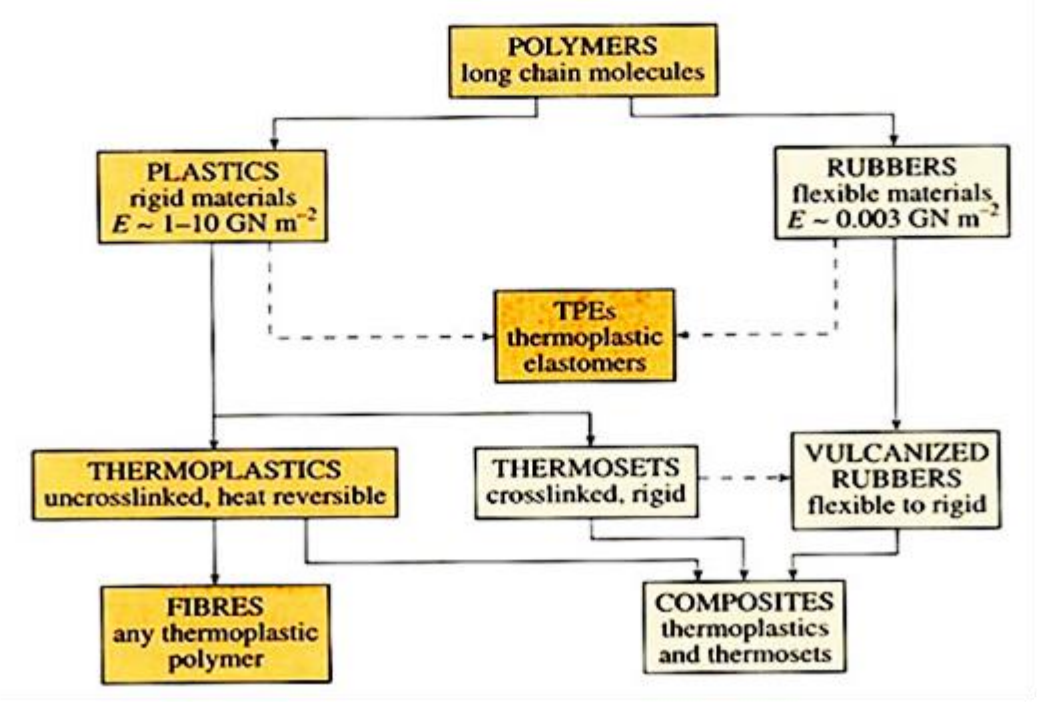

Figure.1. Classification of polymers by properties

Another way of classifying polymers is in terms of their form or function, varying from additives to other bulk materials (e.g. viscosity modifiers in plaster), coatings to products (e.g. paints), film and membranes to fibres (e.g. textiles) and bulk products such as pipe, containers and mouldings (Figure 2). Some of these materials are of course used as products in their own right, or manipulated further into finished products. This does not always happen, however, some polymers being a disposable intermediary in certain industrial processes. Thus photoresists are used to create the circuit patterns on semiconductor chips through controlled degradation, and are entirely absent in the final product.

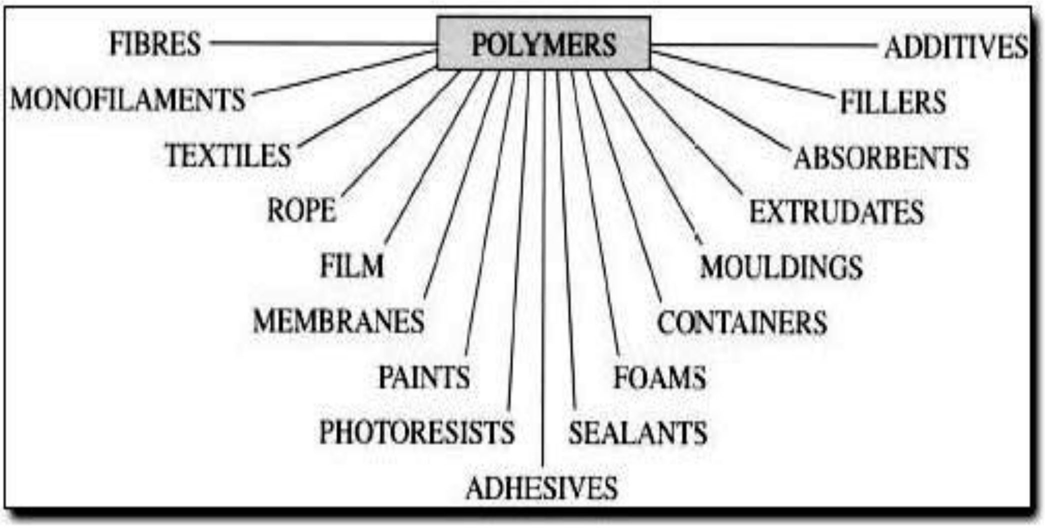

Figure 2. Classification of polymers by design function

CLASSIFICATION OF POLYMERS

Natural and Synthetic Polymers

Depending on their origin polymers can be grouped as natural and synthetic. Those polymer which isolated from natural materials are called natural polymers i.e. cotton, silk, wool, rubber, cellophane, cellulose, leather etc. Man-made polymers or polymers synthesized from low molecular weight compounds are called as synthetic polymers, i.e. polyethylene, PVC, nylon etc.

Synthetic polymer materials such as nylon, polyethylene, Teflon, and silicone have formed the basis for a burgeoning polymer industry. Most commercially important polymers today are entirely synthetic and produced in high volume on appropriately scaled organic synthetic techniques. Synthetic polymers today find application in nearly every industry and area of life. Polymers are widely used as adhesives and lubricants, as well as structural components for products ranging from children's toys to aircraft. They have been employed in a variety of biomedical applications ranging from implantable devices to controlled drug delivery. Polymers such as poly (methyl methacrylate) find application as photo-resist materials used in semiconductor manufacturing and low-k dielectrics for use in high-performance microprocessors. Recently, polymers have also been employed as flexible substrates in the development of organic light-emitting diodes for electronic display.

Thermoplastic and Thermosetting polymers

Thermoplastics are polymers which melt when heated and resolidify when cooled, while thermosets are those which do not melt when heated but, at sufficiently high temperatures, decompose irreversibly. This system has the benefit that there is a useful chemical distinction between the two groups. Thermoplastics comprise essentially linear or lightly branched polymer molecules, while thermosets are substantially crosslinked materials, consisting of an extensive three-dimensional network of covalent chemical bonding. The most important thermosetting resins, both from a historic standpoint and in current commercial application, are formaldehyde condensation products with phenol *(phenolic resins)* or with urea or melamine *(amino resins).* Other thermosetting types include the epoxy resins, the unsaturated polyester resins, urethane foams and the alkyds widely used for surface coating, and minor types.

Organic and Inorganic Polymers:

A polymer whose backbone chain is essentially made of carbon atom is termed as organic polymer. Generally to the backbone of carbon chain atoms like hydrogen, oxygen, nitrogen and sulfur is also attached. The majority of synthetic polymer is organic polymers. Inorganic polymers are those polymers which does not contain carbon atom in their backbone chain, i.e. Glass and silicone rubber.

Plastics, Elastomers, Fibres and liquid resins:

Depending on its ultimate form and use, polymers are classified as plastics, Elastomers, Fibres and liquid resins. When polymers are converted into hard and tough utility articles by heating are known as ‘plastics’. Polystyrene, PVC, and polymethyl mathacrylates are plastic material. When they are vulcanized into rubbery products are called as ‘elastomers’ such as natural rubber, synthetic rubber and silicon rubber. If polymers are drawn into long filament like materials then it is called as ‘fibres’. Nylon and terylene is the best example of fibres. Polymers can also be used as adhesive, potting compounds, sealants etc in liquid form are described as liquid resins.

POLYMERIZATION

In polymer chemistry, **polymerization** is a process of reacting monomer molecules together in a chemical reaction to form three-dimensional networks or polymer chains.

The size of a polymer molecule may be defined either by its mass or by the number of repeat units in the molecule. This latter indicator of size is called the *degree of polymerisation,* [DP]. The relative molar mass of the polymer is thus the product of the relative molar mass of the repeat unit and the DP.

Another classification system, first suggested by Carothers in 1929, is based on the nature of the chemical reactions employed in the polymerization. Polymerization is a chemical reaction in which polymers are formed from monomers. Here the two major groups are the *condensation (*Step-growth polymerization) and the *addition* (Chain-growth polymerization) polymers [27, 84-90]. Condensation polymers are those prepared from monomers where reaction is accompanied by the loss of a small molecule, usually of water, for example polyesters which are formed by the condensation shown in Reaction 1.1.

$$\mathbf{nHO - R - OH + nHOOC - R' - COOH}$$
$$\mathbf{\rightarrow HO[-R - COO - R' - COO -]nH + (n-1)H_2O}$$

By contrast, addition polymers are those formed by the addition reaction of an unsaturated monomer, such as takes place in the polymerisation of vinyl chloride (Reaction 1.2).

$$\mathbf{nCH_2 \ = CHCl \ \rightarrow \{-CH_2 - CHCl -\}n}$$

This system was slightly modified by P. J. Flory, who placed the emphasis on the mechanisms of the polymerization reactions. He reclassified polymerization as *step* reactions or *chain* reactions corresponding approximately to condensation or addition in Carother’s scheme, but not completely. A notable exception occurs with the synthesis of polyurethanes, which are formed by reaction of isocyanates with hydroxy compounds and follow ‘step’ kinetics, but without the elimination of a small molecule from the respective units (Reaction 1.3).

$$\mathbf{nOCN - R - NCO + NHO - R' - OH \ \rightarrow OCN\{-RNHCO_2\text{-}R'\text{-}\}n.\,OH}$$

In the first of these, the kinetics are such that there is a gradual build up of high relative molar mass material as reaction proceeds, with the highest molar mass molecules not appearing until the very end of the reaction. On the other hand, chain reactions, which occur only at a relatively few activated sites within the reacting medium, occur with rapid build up of a few high relative molar mass molecules while the rest of the monomer remains unreacted. When formed, such macromolecules stay essentially unchanged while the rest of the monomer undergoes conversion. This means that large molecules appear very early in the polymerization reaction, which is characterized by having both high relative molar mass and monomer molecules present for most of the duration of the reaction. Step reactions can give molecules having a variety of morphologies from the simple unbranched linear to the heavily crosslinked network. The final structure depends on the number of functional groups in the parent monomers, the greater the proportion with a functionality of greater than two, the more extensive will be the branching until, at sufficient degrees of branching, and a highly crosslinked network emerges. Chain reactions, by contrast, give only linear or lightly branched polymers. Thus, in terms of the thermoplastic/thermoset classification, chain reactions give thermoplastics, while step reactions may give either thermoplastics or thermosets.

COPOLYMER

A heteropolymer or copolymer is a polymer derived from two (or more) monomeric species, as opposed to a homopolymer where only one monomer is used. Copolymerization refers to methods used to chemically synthesize a copolymer [29-30]. Commercially relevant copolymers include ABS plastic, SBR, Nitrile rubber, styrene-acrylonitrile, styrene-isoprene-styrene (SIS) and ethylene-vinyl acetate.

There are two types of copolymers and their graphical representations are presented here (Figure 3 and Figure 4);

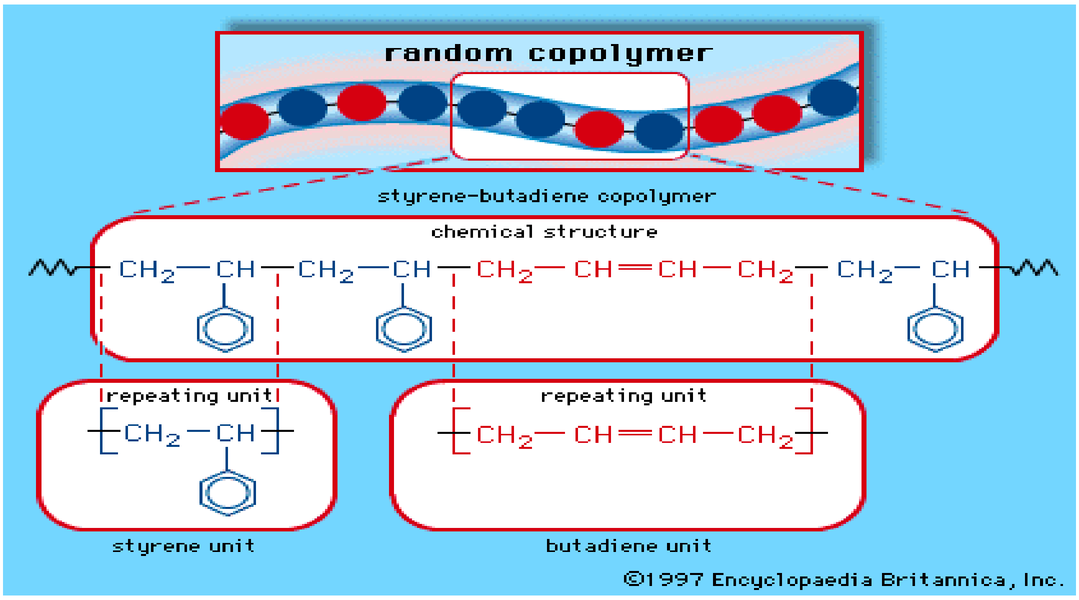

Figure. 3. Copolymer: random arrangement

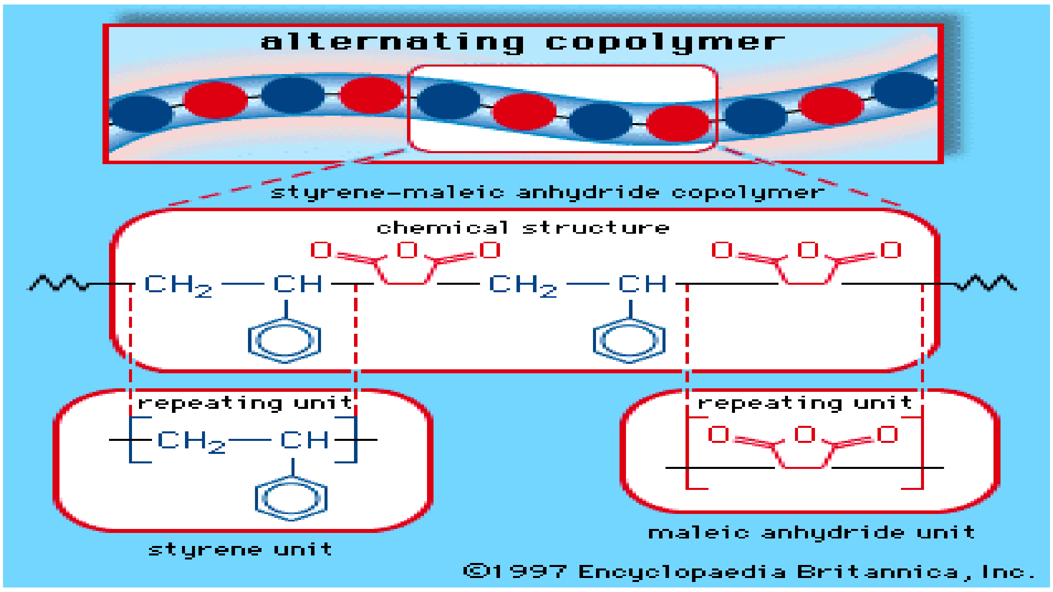

Figure.4. Copolymer: alternating arrangement

AROMATIC POLYMERS

A generic name for an aromatic polymer containing 52% by volume of continuous carbon fiber reinforcement in polyether ether ketone (Victrex). APC-1 is used as an aromatic thermoplastic composite for aerospace applications [88-89].

As an aromatic polymer *aromatic polyamides* were first introduced in commercial applications in the early 1960s, with a meta-aramid fiber produced by DuPont under the trade name Nomex. This fiber, which handles similarly to normal textile apparel fibers, is characterized by its excellent resistance to heat, as it neither melts nor ignites in normal levels of oxygen. It is used extensively in the production of protective apparel, air filtration, thermal and electrical insulation as well as a substitute for asbestos. Meta-aramid is also produced in the Netherlands and Japan by Teijin under the tradename Teijinconex, in China by Yantai under the trade name New Star and also by SRO Group (China) under the trade name X-Fiper, in France by Kermel under the tradename Kermel [81-82].

Liquid-crystal polymers (LCPs) are a class of aromatic polyester polymers. They are extremely unreactive and inert, and highly resistant to fire. Liquid crystallinity in polymers may occur either by dissolving a polymer in a solvent (lyotropic liquid-crystal polymers) or by heating a polymer above its glass or melting transition point (thermotropic liquid-crystal polymers). Liquid-crystal polymers are present in melted/liquid or solid form. LCPs are the commercial aramid known as Kevlar. Chemical structure of this aramid consists of linearly substituted aromatic rings linked by amide groups. In a similar way, several series of thermotropic LCPs have been commercially produced by several companies (e.g., Vectra).

