Chapter - 1

Introduction

1.0 INTRODUCTION

To put polymer science into it's proper perspective, its worth recalling that historically, the age of civilization have been named according to the materials that dominated that period. First there was the Stone Age eventually followed by the Tin, Bronze, Iron and Steel Ages. Today many historians consider us in the Age of synthetic: Polymers, Fibers, Plastics, Elastomers, Films, Coatings, Adhesives etc. it is also interesting to note that in the early 1980's Lord Todd, then president of the Royal Society of Chemistry was as ked what has been chemistry's biggest contribution to society. He felt that despite all the marvelous medical advances, chemistry's biggest contribution was the development of polymerization.

Polymer science is a relatively new field and it continuous to grow at an exciting pace. Polyolefins, polyvinyl chloride and polystyrene are good enough to justify annual sales of a score of millions of tons. Yet they are not satisfactory for use at the temperature of boiling water. Thus, there was a need for polymers with greater strength and greater resistance to elevated temperatures.

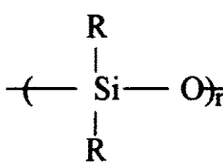
During the last 40 years the plastics industry has experienced tremendous growth, a growth catalysed and allowed by the unprecedented technological advances. These advances have culminated in a new class of synthetic materials often referred to as " engineering thermoplastics". This class of polymers is characterized by unusual toughness and good load – bearing capabilities. These materials has opened many new horizons for designers and have found applications in market previously dominated by metals, wood, ceramic, glass etc.

The approaches to the new engineering / advanced polymer developments cover a multitude o areas. Among these " High Performance Polymers" not only meet unusual requirements for long term durability at elevated temperature; they may also have unique and diverse characteristics such as conductivity, insulating properties, chemical resistance, self-extinguishing, selective gas barrier properties. They are used in normal applications as films, fibers, elastomers, adhesives and coatings as well as injection moldable materials, in vast number of areas including automobile, construction, medical, sophisticated high tech instruments, agriculture and aero-space etc. Some of the industrially important classes of high performance and thermally stable classes of polymers are briefly discussed below.

1.1.0 High performance polymers : -

1.1.1 Inorganic polymers: -

Much efforts were devoted to synthesizing inorganic polymers[1-4]. Silicon rubber elastomers is outstanding in maintaining its elastic properties over the widest temperature range and especially at the low temperatures. However, with the single exception of the silicon polymers i.e. polysiloxanes, consisting of following repeating unit, none has achieved commercial significance. Polysiloxanes often import poor stability to hydrolysis.



polysiloxanes

Silicon polymers with R – either methyl or mixed – phenyl groups have very low Tg values (about - 100°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 silicons have found minor use as glass reinforced thermosetting plastics for high temperature electric insulation purpose and other special applications.

1.1.2 Fluoropolymers : -

The polymer of tetrafluoroethylene was discovered by R. J. Plunkett[5]. Carbon – fluorine bonds have higher bond strengths than carbon – carbon and carbon – hydrogen bonds. Fluoropolymers 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.

e.g. polytetrafluroethylene [PTFE]. $-[CF_2-CF_2]_n-$

Fluoropolymers applications include electrical (coaxial cable, tapes), mechanical (seals, piston rings, bearings), antistick coating for cookware, self lubricating parts, chemical (pipe liners, gaskets, tapes) and micro powders (used in plastics, links, lubricants, lacquer, furnishes). A unique application of Fluoropolymers is protection of Statue of Liberty against corrosion. The applications for fluropolymers are specialty applications[6], however they are limited by their high cost.

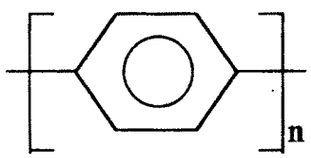
1.1.3 Aromatic polymers : -

The most successful approach to the design of high temperature resistant polymers, especially for the most important areas of application as plastic material, has been to utilize the advantageous features of polymer chains composed of linked benzene rings i.e. of aromatic rings. Polymer combine two

main requirements for high temperature resistance. First, they have good oxidation resistance, since the C – H bonds of the benzene rings resist abstraction by the chain propagating free radicals compared with aliphatic C – H bond. It is roughly true that a polymer susceptibility to thermal oxidation correlates with its aliphatic C – H bond content. Second, the incorporation of the benzene ring structure into the polymer chain stiffens the chain and hence raises the Tg (and Tm if the polymer is crystalline). However the stiffening effect may be overdone.

