

## Chapter-1

### General Introduction and Literature Survey

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#### 1.0 Introduction:-

Much of the humanity's progress has been marked by dramatic improvements in the materials that chemists have developed, from the 'Stone Age' to the "Iron Age" to the "Bronze Age" and now to the "Polymer Age". The development of polymers is perhaps the biggest achievement chemistry has made and it has a significant effect on every day life. "Polymer" is now a household word. Polymers are big molecules, the materials that constitute most of our natural and synthetic environment. The world would have appeared totally different without artificial fibers, plastics, elastomers, etc. and as cheaper, better and stronger synthetic materials are developed, their use will undoubtedly increase further. Polymer materials, as they are constantly being modified, improved and fine-tuned for current and additional needs are readily accepted by the public, will have an ever-expanding influence on everyday life. Today polymers are used as replacements for woods, glass and metals and for a wide variety of applications in industries such as packaging, automobiles, building and construction, electronics, aerospace, electric equipments etc. In the high technology microelectronics area, many opportunities exist for polymers to serve as improved dielectrics, improved plasma etch resistance barriers and improved lithographic resists etc.

Polymers for biomedical applications, likewise, provide a rich opportunity for synthetic innovation. Polymers are materials for the future and are versatile substances that can be tailored in an almost infinite number of ways to meet evolving needs. It is not surprising then that much of the high technology in future, from biotechnology to microelectronics, will depend on our ability to synthesize and manipulate polymers.

Syntheses of new monomers with special functionalities are greatly needed to fine-tune polymers for specific tasks. The raw materials cost, market size, energy needs, and health environmental concerns have been the important factors especially for invention / discovery and introduction of new monomers. There have been always constant searches for new cost effective monomers that can be used in the synthesis of polymers for specialty applications. In this respect, the synthesis of polymers from renewable resources has attracted considerable attention of research workers throughout the world.

#### 1.1 Classification of polymers:-

W. H. Carother<sup>1a,b</sup> classified synthetic polymers into addition and condensation polymers based on the classical definition of organic chemistry of addition and condensation reactions through which polymers are synthesized. P. J. Florry, classified the polymers based on the mechanism into chain growth and step growth polymerization

##### a) Addition polymerization:-

The addition polymerization involves the addition of individual monomers to each other directly without any change in the composition and a long chain is formed. Vinyl compounds with  $[-C=C-]$  are prime examples forming polymers such as

polyethylene, polypropylene, polyvinyl chloride, polystyrene, polymethyl methacrylate etc, by chain growth mechanism.

### **b) Condensation polymerization:-**

In this polymerization, two or more functional monomers react with each other with elimination of byproduct to form a linear polymer. The reacting monomer should carry appropriate functional groups, which react with each other to form high molecular weight linear polymer. The byproduct, which is formed during the reaction, is removed or trapped to achieve high molecular weight polymer. Polyesters (PET), polyamides (Nylons, Aramids), are examples of condensation polymers which are formed by step growth mechanism.

Thus diacids, diacid chlorides, diphenols, diamines, dialdehydes etc are the main classes of condensation monomers<sup>2-12</sup>. The commercially important polycondensation reactions are the polyesterification, polyamidation producing polyamides and reaction between diamines with dianhydrides yielding polyimides. The nucleophilic substitution reactions lead to the polymers like poly(sulphone)s, poly(phenylenesulfide)s, poly(ether amide)s etc.

### **1.2 High performance polymers:-**

The first man-made plastic was created by Alexander Parkes who first publically demonstrated it at the 1862 great international exhibition in London. The material called Parkesine was an organic material derived from cellulose that once heated could be molded and retained its shape when cooled.

It is generally accepted that plastic materials fall into three categories commodity plastic, engineering plastics, and speciality or advanced plastics. The commodity plastics constitute the highest volume of usage, their consumption exceeding one million tones per annum on global scale. Engineering plastics are defined as those plastics that possess high performance multiple engineering properties at an economically feasible cost and may be processed by conventional technique. These polymers are generally containing high aromatic contents and/or heterocyclic units with relatively rigid segments that impart high  $T_g$ , good thermal oxidative stability and excellent mechanical properties.

These materials require the high purity monomers for synthesis of high performance polymers. The polymer properties are determined by the intensity of intermolecular forces, presence of cross-links, crystallinity etc. Four principles used in the molecular design of high performance polymers are;

1. Use of rigid chain
2. Orientation
3. Crystallization
4. Cross-linking

#### **1.2.1 Brief History of High Performance Polymers:-**

High temperature organic polymers were synthesized in the late 1950s primarily to meet the needs of aerospace and electronic industry. The flurry of activity in the synthesis of new polymers in the mid of 1960s was due to success of polybenzimidazoles, the longtime goals of the high temperature polymer chemists have been to achieve a material, which can exist for a long period in air 500 °C. In the

beginning of era of high performance polymers, the stabilities were in the range of 400-500 °C in air. Within six years the development of these polymers for thermal properties upto 600 °C in air were realized. Amongst all these types polymers, up to that stage, poly(phenylene)s and poly(quinoxaline)s were of the highest thermal stability. Since then, many different heat resistant polymer systems have been reported and some of these materials are now commercially available. The evolution of these types of the polymers is outlined in [Table 1.1].

**Table 1.1. High performance polymers (HPP) along with their year of reporting / commencement.**

Polymer	Year Reported	References
Poly(phenylene sulfide)s	1948	13
Poly( benzimidazole)s	1961	14
Polyimides	1962	15-17
Poly(quinoxaline)s	1964	18-19
Poly(amide-imide)s	1965	20
Poly(aryl-sulfone)s [Astrel*3600]	1967	21
Poly( phenyl quinoxaline)s	1967	23
Poly(imide)s containing Hexafluoroisopropylidene group	1968	24 <sup>a</sup>
Aromatic polyamides [PRD49, Kevlar]	1970	24 <sup>b</sup>
Bismaleimide resins	1970	25
Norbornene-terminated polyimides [PMR-15]	1972	26
Ethynyl-terminated polyimides [Thermid*600]	1974	27
Poly(ether-imide)s [Ultem]	1974	28
Poly-imide containing indane [Matrimid*]	1975	29
Liquid crystalline polyesters Poly(4-benzoate) Konol*	1976	30
Poly(ketoimide)s (LARC-TPI)	1976	31,32
Rigid rod like poly(benzoate)s (PBT, PBI, PBO)	1981	33,34
Semicrystalline polyimides (LARC-CPI.)	1987	24 <sup>b</sup>
Poly(arylsulfone)s [Radel*]	1989	35

By the mid 1960s inherent limitations in the stability were suspected and problem of tractability was readily apparent. The research at that point began for modification of known systems to make them more soluble and processable materials. These structural modifications included reduction of crystallinity, phenylation of the backbone and introduction of flexible / bridging functional groups such as ether, sulphone, alkylene etc; copolymerization and constructing random dissimilar backbone structured.