Aramid fibers are a class of heat-resistant and strong synthetic fibers. They are used in aerospace and military applications, for ballistic rated body armor fabric and ballistic composites, in bicycle tires, and as an asbestos substitute. The name is a shortened form of "aromatic polyamide" is arearomatic. The arearomatic polymers in which the chain molecules are highly oriented along the fiber axis, so the strength of the chemical bond can be exploited.

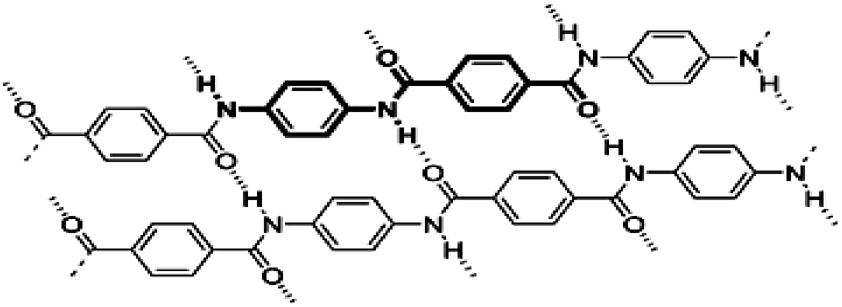

Figure. 5. Molecular structure of Aramide(Aromatic polyamide)

A high number of LCPs, produced in the 1980s, displayed order in the melt phase analogous to that exhibited by non-polymeric liquid crystals. Processing of LCPs from liquid-crystal phases (or mesophases) gives rise to fibers and injected materials having high mechanical properties as a consequence of the self-reinforcing properties derived from the macromolecular orientation in the mesophase. Today, LCPs can be melt-processed on conventional equipment at high speeds with excellent replication of mold details. In fact, the high ease of forming of LCPs is an important competitive advantage against other plastics, as it offsets high raw material cost.

A unique class of partially crystalline aromatic polyesters based on p-hydroxybenzoic acid and related monomers, liquid-crystal polymers are capable of forming regions of highly ordered structure while in the liquid phase. However, the degree of order is somewhat less than that of a regular solid crystal. Typically LCPs have a high mechanical strength at high temperatures, extreme chemical resistance, inherent flame retardancy, and good weather ability. Liquid-crystal polymers come in a variety of forms from sinterable high temperature to injection moldable compounds. LCP can be welded, though the lines created by welding are a weak point in the resulting product. LCP has a high Z-axis coefficient of thermal expansion.

Because of their various properties, aromatic polymers such as LCPs are useful for electrical and mechanical parts, food containers, and any other applications requiring chemical inertness and high strength. LCP is particularly attractive for microwave frequency electronics due to low relative dielectric constants, low dissipation factors, and commercial availability of laminates. Packaging Micro-electromechanical Systems (MEMS) is another area that LCP has recently gained more attention [82-91].

Ken Yoshimura and Katsuhiko Iwasaki [94] synthesized aromatic Polymer (Figure 6) with pendant perfluoroalkyl sulfonic acid for fuel cell applications.

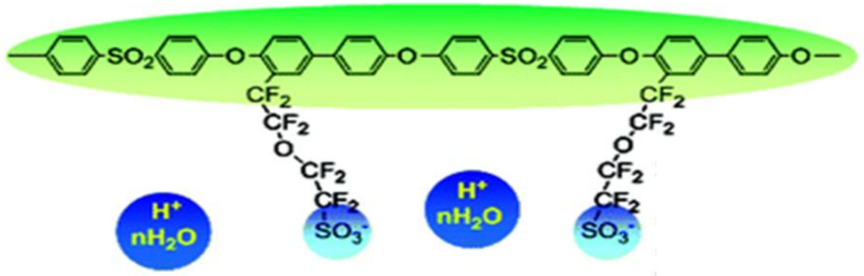

Figure. 6. Aromatic Polymers having poly(arylene ether sulfone) in the main chain and $-CF_2CF_2OCF_2CF_2SO_3H$ in the side chain (PES-PSA).

Aromatic polymers such as poly(phenylene), poly(p - phenylene vinylene) (PPV) , and poly(p- phenylene sulfide) (PPS) have been shown to undergo dramatic increases in electrical conductivity, of up to 16 orders of magnitude, when exposed to various electron donor or acceptor compounds [88-90].

PHENOL-FORMALDEHYDE RESINS *(PHENOLPLAST)*

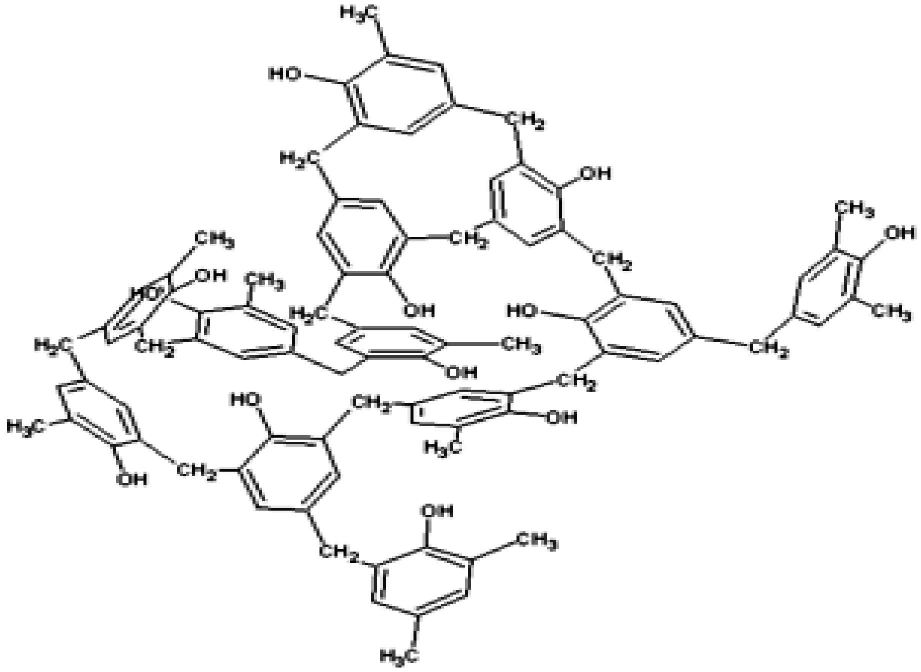

Figure. 7. Example of a possible structure in a phenol-formaldehyde resin

Bakelite, a phenol-formaldehyde polymer (Figure 7), was the first completely synthetic plastic, first made by Leo Baekeland in 1907. Baekeland and an assistant started their research in 1904 looking for a synthetic substitute for shellac. Bakelite was commercially introduced in 1909. Bakelite was first used to make billiard balls, but, later, was used to make molded insulation, valve parts, knobs, buttons, knife handles, many types of molded plastic containers for radios and electronic instruments, and more.

Phenol formaldehyde resins (PF) include synthetic thermosetting resins such as obtained by the reaction of phenols with formaldehyde. Sometimes the precursors include other aldehydes or other phenol. Phenolic resins are mainly used in the production of circuit boards. They are better known however for the production of molded products including pool balls, laboratory countertops, and as coatings and adhesives. In the form of Bakelite (Figure 8), they are the earliest commercial synthetic resin [1-4].

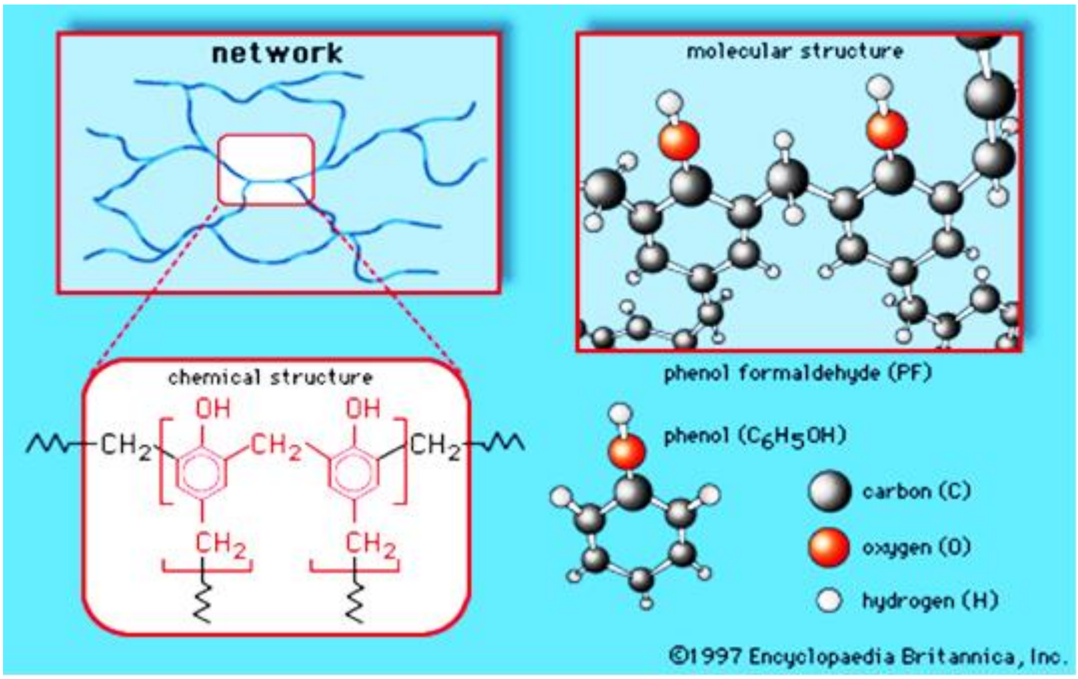

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Figure.8. Bakelite network, molecular structure and its chemical structure

Phenol-formaldehyde resins, as a group, are formed by a step-growth polymerization reaction that can be either acid- or base-catalyzed. Since formaldehyde exist predominantly in solution as a dynamic equilibrium of methylene glycol oligomers, and the concentration of the *reactive* form of formaldehyde depends on temperature and pH.

Phenol is reactive towards formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. The initial reaction in all cases involves the formation of a hydroxymethyl phenol (Reaction 1.4).

$$\mathbf{HOC_6H_5 + CH_2O \rightarrow HOC_6H_4CH_2OH}$$

The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction gives a methylene bridge, and the second forms an ether bridge (Reaction 1.5).

$$\mathbf{HOC_6H_4CH_2OH + HOC_6H_5 \rightarrow (HOC_6H_4)_2CH_2 + H_2O}$$

The diphenol $(HOC_6H_4)_2CH_2$ (sometimes called a "dimer") is called bisphenol F, which is itself an important monomer in the production of epoxy resins. Bisphenol-F can further link generating tri- and tetra-and higher phenol oligomers (Reaction 1.6).

$$\mathbf{2\ HOC_6H_4CH_2OH \rightarrow (HOC_6H_4CH_2)_2O + H_2O}$$

Novolacs are phenol-formaldehyde resins made where the molar ratio of formaldehyde to phenol of less than one. The polymerization is brought to completion using acid-catalysis. The phenol units are mainly linked by methylene groups. Novolacs are commonly used as photoresists. Hexamethylene tetramine or "hexamine" is a hardener that is added to crosslink novolac. At ≥180 °C, the hexamine forms crosslinks to form methylene and dimethylene amino bridges. We know that earliest commercial synthetic resin is based on a phenol formaldehyde resin (PF) with the commercial name Bakelite, and is formed from an elimination reaction of phenol with formaldehyde [5-7]. This forms a hydroxymethyl phenol, which is not usually isolated in novolacs but is found in resoles. The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction forms a methylene bridge, and the second forms an ether bridge. Phenol formaldehyde resins, as a group, are formed by a step-growth polymerization reaction which may be either acid or base catalysed. The pathway the reaction follows varies depending on the catalyst type used.

Acid catalyzed phenol formaldehyde resins are made with a molar ratio of formaldehyde to phenol of less than one and are called novolacs (Figure 9). Owing to the molar ratio of formaldehyde to phenol, they will not completely polymerize without the addition of a crosslinking agent. Novolacs are commonly used as photoresists.

Figure. 9. Synthesis of acid catalyst phenol formaldehyde resins

Common cross-liner used for novolak is paraformaldehyde. Base catalyzed phenol formaldehyde resins (Figure 10) are made with formaldehyde to phenol ratio of greater than one (usually around 1.5). Phenol, formaldehyde, water and catalyst are mixed in the desired amount, depending on the resin to be formed, and are then heated. The first part of the reaction, at around 70 °C, forms hydroxymethyl phenols. This results in a thick reddish-brown goo, the resin. The rate of the base catalysed reaction initially increases with pH, and reaches a maximum at approx. pH = 10. The reactive species is the phenolic anion formed by deprotonation of phenol. The negative charge is delocalized over the aromatic ring, activating sites 2, 4 and 6, which then react with the formaldehyde. Formaldehyde in solution does not exist as the aldhehyde, but instead a dynamic equilibrium is formed creating a range of methylene glycol oligomers, and the concentration of the *reactive* form of formaldehyde depends on the exact conditions (temperature, pH) under which the reaction occurs. Thus the reaction rate law describing phenol and formaldehyde is not a simple one, and the chemical kinetics is highly complex. Hydroxymethyl phenols will crosslink on heating to around 120 °C to form methylene and methyl ether bridges. At this point the resin is starting to crosslink, to form the highly extended 3-dimensional web of covalent bonds which is typical of polymerised phenolic resins. It is this highly crosslinked nature of phenolics which gives them their hardness and their excellent thermal stability and which makes them impervious to most chemical attack and solvation. It is also the reason they are called thermosets.

Figure. 10. Synthesis of base catalyzed phenol formaldehyde resins

In both cases, further condensation between methylol phenols and phenol occurs to give the methylene compounds.

Resols are also base-catalyzed phenol-formaldehyde resins and made with a formaldehyde to phenol ratio of greater than one (usually around 1.5). Phenol, formaldehyde, water and catalyst are mixed in the desired amount, depending on the resin to be formed, and are then heated. The first part of the reaction, at around 70 °C, forms a thick reddish-brown tacky material, which is rich in hydroxymethyl and benzylic ether groups.

The rate of the base-catalyzed reaction initially increases with pH, and reaches a maximum at about pH = 10. The reactive species is the phenoxide anion ($C_6H_5O^-$) formed by deprotonation of phenol. The negative charge is delocalized over the aromatic ring, activating sites 2, 4 and 6, which then react with the formaldehyde. Being thermosets, hydroxymethyl phenols will crosslink on heating to around 120 °C to form methylene and methyl ether bridges. At this point the resin is 3-dimensional network, which is typical of polymerized phenolic resins. The high crosslinking gives this type of phenolic resin their hardness, good thermal stability, and chemical imperviousness.

When the molar ratio of formaldehyde:phenol reaches one, in theory every phenol is linked together via methylene bridges, generating one single molecule, and the system is entirely crosslinked. Resols resins are synthesized by a molar excess of formaldehyde ($1<F/P<3$). Lim Chee Siong have been studied the physical properties of Phenol-formaldehyde poly(Vinyl Alcohol) resin as fibre-reinforced film adhesive [8].

Phenolic resins are found in myriad industrial products. Phenolic laminates are made by impregnating one or more layers of a base material such as paper, fiberglass or cotton with phenolic resin and laminating the resin-saturated base material under heat and pressure. The resin fully polymerizes (cures) during this process [22-25]. The base material choice depends on the intended application of the finished product. Paper phenolics are used in manufacturing electrical components such as punch-through boards and household laminates. Glass phenolics are particularly well suited for use in the high speed bearing market. Phenolic micro-balloons are used for density control [26]. C. Harwood, G. H. Wostenholm , B. Yates , D. V. Badami had prepared phenol formaldehyde resins and find out its thermodynamic properties.

These thermoset polymers made from phenol or less commonly, phenolic type compounds such as the cresols, xylenols, and resorcinol together with formaldehyde. Morgan discovered them in the early 1890s when attempting (unsuccessfully) to make artificial dyestuffs by reaction of phenol with formaldehyde. But this knowledge had not been exploited before 1907, the year in which Leo Baekeland in America obtained his first patent for materials prepared from these two compounds. In 1910 he founded the General Bakelite company to exploit this development, in the process making phenol-formaldehydes, the first synthetic polymers to achieve commercial importance. Baekeland had to make important discoveries before he could bridge the gap between the initial concept and final products. In particular, he found that the base-catalyzed condensation of phenol and formaldehyde can be carried out in two parts. If the process is carefully controlled, an intermediate product can be isolated, either as a liquid or a solid, depending on the extent of reaction. At this stage, the material consists of essentially linear molecules and is both fusible and soluble in appropriate solvents. When heated under pressure to 150 °C, this intermediate is converted to the hard, infusible solid known as ‘Bakelite’. This second stage is the one at which the three-dimensional cross-linked network develops.