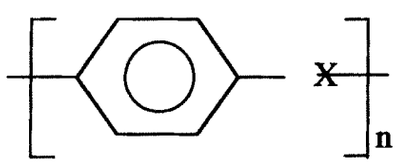
1.1.3.1 Polyphenylenes : -

The polymer consisting entirely of benzene rings linked together i.e. poly-*p* –phenylene[7-8], although superbly resistance to oxidation, has a softening point of over 500°C and so it is not melt processable.



This example illustrates the need to achieve a compromise between high softening point and adequate process ability, preferably by conventional melt processing techniques such as extrusion and injection molding. However, for polymers whose end use requires the highest softening points, special processing technique more akin to metallurgical techniques may be needed.

Therefore commercial polymers those achieve the required compromise are mostly of the type;

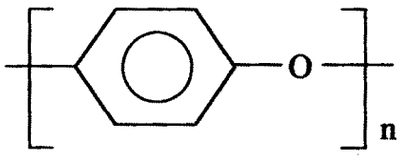


where "X" is an atom or group of atoms, giving the polymer chain a certain degree of flexibility and hence melt processability. In most commercial polymers the benzene rings are joined through the *p* - positions providing the most symmetrical type of structure and hence the best possibility for crystallization .

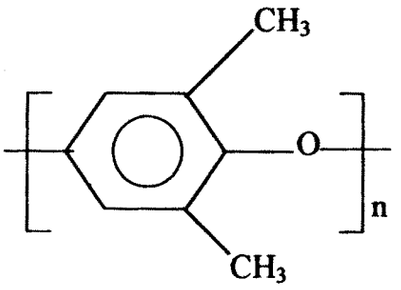
A great variety of flexibilising atoms or group is sulfone, amide, ester, keto etc.

1.1.3.2 Polyethers : -

Ether links provide a very good choice of flexibilizing group since – C – O – C – link is itself very flexible and is also highly resistant to thermal oxidation. The commercial polyphenylene oxide (PPO).



is based on the 2, 6 dimethyl substituted phenol as starting monomer, with a Tg of 208°C. It does not crystallize from the melt.

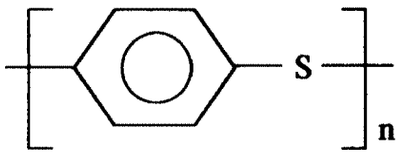


Aromatic polyethers[9-11] are relatively new group of polymers in the field of engineering plastics. The mechanical properties of PPO / polystyrene blends are significantly better than those of virgin polystyrene and hence such blends find increasing interest as engineering plastics[12-13].

It become evident in the past two decades that aromatic polyethers is a versatile group of polymers that may be useful as thermo stable engineering plastics, as resins for high performance composites, as high temperature adhesives and as basis materials for the production of membranes[14-15]. A wide range of applications is found for modified poly (p – phenylene oxide); automotive (dashboard, wheel covers, metalised grills, trim), electrical (fuse boxes, wiring splice devices), consumer and business (refrigerator door liners, computer housing, keyboard frame, iron) and liquid handling (pipe, values, pumps) etc.