### 1.2.2 Factors Influencing Heat Resistance Property: -

Early work uncovered many factors that contribute to the thermal stability of polymers. Some of these are primary bond strength, resonance stabilization, secondary

bonding forces, rigid intra-chain structure, molecular weight, molecular weight distribution and stable end groups on the molecules. The chemical factors that influence thermal stability, toughness, and mechanical properties of these polymers are as follows<sup>36-39</sup>.

### **1) Primary Bond Strength:-**

Primary bond strength is the single most important factor which influences heat resistance. Bond dissociation energy<sup>40,41</sup> of carbon-carbon single bond is 350 KJ/mol, that of carbon-carbon double bond is 610 KJ/mol and of aromatic systems it is even higher. As a result aromatic and heterocyclic rings are widely used in the thermally stable polymers. The main requirements for high temperature resistant polymers are high softening point and resistance to thermal oxidation. In terms of molecular structure these demand may be met in several ways. The high bond strength in inorganic polymers could provide the potential for good high resistance property. Carbon-fluorine bonds have higher bond strength than carbon-hydrogen or carbon-carbon bonds; therefore fluoro polymers are extremely resistant to oxidative degradation. They have also excellent resistance to chemical and solvent attack.

### **2) Secondary or Vander Waals Bonding:-**

The presence of secondary or Vander Waals forces provide additional strength and thermal stability to the polymer. Dipol-dipol interactions and hydrogen bonding contribute towards molecular stability and affect the cohesive energy density, which influences the stiffness,  $T_g$ , melting points and solubility.

Resonance stabilization, mechanism of bond cleavage, molecular symmetry (structural regularity), and rigid intra-chain structure, cross linking and branching also affect the properties of a polymer. Physical properties of polymer are also influenced by atomic interaction between chain carbon atoms, the ability of polymers to crystallize, the flexibility of the chains and the spacing of polar groups. The heat resistant polymers often contain polar groups e.g. -CO-, -SO<sub>2</sub>- etc that participate in strong intermolecular association. Polymer containing electron withdrawing group e.g. -CO-, -SO<sub>2</sub>- etc, as connecting groups are generally more stable than those containing electron-donating group like -O-.

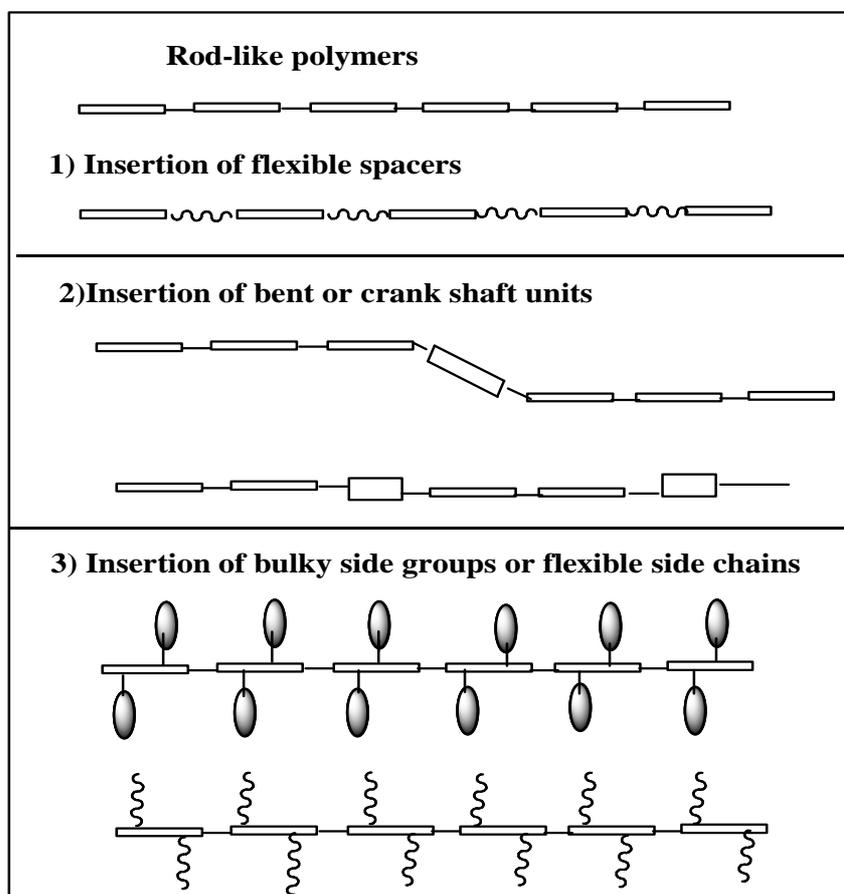
### **3) Stability and Processability of Polymer:-**

Most high temperature polymers are composed predominantly of aromatic or hetero-aromatic units. The chemical structure that makes a polymer thermally stable also makes it difficult to form into useful items because of limited solubility and moldability.

A) The aromatic or heterocyclic ring in the polymer backbone leads to rigid structure. The p-oriented aromatic polymers have lower solubility and processability. Cross-linking improves heat resistance of a polymer and branching in a polymer tends to lower thermal stability. The high regularity and rigidity of the backbone of certain high performance polymers results in strong chain-chain interaction, high crystallinity, high melting point and low solubility. Thus processing of rod like polymers is often impossible. The research at the present is to modify the known thermally stable polymers than finding new classes to improve the thermal stability. Several approaches have been used to modify the structural unit of rod like polymers, they are,

1. Insertion of flexible spacers in the rigid units.

2. Insertion of “bent” or “crank shaft” units, along the aromatic backbone to form random or alternate copolymers and
3. Appending of bulky pendant groups or flexible side chains to aromatic backbone.



B) Thermal stability of polymers is related to high rigidity, crystallinity and cross-linking. To achieve good thermal stability, weak links to be avoided are mostly alkylene, alicyclic, unsaturated and non aromatic hydrocarbons. There should be favorable balance of thermal stability and solubility.

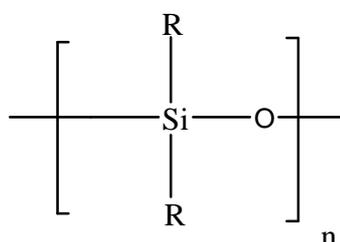
C) Sulfone, Carboxylic acid derivatives (amide, imide) in the backbone of polymers are proven to be good attempts for improving high temperature resistance. The insertion of aromatic pendant group imparts good solubility without compromising the thermal stability.

### 1.3 Types of high performance polymers:-

#### 1.3.1 Inorganic polymers:-

The polymers containing elements of the IV-VI groups in the periodic table are known as inorganic polymers. Many efforts were devoted to synthesize inorganic polymers<sup>42-45</sup>. Silicon elastomers are outstanding in maintaining its elastic properties over wide temperature range and especially at the low temperatures. However, with the

single exception of the silicon polymers i.e. Polysiloxanes, consisting of following repeating units, none has achieved commercial significance. Polysiloxanes, impart poor stability to hydrolysis.