Phenol–formaldehydes may no longer hold the centre-stage where synthetic polymers are concerned, but they are still of some commercial importance. They are produced for electrical mouldings, appliance handles, household fittings, and also as adhesives and specialized surface coatings. Cured phenol–formaldehydes are resistant to attack by most chemicals. Organic solvents and water have no effect on them, though they will swell in boiling phenols. Simple resins are readily attacked by sodium hydroxide solutions, but resins based on phenol derivatives, such as cresol, tend to be less affected by such solutions. Simple phenol–formaldehyde polymers are resistant to most acids, though formic and nitric acids will tend to attack them [16-22, 36, 77, 78, 79, 80, 81, 82]. Again, cresol-based polymers have resistance to such attack.

Phenolic resole are the most useful thermosetting materials for the manufacture of composite panels, based on wood such as plywood. After curing the resole resin is a solid, insoluble, rigid material with a high fire resistance, long term thermal, mechanical stability, high strength, low toxic and excellent insulating properties. Subhas Chandra Bajia et al.[9] synthesized phenol-formaldehyde resin and proposed two reaction scheme for synthesis. During synthesis of phenol-formaldehyde resole two main reactions occur.

(I) Addition reaction (II) Condensation reaction.

Step I. Addition reaction:

Step II. Condensation reaction:

In summary, the four major reactions in phenolic resin chemistry are (a) addition to give methylol phenols, (b) condensation of a methylol phenol and a phenol to give a methylene bridge, (c) condensation of two methylol groups to give an ether bridge, and (d) decomposition of ether bridges to methylene bridges and formaldehyde, the latter reacting again by the first mode.

Under the trade names **“**Bakelaque” is a rigid laminate or tube made from phenolic resin on a substrate cotton fabric, paper or glass**.** Bakelite is made from phenolic resin and wood flour**,** Novotext is cotton fibre-reinforced phenolic, using randomly oriented fibres**.** Paxolin and Richlite are made from phenolic resin and paper and Tufnol is made from phenolic resin and woven cotton or linen fabric. Umezawa and Ohtsuka[10] have prepared ion-exchange resins by condensing mixture of phenol and salicylic acid with formaldehyde in presence of 50 % H_2SO_4 followed by curing with NaOH. Pennington and Williams [11] have prepared a resin from 2, 4-dihydroxybenzoic acid and formaldehyde and studied their ion-exchange properties. The following structure was proposed for the resin (Figure 11).

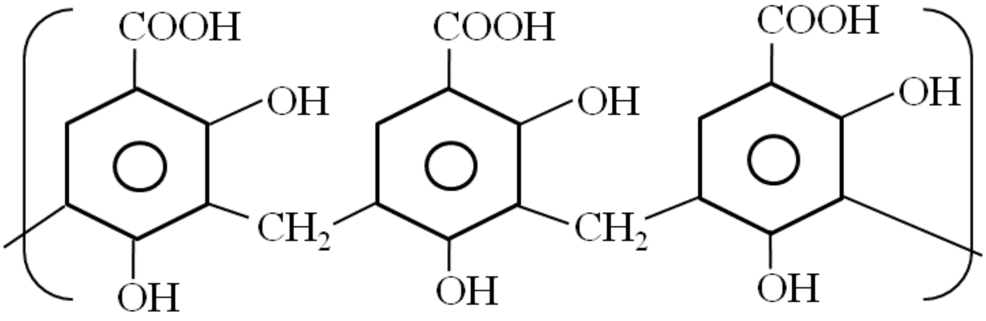


Figure.11.Suggested structure of 2,4-dihydroxybenzoic acid-formaldehyde copolymer

Aniline modified phenol-resorcinol copolymer resins have been reported in literature [12]. Copolymer derived from 3,5-dimethyl phenol with formaldehyde in presence of base catalyst give linear and highly condensed structure, shows oxygen sensitivity and graphitizability [13]. Polymer composite derived from resols can be used for fuel cell separator and electrolyzer frames, having thermal and acid resistance [14]. The independence between curing conditions, structure and mechanical properties of low heat resin systems, resol DW247 have been discussed. Backelite-Au and a phenolic resin with p-toluene-sulphonic acid and phenol sulphonic acid as hardener was studied by Eapen K. C et al [15] and concluded that hardener concentration and the degree of cure has a strong influence on the mechanical property.

Gary Trammell , Steve Dykema , Greg Minix and Jerrold J. Jacobsen formed phenol-formaldehyde resin. In this process Aqueous formaldehyde is added to solid phenol. Next glacial acetic acid is added and the mixture is stirred. Concentrated hydrochloric acid is then mixed with the resulting solution. After a few minutes, the solution becomes cloudy and the red solid phenol-formaldehyde copolymer forms. The polymerization occurs by electrophilic aromatic substitution between the ortho and para positions of phenol and protonated formaldehyde (Figure 12). The resulting polymer is made by methylene bridges between phenol molecules.

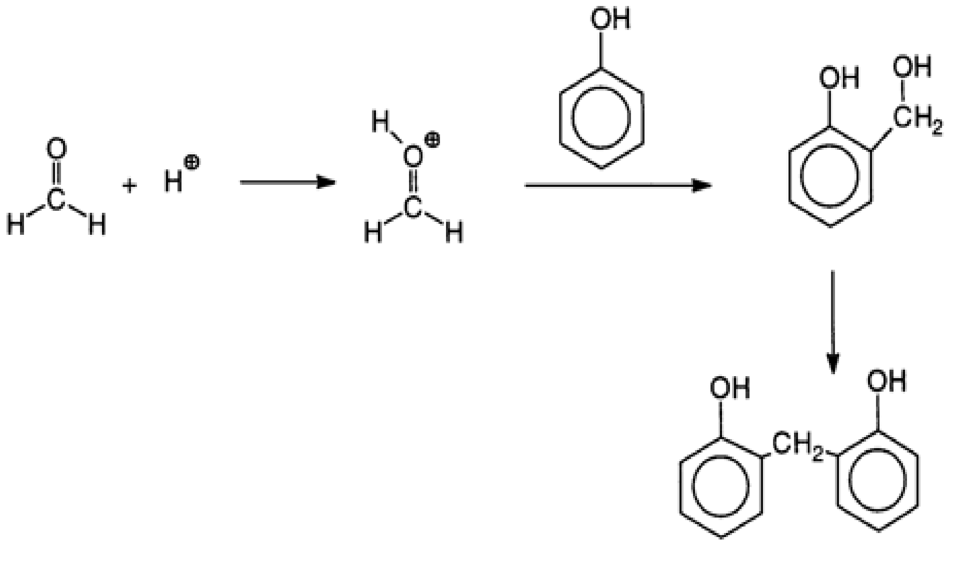


Figure. 12. Synthesis of phenol-formaldehyde [PF] resin

Gregor et al [16] studied the first of a new class of ion exchange copolymer resins in which the chelating groups are substituents in a highly crosslinked and therefore insoluble hydrocarbon matrix. These ion-exchange resins are composed by phenol-formaldehyde resin. Some important phenol-formaldehyde resins are synthesized and carried out the viscometric measurement as well as spectroscopic spectra's [23,24,25,37,54,112]. Lebach [32] was a contemporary of Backland, who introduced the term resole for fusible basic condensation products, recite of infusible insoluble mass and resitol for those intermediates, which are fusible but not soluble.

Extensive literature is available on phenol-formaldehyde resin. Maldas, Shiraish and Harode [33] had prepared phenolic resole resin adhesive from alkyl catalyzed liquefied phenolated wood and used to bond hard wood. NMR spectroscopy has been applied to the analysts of formaldehyde containing resins by Aloysius et al. Chow and Steiner [34] were made comparisons of the cure of phenol-formaldehyde novolac and resole systems by differential scanning calorimetric. Samal, Des and Mohoputra [35] had synthesized, characterized and studied metal ion uptake of chelating resins derived from formaldehyde condensed dodges of aniline and 4, 4'-diaminodiphenyl methane coupled with phenol/resorcinol. Nair, Thachil and Paul have been studied the influence of different side groups in the phenol molecule on properties of compositor made of phenolic resins and cement pastes was investigated. The three phenolic resins considered were phenol-formaldehyde, resorcinol-formaldehyde and m-cresol-formaldehyde which differ in the nature of the side groups in the make positions of the phenolic ring. The study shows that resorcinol formaldehyde resin cement poster possess superior chemical resistance [37, 38, 39,77,78, 80, 81, 82].

Anthony H. Conner, Linda F. Lorenz [75] synthesized new carbohydrate modified phenol-formaldehyde resin, which can be economically beneficial to processes producing alcohol and chemicals from wood as well as to the wood industry and consumers of bonded wood products.

Some Phenol formaldehyde resins are used as precursors in the fabrication of glassy carbons [76, 79]. Glassy carbons are hard, stiff (--25MPa), usually pore free structures with non wetting ultra smooth surfaces.

AMINO-FORMALDEHYDE RESINS [AMINOPLAST]

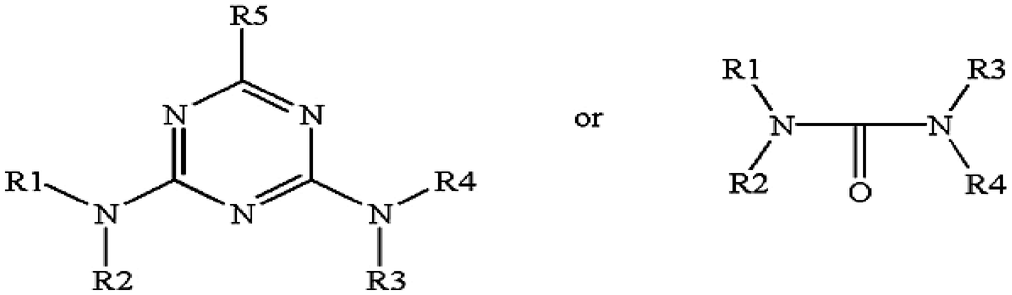


Figure.14. Possible Amino-formaldehyde resin from (a) Melamine (b) Urea

Amino-formaldehyde resins are thermosetting polymers synthesized by the reaction of an aldehyde with an amino compound containing -NH_2 group. Term amino-formaldehyde resin is applied to a broad class of materials regardless of their application. Generally amino-formaldehyde resins formed by the interaction of urea, thiourea, melamine, biuret, oxamide with formaldehyde [40-46].

The two important classes of amino-formaldehyde resins are the condensation products of urea and of melamine with fbrmaldehyde. They are considered together here because of the similarity in their production and applications In general, the melamine resins have somewhat better properties but are higher in price production of amino resins in the United States in 1982 was about 1 billion.

Chemistry and Production: Both melamine (a trimmer of cyanamide) and urea react with formaldehyde, first by addition to form methylol compounds and then by condensation in reactions much like those of phenol and formaldehyde. The methylol reaction takes place from the following reaction (1.3). These may polymerize to crosslinked resins by loss of water. Other reactions that may enter into the condensation include the formation of' methyleneurea, and the following crosslinking reactions (Figure 15):

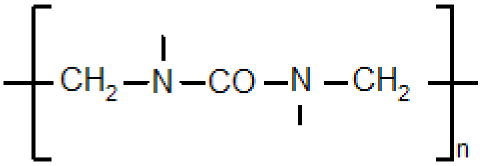
Figure.15. Chemistry and Production of amino-formaldehyde resin by crosslinking

The production of the amino resins is similar to that of phenolic resins. Since the resin is water soluble, it is only partially dehydrated, the water solution being used to impregnate the filler. The molding resins are almost always filled with cellulose obtained from good-quality sulfite-bleached paper. A distinct advantage of the amino resins over the phenolic resins is the fact that they are clear and colorless, so that objects of light or pastel color can be produced. The tensile strength of the amino resins are better than those of the phenolic resins, but their impact strength and heat and moisture resistance are lower, although still characteristic of thermosetting resins. The melamine resins have better hardness, heat resistance, and moisture resistance than the urea [68-69,]. Almost three-quarters of' the amino resins are used for adhesives, largely fibres, plywood and furniture. The melamine resins give excellent, boil-resistant bonds, but for economy are usually blended with the urea. The remaining quarter of production is divided roughly equally among uses as textile treatment and coatings resins, protective coatings, molding compounds, and paper treatment and coating resins. Practically all urea molding compounds are cellulose filled, whereas the melamines, although predominantly cellulose filled, are also used with asbestos, glass or silica, and cotton fabric [72-74]. Because of their poorer flow characteristics, the urea resins are usually compression molded, but injection molding is now common with both resins. Both resins can be preheated by high-frequency curxent because of their high polarity.

Because of' their color ability, solvent and grease resistance, surface hardness, and mar resistance, the urea resins are widely used for cosmetic container closures, appliance housings, and stove hardware [75-76]. The production of high-quality dinnerware from cellulose-filled compounds is the largest single molding use for the melamine resins.

The amino resins modify textiles such as cotton and rayon by imparting crease resistance, stiffness, shrinkage control, fire retardance, and water repellency [77-79]. They also improve the wet strength, rub resistance, and bursting strength of paper. Alkylated resins, in which butyl- or amyl-substituted monomethylol, ureas or melamines are used, are combined with alkyd resins to give baking enamels. The urea-based enamels are used for refrigerator and kitchen appliances, and the melamine-based enamels are used in automotive finishes.

UREA-FORMALDEHYDE RESINS (UREA-METHENAL)



$$\left[-CH_2-\overset{|}{N}-CO-\underset{|}{N}-CH_2- \right]_n$$

Urea-formaldehyde, also known as urea-methanal, named so for its common synthesis pathway and overall structure, is a non-transparent thermosetting resin or plastic, made from urea and formaldehyde heated in the presence of a mild base such as ammonia or pyridine. These resins are used in adhesives, finishes, MDF, and molded objects. Urea-formaldehyde resin's attributes include high tensile strength, flexural modulus and heat distortion temperature, low water absorption, mould, high surface hardness, elongation at break, and volume resistance. It is also used to glue together wood.

Urea formaldehyde was commonly used when producing electrical appliances casing e.g. desk lamps. Urea-formaldehyde foam insulation (UFFI) started being used in the 1950s. In the 1980s, concerns began to develop about the toxic formaldehyde vapor emitted in the curing process, as well as from the breakdown of old foam. Consequently, its use was discontinued. Modern replacement options include melamine formaldehyde resin and polyurethane. Urea formaldehyde (UF) is a cost-effective thermosetting resin that is widely used in the wood product industry. These resins cure easily and are scratch resistant. They are mainly used in the manufacture of pressed wood products.

Approximately 1 million metric tons of urea-formaldehyde resin is produced annually. More than 70% of this urea-formaldehyde resin is used by the forest products industry for a variety of purposes. The resin is used in the production of an adhesive for bonding particleboard (61% of the urea-formaldehyde used by the industry), medium density fiberboard (27%), hardwood plywood (5%), and a laminating adhesive for bonding (7%), for example, furniture case goods, overlays to panels, and interior flush doors. Urea formaldehyde is also used in agriculture as a controlled release source of nitrogen fertilizer. Urea formaldehyde’s rate of decomposition into CO_2 and NH_3 is determined by the action of microbes found naturally in most soils. The activity of these microbes, and therefore the rate of nitrogen release, is temperature dependent. The optimum temperature for microbe activity is approximately 70°-90°F [47-52].

The major drawback of urea formaldehyde resin is that it hydrolyzes, or decomposes, in extremely humid conditions and at high temperatures, which limits its usage as an outdoor construction material. Further, when pressed wood products with urea formaldehyde resins are used indoors, there is a noticeable increase in the formaldehyde levels in indoor air. The increased usage of pressed wood products, such as fiberboards, particle boards, and hardwood plywood paneling, within a limited space can be considered a significant reason for deterioration in the indoor air quality (IAQ).

Rossiter and Ripper [48] synthesized a new commercial polymer with equimolar mixture of urea, thiourea and formaldehyde, reinforcing it with purified cellulose fiber and were named as Beetle [49]. Patel and Joshi [50-52] have characterized terpolymer resins of ortho/para-hydroxy benzoic acid-urea-formaldehyde in presence of acid as a catalyst and also studied their ion - exchange properties for some heavy metal ions. The suggested structure for p-hydroxybenzoic acid - urea- formaldehyde polymer is given below (Figure 16).