1.1.3.3 Polyphenylene sulphides : -

One important member of engineering resins is polyphenylene sulphide[16], which show good thermal and thermo oxidative stability. It has the following repeat unit structure,



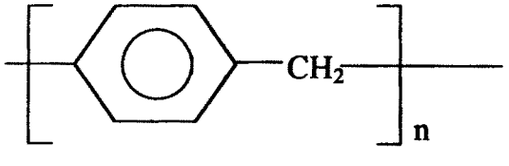
It may be used in air at temperatures above 200°C for long periods. Poly (*p*–phenylene sulphide)[17-18] is synthesized by the reaction of sodium sulphide with

p – dichlorobenzene in a polar solvent. Polyphenylene sulphide (PPS) is a highly crystalline polymer with Tm = 285°C and Tg = 85°C. It is rated for continuous service at 200 – 240°C, placing PPS between the polysulphones and the polyketones. It has inherent flame resistance, and its stability towards both organic and aqueous environment is excellent. Application of PPS includes automotive, industrial blends with fluorocarbon polymers and protective coatings.

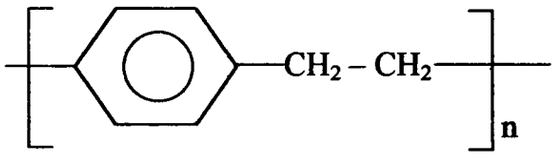
1.1.3.4 Aromatic – aliphatic hydrocarbon polymers : -

As high molecular weight polyphenylene is a highly intractable material so despite it's superb high temperature resistance to oxidation, it is not commercially useful. However low molecular weight branched polymers with mixed isomeric linkages (H – resin) have been used as soluble, flexible precursor polymers for fabrication of high temperature resistant composites with glass fibers of asbestos which forms cross – linked networks on curing at high temperature (upto 250°C). Maximum use temperature in air is 215°C (continuous) or 350°C for short times.

Linking the benzene rings through aliphatic methylene $-(CH_2)-$ groups is one way of introducing chain flexibility and hence improving process ability. However, the presence of aliphatic groups reduces resistance to thermal oxidation.



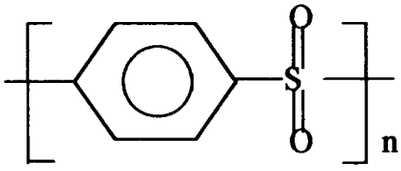
The simplest such polymers has not been synthesized. Polymers of the type poly (p – xylenes)[19-20],



are useful as electrically insulating coatings. Other potential uses include coating of orthopedic parts (bone pins and joint prosthesis) to make them biocompatible and conversation of archival and artifact objects.

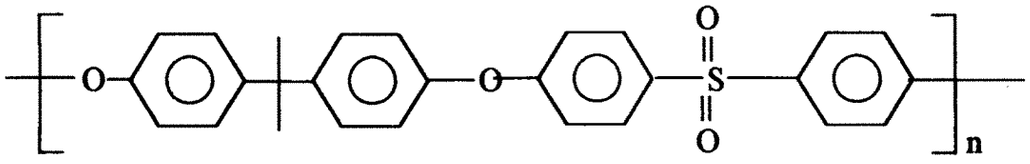
1.1.3.5 Polysulphones : -

They are synthesized by nucleophilic aromatic substitution reaction between aromatic dihalides and diphenolate salts[21]. Poly– p - phenylene sulphone has the following repeat unit structure



Another potential monomer that would not eliminate hydrogen chloride and would contribute to the goal of high thermal stability was

4,4' – dichlorodiphenylsulphone. The electron withdrawing character of the sulfone group strongly activated the chlorides towards displacement by nucleophiles such as phenoxide anion.



Polysulphone

These polyether sulfones have Tg in the range of 150° - 250°C and are insensitive to oxidation possessing short term thermostabilities upto 450°C.

Polyarylethersulphones were reported in the patent literature as new materials prepared by novel polycondensation reaction during the early 1960's. The effect of chain rigidity and polarity on Tg and Tm increase in either of these parameters leading usually to an increase in the transition temperatures was well known. Incorporating phenylene rings in polymer chains was an obvious method of increasing chain rigidity. However, the predictive power of knowledge available was limited by it's qualitative nature and there was a major problem in predicting the softening points of aromatic polymers because the relationships between crystallisabillity and molecular structure were less well known for the polymers than for their low molecular weight analogues.