### Polysiloxane

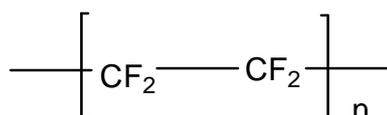
Silicon polymers with –R either methyl or mixed phenyl groups have very low T<sub>g</sub> values (about-100<sup>0</sup>C) and hence if of high molecular weight, are heat resistant fluids, oils and grease. The high molecular weight silicon rubbers offer not only good high temperature resistance but also good low temperature flexibility. Cross –linked silicon have found minor use as glass reinforced thermosetting plastics for high temperature electric insulation purpose and special applications.

### 1.3.2 Organic polymers:-

There have been continuing and strong efforts since the late 1950's to synthesize high temperature resistant polymers. The organic heat resistant polymers possess the properties such as high mechanical strength and modulus, stability to various environment (chemical, solvents, UV, and oxygen), and dimensional stability at high temperature that match to other polymers at low temperature. The impetus for heat resistant polymers comes for the needs in such a technological area as advanced air and space-craft, electronics and defense as well as consumer applications.

### 1.3.3 Fluoropolymers:-

The polymer of tetrafluoroethylene was discovered by R. J. Puckett. Carbon fluorine bond have higher bond strength than carbon-carbon and carbon –hydrogen bonds. Fluoro polymers are extremely resistance to attack by the free radicals involved in oxidative degradation and hence to thermo –oxidative degradation. In addition they have excellent resistance to chemicals and solvent attack<sup>46-47</sup>.



### Polytetrafluoroethylene (PTFE)

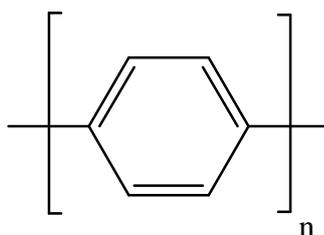
Fluoropolymers applications include electrical (coaxial cable, tapes), mechanicals (seals, piston rings, bearings), antistick coating for cookware, self lubricating parts, chemical resistance parts (pipe liners, gaskets, tapes) and micro powders (used in plastics links, lubricants and lacquer).

### 1.3.4 Aromatic polymers:-

The most successful approach to the design of high temperature resistant polymers has been to utilize the advantageous features of polymer chains composed of linked benzene rings i.e. of aromatic rings. These polymers have good oxidative resistance, thermal and mechanical properties.

### 1.3.5 Polyphenylene:-

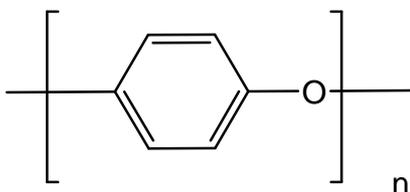
The polymer consisting of entirely of benzene rings linked together i.e. Poly-p-phenylene<sup>48-54</sup>, although superbly resistance to oxidation has a softening point over 500 °C and so it is not melt processable.



**Poly(p-phenylene)**

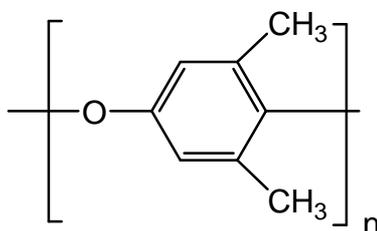
### 1.3.6 Polyether:-

Ether links provide a very good choice of flexibilizing group since -O- link is itself flexible and it's also highly resistance to thermal oxidation. The commercial polyphenylene oxide (PPO) is based on the 2, 6 -dimethyl substituted phenol as starting materials, with a  $T_g$  of 208 °C, and it does not crystallize from the melt.



**Poly(p-phenylene oxide)**

Aromatic polyethers are relatively new in the field of engineering plastics. It is a versatile group of polymers that may be useful as thermo stable plastics, as resins for high performance composites, adhesives and basic material for membranes<sup>55-56a</sup>.

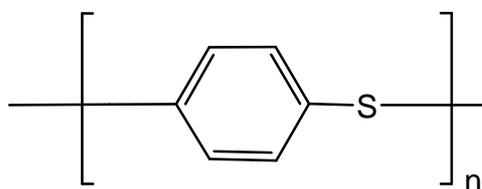


**Poly(oxy-2,6-dimethyl phenylene)**

Applications of modified PPO are in automotive (dashboard, wheel covers, metalizer grills, trim), electrical (fuse boxes, wiring devices), consumer and business (refrigerator door liners, computer housing, keyboard frame) and liquid handling (pipes, valves, pumps) industries<sup>56b</sup>.

### 1.3.7 Polyphenylene sulfide:-

It is important engineering plastic having good thermal and thermo oxidative stability.

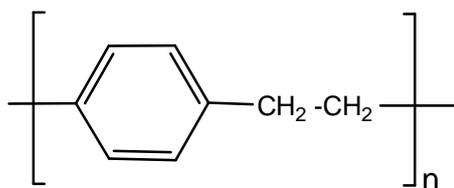


**Poly(p-phenylene sulphide)**

PPS may be used in air at temperature above 200 °C. It is highly crystalline polymer with T<sub>m</sub> 285 °C and T<sub>g</sub> 85 °C. It has flame resistance and stability towards both organic and aqueous environment. It is used in automotive, industrial blends with fluorocarbon polymer and protective coatings<sup>57-59</sup>.

### 1.3.8 Aromatic- Aliphatic hydrocarbon polymers:-

Linked benzene rings through aliphatic methylene -(CH<sub>2</sub>)- group are one way of introducing chain flexibility and hence improving processability. However, the presence of aliphatic groups reduces resistance to thermal oxidation.

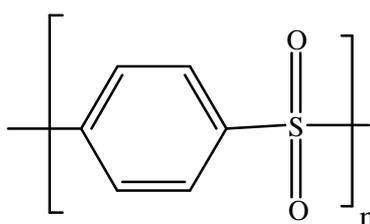


**Poly(p-xylylene)**

Polymers of the type poly (p-xylylene) are useful as electrically insulating coating, coating of orthopedic parts (bone pins and joint prosthesis) to make them biocompatible and conservation of archival and artifact objects<sup>60,61</sup>.

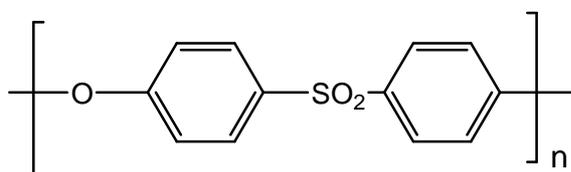
### 1.3.8 Polysulphones:-

They are synthesized by nucleophilic substitution reaction between aromatic dihalides and disulfonolates salts<sup>62</sup>. Poly (p-phenylene sulphone) has the following structure.