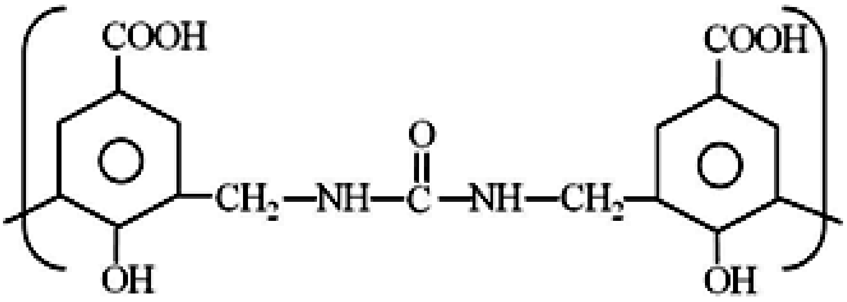
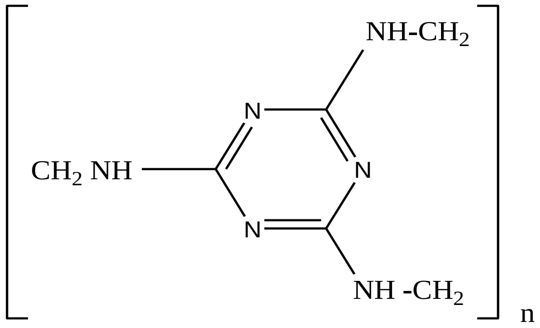


Figure.16.Suggested structure for p-hydroxybenzoic acid - urea- formaldehyde Terpolymer resin

Some urea-formaldehyde oligomers synthesized which find wide applications as spray drying polymers. U-F polymers have also been used as foam forming compound [53-57], ore flotation agents [58], board manufacture [59] and as rubbery polymers. Henkel and Co workers [60] developed melamine-formaldehyde copolymer resins. They are applicable for moulding, laminations and bonding. Amino-formaldehyde resins have great affinity for cellulose and other trisecherides [61]. They are also used in textile treatment and increasing the wet strength of paper [62], in metal foundry [63] and shell moulding process [64].

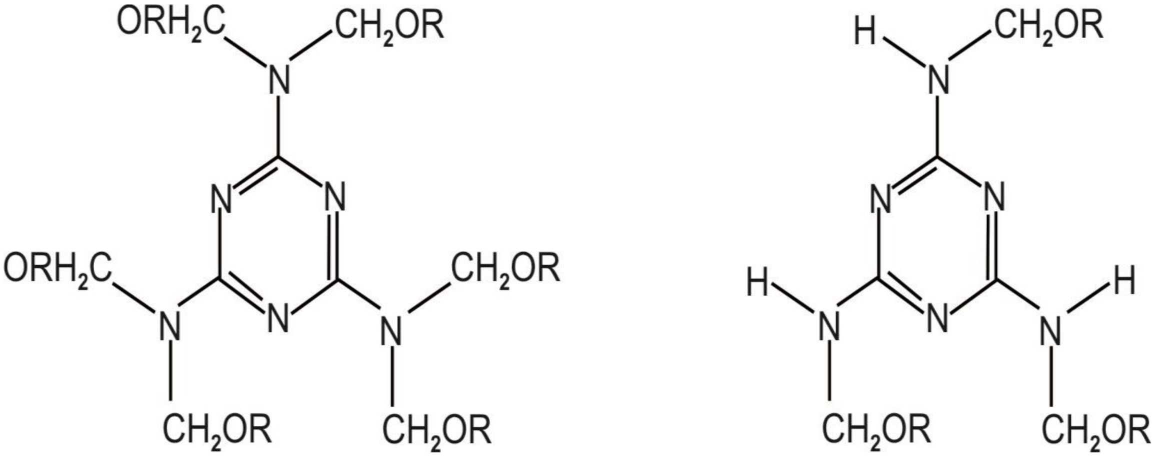
Melamine-formaldehyde resin



Melamine-formaldehyde resin is hard, thermosetting and water soluble resin. These are formed by the polymerization of melamine with formaldehyde. MF resins have versatile applications such as in preparing kitchen utensil, table ware, furniture, automotive industry, clutch facing, break pads, friction materials, for clutch and break, coated abrasive, grinding wheels, laminated paper and cloth, wood panel industry, composite wood panels, electrical molding, binder for leather tanning. Melamine resin is often used in kitchen utensils and plates (such as Melmac). Melamine resin utensils and bowls are not microwave safe, as they absorb the microwave radiation and heat up. As with all thermosetting materials, melamine resin cannot be melted and, therefore, cannot be recycled through melting. During the late 1950s and 1960s melamine tableware became highly fashionable. Aided crucially by the stylish modern designs of A. H. Woodfull and the product design unit of “British Industrial Plastics”, it was thought to threaten the dominant position of ceramics in the market. The tendency of melamine cups and plates to stain and scratch led sales to decline in the late 1960s, however, and eventually the material became largely restricted to the camping and nursery market.

Subhash Bajia, Rashmi Sharma and Birbal Bajia [9] synthesized melamine-formaldehyde resin using conventional as well as microwave irradiations (without and with solid support) in different molar ratio. Microwave irradiation is well known technique to promote the synthesis of a variety of compounds, where chemical reactions are accelerated because of selective absorption of microwaves by polar molecules [188-192].

In the synthesis of melamine formaldehyde resins, the first step is methylolation, when melamine and formaldehyde having stichometric role ratio is 1:6 undergo reaction they form a mixture of partially methylolated derivative (Figure 17a) while if formaldehyde is taken in excess than it forms the complexly methylolated derivative of melamine (Figure 18b). Methylolmelamine resins are often used to fabricates terminates and plastics but are rarely used in coating.



(a) **(b)**

Figure. 17. Structure of methylolated of melamine-formaldehyde resin.

For using methylolmelamine for coating the second step is performed which is acid catalyzed etherification of methylolmelamine with an alcohol. Melamine content significantly affected resin properties and glue bond quality. Therefore in recently phenol modified melamine urea formaldehyde resin has been used for the manufacture of exterior grade particleboard. In the melamine modified UF resins [112] the content of melamine get reduced which develop to improve durability and moisture resistance properties and cost also became less. Therefore these low melamine content UF resins have been relatively popular in Europe and the Asia Pacific region.

Thus both uncrosslinked UF and MF resins (also known as amino resins) are water soluble and, hence, find use as sizing agents and textiles-finishing resins. They are also used in paper industry, plywood industry and as adhesives.

Polyamide

A polyamide (PA) is a polymer containing monomers of amides joined by peptide bonds. They can occur both naturally and artificially, examples being proteins, such as wool and silk, and can be made artificially through step-growth polymerization, examples being nylons, aramids, and sodium poly(aspartate). Polyamides are commonly used in textiles, automotives, carpet and sportswear due to their extreme durability and strength (100).
According to the composition of their main chain, polyamides are classified as follows:

Polyamide family	**Main chain**	**Examples of polyamides**	**Examples of commercial products**
Aliphatic polyamides	Aliphatic	PA 6 and PA 66	Nylon
Polyphthalamides	Semi-aromatic	PA6T hexamethylenediamine terephthalic acid	Trogamid from Evonik Industries
Aramides(aromatic polyamides)	Aromatic	Paraphenylenediamine terephthalic acid	Kevlar and Nomex from DuPont, Teijinconex, Twaron and Technora from

Teijin

These materials are commonly completely insulating, and generate static electricity, which can cause dangerous sparks that can damage electronics in manufacturing plants and in consumer products. This has resulted in an interest in incorporation of conductive fillers such as carbon black, metals and conducting polymers. The most common conducting fillers are silver and carbon black. Both of these materials have processing deficiencies.

Quality polyamide resins offered by us are widely used in the adhesives and cater to the requirement of printing ink, ball point pen ink, lacquers, varnishes, paints and rubber industries. Polyamide resin is a high performance semi-transparent penetrating finish that helps prevent the destructive effects of water, fungi and UV radiation on exterior wood. With its unique fortified synthetic resin, this product is able to penetrate wood pores to block out the damaging effects of weather while allowing the natural beauty of the wood to shine through. These are in high demand by our clients spread across the world and can be availed at industry leading prices.

Polyimide

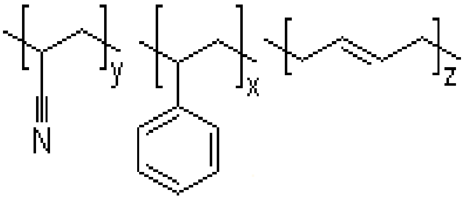
Polyimide (PI) is a polymer of imide monomers. Polyimides have been in mass production since 1955. Typical monomers include pyromellitic dianhydride and 4,4'-oxydianiline. According to the type of interactions between the main chains, polyimides can be:

1. Thermoplastic: very often called pseudothermoplastic.
2. Thermosetting: commercially available as uncured resins, polyimide solutions, stock shapes, thin sheets, laminates and machined parts.

The polyimide materials are lightweight, flexible, resistant to heat and chemicals. Therefore, they are used in the electronics industry for flexible cables, as an insulating film on magnet wire and for medical tubing. For example, in a laptop computer, the cable that connects the main logic board to the display (which must flex every time the laptop is opened or closed) is often a polyimide base with copper conductors. Examples of polyimide films include Apical, Kapton, UPILEX, VTEC PI, Norton TH and Kaptrex. The semiconductor industry uses polyimide as a high-temperature adhesive; it is also used as a mechanical stress buffer. Some polyimide can be used like a photoresist; both "positive" and "negative" types of photoresist-like polyimide exist in the market [101]. An additional use of polyimide resin is as an insulating and passivation layer in the manufacture of digital semiconductor and MEMS chips. The polyimide layers have good mechanical elongation and tensile strength, which also helps the adhesion between the polyimide layers or between polyimide layer and deposited metal layer. The minimum interaction between the gold film and the polyimide film, coupled with high temperature stability of the polyimide film, results in a system that provides reliable insulation when subjected to various types of environmental stresses.

Polyimide powder can be used to produce parts and shapes by sintering technologies (Hot compression moulding, Direct forming, Isostatic pressing). Because of their high mechanical stability even at elevated temperatures they are used as bushings, bearings, sockets or constructive parts in demanding applications. To improve tribological properties compounds with solid lubricants like graphite, PTFE or molybdenum sulfide are common. Polyimide parts and shapes include P84 NT, VTEC PI, meldin, vespel and plavis. In coal fired power plants, waste incinerators or cement plants, Polyimide fibres are used in hot gas filtration. A Polyimide needle felt separates dust and particulate matter from the exhaust gas. Polyimide is also used for filter membranes used in osmosis processes.

TERPOLYMER



A polymer that consists of three distinct monomers, as ABS resin known as terpolymer. A terpolymer is a polymer derived from three different monomeric species, as opposed to a homopolymer where only one monomer is used [102-115].

Terpolymer is a copolymer made from three different monomers. Since the discovery of polymerization, a new field of terpolymer is the recent and spectacular development of polymer chemistry. From the last few decades terpolymer have attracted the attention of scientists as a spectacular development in polymer chemistry. Terpolymer is the recent innovation in polymer science. Terpolymers are generally resinous, amorphous, or crystalline in nature [116-120]. These terpolymers are found to be insoluble in common organic and inorganic solvents [115]. The present invention relates to a novel terpolymer useful for inhibiting the formation of scale in water systems. More specifically, the terpolymer comprises monomers of acrylic or methacrylic acid, vinyl acetate and/or vinyl alcohol formed by hydrolysis of vinyl acetate, and sodium-1-allyloxy-2-hydroxypropyl sulfonate. These novel terpolymers are particularly effective in inhibiting the formation of inorganic scales derived from sparingly soluble salts of calcium, barium, magnesium, and the like.

U.S. Pat. No. 4,532,048 suggests the use of a terpolymer in method for inhibiting scale formation. The terpolymer includes monomer units of (i) acrylic or methacrylic acid; (ii) a lower alkenyl carboxylate; and (iii) a salt of a lower alkenyl sulfonate. terpolymer or interpolymer useful for treating aqueous systems. The terpolymer of the present invention is added to the aqueous system for which corrosion inhibiting and/or deposit activity is desired in an amount effective for the purpose. the terpolymers are particularly effective against the formation of calcium phosphate and calcium carbonate scales and may be used in association with any type of aqueous system. For example, they may be used in boiler and cooling water and in scrubber systems where corrosion and/or the formation of scale deposits pose problems. Other environments in which the terpolymer may be used include heat distribution type sea water desalting apparatus [121], in oil field services to remove scales from pipe walls, in mining applications such as gold heap leaching, in reverse osmosis systems and as a dispersant in the pulp and paper processing industries. They also could be used as mineral beneficiation aids such as in iron ore, phosphate and potash recovery. The terpolymer are found very useful applications as an adhesive[122-127], high temperature flame resistant[128-130], fibers, coating materials, semiconductors[131-134], catalysis and ion exchange resins [122,125, 130]. Ion exchange resins have attracted much attention in the recent years due to their applications in waste water treatment, metal recovery and for the identification of specific metal ions. Now a day’s high temperature resistance and ion-exchange terpolymer have renowed interest.

Recent literature survey reveals that various kinds of terpolymers were synthesized, their structural determination by various physico-chemical techniques and spectral analysis have been carried out along with their study of different applications by various workers [11,23, 27,29,37,44, 75,85,92,102,118,125,128,131].

G. C. Patel, H. B. Pancholi and M. M. Patel [121] Synthesized, characterized and determined ion exchange properties of 2,4-Dihydroxybenzoic Acid-Urea-Formaldehyde teropolymers. The terpolymers were characterized by elemental analyses, IR spectral studies, number average molecular weight determination, viscosity measurements and thermogravimetry. Ion exchange properties have been studied employing the batch equilibration method. The terpolymer showed a higher selectivity for UO^{2+} and Fe^{3+} ions than for Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+}ions.

Pratik E.P. Michael, J.M and coworkers [122] synthesized (8-HQGF) terpolymer by using the monomers 8-hydroxyquinoline, guanidine and formaldehyde in 1:1:2 molar proportions. They elucidated the structure of 8-HQGF terpolymer on the basis of elemental analysis and various physicochemical techniques, i.e. UV–Visible, FTIR–ATR and ^{1}H NMR spectroscopy. Detailed thermal degradation study of the new terpolymer has been carried out to ascertain its thermal stability. They discussed the thermal degradation curve which shows two decomposition steps (265–475 °C and 540–715 °C).

Xin-Gui Li, Mei-Rong Huang et al [123] synthesized a series of soluble terpolymer by oxidative polymerization of 2-pyridylamine, aniline and 2,3-xylidine using ammonium persulfate as oxidant in 1 M HCl aqueous solution. The yield, intrinsic viscosity, and solubility of the terpolymers were studied by changing monomer ratio and the polymerization time. At a fixed xylidine content of 10 mol%, the yield and intrinsic viscosity of the terpolymer decrease with increasing pyridylamine content and remain almost constant with polymerization time. The resulting terpolymers were characterized by FT-IR, ^{1}H-NMR, wide-angle X-ray diffraction, and thermogravimetry. The polymers are amorphous terpolymer and exhibit good solubility, decomposition temperature of 375–495°C, the maximum weight-loss rate of 0.9–5.8%/min, high char yield of 65 wt.% at 700°C in nitrogen, and thermal degradation activation energy of 25–81 kJ/mol. Various co-workers works extensively on terpolymer, synthesis, characterization and their applications as a higher thermal stable materials [119,120,124,134,135,136]

The literature survey reveals that few terpolymers are used as a novel Polymers for controlled drug delivery in medical science. Jie Fu, Jennifer Fiegel, and Justin Hanes [124] synthesized a series of biodegradable poly(ether−anhydrides) composed of poly(ethylene glycol) (PEG), sebacic acid (SA), and 1,3-bis(carboxyphenoxy)propane (CPP) were synthesized for use in advanced drug delivery applications. PEG (M_n = 8000 Da) was incorporated to reduce polymeric particle clearance rates by the immune system and improve particle resuspension and aerosolization efficiencies. CPP and SA were selected to render the polymer insoluble in water and allow control over polymer degradation and drug release rates. In particular, CPP incorporation caused a significant decrease in polymer degradation rates and release kinetics of model drugs incorporated into poly(ether−anhydride) microparticles. Terpolymers were synthesized with weight-average molecular weights over 65 kDa without catalyst. The first thermal transition in polymers containing ≤10 wt % PEG was ~80 °C (well above typical storage conditions and body temperature), and there was no evidence of a glass transition (−100 to 200 °C). Several of the polymers were used to produce particles suitable for injection or inhalation; these particles released model drugs, with molecular weights ranging from 443 to 5 143 000 Da, in a continuous fashion for up to 7 days.

The perusal of literature reveals that the terpolymers are very useful in waste water treatment, metal recovery and bioinorganic chemistry. Recently, the use of chelating polymers for remediation of water and soil has attracted much attention [137-140]. Chelating groups are incorporated into the polymeric side chains or backbone. The choice of the type of ligands, ligand density, structure and solubility of the polymer, as well as pH, govern the metal ion affinity, retention efficiency and selectivity [141-143].