Thus, by 1960 there was sufficient information available to suggest that in the search for new thermoplastics suitable for continuous use above 125°C attention should be directed towards polymers consisting of linked aromatic

rings. But there was little guidance on the choice of inter – ring linkages. It can now be seen that the combination of flexible arylether bonds with polar aryl sulphone (or ketone) linkages provides an effective solution to this problem but the discovery of these combinations arose mainly from the chemistry of the polycondensation processes investigated, rather than from properties versus structure predictions. In this environment, new synthesis of novel aromatic polymers appeared to be a good topic for research as there attention was directed towards the aryl sulphone linkage because of its high polarity and because phenyl sulphone was known to distill unchanged at 379°C indicating high thermal stability of the moiety.

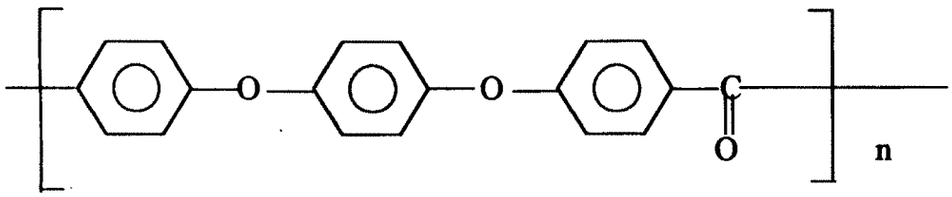
These polysulphones have found widespread use as injection molding materials when good dimensional stability at elevated temperature is required e.g. electrical components, including circuit boards, connectors, coil bobbins and relays applications operating at high temperature e.g. fan, heaters, hair driers, microwave ovens, and pumps, valves and lamp housings. 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.

1.1.3.6 Polyether ketones and polyetherether ketones : -

Polyether ketone was reported independently by ICI and du Pont as new novel material at about same time as the corresponding polyethersulphones in the early 1960s. Union Carbide was also interested in polyetherketones at this time and exemplified a polyarylether ketone – sulphone and a polyaryl ether ketone containing a bisphenol.

The first preparation of completely aromatic polyetherketones was reported by Bonner of du Pont. Aromatic polyketones are the most recently

developed type of aromatic polymer and probably offer the best high temperature resistance of any melt processable thermoplastic material. Polyetheretherketone [PEEK] has been available since 1978 and has the following repeat unit structure.



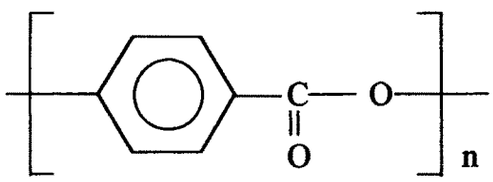
PEEK

Polyketones are partially crystalline. They have excellent resistance to a wide range of aqueous and organic environment. The resistance to organics matches that of the polyamides, while their resistance to aqueous environment matches that of polysulphone. The polyketones are finding applications in parts subjected to high temperature and aggressive environment, automotive (bearings, piston, parts), aerospace (structural components), oil and chemical (pumps, compressor, valves plates) and electrical – electronic (cable insulation) applications.

Special class of the photosensitive PEEK has been reported. The application area for the polymer was an extruded insulation for high performance wires and cables, injection molded parts, chemically resistant surface coating, monofilament for industrial belts and filters and as the matrix in carbon fiber composites for aerospace components.

1.1.3.7 Polyester : -

Various combinations of reactants and process conditions are potentially available to synthesize polyester[22]. The partially aromatic polyesters, poly(ethylene terephthalate) and poly(butylene terephthalate) are well established as plastics and fiber forming materials. However, they have limited heat resistance. The earliest commercial wholly aromatic polyester was Ekonol (polyhydroxybenzoic acid), which is crystalline and soften only above 500°C, so it must be processed by metallurgical techniques such as sintering and hammering. It may be used at temperatures up to 320°C and has found use as a bearing material.



Completely aliphatic polyesters are not of major industrial importance because of their low melting temperatures and poor hydrolytic stability. Low molecular weight aliphatic polyesters are used as a plasticizers and prepolymer reactants in the synthesis of polyurethanes.