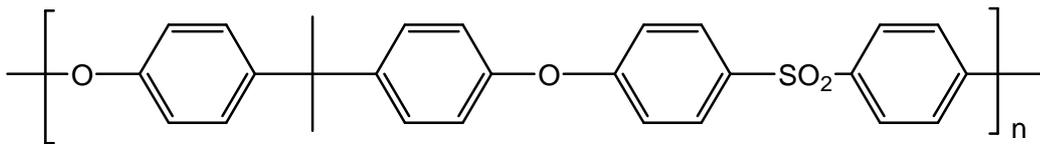
**Poly(phenylene sulphone)**

Another potential monomer that would not eliminate hydrogen chloride and would contribute to the goal of high thermal stability was 4, 4'-dichloro diphenyl sulphone. The electron withdrawing effect of the sulphone group strongly activated the chlorides towards displacement by nucleophiles such as phenoxide anion. These polyether sulphone have T<sub>g</sub> 150-250 °C and insensitive to oxidation possessing short term thermo stabilities upto 450 °C.



**Poly(ether sulfone) PES**

During the early 1960's, polyarylethersulphones were reported in the patent literature as new materials prepared by novel polycondensation reaction of 4, 4'-dichloro diphenyl sulphone with bisphenol-A.



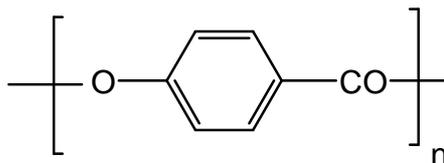
**Poly(ether ether sulphone) PEES**

The Polysulphones have found widespread use as injection molding materials, electrical components including circuit's boards, connectors, coil bobbins and relays application. They are also used for fan-heater, hair driers, microwave ovens, pumps, valves and lamp housing. The resistance of polysulphones to aqueous environment including acids, bases and oxidants is excellent. Their outdoor use is limited because of relatively low UV stability.

### 1.3.9 Polyether ketones and polyether ether ketones:-

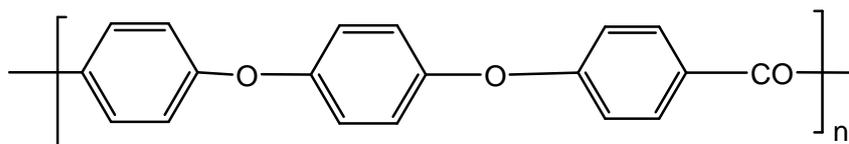
Polyether ketone (PEK), was reported independently by ICI and DuPont as new novel material at about same time as the corresponding polyethersulphone in the early 1960's. Union Carbide was also interested in polyetherketones at this time and exemplified a polyether ketone sulphone and poly ether ether ketone containing a bisphenol.

The first preparation of completely aromatic polyetherketones was reported by Bonner<sup>63, 65</sup> of DuPont. PEKs are partially crystalline, have excellent resistance to aqueous and organic environment, and are useful in automotive (bearings, piston parts), aerospace (structural components), oil and chemical transport, (pumps, compressor, valves plates) and electrical-electronic (cable insulation) industries.



**Poly(ether ketone) PEK**

Poly ether ether ketone (PEEK) has been available since 1978 and has the following repeat unit structure.

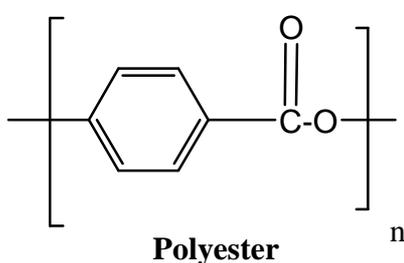


**Poly(ether ether ketone) PEEK**

The application area for the polymer was an extruded insulation for performance wires and cables injection molded parts, chemically resistant surface coating and monofilaments for industrial belts / filters and as the matrix in cable fiber composites for the aerospace components<sup>66a,b</sup>.

### 1.3.10 Polyesters:-

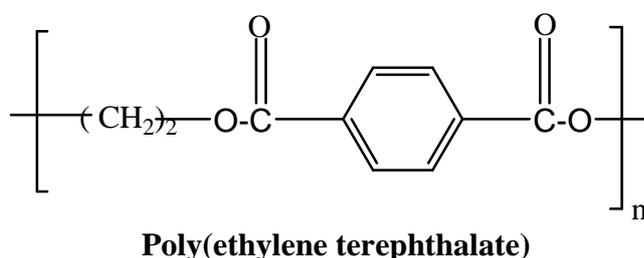
Various combinations of reactants and process conditions are potentially available to synthesize polyester<sup>67</sup>. The partially aromatic polyesters, poly (ethylene terephthalate); PET, poly (butylene terephthalate); PBT, are well established as plastics and fibre forming materials. The earliest commercial polyester was Ekonol (polyhydroxy benzoic acid), which is crystalline and softens only above 500 °C, so it can be processed by metallurgical techniques such as sintering and hammering.



It can be used at temperature up to 320 °C and used as bearing material. Commercially aliphatic polyesters have no industrial importance because of their low melting temperatures and poor hydrolytic stability. Low molecular weight polyesters are used as plasticizers and prepolymer reactants in the synthesis of polyurethanes.

### 1.3.11 Poly(ethylene terephthalate):-

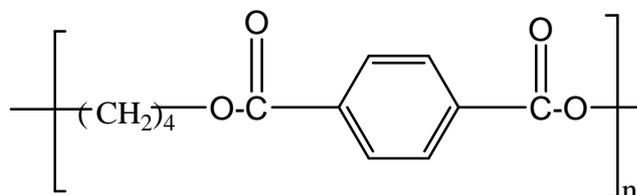
PET was first synthesized by J. R. Winfield in England in the 1940's. It is used as fibre for apparel, film for packaging, insulation and in the bottles of beverages.



Several factors keep PET accepted, the most important of these was that, PET did not crystallize completely in conventional water heated molds. First commercial engineering PET resins for injection molding were introduced by Akzo Chemie in Europe and Teisin in Japan. They used conventional nucleating agents such as Talc, but did not increase crystallization rate.

### 1.3.13 Poly(butylene terephthalate):-

It is linear condensation polymer based on terephthalic acid and 1, 4 butane diol. The more definitive name of PBT is poly (tetramethylene terephthalate), PTMT.

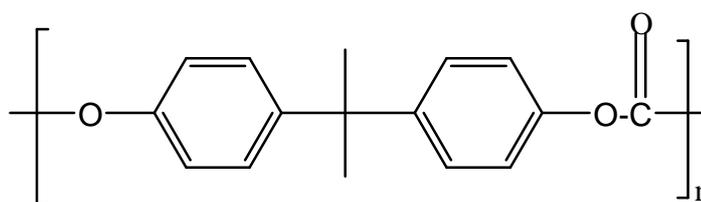


**Poly(butylene terephthalate)**

There is evidence of some interest in the materials, in the form of patent issued to ICI. PBT finds use in stretch fabrics and carpets.