Chelating polymers or polychelatogens are used for remediation in homogenous reactions with water soluble polymers coupled with ultra filtration, or in heterogeneous reactions of solid polymer beads or semi-permeable membranes [144]. Bhavna A. Shah et.al [130] has been prepared chelation ion exchange resin [AFR] derived from anthranilic acid-formaldehyde and resorcinol (Figure 18). The physico-chemical properties, the studies of total ion exchange capacity, effect of pH, and concentration for different metal ions were carried out. Terpolymers are used as ion-exchangers. Ion exchangers have been used commercially on a worldwide basis for almost a century due to diverse applications in many fields such as water softening and deionization [146], sugar purification [147], extraction of uranium [148], glycerol refining [149], isolation and purification of antibiotic [150], in hydrometallurgy for separation and purification of [151] in waste water treatment and pollution control [152]. Since long, considerable interest has been developed in the synthesis of ion exchange resin having special properties and containing specific functional groups.

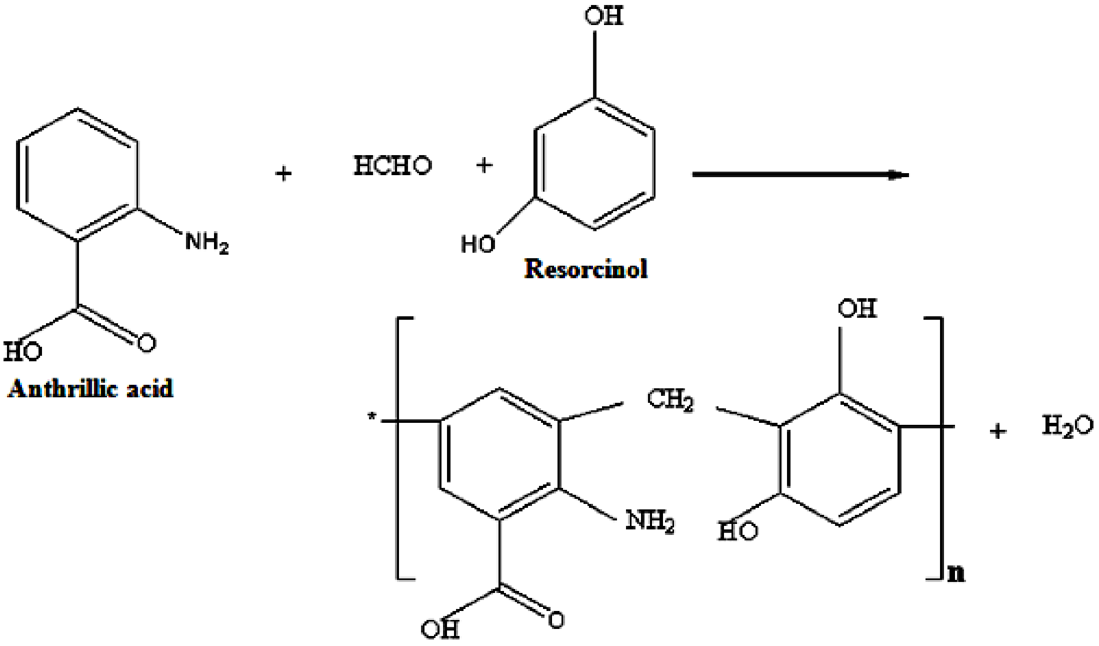


Figure.18. Synthesis of APF terpolymer resin

Literature survey reveals that few terpolymer are applicable as a lubricating mineral oils. This property is depend on monomers which used to form the polymer . Ante Jukic, Elvira Vidovic and Zvonimir Janovic [150] have been synthesized alkyl methacrylate and styrene terpolymer as lubricating oil viscosity index improvers. The properties of styrene/dodecyl methacrylate/octadecyl methacrylate terpolymer as viscosity index improvers of lubricating mineral oils were investigated. Terpolymer of different composition and molar mass were prepared by peroxide-initiated polymerization of the monomer mixture in a mineral base oil solution. All the terpolymer solutions in base oil exhibited high kinematic viscosity and viscosity index values (> 130), proving their high thickening efficiency. The ratio of viscosity values at 100°C and 40°C of styrene/alkyl methacrylate additive solutions was between 0.95 and 1.0, showing the coherent thickening effect in a wide temperature range, comparable with pure alkyl methacrylate additives. Increasing content of styrene in the additive and decreasing molar mass of the terpolymer resulted in a decrease in viscosity and viscosity index while the shear stability increased [166-167]. C. Becker, H. Krug and H. Schmidt [165] have been studied the mechanical properties of copolymers.

In the past decades, it has been studied that the thermal stability of polymers and terpolymer depend on the monomers used in synthesis. In recent years, meleic anhydrite has become an important monomer of copolymers and terpolymer [137-138]. Ali Boztug, Satlms Basan [139] have been prepared maleic anhydride- styrene-allyl propionate (MA-St-AP) terpolymer (Figure 19) and its ester derivatives. Thermal stabilities of the terpolymer and its ester derivatives were compared by using various measurements plotted as TGA, DTA, DSC, and TMA curves. The thermal stability of polymers and terpolymer has been extensively studied employing the method of thermogravimetric analysis (TGA) by several authors [158, 159, 160, 161, 162, 163, 171, 198] in the past because of its application in various polymer industries.

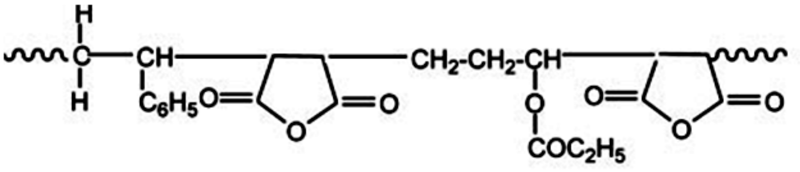


Figure.19. Chemical structures of the MA-St-AP terpolymer

The main objective of the most studies on chelating resin is preparation of insoluble functionalized polymer which can provide more flexible working conditions together with good stability and high capacity for certain metals ions [55, 56, 117, 120, 126]. Generally for the determination of metal ions, salicylic acid has been used extensively as a catalytical agent due to its chelating property. T. K. Pal, and R. B. Kharat [148] synthesized terpolymer resins (SBT) by the condensation of salicylic acid and biuret with trioxane in the presence of 2MHCl acid catalyst and using varied molar ratios of reacting monomers. They have studied the chelation ion-exchange properties by employing the batch equilibration method. De-Geiso et. al. [149] studied the ion-exchange capacity and selectivity of selicylic acid-formaldehyde copolymer resin with Fe^{3+} and $UO_2{}^{2+}$ ions as function of pH [150-151].

APPLICATIONS OF TERPOLYMERS

Macromolecular science has had a major impact on the way we live. It is difficult to find an aspect of our lives that is not affected by polymers. Just 50 years ago, materials we now take for granted were non-existent. With further advances in the understanding of polymers, and with new applications being researched, there is no reason to believe that the revolution will stop any time soon. Polymers are an important part of everyday life.

Terpolymer, very special class of polymer, are known for their versatile uses and are found to be amorphous, crystalline or resinous in nature among the most important and versatile of the hundreds of commercial plastics is polyethylene. Polyethylene is used in a wide variety of applications because, based on its structure, it can be produced in many different forms. The first type to be commercially exploited was called low density polyethylene (LDPE) or branched polyethylene. HDPE is much more rigid than branched polyethylene and is used in applications where rigidity is important. Major uses of HDPE are plastic tubing, bottles, and bottle caps. Other forms of this material include high and ultra-high molecular weight polyethylenes. HMW and UHMW, as they are known. These are used in applications where extremely tough and resilient materials are needed.

Fibers represent a very important application of polymeric materials, including many examples from the categories of plastics and elastomers. Natural fibers such as cotton, wool, and silk have been used by humans for many centuries. In 1885, artificial silk was patented and launched the modern fiber industry. Man-made fibers include materials such as nylon, polyester, rayon, and acrylic. The combination of strength, weight, and durability has made these materials very important in modern industry. Nylon (a generic term for polyamides) was developed in the 1930's and used for parachutes in World War II. This synthetic fiber, known for its strength, elasticity, toughness, and resistance to abrasion, has commercial applications including clothing and carpeting. Nylon has special properties which distinguish it from other materials. One such property is the elasticity. Nylon is very elastic, however after elastic limit has been exceeded the material will not return to its original shape. Like other synthetic fibers, Nylon has a large electrical resistance. This is the cause for the build-up of static charges in some articles of clothing and carpets. From textiles to bullet-proof vests, fibers have become very important in modern life. As the technology of fiber processing expands, new generations of strong and light weight materials will be produced.

Polymeric materials are used in and on soil to improve aeration, provide mulch, and promote plant growth and health. Many biomaterials, especially heart valve replacements and blood vessels, are made of polymers like dacron, teflon and polyurethane. Plastic containers of all shapes and sizes are light weight and economically less expensive than the more traditional containers. Clothing, floor coverings, garbage disposal bags, and packaging are other polymer applications. Automobile parts, windshields for fighter planes, pipes, tanks, packing materials, insulation, wood substitutes, adhesives, matrix for composites, and elastomers are all polymer applications used in the industrial market. Playground equipment, various balls, golf clubs, swimming pools, and protective helmets are often produced from polymers [153-157].

Some cyclo-olefin copolymers are engineering thermoplastics derived from the ring-shaped norbornene molecule. Cyclo-Olefins are used for light guide panel, laptop computer screens-contact lenses, compact discs, barrier sheets in medical applications, packaging films and blister packs for medication packaging in which case a layer of cyclo-olefin copolymer may be laminated between layers of polypropylene, Bottles such as those used for cosmetic packaging, lenses, automotive parts and industrial parts etc.

Recently, the use of chelating polymers for remediation of water and soil has attracted much attention [158]. M. M. Patel, R. Manavalan [159] has been studied magnetic, spectral, thermal, and electrical properties of coordination polymers derived from terpolymer. Chelating groups are incorporated into the polymeric side chains or backbone. The choice of the type of ligands, ligand density, structure and solubility of the polymer, as well as pH, govern the metal ion affinity, retention efficiency and selectivity [160, 161,162].

A batch equilibration method was used in the study of the selectivity of metal ion uptake. The method involved the measurement of distribution of a given metal ion between an aqueous solution and the resin. The ion exchange study was carried out over a wide pH range and in media of various ionic strengths. The sorption properties of the commercially available cationic exchange resin Amberlite IRC-718, that has the iminodiacetic acid functional group were determined toward the divalent metal-ions, Fe^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} by a batch equilibration technique [114]. Results of the study revealed that the resin exhibited higher capacities and a more pronounced adsorption toward Fe^{2+} and that the metal-ion uptake follows the order: $Fe^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. Many of the researchers prepared the ion exchange terpolymer resins and studied their ion exchange capacities for different metal ions using batch equilibrium technique at different pH with different electrolytes.

Chelating polymers or polychelatogens are used for remediation in homogenous reactions with water soluble polymers coupled with ultra filtration, or in heterogeneous reactions of solid polymer beads or semi-permeable membranes [163-168]. The environmental remediation ability and selectivity of chelating polymers depends strongly on ligand composition and pH. Sauer et al. [154] examined the use of polyethyleneimine (PEI) functionalized with full and partial molar equivalents of carboxylic acids for homogenous lead extraction from contaminated soils (figure 20). Highly branched polymers such as nanoscale dendrimers will continue to be explored for homogenous filtration applications due to their high number of chain ends and hence chelating groups.

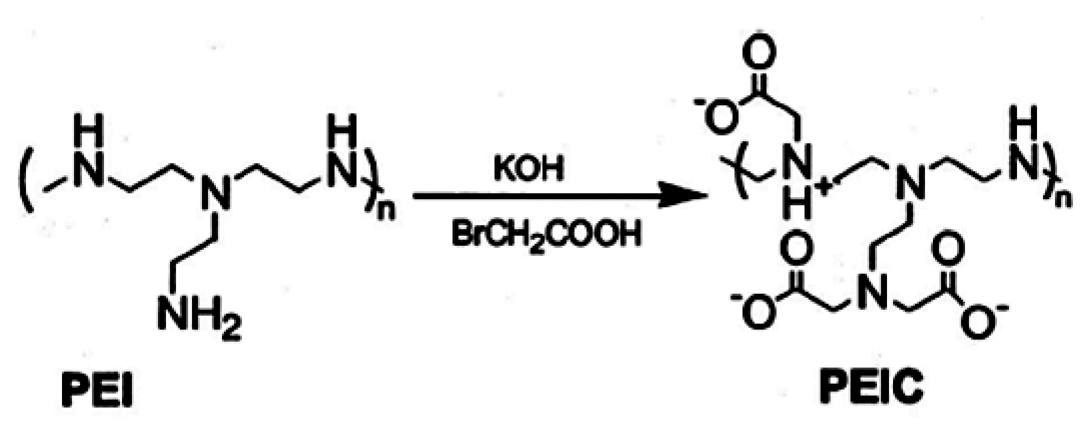


Figure.20. Functionalization of PEI with bromoacetic acid

Literature survey reveals that an alicyclic methacrylate terpolymer plays very important role for the manufacture of photoactive polymers which applied in advanced microelectronic devices. Katsuhiro Mizoguchi and Etsuo Hasegawa [160] synthesized organic photopolymers for opto-electronic devices, which are contributing to the realization of the “Multimedia World” in the 21st century. For this purpose two photoactive polymers were developed for Gbit-scale dynamic random access memory (DRAM) chip fabrication and for liquid crystal displays, respectively. For first Gbit DRAM fabrication mask, a novel and positive resist of the chemically amplified type was developed for ArF excimer laser lithography. It consists of new organic materials, an alicyclic methacrylate terpolymer and a photoacid generator called NEALS. A 0.20 μm line-and-space pattern was formed using an ArF excimer laser exposure system (numerical aperture of 0.55) and an aqueous base developer. For a bright and low-energy consumption display, a new polymer (poly(diacryloyloxy diethylstilbene)) was developed for a polymer stabilized cholesteric textures film, which operates without a polarizer. The film with a chlorine liquid crystal mixture shows good electro-optic properties, such as low driving voltage (V^{10} of 9.2 V), large charge holding ratio (92%), low width of hysteresis (0.4 V) and contrast ratio of 20, which demonstrate its potential for use in a display driven by a thin film transistor [161].

In addition to these novel applications various terpolymer showed an antibecterial properties. Nonaka Takamasa et.al. [162] synthesized a terpolymer by graft copolymerization of a crylamide (AAm) and tri-n-alkyl-4-vinyl-benzyl phosphonium chloride (TRVB) on poly(vinyl alcohol) (PVA), and crosslinking with glutaraldehyde (GA). They examined that this terpolymer behaves swelling properties and antibacterial activity against *staphylococcus aureus(S aureus).* They found that swelling ratio of antibacterial polymer increased with incresing content of TRVB, and decreased with increasing alkyl chain length of TRVB in the terpolymer, as well as increasing concentration of GA during crosslinking. The antibacterial activity of the terpolymer increased with increasing content and alkyl chain length of TRVB in the terpolymer. Brahmbhatt et al. prepared poly (3-phenoxy-cumarinethylene]s and determined their toxicity effect on various fungal and bacterial strains [174]. These polymers showed good biological activity.

In recent years, the synthesis of resins from hydroxy aromatic compounds like acetophenone, Phenacyl bromide and chalcones has also attracted attention, because of their antifungal, antibacterial and biological applications. The characteristic properties of tercopolymer resins would indicate their utility as ion-exchangers.

Garland W. Fusel and Stuart L. Cooper [163] design a biomaterial, using acrylic terpolymer with RGD peptides, which could support endothelial cells and function in small diameter vascular graft applications (Artificial Organs) in biomedical science. R. Narayani, V. Bagavad Gita and T. Amarnathan [164] prepared and evaluated alginate films of polymer for peridontal (a common dental disease) drug delivery.

A series of thermally stable, elastomeric and hydrophobic fluoro-terpolymers of tetrafluoroethylene (TFE), vinyl acetate (VAc), and poly (dimethylsiloxane) methyl acrylate-terminated (PDMSMA), P(TFE-ter-VAc-ter-PDMSMA), were synthesized [165]. These novel P(TFE-ter-VAc-ter-PDMSMA) terpolymer exhibit the properties associated with polysiloxanes and fluoropolymers, making them useful for coatings applications [166].

William Dickstein and Otto Vogl have been prepared functional co- and -terpolymer which can be used as an Ultraviolet stabilizers and antioxidants [167]. Ethylene propylene terpolymer [168-169] is used as paint films. Ethylene acrylate based terpolymer is the suitable choice of modifying engineering polymers and design flexible films, packaging etc.