1.1.3.7.1 Polyethylene terephthalate : - (PET)

Glass reinforced injection moldable PET resins have become a major engineering thermoplastics. PET was first synthesized by J.R.Winfield in England in the 1940's. PET was used as a fiber for apparel, film for packaging / insulation and in the bottles of beverages.

Several factors kept PET from been 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. This did increase crystallization rate but would not allow full crystallization in water-heated molds.

1.1.3.7.2 Poly (butylene terephthalate) : -

It is a linear condensation polymer based on terephthalic acid and 1,4 – butanediol. The more definitive name is poly(tetramethylene terephthalate) or PTMT.

There is evidence of some interest in the material, in the form of patents issued to ICI over the period 1957 through 1962, which deal with formation of PBT from both DMT / 1,4 butanediol and terephthalic acid / 1,4 butanediol. PBT finds used in stretch fabrics, and carpets.

Other classes of polyesters of commercial importance are polycarbonate, liquid crystal polyester and unsaturated polyester.

1.1.3.7.3 Polycarbonates : -

It is a special class of polyester derived from carbonic acid and diol. Aromatic polycarbonates were first disclosed by A.Einhorn in 1898. He reacted pyridine solution of hydroquinone, resorcinol and catechol with phosgene to produce polycarbonate. Four years latter C. Bischoff and A.Von Hedenstrom produced and reported the same products employing transesterification, and then the subject of aromatic polycarbonates was apparently forgotten. More than 50 years later Dr. Herman Schnell at Bayer A.G and General Electric Corporation

laboratory in Schenectady, N.Y. independently synthesized aromatic polycarbonates based on bisphenol –A. Bisphenol polycarbonates have found broad application around the world as a premier engineering plastics. Features which qualify bisphenol - A polycarbonate as "Engineering Plastics" include outstanding toughness, dimensional stability, load bearing properties over a very broad temperature range, transparency, resistance to burning, excellent electrical properties, high impact strength and a Tg of 149°C etc.

1.1.3.8 Polyamides : -

In the early 1930's the pioneering work of Wallace Carothers and his associates at du Pont gave us polymer such as nylon, which can be melt spun into fibers.

1.1.3.8.1 Nylons : -

Nylon is a generic term for any long chain synthetic polymeric amide, which has recurring amide groups as an integral part of the main polymer chain. The first commercial use of nylon was in bristles for toothbrushes and hairbrushes.

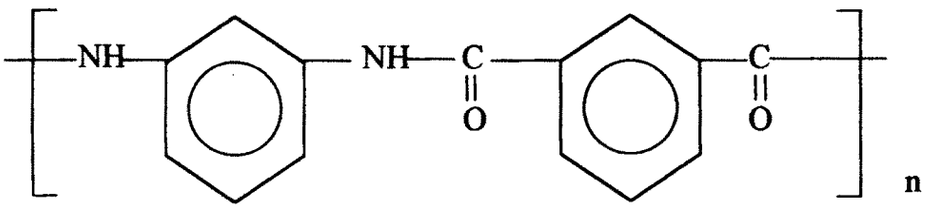
Nylon – 6,6 an invention of Carothers [a man with broad talent and scientific contribution] is industrially important material. The polyamide from 9 – aminononanoic acid was the made and found to have low melting point of 195°C but fiber properties comparable to silk. This lead initiated extensive studies on polymers from amino acids or diamines and dibasic acids. On February 28, 1935 the superpolymers from HMDA and adipic acid was first made having melting point over 260°C, safely higher than ironing temperature.

Nylon – 6, derived from ω – amino caperic acid Є-caprolactuem, has also gained commercially significance.

Aliphatic polyamides have amongst the highest softening / melting points for wholly aliphatic polymers. These high values arise from the complete hydrogen bonding of the amide groups in the crystalline regions. Recently an higher melting nylon, nylon - 4,6 with a Tm of 295°C has become available. The polymer has claimed maximum working temperature of above 150°C. The polymers may be competitor with polysulphones as a reasonably high temperature resistant materials in electrical and automotive applications.