### 1.3.14 Polycarbonates:-

It is class of polyesters derived from carbonic acid and diol. There are two major classes of poly (carbonate)s, aliphatic and aromatic. Aliphatic (polycarbonate)s, have not found any significant commercial use as thermoplastic. Most of them are semicrystalline materials with low melting points, normally less than  $120^\circ\text{C}$ . Aromatic polycarbonates were first reported by A. Einhorn in 1898, by reacting pyridine solution of hydroquinone, resorcinol and catechol with phosgene to produce aromatic polycarbonate. Bischoff and Hedenstrom reported the same polycarbonates by employing transesterification process. More than 50 years later Dr. Herman Schnell at Bayer A. G. and Brunel at General Electrical Corporation Laboratory in Schenectady, N. Y. independently synthesized aromatic polycarbonates based on bisphenol-A.



**Bisphenol-A polycarbonate**

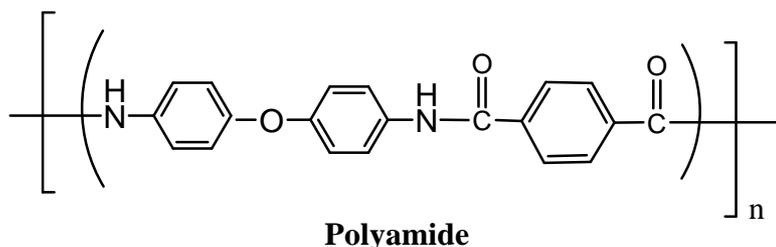
These Polycarbonates have found broad application around the world as a premier “Engineering plastic” due to their properties, like toughness, dimensional stability, Load bearing properties over a very broad temperature range, transparency<sup>68-70</sup> resistance to burning, excellent electrical properties, high impact strength and moderately high  $T_g$  ( $149^\circ\text{C}$ ) etc.

### 1.3.15 Polyamides:-

Polyamides are polymers with recurring amide groups (-CO-NH-) as an integral part of the main polymer chain. The polyamides are generally divided into two groups.

- Aliphatic polyamides (nylons),
- Aromatic polyamides (aramids).

In 1974, the aliphatic and aromatic polyamides were given separate generic nomenclature by the U.S. Federal Trade Commission. The aliphatic polyamides are termed as nylons and aromatic polyamides are termed as aramids<sup>71-74</sup>.

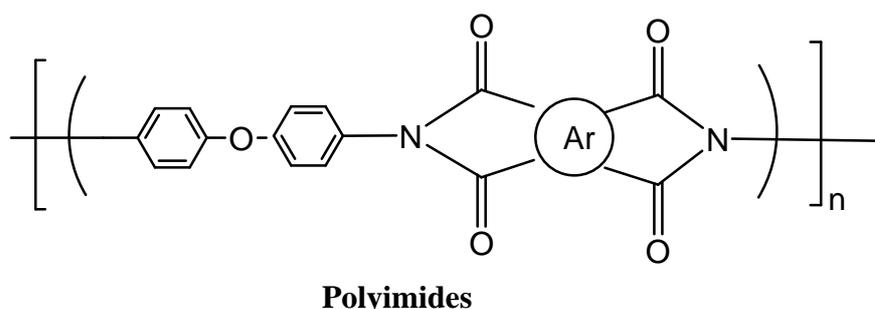


Historically, the chemistry of polyamides was first studied in 1862 by Harbordt and the first aliphatic polyamide was reported in 1899 by Gabriel and Mass, where as high molecular weight –polyamides were prepared in 1933 by Carothers.

Aromatic polyamides because of their special properties like polarity and hydrogen bonding are highly versatile and find a great variety of application as high performance polymers. Aramids are heat resistant, flame resistant, highly crystalline and have high tensile strength, high Young's modulus, some of the aramids show liquid crystal (lyotropic) behavior, and used in the resin, membrane, fiber, films and plastic etc<sup>75-78</sup>.

### 1.3.16 Polyimides:-

Aromatic polyimides are an important class of high performance polymers due to their excellent thermo-oxidative stability, mechanical strength, electrical properties and high radiation and solvent resistance. They are condensation polymers incorporating the imide group CO-N-CO in their repeating units either as open chain or as rings and are generally derived from the reaction of organic diamines with organic tetracarboxylic acids or their dianhydrides<sup>79-81</sup>.



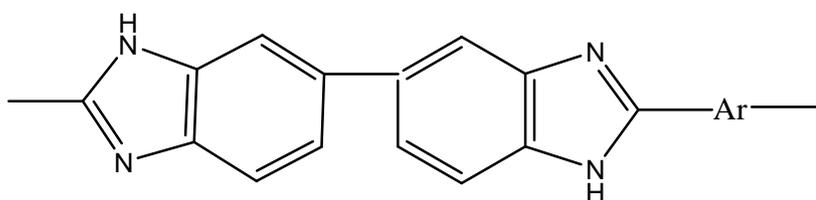
Bogart and Reshow in 1908, obtained first polyimide, from 4-amino phthalic anhydride a relatively stable compound, which did not melt upon heating but evolves water at elevated temperature with the formation of a poly molecular imide.

Edward and Robinson prepared first aliphatic polyimides by melt fusion method from aliphatic diamines and tetra acids or diacids/diester<sup>82</sup>.

### 1.3.17 Poly(benzimidazole) s (PBI):-

Poly (benzimidazoles) were first claimed in the US patent in 1959 and then published in a scientific report by Vogel and Marvel in 1961 with anticipation that these polymers would have exceptional thermal and thermo-oxidative stability<sup>83-84</sup>.

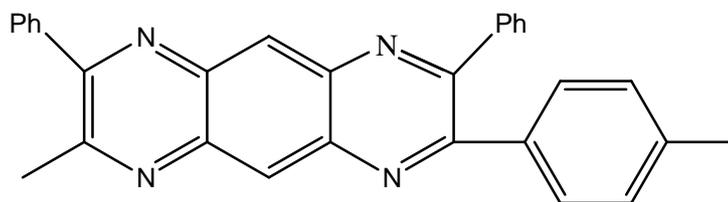
These polymers are a class of polymers, having outstanding properties such as thermal stability, flame resistance, radioactive stability, excellent mechanical and dielectrical strength and chemical inertness. Due to these properties polybenzimidazoles find applications in aerospace and defense industries.



**Poly(benzimidazole) (PBI)**

### 1.3.18 Poly(quinoxaline)s (PQ):-

Poly (quinoxaline)s are heterocyclic polymers, synthesized by the Friedlander reaction of a bis (o-aminoaromaticaldehyde/ ketones) with bis keto methylene) reactant<sup>85</sup>. They can be also synthesized by polymerization of bis (o-diamine) and bis (o-keto aldehyde) reactants in m-Cresol<sup>86</sup>. These polymers have excellent thermal, oxidative stability, resistance to acids and bases, high  $T_g$  and high strength / modulus.