Stejskal J. and Gilbert R. G [170] prepared a Polyaniline (PANi) conducting polymer with electrochemical activity that has been widely investigated in the past decade [171-173]. Several applications of the polymer have been proposed and demonstrated [174-176]. Whereas, most of the applications deal with the electrochemical activity and electronics, a few are concerned with its ion-exchange properties [177]. Because of the attractive electrical, optical and chemical properties of PANi and (PPy), both polymers have recently been used in the surface modification of various substances. A particularly interesting example is the use of PANi modified glassy carbon particles as the stationary phase in ion-exchange chromatography [178]. It has often been observed that glass surfaces immersed in the aqueous reaction mixture used in the oxidation of aniline became coated with a thin PANi film [179]. The typical film thickness varied between 50 and 400 nm depending on the reaction conditions. The coating protocol can be applied to the surface modifications of microspheres of the same chemical nature, SiO2 with PANi hydrochloride. The deposition of thin PANi and PPy coating onto monodisperse silica particles of 1 m diameter was reported by Armes et al. Stejskal and co-worker [180] prepared PANi in the presence of silica having 7 m diameter and 35 nm pore size. Electron microscopy showed that a solid film of PANi was produced on the surface of silica microspheres. PANi over-layer has been similarly produced on silica gel microspheres of 15 m in size [181-183]. Also 60- 125 m porous silica gel was coated with PPy. The silica gel modified with conducting polymers was proposed to be used in chromatographic and ion-exchange separations[184-186].

Literature survey reveals that polyfluorene terpolymer containing phenothiazine and fluorenone posses photoluminescence and electroluminescence. Abhishek P. Kulkarni, Xiangxing Kong, and Samson A. Jenekhe [187] synthesized five new conjugated terpolymer containing 9,9-dihexylfluorene, 10-hexylphenothiazine (HPT) donor, and 9-fluorenone (FLO) acceptor (Figure 21). They studied the effects of competing energy and intramolecular charge transfer processes on the photoluminescence (PL) and electroluminescence (EL) of multichromophore copolymers. The HPT and FLO moieties were found to act as emissive exaction traps on the terpolymer chains, leading new blue-green (475−485 nm) and green (520−525 nm) emission bands in addition to the blue (415 nm) emission of the fluorene segments. As the emissive materials in light-emitting diodes (LEDs), the terpolymer showed green to yellow EL with luminances of 1900−8970 cd/m^2 and efficiencies of 0.5−3.5 cd/A that varied with terpolymer composition. It can be used for the design of multichromophore EL copolymers for white LEDs [188-192].

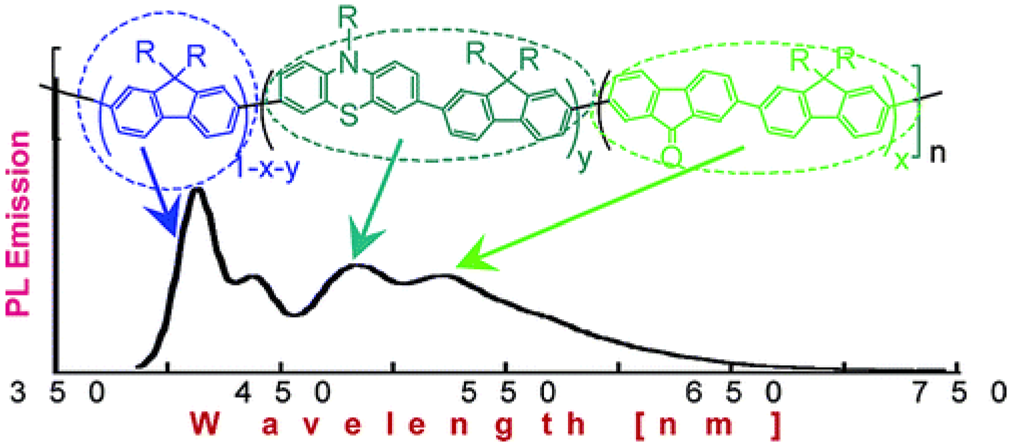


Figure.21.Synthesis of new conjugated terpolymer containing 9,9-dihexylfluorene, 10-hexylphenothiazine (HPT) donor, and 9-fluorenone (FLO) acceptor

Copolymers and terpolymer, based on vinyl ethers from linseed conjugated fatty alcohols and selected as having the most potential for commercial use, were evaluated as chemically resistant coatings, metal-decorating coatings, small-applicance [181] and architectural finishes, wire coatings, and adhesives. Studies show these materials to have promise in areas where a high-temperature baking schedule can be tolerated and where color is not of prime importance [182-186]. Good compatibility with most commonly used pigments was observed. As wire coatings, film showed good continuity and had superior dielectric strength and resistance to cut-through; however, improvement in flexibility and adhesion to copper would be needed for successful application. Performance as adhesives was disappointing, since curing in the absence of air was poor. The polymers showed some promise as can coatings, but the need for modifications in them was demonstrated.

In addition to these novel applications various terpolymer can be used in large number of applications. Terpolymer plays very important role as an ion exchangers for isotope separation in nuclear industry. It can be used in electronics and microelectronics , as a photoactive polymers, in nuclear industry, in water-treatment technologies, semiconductors manufacturing, as a fire proofing agent, optical storage data device, binding agents, additives, binders, molding materials, optical lithography, , removal of specific constitute water such as dealkalisation, fluoride removal, removal of organic matter, oxygen removal, nitrate removal, ammonia removal and removal of other harmful ions from drinking water, in pulp and paper industry for removal of inorganic salts from liquors, detoxification of by-products transferred for bio-cultivation, purification of sugars and polyhydric alcohols and extraction of lactoperoxidase and lactoferrin, purification of casein in dairy.

Terpolymers are the best for extrusion coating process, crystallinity control, transparency, automotive, melting temperature control, flexibility impact modifier for engineering plastic, heat sealing film in car interior, coating, pipelines, electrical resistance textiles, bullet-proof vests biomaterials, light guide panel, laptop computer, screens-contact lenses, compact discs, barrier sheets in medical applications and act as a Ultraviolet stabilizers, antioxidants, fungicides in plant and living tissues, bio-sensors etc and many more others. These applications made the terpolymer modernistic , extraordinary and encrediable substances in polymer chemistry.

This extensive work has been accounted in our laboratory on copolymer/terpolymer resins derived from ortho-aminophenol/4-hydroxy benzophenone /substituted phenols , melamine/urea/biurate and formaldehyde. These newly synthesized Terpolymer resin analyzed by elemental analysis, molecular weight determination by non-aqueous conductometric titration method, viscosity measurements, spectral methods (UV-Visible, FTIR , ^{1}H NMR , ^{13}C NMR), scanning electron microscopy (SEM). Terpolymers and their application as ion exchangers and their comparison with those which was studied by earliar workers [37.44, 56, 110, 115, 120, 126, 130, 132, 136, 139, 192] with respect to electrical conductivity and thermal stability. Terpolymer resins have been also studied in the light of photoluminescence properties.

Aims and Scope of Project

The aim of this thesis is to enhance the fundamental understanding regarding the development of new terpolymer resin and their applications. The work has been carried out within several research disciplines. New chemical products based on ortho-amino phenol/4-hydroxy benzophenone /substituted phenols, melamine/urea/biurate and formaldehyde have been developed with good performance such as electronics and microelectronics , as a photoactive polymers, in nuclear industry, in water-treatment technologies, semiconductors manufacturing, as a fire proofing agent, optical storage data device, binding agents, additives, binders, molding materials, optical lithography, , removal of specific constitute water such as dealkalisation, fluoride removal, removal of organic matter, oxygen removal, nitrate removal, ammonia removal and removal of other harmful ions from drinking water, The foremost aim of this thesis is:

1. To develop a new technique to synthesize different ion-exchangers.
2. Characterization of these terpolymer resins as an ion-exchangers.
3. Setting the methods and parameters related with the synthesis of copolymer resins
4. For studying the effect of temperature on the properties and structure of terpolymer.
5. Study an ion exchange properties, electrical conductivity and photoluminescence of the terpolymer.
6. Provide contribution to knowledge of the chemist.

The important chemicals used in the preparation of various new terpolymer resins were procured from the market and were of chemically pure grade, and wherever necessary the purity was tested and confirmed by thin layer chromatography. All the reagents were of the analytical grade and metal solutions were prepared by dissolving appropriate amount of the nitrates of the metals in double distilled water and standardized by EDTA titrations.

The A.R. grade or chemically pure grade chemicals which are used in the synthesis of organic polymeric resin are as: 2-amino-6-nitrobenzothiozole, p-methyl acetophenone, 4,4'-Dihydroxybiphenyl, Dithiooxamide, Biuret, 1,5-Diaminonapthalene, Hexamethylenediamine with Formaldehyde.

The organic polymeric resin have been synthesized using hydrochloric acid as a catalyst under various experimental condition viz. the concentration of catalyst, reaction time and temperature of reflux etc. All the terpolymer resins have been synthesized in four different terpolymer and total 16 terpolymer have been prepared by using mole ratios of monomers viz. (1:1:2), (2:1:3), (3:1:4) and (4:1:5) and (1:1:3), (2:1:4), (3:1:5) and (4:2:7). These organic polymeric resins have been abbreviated as follows.

1. 2-Amino-6-nitrobenzothiozole-Biuret– Formaldehyde
   (2-ANBF-I, 2-ANBF-II, 2-ANBF-III, 2-ANBF-IV)
2. 2-Amino-6-nitrobenzothiozole-Dithiooxamide – Formaldehyde
   (2-ANDF-I, 2-ANDF-II, 2-ANDF-III, 2-ANDF-IV)
3. 2-Amino-6-nitrobenzothiozole-1,5-Daminonaphthalene – Formaldehyde
   (2-AN-1-5-DF-I, 2-AN-1-5-DF -II, 2-AN-1-5-DF -III, 2-AN-1-5-DF -IV)
4. 2-Amino-6-nitrobenzothiozole-Hexamethylenediamine – Formaldehyde
   (2-ANHF-I, 2-ANHF-II, 2-ANHF-III, 2-ANHF-IV)
5. P-Methyl Acetophenone-Biuret– Formaldehyde

(PMABF-I, PMABF-II, PMABF-III, PMABF-IV)

6. P-Methyl Acetophenone -Dithiooxamide – Formaldehyde
   (PMADF-I, PMADF-II, PMADF-III, PMADF-IV)
7. P-Methyl Acetophenone -1,5-Daminonaphthalene – Formaldehyde
   (PMA-1-5-DF-I, PMA-1-5-DF -II, PMA-1-5-DF -III, PMA-1-5-DF -IV)
8. P-Methyl Acetophenone -Hexamethylenediamine – Formaldehyde
   (PMAHF-I, PMAHF-II, PMAHF-III, PMAHF-IV)
9. 4, 4’-Dihydroxybiphenyl-Biuret– Formaldehyde
   (4,4’-DBBF-I, 4,4’-DBBF-II, 4,4’-DBBF-III, 4,4’-DBBF-IV)
10. 4, 4’-Dihydroxybiphenyl -Dithiooxamide – Formaldehyde
    (4,4’-DBDF-I, 4,4’-DBDF-II, 4,4’-DBDF-III, 4,4’-DBDF-IV)
11. 4, 4’-Dihydroxybiphenyl -1,5-Daminonaphthalene – Formaldehyde
    (4,4’-DBDF-I, 4,4’-DBDF -II, 4,4’-DBDF -III, 4,4’-DBDF -IV)
12. 4, 4’-Dihydroxybiphenyl -Hexamethylenediamine – Formaldehyde
    (4,4’-DBHF-I, 4,4’-DBHF-II, 4,4’-DBHF-III, 4,4’-DBHF-IV)

All the organic polymeric resins have been purified by suitable technique like reprecipitation, crystallization etc. their purity has been checked by thin layer chromatography.

Melting points for all organic polymeric resin have been determined. The solubility of the organic polymeric resin has been tested by various organic as well as inorganic solvents. All the organic polymeric resin was found to be soluble in DMF, DMSO, THF and NaOH and KOH while insoluble in almost all other solvents.

The most significant physicochemical techniques and spectral studies have been used for the characterization of these newly synthesized organic polymeric resins.

A brief description of theoretical aspect of various physicochemical methods such as elemental analysis, molecular weight determination by conductomeric titration in non – aqueous medium, intrinsic viscosity, UV-visible spectra, IR spectra, ^{1}H NMR and ^{13}C NMR spectral studies, thermo gravimetric analysis, used for characterization of organic polymeric resins, and study of morphology of the organic polymeric resins by SEM has been included in this project work. SEM provides the information regarding surface topography at a very high magnification.

On the basis of physico-chemical and spectral evidences the most probable structures have been assigned to these new terpolymer resins.

Finally ion exchange properties of the newly synthesized and characterized resin have studied in detail and attempts have been made to interpret the experimental results in the light of practical applicability of these new tercopolymer resins.

Polymer chemistry is a rapidly changing field in course of time and each year, new exciting advances are made. Today polymer chemistry is promising area with applications in physical, chemical, biological and environmental science. The purpose of present investigation is to incorporate synthesis, characterization and applications of newly synthesized terpolymer resins in which electronic and metal sorption application are emphasized.

The objective has been to convey a deep understanding of various polymers and their advanced applications rather than to ring out a reference text. An attempt has been made to incorporate several important and recent developments in the subject. A fairly comprehensive review of organic polymers and copolymers which provide background to the study of synthesis and characterization of our newly synthesized copolymer resins is provided in each chapter. An excessive weight age has been given on structural determination, properties and various relevant and advanced applications. The characterization of the polymers by UV-visible, IR and NMR spectra as well as scanning electron microscopy are adequately covered, in elucidation the structure of synthesized terpolymer. The chelating ion-exchange properties and semiconducting properties along with thermal degradation study are also incorporated.

The literature in polymer chemistry is rapidly growing and it is almost impossible to cite exhaustive references for each topic. Therefore an attempt has been made to give at end of each chapter references to well known books and papers of authors at various reputed journals.

The present thesis is divided into five chapters. Each chapter has been tried to improve the logical flow to help in correlation with other chapters.

This chapter includes different types of polymers such as natural polymer, organic polymers, inorganic polymers, aromatic polymers, phenolplast, aminoplast, elastomers, thermosetting and thermoplastic, fibers, plastics, coating, adhesive etc. The focus has been given to overall information of polymers and provided the enough knowledge regarding aromatic polymers, phenol-formaldehyde polymers, amino-formaldehyde polymers and lastly terpolymers, their literature surveys, synthesis, characterization and applications in various sectors.

All newly synthesized terpolymer resins were purified by re-precipitation technique and have been tested and confirmed by thin layer chromatography (TLC) using dimethyl sulphoxide solvent. The melting points of each terpolymer resins samples have been determined and are found to be in the range of $125 \pm 2\ ^0C$.

The solubility of each terpolymer resin has been checked in various organic and inorganic solvents. The terpolymer resins are insoluble in almost all other solvents indicates higher moleculer weight polymeric nature of resins but soluble in dimethyl sulphoxide, dimethyl formamide, concentrated aqueous sodium hydroxide and potassium hydroxide [19-23, 26, 28, 32].

The terpolymer resins has been characterized by physico-chemical technique and spectral studies. The elemental analysis decided the empirical formula and empirical formula weight. Conductometric titration has been determine degree of polymerization $(\overline{DP})$ and number average molecular weight $(\overline{Mn})$ and the intrinsic viscosity has been determined molecular weight [1, 10, 19, 26, 32]. In the spectral study UV-visible spectra and IR spectra have been provided information regarding bonding in the molecular structure, composition and functional groups present in terpolymer resins [3,5,50]. Proton NMR spectra provided information about the types of proton, substituted groups and functional groups [56]. The morphology of the polymer can be confirmed by scanning-electron microscopy (SEM) [15, 37, 52].

The thermogravimetric analysis (TGA) has provided the information of thermal behaviour, thermal stability, decomposition and degradation products at various temperatures [2, 3, 19, 20, 26, 32]. The electrical conductivity and ion-exchange properties also studied. The introduction and experimental procedure of each physico-chemical technique and spectral method have been discussed in this chapter.

The various physico-chemical techniques and spectral methods reported are elemental analysis, non-aqueous conductometric titration for determination of number average molecular weight, determination of intrinsic viscosity, UV-visible spectra, IR spectra, ^1H NMR spectra, scanning electron microscopy (SEM) and thermal study by thermogravimetric analysis (TGA). Each technique has been elaborated with theoretical aspect and literature review in addition to result and discussion with conclusion.

Empirical formula of each repeat unit structure of each terpolymer resin has been determined on the basis of elemental analysis [32, 40, 43, 44]. Degree of polymerization $(\overline{DP})$ and the number average molecular weight $(\overline{Mn})$ has been determined by conductometric titration for different molar ratio of reacting monomers [6, 19, 26, 32, 40, 42, 44, 45]. The intrinsic viscosity has been determined in dimethylsulphoxide, found to be increase with increasing molecular weight of terpolymer resins, similar to earlier co-workers [19, 26, 32].

Absorption of visible and ultraviolet (UV) radiation is associated with excitation of electrons, in both atoms and molecules, to higher energy states. UV-visible spectra of all terpolymer resins have been analyzed minutely and the results indicated that absorption maxima (λ_{max}) and intensity maxima (ε_{max}) increased with increasing molar ratio of reacting monomers. UV-visible bands can also be determined the presence of aromatic rings and clue about functional groups like –OH, -NH, $-CH_3$, $-SO_3H$ etc in the terpolymer resins. The observations are in good agreement with earlier co-workers [1, 69, 10, 16, 19, 26, 29, 31, 32, 33, 40, 42].

IR spectra, it has been indicated the presence of phenolic -OH group, $-CH_2$ group, -NH group, >C=O group, $-SO_3H$ group, aromatic ring and substituted aromatic ring, their various stretching, bending vibrations, substitution pattern of aromatic ring, various tautometric forms and intramolecular hydrogen bonding involved in the polymeric chains, proton exchange reaction among various polymeric chains. These indications have made on the basis of various infrared absorption bands appeared in IR spectra [5, 6, 10, 16, 19, 26, 32, 40, 43, 44, 50, 53].

In ^1H NMR spectra of all terpolymer resins have analyzed, the results obtained indicated the presence of -OH, -NH, $-CH_2$, $-SO_3H$, -COOH groups in terpolymer resins. The signal of -OH group has been found to be shifted towards down field (generally at $\delta = 9$ ppm). The downfield shift of -OH signal may be due to intramolecular hydrogen bonding between -OH and -NH group or >C=O group or may be due to the exchange of proton between different polymeric chains or may be due to the isomerisation taking place in the polymeric structure [19, 26, 32, 40, 43, 44, 53, 56, 59].

The study of surface topography the micrograph of scanning electron microscopy (SEM) have been scanned for the representative terpolymer resins and has incorporated in this chapter. The SEM can produced very high resolution image of sample surface, revealing details about 1-5 nm in size and large depth of field yielding a characteristics three dimensional appearance of sample. During polymerization the crystalline nature of reactants monomenes may be converted into amorphous nature. The amorphous nature of the terpolymer resin samples shows the ion exchange capacity, indicating to use as ion-exchanger for certain ions [15, 29, 49, 51, 57].

The study of thermogravimetric analysis (TGA) of all terpolymer resins indicates that the decomposition reaction is taking place in the temperature range of 40º-800ºC in three steps after loss of crystalline water molecule. The three steps involved – 1) the degradation of substituted groups of aromatic ring, 2) degradation of aromatic ring, and 3) degradation of side chain [2, 3, 6, 20, 27, 35, 36]. The energy of activation obtained from both the methods is found to be in good agreement. From the data of Freeman-Carroll method different thermodynamic parameters such as change in Free Energy (ΔF), Change in Entropy (ΔS), Frequency Factor (Z), apparent entropy (S*), order of reaction (n) have been determined. The value of order of reaction (n) obtained from Freeman-Carroll plots, is nearly one. Thus the value of n has not obtained perfectly one, which indicates that the degradation reaction does not obey first order reaction. The thermal stability of terpolymer resins found to be increased by increasing molar ratio of resins. This sequence of thermal stability may be due to allowing formation of stronger intermolecular and intramolecular hydrogen bonding by increasing molar ratio of terpolymer resins and linear structures and establishing the intramolecular force of attraction.[2, 3, 6, 19, 26-28, 30, 32, 35-36, 40, 43-44, 60].

Semiconducting nature of polymers are new and promising materials for the development of new technology such as plastic electronics. The field of semiconducting polymer has experienced dramatic advances during last-decades. The terpolymers under investigation are semiconductor and measured their D.C. electrical conductivity in the temperature range of 313K to 463K by LCR-Q meter 4910. The pellet was fixed in sample holder and has been kept in the specially designed muffle furnace having auto regulating system by increasing temperature of 5K at each time and the resistance was recorded in LCR meter. The resistance has been converted into conductivity (σ). The results of the D.C. conductivities have been presented in the form of plots of logσ versus 1000/T for each set of data, has found that there is a consistent increase in electrical conductivity as temperature increase. This trend is the characteristics of the semiconductor which has shown by all synthesized terpolymer resins.

The increasing order of electrical conductivity and decreasing order of activation energy on increasing molar ratio of terpolymer resins, may be due to introduction of more and more aromatic skeleton and therefore more π electrons in the repeat unit structure of terpolymer resins, which has in good agreement with the most probable structure proposed for the newly synthesized terpolymer resins under study. The trend is also in good agreement with earlier co-workers [6, 7, 18, 19, 37, 54, 55].

Copolymer resins may be used to make a wide range of semiconducting electronic devices such as transistors, light-emitting diodes, solar cells etc. which can be manufactured by much simpler way than conventional inorganic semiconductors [18, 23, 24, 37, 47].

This chapter, the chelating ion-exchange properties of terpolymer resins under study were studied for different metal ions such as Fe (III), Cu (II), Ni (II), Co (II), Zn (II), Cd (II) and Pb (II). A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurements of distribution of a given metal ion between the terpolymer sample and a solution containing the metal ion only. The study was carried out over a wide pH range, rate of uptake time (staking time) and in media of various ionic strengths. The terpolymer resins under investigation provide to be a selective chelating ion-exchanger for certain metals. The terpolymer resins showed a higher selectivity for Fe (III), Cu (II) and Ni (II) ions than Co (II), Zn (II), Cd (II) and Pb (II) metal ions.

Ion-exchange study reveals that the metal uptake capacity of all synthesized terpolymer resins increase with, increasing molar ratio of terpolymer resins. This is because by increasing molar ratio resins, increase the chelating groups which can form the more chelation with more metal ions, which ultimately increase the uptake capacity [4, 9, 11, 12, 14, 19, 21, 22, 25].

$$\text{Polymer + metal ion solution} \xrightarrow{\text{Shaking}} \text{polymer- metal ion chelates}$$

Metal ion uptake capacity of polymer depends on stability of polymer- metal ion chelates. The metal uptake capacity in the form of distribution ratio increased with increasing pH of the solution, this is because at higher pH the hydrogen ion (H^+) concentration is less in solution. On decreasing pH, the hydrogen ion concentration is increased the dissociation tendency of resin to liberate H^+ ion is decreased, hence ion-exchange reaction tend to proceed in the reverse direction., therefore adsorption of metal ion on exchange is decreased on decreasing pH i.e. the uptake of metal ion decreased.

Distribution ratio of Fe^{3+} ion is lower, at pH=3. At high pH Cu^{2+} shows highest adsorption ratio followed by Ni^{2+} and the metal ion Co^{2+} has moderate value while Zn^{2+}, Cd^{2+} and Pb^{2+} have lower distribution ratio.

Fe^{3+} forms octahedral complexes with ligands of electrolyte, which involve more number of ligands in complex formation. For Cu (II), Ni (ii) and Co (II) metal ions atomic number decrease, the ion uptake capacity is decreases at particular pH. Ni (II) forms strong complex and Co (II) still forms strong complex with ligands, hence Cu (II) may show higher distribution ratio than Ni(II) which has higher than Co(II) ions. Zn (II) ion has completely filled 3d orbital, having less tendency towards the complex formation, hence it may show lower distribution ratio. In case of Cd (II) and Pb (II) purely electrostatic factors are responsible. The metal uptake capacity may depend on the degree of polymerization. Lower value of DP may favours the complexation [11, 19, 21, 22, 26, 32, 34, 40].

Concentration of an electrolyte affects the metal ion uptake capacities of terpolymer resins. SO_4^{2-} ligands of sodium sulphate electrolyte, forms stable complex with metal ions, hence on increasing concentration of SO_4^{2-} electrolyte the metal uptake capacity may decrease. Concentration favours the stability of the complexes. Cl^-, NO_3^- and ClO_4^- electrolyte are comparatively weak ligands, forms weak complex with Fe (III), Cu (II), Ni (II) and Co (II), therefore metal uptake of resins increases, while these ions may form more stable and strong complex with Zn (II), Cd (II) and Pb (II) therefore on increasing concentration of these electrolyte the metal uptake capacity decrease.

The metal ion uptake capacity thus depends upon the stability of complex formed between the metal ligand of electrolyte and metal ligands of resins. The trend is similar to earlier co-workers [10-12, 19, 21, 22, 25, 26, 34, 41, 43-46, 59].

The metal ion uptake capacities also depend upon the shaking time. As the shaking time increase the polymer resin get more time in contact with metal ion solution, therefore increase the metal uptake capacity. Thus the rate of metal ion uptake follows the order –

Metal ion	$Fe^{3+} >$	$Cu^{2+} \approx$	$Ni^{2+} >$	$Co^{2+} \approx$	$Zn^{2+} >$	$Cd^{2+} \approx$	Pb^{2+}
Ionic size	0.55	0.57	0.69	0.90	0.90	1.10	1.19

The sequences of rate of metal ion uptake indicate that the rate may depend on size of the ion. The rate is directly proportional to the size of the metal ion. For example Fe^{3+} has more charge and small size, therefore equilibrium is attained within three hours, while other first transition ions Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} have nearly equal cationic size, charges are some: therefore required 5 hrs to attain equilibrium, while Cd^{2+} and Pb^{2+} have large atomic size, therefore requiring 6 hrs to attain equilibrium. This order may be explained on the basis of their stability constants of the complexes formed by the resin to metal ions. The metal uptake capacities of resins have found to be increased by increasing the molar ratio of reacting monomers. This may due to increasing more ligands groups per unit structure of resin, which increase the ability to form the complex with metal ions by the resin.This type of trend has also observed by earlier co-workers [11, 12, 19, 21, 22, 25, 26, 32, 40, 41, 43, 44, 45, 46, 48, 59].

Overall study of terpolymer resins indicates that the terpolymer resins under investigations may be used as semiconducting materials in various electronic industries for making a wide rage semiconducting electronic devices such as transistors, light-emitting diodes, solar cells etc. The ion-exchange study reveals that the terpolymer resins under study, are very good ion-exchangers for various metal ions, therefore these resins can be used as ion-exchanger in the purpose of purification of waste solutions, one of the important application of chelating and functional polymer is the capability to recover metal ions from waste solution. In addition to semiconducting and chelating application the terpolymer resins under study can also be used as coating material, in automotive industry, in foundry etc. The resins under study are stable at elevated temperature therefore may be used in aerospace industry and industries requiring the polymer resistance to harsh environment and thermally stable polymers.

FUTURE WORK

In future copolymer metal complexes can be synthesized with various metal ions especially the lanthanides series. Owing to their versatile applications, the metal complexes can be used as semiconductors, super capacitors, heat resistant materials, antibacterial agents, light emitting diods and effective catalysts. Further, the new combination of copolymers will also satisfy the present day needs of cost effective ion-exchange resins for the removal of hazardous and toxic ions. These types of research work definitely generate the clean and pollution free environment.

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REFERENCES

1. Baeckland L.H., U.S. Pat. 939, 966 (1909) 942, 852 (1909).
2. Baeckland L.H., J.Ind.Eng.Chem. 1, 149 (1909) C.A. 3, 1471 (1909)
3. Baeckland L.H.,U.S. Pat., 939, 988 (1909) C.A. 4, 521 (1910)
4. Baeckland L.H., J. Ind. Eng. Chem. 1, 545 (1909) C.A. 3, 2863 (1909)
5. Beayer A., Ber. 5, 25, 280, 1094 , Vol.10 Encyclopedia of polymer Sci. and Tech, Wiley (inter science) (1872),
6. Lederer L., J. Park Chem; 50, 224 (1960)
7. Baeckland L.H., J. Ind. Engg. Chem., 1, 545 (1909) C.A. 3, 2863 (1909)
8. Lim, Chee Siong, Masters thesis, Universiti Putra Malaysia (2004).
9. Bajia Subhas Chandra, Swarankar Pawan, sudesh Kumar and Bajia Birbal, E-Journal of Chemistry, 4, 457-460, (2007).
10. Umezawa S., Ohtsuka U., Japan, 1598, (1953), C. A. 48, 2290 (1954).
11. Pennington L. D., Williams M. B., Ind. Eng. Chem., 51, 759 (1959).
12. Maldas D., Shiraishi N., Harada Y., J. of Adhesion Sci. and Technol., Netherland, 11, 305-316 (1997).
13. Chow S., Steiner R. R., J.Appl. Polym. Sci. 86, 3256-3263 (2002).
14. Nair P., Thachil E. T., Paul A., Thomas Telford of Journal Home, 19(3), 101-108 (2007).
15. Eapen K. C., Veddanapalli I. M., Macromol Chem., 119, 4(1968).
16. Gregor P.H., Taifer M. Cilard L, Becker E.I., Ind. Eng. Chem. 44, 2834 (1952)
17. Kriplani Prashant, Swarnkar Pawan, Maheshwari Rinku, Ojha K G, E-J.Chem, 3(13), 307 (2006).
18. Rajanarendar E and Karunakar E, Indian J Chem. 43,805 (2006).
19. Caddick S, Tetrahedron,51,10403 (1995).
20. Kuhnert N, Angew Chem Int Ed., 41, 1863 (2002).
21. Gabilondo N, Martin M D, Mondragon I and Echeverria J M, High Performance Polymers, 14, 415 (2002).
22. Young-Kyu Lee, Dae-Jun Kim, Hyun-Joong Kim, Teak-Sung Hwang and Miriam Rafailovich, J Applied Polymer Science, 89, 2589 (2003).
23. ASTM, Annual Book of ASTM Standards, D 1084-88, 1991, Vol.15, American Society for Testing and Materials, Philadelphia, Seattle, WA, (1957).
24. Walker J F, Formaldehyde, Krieger Publishing Co., Huntington, New York, p

493,(1975).

25. Gardziella, L.A. Pilato, A. Knop, Phenolic Resins: Chemistry, Applications, Standardization, Safety and Ecology, 2nd edition, Springer, (2000).
26. Wolfgang Hesse "Phenolic Resins" in Ullmann's Encyclopedia of Industrial Chemistry, 2002, Wiley-VCH, Weinheim.
27. Odian, G. "6". Principles of Polymerization. WileyInterscience. p. 464, (2004).
28. Jenkins, A. D. "Glossary of Basic Terms in Polymer Science". Pure Appl. Chem. 68: 2287–2311, (1996).
29. R. Mayo and Frederick M. Lewis J. Am. Chem. Soc.; 66(9) pp 1594 – 1601,(1994).
30. Painter P. C. and Coleman M. M., Fundamentals of Polymer Science, CRC Press, , p 14 (1997).
31. Knop A. Pilato L. A., Phenolic resins, Springer Verlags, Barlin (1995)
32. Lebach H. Z., Angew Chem., 22, 1599 (1909).
33. Maldas D., Shiraishi N., Harada Y., J. of Adhesion Sci. and Technol., Netherland, 11, 305-316 (1997).
34. Chow S., Steiner R.R., Appli. Polym, Sci. 23(7), 1973-1985 (2003).
35. Samal U. K., Nayak P. L., Lenkas., J. Appl. Polym. Sci., 47, 1315 (1993).
36. GeoigeL Brode, "Phenoltc Reslns," pp 384-416 In ECT, Vol 17, (1982)
37. Micioi, M.; Albu, A.; Mateescu, C., Voicu, G., Rusen, E., Marculescu, B., Mutihac, L. J., Applied Polymer Science , 103, 1397–1405 (2007).
38. Fu, F.; Chen, R.; Xiong, Y. Separation and Purification Technology, 52, 388–393, (2006).
39. Lebrun, L.; Vallée, F.; Alexandre, B.; Nguyen, Q. Desalination, 207, 9–23 (2007).
40. Zalloum, R.; Mubarak, S. Journal of Applied Polymer Science, 109, 3180-3184 (2006).
41. Zhu, Y.; Millan, E.; Sengupta, A. Reactive Polymers, 13, 241–253 (1990).
42. Spivakov, B.; Geckeler, K.; Bayer, E. Nature, 315, 313–315 (1985).
43. Rivas, B.; Maureira, A. Inorganic Chemistry Communications, 10, 151–154 (2007).
44. Williams L. L., Howe-Grant, M.Eds; John Wiley & Sons; New York, Vol 2, pp 604-637 (1991).
45. Updegratt, H, 3rd ed, van Nostrand Reinhold, New York, , 341-346 (1990).
46. Pizzi A, In wood Adhesives, Chemistry and Technology; Marcel Dekker, New York, (1983).
47. Pratt T, John W. E., Rammon R M, Plagemann W L, , 17, 275 (1985).