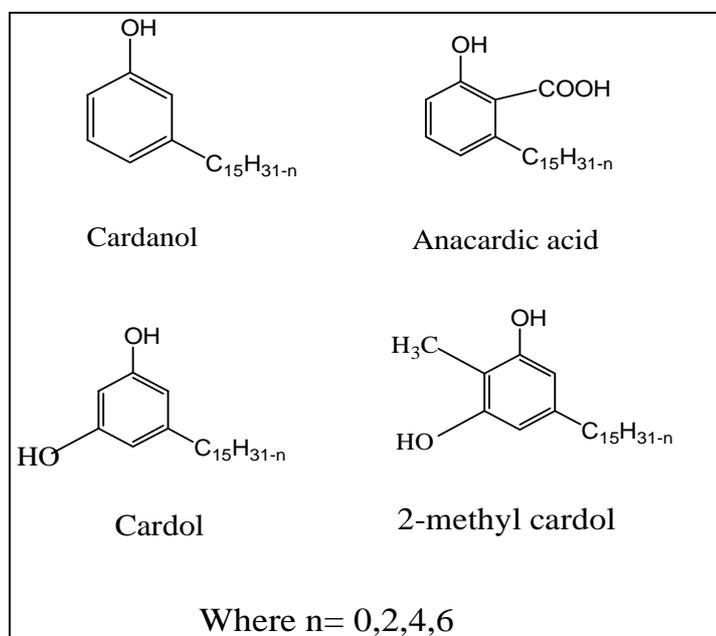
**Poly(phenyl quinoxaline) (PPQ)**

### 1.3.19 Aromatic phenols and cardanol:-

Synthetic high performance polymers are constantly being modified and improved for current and future need. This necessitates a look at the renewable natural resources that can serve as alternative feed stocks for monomers of the polymer industry. In this regard cashew nut shell liquid (CNSL), an agricultural byproduct abundantly available in the country, is one of the few major and economic sources of naturally occurring phenols and can be regarded as a versatile and valuable raw material for polymer production<sup>87a-d</sup>. Cardanol, a natural alkylphenol from cashew nut shell liquid (Anacardium occidentale), a potential natural source for biomonomers, cannot even today be said to have found its niche in terms of an appropriate industrial application. Considerable research works have been done by scientists all over the world to find out the multifarious uses of CNSL. Recent investigations have revealed that the constituents of CNSL possess special structural features, which can be chemically transformed into specialty and high value products / polymers.

Cashew nut shell liquid occurs as a brown viscous fluid in the soft honeycomb structure of the shell of cashew nut, a plantation product obtained from the cashew tree. Many researchers have investigated its extraction<sup>88(a-d)</sup> chemistry and composition. The components of cashew nut shell liquid are shown in Figure 1. Cardanol is formed when anacardic acid is heated and can be isolated from the raw oil by double vacuum distillation, at 245°C at 6 mm Hg<sup>89(a-j)</sup>.

The literature on cardanol is replete with innumerable patents<sup>90-91</sup> and reports and many reports deal with the synthesis of several futuristic products from CNSL namely melt processable liquid crystal polymers, melt / solution processable polyurethanes, cardanol grafted cellulose, multi-functional additives for natural rubber, azobenzene based cross linked network structures for liquid crystal phase stabilization etc.



**Figure.1. Components of cashew nut shell liquid**

By far the greatest amount of work on polymeric materials derived from CNSL have been concerned with its use in the manufacture or modification of phenolic resins<sup>92</sup>. The phenolic nature of the material makes it possible to react under a variety of conditions to form both resols (condensation in presence of alkaline catalysts) and novalcs (condensation in presence of acid catalysts). Lima et al. condensed the phenolic monomers, cardol, cardanol and anacardic acid present in CNSL. Studies have shown that the phenolic resins made from a mixture of cardanol, phenol and formaldehyde have improved chemical resistance and mechanical properties such as tensile, flexural, and Izod impact strengths than those of pure phenol-formaldehyde resins<sup>93</sup>. The cardanol-formaldehyde resins have been studied for producing protective varnishes with improved properties in food industry. Cardanol have been used for the manufacture of special phenolic resins for coatings, laminates and friction materials<sup>94</sup>. The phenolic resins made from cardanol can also be used for breaking crude oil emulsions and as selective ion exchangers for certain metal ions<sup>95</sup>. Hydroxyalkylated cardanol-formaldehyde resins have been used for the synthesis of polyurethanes with good thermal and mechanical properties<sup>96a</sup>. Poly(vinyl formal) (PVF) was modified by phenol-cardanol-formaldehyde resins (PCF)<sup>96b,c</sup> to improve properties of the insulating enamel varnish for copper wires. The varnish films prepared from modified PVF showed better physico-mechanical properties, heat resistance and electrical properties.

CNSL can be used to manufacture epoxy by reacting with glycidyl ethers and phenol (followed by epoxidation); Tan et al<sup>97</sup> reported the synthesis of cardanol-lignin based epoxy resins. A study of their mechanical properties indicated that an increase of the cardanol content increases the tensile strength and Young's modulus of the film products. Cardanol was treated with phenol using boron trifluoride as catalyst to give 1, 8 -bis(hydroxyphenyl) pentadecane, which was polymerized with epichlorohydrin to give epoxy resins useful for the preparation of baked coatings having comparable corrosion and chemical resistance and better flexibility to conventional epoxy resins prepared from bisphenol A<sup>98</sup>. The cardanol epoxy resin could be further modified with vinyl monomers to give air drying components which were cheaper than the conventional epoxy coatings. Cardanol based epoxy resins are also used as binders for cathodic electro depositions and in automated bonding processes in electronics industry<sup>99</sup>. Phosphate ester-terminated epoxy novolac / phenolic resins having higher thermal stability than the conventional epoxy resins were also synthesized from cardanol and used in interpenetrating network coatings. There are patent reports on the use of cardanol for the synthesis of modified epoxy resins<sup>100</sup>.

Cardanol functionalized with methacrylate was found to have application in the synthesis of several heat-resistant resins. Copolymers of MMA and cardinyl acrylate having a small fraction of cardinyl acrylate showed better thermal stability than the PMMA homopolymer.<sup>101</sup>

Cardanol was also used in the synthesis of thermoplastic polyurethanes. Bhunia et al<sup>102</sup> investigated the synthesis of novel polyurethanes by solution polycondensation reaction of 1, 6-diisocyanatohexane with 4-[(4-hydroxy-2-pentadecenyl)phenyl] azo] phenol (HPPDP) and 1, 4-butanediol.

Liquid crystal (LC) polymers with cross-linked network structures containing azobenzene mesogens were synthesized from cardanol, the unsaturated -C<sub>15</sub> hydrocarbon side chain of which was utilized for crosslinking reactions<sup>103a</sup> 8-(3-hydroxyphenyl) octanoic acid obtained by the side chain oxidation of cardanol was used in the synthesis of thermotropic liquid crystalline copolyesters and these polyesters were found to be anisotropic under crossed polarized light at 200-409 °C<sup>103b</sup>.

The fuel blends of norborne diene and careen (50:50 by wt.) and norborne diene, careen and cardanol (40:40:20 by wt.) exhibited good ignition with red fuming nitric acid (RFNA) as oxidizer. The fuel blends with their low cost and toxicity and relatively high density can replace G-fuel, used in several Indian missiles, without impairing the performance<sup>103c</sup>.

A number of semi-interpenetrating polymer networks (semi-IPNs) have been synthesized using polyurethane and cardanol derivatives like acetylated cardanol and phosphorylated cardanol. Mohapatra et al<sup>103d</sup> synthesized some semi-interpenetrating networks by condensing cardanol-formaldehyde, p-hydroxyacetophenone or furfural novalc resins with polyurethanes prepared from castor oil and diisocyanates. The thermal characteristics of poly(methylmethacrylate) (PMMA) interpenetrated with cardanol-formaldehyde resin was studied by Manjula et al.<sup>103e</sup>. The interpenetrating networks showed only 15% weight loss at 350 °C whereas PMMA showed around 50% weight loss at this temperature.

Syntheses of new polyphenols with attractive properties from natural phenolic compounds such as cardanol by oxidative polymerization using enzymes have been reviewed by Uyama et al<sup>104a</sup>. Enzymic homo and copolymerization of alkylphenols derived from cashew nut shell gave homopolymers that are soluble in organic solvents, but the copolymers were crosslinked, with negligible solubility<sup>104b</sup>. The enzymic polymerization was found to be dependant on the solvent mixture used. Polymerization in a dioxane-water solvent mixture resulted in spherical particles in the case of homo polymerization while structures without distinctive morphologies were obtained in the case of copolymerization. There are many reports on the synthesis of polyethers from cardanol. A novel polyether was synthesized by cationic polymerization of glycidyl 3-pentadecenylphenyl ether (GPPE) in the presence of a latent thermal initiator, N-(benzyl) N, N-di-Me anilinium hexafluoroantimonate (BDAHA). Nguyen et al<sup>104c</sup> reported the modification of unsaturated polyester with maleated cardanol-epoxy resin.

The suitability of a flame retardant, 3-(tetrabromopentadecyl)-2,4,6-tribromophenol (TBPTP) developed from cardanol was evaluated by Pillai et al.<sup>105</sup> for use in cable insulating and jacketing materials based on low density polyethylene (LDPE) and ethylene vinyl acetate copolymer (EVA). Simple chemical modifications of cardanol such as introducing phosphorus and/or bromine gave a series of multi-purpose resins that can be used as flame retardants (FRs), adhesives, matrix resins for brake linings and composites. Asbestos short fiber-filled phosphorylated cashew nut shell liquid (PCNSL) polymers are used for automobile brake lining applications. PCNSL polymer-based brake linings gave a coefficient of friction within the recommended value for medium-range brake linings. Phosphorylated cardanol was also used as a dopant for conducting polyaniline. The resulting complexes induced solubility of polyaniline in commonly used weakly polar or non-polar organic solvents such as xylene, THF, chloroform, etc.

Hydrophobe-modified hydroxyethylcellulose polymers for use as rheology modifiers in latex paints were prepared by using cashew nut shell liquid as a source of the hydrophobe. Cardanol was grafted onto cellulose (filter paper) using BF<sub>3</sub>. Et<sub>2</sub>O as carbocationic initiator and the resulting filter paper showed extensive water repellency.<sup>106</sup>

Novel blends were prepared from elastomeric materials and thermosetting resins, for example natural rubber and cardanol-formaldehyde resins, in order to improve mechanical properties (such as toughness) and thermal properties (such as high-temperature resistance). Cardanol-formaldehyde resin (CF) and cardanol glycidyl ether (CGE) were synthesized for reinforcing natural rubber (NR)<sup>107</sup>. The novolac CF resin

reinforced NR, SBR, and NBR and the resole CF were found to be a hardener for NBR. The CGE could be used as a reinforcing agent for NR and for crosslinking maleated NR.

Even though the application of cardanol in the synthesis of a variety of polymers have been extensively reviewed, reports on its application for the synthesis of polyamides and polyimides are limited. Maldar<sup>108</sup> reported the synthesis of some polyimides from substituted p-phenylene diamines based on cardanol. Vernekar et al<sup>109</sup> reported the synthesis of novel polyimides and polyamides from a cardanol based diamine 4, 4' -[sulfonyl bis (p-phenyleneoxy)]-3-pentadecyl bis (benzeneamine). Most of the polyimides were soluble in aprotic polar solvents like N-methyl-2-pyrrolidone (NMP), N, N'-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO) and m-Cresol and some were soluble in common organic solvents like chloroform. These polyimides had glass transition temperatures between 114-125 °C and their 10% wt. loss temperatures were recorded in the range of 441-526 °C in nitrogen atmosphere. The polyamides were also soluble in a variety of solvents and they were stable up to 422 °C in nitrogen atmosphere.

An analysis of literature on cardanol shows that the important structural factor that makes cardanol suitable for a variety of applications is its pendant long alkyl group<sup>110,111</sup>. Pendant alkyl groups and alkoxy groups are known to improve the solubility and processability of polyamides and polyimides. These alkyl groups can be attached directly to the main chain or can be substituents of the side chain, which in turn is connected to the main chain through some flexible connecting groups. In both these cases literature are mainly based on the incorporation of small and bulky alkyl groups like methyl and t-butyl and there are only very few reports on the incorporation of long pendant alkyl groups because of the difficulty in synthesizing monomers containing them. Phenols containing alkyl group substituents are useful starting materials for the synthesis of these monomers and the corresponding polymers. Most of the phenols reaction with alkyl halides, which usually give ortho, and para alkylated products. The position and length of pendant alkyl group can affect the final properties of the polymers and therefore it will be interesting to study the properties and applications of polyamides and polyimides synthesized from phenols having long alkyl groups in the meta position. In this regard cashew nut shell liquid can be considered as a potential natural resource of long chain alkyl phenol like cardanol, where the substitution is at the meta position, which is very difficult to obtain by any synthetic method and can be used in the synthesis of monomers and polymers having pentadecyl groups directly attached to the main chain<sup>112</sup> or as a meta substituents of the pendant phenyl group.