48. Rossister E. C., British Cyanides Co., British Patent, 258-266 (1950).
49. John H., U. S. Patent, 1, 355, 834 (1920).
50. Patel M. M. and Joshi R. M. Pract. Indian Acad. Sci. (Chem. Sci.) 91 (4), 351(1982).
51. Patel M. M. and Joshi R. M., Indian J. Chem. Vol. 21 A No. 6, 637 (1982).
52. Patel M. M. and Joshi R. M., J. Makromol Sci. (Chem.), A 19 (5), 705 (1983).
53. Filatova V. A. et. al., Plast Mascy, 6, 25 (1980).
54. Peiking Well building Inst., Coal Sci. Technol. Peking, 1, 27 (1980).
55. Sakachev P. G. et al., Sh. Tr. TSNLL Bumage, 18, 31 (1979).
56. Pilot B. V., A. Sh. Aiginina USSR, 740289 (1980).
57. Jsu. L. V., et al., Derevoobrah, Prom. St. 4, 28 (1980).
58. Schaudy, Emil Prokoch, Holzforachung, 34 (3), 104 (1980).
59. Otsuka Chem. Co. Ltd. Japan, Jp 8065228 (1980).
60. Henkel and Co., Brit. Patent, 455, 008 (1935).
61. Buller J., Trans Plastic Inst. 20 (41), 8 (1952).
62. Anonymous, Ind. Eng. Chem., 57, 13 (1965).
63. Hedwett, U.S. Patent, 2, 456, 191 (1948).
64. Anon. Plastic, 17, 231 (1952), 29 (8), 155 (1952).
65. John K Backus, "Polyurethanes, In Calvln E Sch~ldknecht, ed , w~th Irving Skeist, Polymerzzatzon Processes, Wiley-Interscience, New York, (1977).
66. Bruzns Paul F Brums, ed , Polyurethane Technology, Wlley-Intersc~ence, New York, (1969).
67. A Brydson, Rubber Chemistry, Applied Science, London, (1978).
68. D J Davld and H B Staley, Analytical Chemistry of the Polyurethanes, Wiley-Interscience, New York, (1969).
69. R J D Domlnguez, "Polyurethane," pp 102, 104, 106, 108 in MPE, (1982).
70. J F Keegan, "Phenolic," pp 42-44 in MPE, (1982).
71. W A Kentgen, "Phenolic Resins," In EPST, Vol 10, pp 1-73 (1969)
72. M. Olivares, J. A. Guzmán, A. Natho and A. Saavedra , Wood Science and Technology,Volume 22, Number 2, Pages 157-165 (1998).
73. Yun-yan Wang, Wen-jie Peng, Li-yuan Chai, Bing Peng and Xiao-bo Min, et al. Journal of Central South University of Technology, Volume 13, Number 1, Pages 53-57 (2006).
74. Walter Sonderegger and Peter Niemz European Journal of Wood and Wood Products, Volume 64, Number 1, Pages 11-20 (2006).

75. Anthony H. Conner, Linda F. Lorenz Journal of wood chemistry and technology, 6(4), 591-613 (1986)
76. Bhatia, G., et al, J.Mat. Sci. 19, 1022, (1984)
77. Cambell, M. I., "Introduction to Synthetic Polymers", Oxford University Press 1994
78. Haupt, A., R., and Sellers T., Ind. Eng. Chem. Res 33, 693 (1994)
79. R.J. Young Chapman & Hall, Introduction to Polymers ,ISBN 0-412-22170-5,(1987).
80. International Union of Pure and Applied Chemistry, et al. "IUPAC Gold Book" Retrieved on 11 May 2007 from "IUPAC Gold Book". (2000).
81. Clayden, J., Greeves, N. et al. "Organic chemistry", p1450-1466 (2000).
82. J.M.G. Cowie "Polymers: Chemistry and Physics of Modern Materials (Chapman and Hall, 2d ed. p.4, (1991).
83. Kim, N.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. Macromolecules, 37, 2427 (2004).
84. Hohenstein, W. P.; Mark, H. J. Polym. Chem1, 127 (1946).
85. Anne Field "Melamine Plastic". Home Maintenance and Repair. Michigan State University Extension . (2003-06-24).
86. Ozawa S ,Polym. J. Japan 19 (1999).
87. Kadolph, Sara J. Anna L. Langford. "Textiles". Pearson Education, Inc. Upper Saddle River, NJ. (2002).
88. J M Garcia, F C Garcia, F Serna, J L de la Peña , High Performance Aromatic Polyamides, Progress in Polymer Science 35: 623-686 (2010)..
89. JWS Hearle "High-performance fibers". Woodhead Publishing Ltd., Abington, UK – The Textile Institute (ISBN 1855735393) (2000).
90. Doetze J. Sikkema "Manmade fibers one hundred years: Polymers and polymer design". J Appl Polym Sci, John Wiley & Sons, Inc. (83): 484–488 (2002).
91. Kh. Hillermeier and H.G. Weijland. "An aramid yarn for reinforcing plastics". Plastica (11): 374–380 (1977).
92. Callister "Materials Science and Engineering - An Introduction," 557-558 (2007).
93. Charles A. Harper, ed., Modern Plastics Handbook, ISBN 0-07-026714-6, (2000).
94. Ken Yoshimura and Katsuhiko Iwasaki Macromolecules, , 42 (23), pp 9302–9306 (2009)
95. Kunio Kimura, Shin-ichiro Kohama and Shinichi Yamazaki Polymer Journal 38, 1005-1022 (2006).
96. James M. Margolis, editor in chief, Engineering plastics handbook , ISBN

0071457674 , McGraw-Hill, (2006).

97. Patel, M.C. and Shah, A.D., Poly(amides-imides)based on amino end-capped polyoligomides, Oriental J. Chem, 19(1), (2002).

98. Ivory D.M. , Miller G.G. , Sowa J.M. , Shacklette L. W. , Chance R. R., Baughman R.H., J.Chem. Phys., B,(1979) 1506.

99. Wnek G.E., Chin J . C, Karasz F.E. ,and Lillya C.P., Polymer, 20,1441 (1979).

100. Arket C., Kanazawa K. K., Lee V. Y., Rabolt J. F., Reynolds J. R. ,and Strest G. B. , J.Polym. Sci., Polym. ,Phys. Ed., 20, 117 (1982).

101. Bastia T. K., Lenka S., Nayak P. L., J. Appl. Polym. Sci., 46, 739(1992)

102. Gurnule W. B., Juneja H. D., paliwal L. J., Oriental J. Chem., 39(A), 1110-1113 (2000)

103. Gurnule W. B., Juneja H. D., paliwal L. Research Journal of Chem. And Environ., 3(1), 23 (1999).

104. Gurnule W. B., Juneja H. D., paliwal L. J., Reactive and Functional polymer, 50, 95-100(2002).

105. Kapadia R. N., Dalal A. K., Indian J. Chem., 19A, 280-282 (1980)

106. Kapadia R. N., Dalal A. K., Indian J. Technol., 19, 127-130 (1981)

107. Patel K.D., Patel M. M., Synth. React. Inorg. Met. Org. Chem., 23(2), 299-325 (1993).

108. Rahangdale P. K., Gurnule W. B., Paliwal L. J., Kharat R. B., Progress in Crystal Growth and Characterization of Materials, 45,155-160(2002)

109. Rath D. K., Nayak P. L., Lenka S., J. Appl. Polym. Sci., 51,1679(1994)

110. Samal U. K., Nayak P. L., Lenka S., J. Appl. Polym. Sci., 47, 1315 (1993)

111. Gurnule W. B., Juneja H. D., paliwal L. J., Ultra Scientist of Physical Sciences, 12(2), 225(2000).

112. Gurnule W. B., Juneja H. D., paliwal L. J., Acta Ciencia Indica, 28(1), 37-40 (2002)

113. Gurnule W. B., Juneja H. D., paliwal L. J., Asian J. Chem., 12(3),753 (2000)

114. Rahangdale SS, Zade AB, Gurnule WB. J App Polym Sci;1 08(2): 747 (2008).

115. Singru RN, Zade AB, Gurnule WB. J App Polym Sci;109(2):859 (2008).

116. Rahangdale SS, Zade AB, Gurnule WB. J Ultra Sci;19(2):213 (2007).

117. Rahangdale SS, Zade AB, Gurnule WB. J App Polym Sci;108(2): 747 (2008).

118. Singru RN, Zade AB, Gurnule WB. J App Polym Sci;109(2):859 (2008).

119. Butoliya SS, Zade AB, Gurnule WB. J App Polym Sci; 113(1):1 (2009)

120. Gupta RH, Zade AB, Gurnule WB. J App Polym Sci; 109(5):3315 (2008).

121. G. C. Patel, H. B. Pancholi and M. M. Patel , High Performance Polymers, Vol. 3, No. 2, 99-106 (1991)

122. Pratik E.P. Michael, J.M. Barbe, H.D. Juneja, L.J. Paliwal, European Polymer Journal, 43 (12), 4995-5000 (2007).

123. Xin-Gui Li, Mei-Rong Huang, Pan Pan, Zhi-Liang Zhu, Yu-Liang Yang, Polymer Degradation and Stability, 71(3), 333-341 (2001).

124. Jie Fu, Jennifer Fiegel, and Justin Hanes Macromolecules, 37 (19), pp 7174–7180 (2004).

125. Patel S.A. et al. Iranian Polymer Journal 13 (6), , 445-453 (2004).

126. Micioi, M.; Albu, A.; Mateescu, C.; Voicu, G.; Rusen, E.; Marculescu, B.; Mutihac, L. J. , Applied Polymer Science, 103, 1397–1405 (2007).

127. Zalloum, R.; Mubarak, S. Journal of Applied Polymer Science, 109, 3180-3184 (2008).

128. Zhu, Y.; Millan, E.; Sengupta, A. Reactive Polymers, 13, 241–253 (1990).

129. Spivakov, B.; Geckeler, K.; Bayer, E. Nature, 315, 313–315, (1985).

130. Bhavna A. Shah et.al, Iranian Polymer Journal 15 (10) , 809-819 (2006).

131. Kunin R. and Preuss A.F., Characterization of a boron specific ion exchange resins, Ind. Eng. Chem. Proc. Rec. Develop., 3, 304-306 (1964).

132. Stromquist D.M. and Reents A.C., Ion exchange purification of sugar solutions, Sugar J., 13, 18-21 (1950).

133. Preuss A. and Kunin R., , Proc. Inter, Conf. Peaceful Uses Atom. Energy- Geneva, 8, 45 (1956).

134. Lyle J.L. and James K.G., Refining glycerol, U.S. Patent 2,578,816 (1951)

135. Bernarda J., Brangera C., Nguyena T. L. A., Denoyelb R. and Margaillana A., React. And Funct. Polym. 68(9), 1362-1370, (2008).

136. Lenka S., Parija A., Nayak P. L., Polym. Intern. 29(2), 103-106, (2007).

137. Patel S. R., Patel H. S., Patel S. R., Macrom. Mate. And Engg. 160(1), 175-186, (2003).

138. Kamble K. J., Patkar D. N., Journ. App. Polym. Sci. Part B, 33(4), 629-632, (2003)

139. Ali Boztug, Satlm;s Basan Journal of Applied Polymer Science, Vol. 103, 600–604 (2007)

140. Rzaev, Z. M. O. J Polym Sci Part A: Polym Chem, 37,1095 (1999).

141. Durgaryan, N. A.; Matosyan, V. H.; Markarian, S. A. Eur Polym J, 39, 921 (2003).

142. Boztugˇ , A.; Basan, S. J Appl Polym Sci, 89, 296 (2003).

143. Wang, K.; Huang, W.; Xia, P.; Gao, C.; Yan, D. React Funct Polym, 52, 143 (2002).
144. Dong, D.; Tasaka, S.; Aikawa, S.; Kamiya, S.; Inagaki, N.; Inoue, Y. Polym Degrad Stab, 73, 319 (2001).
145. Nandan, B.; Kandpal, L. D.; Mathur, G. N. Eur Polym J, 39, 193 (2003).
146. Mu-Yang, H. Polym Test, 19, 105 (2000).
147. Zulfiqar, S.; Masud, K. Polym Degrad Stab, 78, 305 (2002).
148. T. K. Pal, and R. B. Kharat, 173, Issue1, 55–68, (1989).
149. De-Geiso R C, Donaruma L, Tomic E, Analytical chemistry, 34, 845-847, (1962)
150. Ante Jukic, Elvira Vidovic and Zvonimir Janovic Volume 43, Number 5, 386-394,(2007).
151. Hala F. Naguib, Samia M. Mokhtar, Nesren Z. Khalil and Maher Z. Elsabee Journal of Polymer Research, 16, 693-702 (2009).
152. D. Blanco-Gomis, J. M. Le Bourgeois and R. Rosset Chromatographia, , 31, 71-74 (1991).
153. C. Becker, H. Krug and H. Schmidt Volume 8, Numbers 1-3, 625-627 (1997).
154. Sauer, N.; Ehler, D.; Duran, B. J. Environmental Engineering, 130 (5), 585–588 (2004).
155. Micioi, M.; Albu, A.; Mateescu, C.; Voicu, G.; Rusen, E.; Marculescu, B.; Mutihac, L. J. Applied Polymer Science, 103, 1397–1405 (2007).
156. Zalloum, R.; Mubarak, S. Journal of Applied Polymer Science, 109, 3180-3184 (2008).
157. Zhu, Y.; Millan, E.; Sengupta, A. Reactive Polymers, 13, 241–253 (1990).
158. Spivakov, B.; Geckeler, K.; Bayer, E. Nature, 315, 313–315 (1985).
159. M. M. Patel; R. Manavalan, Journal of Macromolecular Science, Part A, 20, ,487 – 501 (1983).
160. Katsuhiro Mizoguchi and Etsuo Hasegawa, Polymers Advanced Technologies, (1998).
161. Mizoguchi, K. and Hasegawa, E, Polymers for Advanced Technologies, 7, Issue 5-6, 471–477 (1996).
162. Nonaka Takamasa, Watanabe Tsutomo, Tomimatsu Yasuhero, Kurihara Seiji, Journal of Network Polymer, Japan, 20; No.2, 55-66 (1999).
163. Garland W. Fussell and Stuart L. Cooper, NCBI PubMed Biomaterials, 25(15), 2971-2978, (2004).
164. R. Narayani, V. Bagavad Gita, T. Amarnathan, Biomaterials & Artificial Organs, 14

Number 1 (2000).

165. Bilal Baradie and Molly S. Shoichet, Macromolecules, 38 (13), 5560–5568, (2005).

166. Chong Cheng, Kenya T. Powell, Ezat Khoshdel, and Karen L. Wooley, Macromolecules 40 (20), 7195-7207 (2007).

167. William Dickstein, Otto Vogl, Journal of Macromolecular Science, Part A, 23, 387 - 402 (2007).

168. R. D. Singer, G. T. Williams, Gerd Angerer Ind. Eng. Chem. Prod. Res. Dev., 10 (3), 287–293, (1971).

169. Ali Boztuğ and Satilmiş Basan Designed Monomers and Polymers, 9, 617-626 (2006).

170. Stejskal J. and Gilbert R. G., Pure Appl. Chem., 74,857-867(2002).

171. Prokes J. and Krivka J., Polym. Deg. Stab., 68, 261-269 (2000).

172. Anand, J., Palaniappan, S., and Sathyanarayana, D.N., Prog. Polym. Sci., 21, 993-1002 (1998).

173. Tallman D.E., Pae Y., Chen G., Wierwagen G.P., Reems B., and Gelling V.J., 201-211, (1999).

174. Hosseini S.H. and Entezami A.A., Polym. Adv.Technol, 12,482-493 (2001).

175. Hosseini S.H. and Entezami A.A., J. Appl. Polym. Sci., 90, 49-62 (2003).

176. Wang J., Synth. Met., 132, 49-52, (2002).

177. Wang J., Synth Met., 132, 53- 56 (2002).

178. Niwas R., Khan A. A., and Varshney K.G., Coll. & Surf. A, 150, 7-14 (1999).

179. V.D.Mane, N.J.Wahne, W.B. Gurnule, *.J.Appl. Polym. Sci*. 111, 3039-3049, 2009.

180. Michael P. E. P., Barbe J. M.,. Juneja H. D., Paliwal L. J., Europ. Polym. J., 43, 4995-5000 (2007)

181. Kim B.J., Oh S.G., Han M.G., and Im S.S.,Langmuir, 16, 5841-5845 (2000).

182. Brahmbhatt D. I., Singh S., Patel K. C., Europ. Polym. J., 35, 317-324 (1999).

183. Kenawy E. R., J. Appl. Polym. Sci. 82, 1364-1347 (2001).

184. Patel M. M., Kapadia M. A., Patel G. P., Joshi J. D., Iran Polym. J., 67(8), 746-757 (2007).

185. Lenka S., Parija A., Nayak P. L., Polym. Intern. 29(2), 103-106, (2007)

186. Parmar J. S., Patel M. R., Patel M. M., Material and Engg. 105(1), 75-81, (2003).

187. Abhishek P. Kulkarni, Xiangxing Kong, and Samson A. Jenekhe Macromolecules, 39 (25), 8699–8711 (2006).

188. F. Cheng, G. Zhang, X. Lu, Y. Huang, Y. Chen, Y. Zhou, Q.Fan, W. Huang, Macromol. Rapid Commun. 27, 799 (2006).
189. Nemli G and Çolakogˇlu G, Build Environ, 40(1), 83 (2005).
190. Roberts R J and Evans P D, Compos Appl Sci Manuf, 36(I), 95 (2005).
191. ahromi S, Polymer, 40(18), 5103 (1999).
192. Saiter A, Devallencourt C, Saiter J M and Grenet J, Materials Lett, 45(3&4), 180 (2002).