The most important areas of applications of polyamides and polyimides include alignment layers in liquid crystal display devices, gas separation membranes and as low dielectric materials in interlayer dielectrics. Earlier reports indicate that the polymers having pendant alkyl groups are suitable candidates for these applications. In the field of liquid crystal display devices the molecular scale orientation at the surface of alignment layers plays a key role in aligning the liquid crystal molecules at the surface. The changes in molecular surface structure affect the pretilt angle (angle between the liquid crystal director and the polymer alignment surface) which is a key parameter affecting the electro-optical properties of liquid crystal displays. Some researchers have shown that long alkyl and fluorinated alkyl side chains generate high pretilt angles of liquid crystals due to hydrophobic interaction with the polar liquid crystal molecules and the length of the alkyl group also affect the pretilt angle. In gas separation applications the pendant alkyl groups are important since they cause an increase in the free volume of the resulting polymer and thereby increase the permeability. Dielectric properties of polymers are dependant on their hydrophobicity and therefore polymers having pendant

alkyl groups are expected to have low dielectric constant, which makes them useful as interlayer dielectrics. The synthesis of polyamides and polyimides from cardanol opens up an easy and economic process for the introduction of a long pendant pentadecyl group into their structure and it is expected that such polyimides and polyamides will have improved properties, which make them useful for the above mentioned applications.

#### **1.4. Applications of high performance polymers:-**

General application of high performance polymers are as follows;

1. Automotive/ truck components (connecting rods, wrist pins, pistons, switches, hinges, etc.)
2. Binding systems in brake shoes, abrasives wheels and cutting discs.
3. Coatings (non-stick interior and decorative exterior cookware, many other)
4. Conveyor belts (treating and drying of materials)
5. Copiers (rollers)
6. Electronic and microelectronic components (circuit boards, moldings insulation, photoresists, interlayer dielectrics etc.)
7. Filters (hot exhaust stacks)
8. Fire resistant materials (protective clothes, parachutes, fire barriers)
9. Functional and structural foams.
10. Gaskets, sealants and tubing (primary elastomers based)
11. Geothermal energy conversion system components (casing, coatings, nozzles, liners)
12. Jet engine components (fan blades, ducting, cowling, bushing, washers, etc.)
13. Labels (for parts that see high temperature)
14. Liquid Crystalline Displays (alleviate distortion of angle viewing)
15. Membranes (separation processes)
16. Medical devices (chemical inertness)
17. Microwave cookware, Moldings (Variety of parts including household items such as curling iron and coffee pots)
18. Nuclear reactor components (coating, coolants, insulation, structural parts etc.)
19. Pipes (chemical processing, energy generating plants, oil wells)
20. Printers (small components)
21. Reinforcements (high modulus/ high strength fibers and ribbons)
22. Structural resins (adhesives, composites, foams and moldings)
23. Wire insulation (coatings)

## 1.5. Scope and Objectives:-

Aromatic poly(ether–ketone)s, PEK; and Aromatic poly(ether– ether–ketone)s, PEEK, are an important class of thermoplastic high performance polymers having excellent mechanical and dielectric properties are well known for their high chemical and heat resistance. These excellent properties make them potentially suitable for a wide range of applications, such as structural adhesives and matrix resins for composites in aerospace applications. However, their aromatic structure and semi-crystallinity result into high melting points (around 340–360 °C), high glass transition temperatures and low solubility in organic solvents often restricting the use of these resins for some application.

Number of modification were adopted to reduce the processing temperature and to soften the chemical backbone. Efforts have been devoted and it is reported that flexible segments, kinks, lateral / pendant substituents or cardo monomers with different dimensions and symmetry can be introduced in the main chain, to enhance solubility and processability of polymers. Hence the present studies were carried out combining some of the above approaches to get PEEKs and Co-PEEKs or modified PEEKs with improved solubility, processability and thermal stability for high performance applications. Thus the work presented in the thesis includes syntheses of several new bisphenols, many novel poly(ether ether ketone)s and corresponding random copolymers by polycondensation of 4, 4' –difluorobenzophenone with bisphenol–A (BPA) and new novel structurally different bisphenols in presence of  $K_2CO_3$  as promoter, Thus the investigations on synthesis of four new, novel bisphenols; HPI(I), HBI(II), HIA(III) and HPIA(IV) and their spectral characterization is presented and the PEEK synthesis were performed using a one pot polymerization method. Starting from different mole percentage of BPA with respect to above mentioned bisphenols as comonomers varying from 25 to 75 mole %; PEEK–copolymers, modified PEEKs, were also obtained copolymerized by means of aromatic nucleophilic substitution reaction<sup>113,114</sup>.

Thus, new novel bisphenols containing preformed imide/amide linkages, pendant C–15 long alkyl substituents, were synthesized and their structural proof was provided by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, mass spectrometry and Elemental Analysis. Further part II and part III of the thesis incorporates the synthesis of new and novel aromatic diamines containing preformed “ether–ether–ketone” linkage with / without C–15 long alkyl substituents, their characterization by spectral techniques and polycondensation with aromatic acids / aromatic acid dichloride or aromatic dianhydrides, to yield several polyamides and polyimides containing ether ketone linkages. Further, copolyamides and copolyimides were prepared using these diamines in combination with phenylated diamine. The structures of polymers were characterized by means of FT-IR, viscosity, solubility, DSC, TGA and XRD. The copolymers were obtained in good yields and had high molecular weights as evident by inherent viscosities upto 1.70 dL/g in NMP. The inherent viscosities have been measured in NMP and not in conc. sulphuric acid, which has been described in literature as a solvent.

In order to study the effect of the copolymerization on the viscosity / solubility / thermal properties etc the structure property study was undertaken. Many of the copolymers of the class PEEK, polyamides, and polyimides had good solubility in polar solvents such as NMP, DMAc and afforded transparent flexible tough films by solution casting.

The solubility of polymers containing bulky pendant phenyl / C-15 alkyl substituents tended to be improved with increase in content of such units; and copolymers become soluble in organic solvent, whereas PEEK (of biphenyl / BPA) is soluble only in conc. H<sub>2</sub>SO<sub>4</sub>. The unsymmetrical and kink structures of the polymer chains, randomness due to copolymer formation, could disturb interchain and intrachain interactions and make them amorphous and readily soluble in polar, aprotic solvents. Thus the effect of the order and ratio of aromatic ether ether ketone linkage, unsymmetrical and kink, m/p – phenyl substitution, pendant alkyl / pendant phenyl groups, amide / imide linkages, and overall effect of the comonomer structures has been analyzed<sup>115</sup>.

XRD and DSC-TGA analysis of PEEK, Co-PEEK, and polyamides, polyimides and copolymers were performed to study morphology of these polymer; and effect of introduction of the pendant phenyl/pendant C-15 long chain alkyl groups.

The results and discussion on the structure property relationship, the crystalline characteristics and the degradation temperatures of the resultant polymers have been investigated and presented. In conclusion, the insertion of pendant phenyl / pendant -C<sub>15</sub> long chain alkyl / amide / imide groups into PEEK backbone allowed us to prepare polymers with modulated properties, from highly crystalline to amorphous samples, according to the type and % content of the co-units. Similar studies with the polyamides and polyimides are performed in part II and III<sup>116,117</sup>.

Thus new engineering materials, with excellent properties and improved solubility / processability for high performance applications, as materials for films, coating for optical devices and electronics, gas separation membranes, aerospace, as fuel cell and nuclear industries, are developed<sup>118,119</sup>.

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