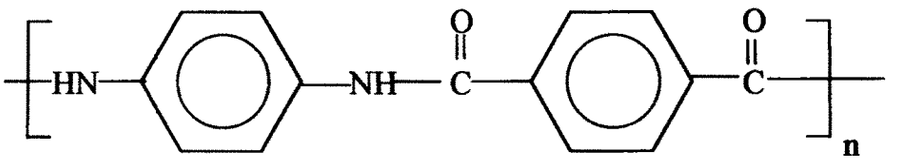
1.1.3.8.2 Aromatic polyamides : -

At the other extreme, wholly aromatic polyamides having such high melting points that they are not melt processables. Hence aramides are not usable as plastic molding materials. However, two long established products are significant commercial polymers. The meta-linked polymer, poly–*m*-phenylene isophthalamide, Nomex has been available since 1972.



It has Tm of above 400°C and is processed into fibers. The maximum use temperature of 370°C is claimed. It is mostly used for its fire resistance in textiles / clothing for racing drivers and astronaut's suits. Nomex film is used as a honeycomb layer in high performance composite laminates, especially when bonded to carbon fiber reinforced plastic outer layers, in air craft and performance speed boats.

Para – linked aromatic polyamides have even higher crystallinities, stiffnesses and melting points owing to the greater symmetry of the structure. Poly – *p* – phenyleneterephthalamide (Kevlar) fibers have been available since 1970. It is used in high performance tyres, the material is better known as a high modulus reinforcing fiber in plastic composites.



The presence of hetero atoms in the main chain, its nature and positions widely modify both the structure and properties of polyamides and they occupy special place, due to the polarity and hydrogen bond forming ability of amide groups. They are highly versatile and flame resistance polymers, high – tensile strength and high Young's modulus polymers and high performance plastics.

They also find utility as functional polymers biomedical polymers, electroactive polymers, polymer liquid crystals and polymer resins and membranes in addition to the classical uses as synthetic fibers, films and plastics. Number of excellent review articles are available on aromatic polyamides[23-26].

1.1.4 Heterocyclic polymers : -

Heterocyclic structures in the polymer chain provide another type of ring structure to stiffen the chain and raise Tg, Tm and softening point. In the earlier days of the search for high temperature resistance polymers, many such polymers were synthesized and their thermal degradation behaviour was investigated. Most important of these materials are the polyimides, polybenzimidazoles etc.

1.1.4.1 Polyimides : -

Polyimides are polymers incorporating the imide group —CO—N —CO— in their repeating units either as an open or as closed rings. Polyimides have been known to be one of the best materials for use in high temperature applications. Polyimides exhibit outstanding resistance to irradiation, mechanical deformation and solvent attack, while maintaining an excellent balance of mechanical and electrical properties. The first synthesis of polyimide was reported by Bogert and Renshaw[27]. Polyimides with aliphatic units in their main chain are generally obtained by thermal polycondensation by heating salts of aromatic tetra-carboxylic acids and aliphatic diamines[28]. Polyimides with aromatic units in their main chain are generally prepared by a two-step polycondensation method. The first report appeared in 1959[29], and aromatic polyimides became highly important because of their excellent thermal stability, along with good mechanical and electrical properties. However, they do not lie at the top of the list of the thermally stable heterocycles. Indeed other heterocycles, such as polybenzimidazoles, polybenzoxazoles, or polyquinolines, show better heat resistance than polyimides[30]. But polyimides have gained a prominent position due to their excellent properties, price, processability balance. Furthermore, while at the beginning polyimides found application in a rather restricted variety of technologies, mainly in the form of films and resins for the aerospace and electrical industries[4, 31].

1.1.4.2 Polyetherimides : -

Polyetherimides were developed by GE's Research and Development Center as a result of research interests in aromatic nucleophilic displacement

chemistry combined with a perceived marketplace need for high performance polymers which could be readily fabricated by standard plastics extrusion and injection molding processes.

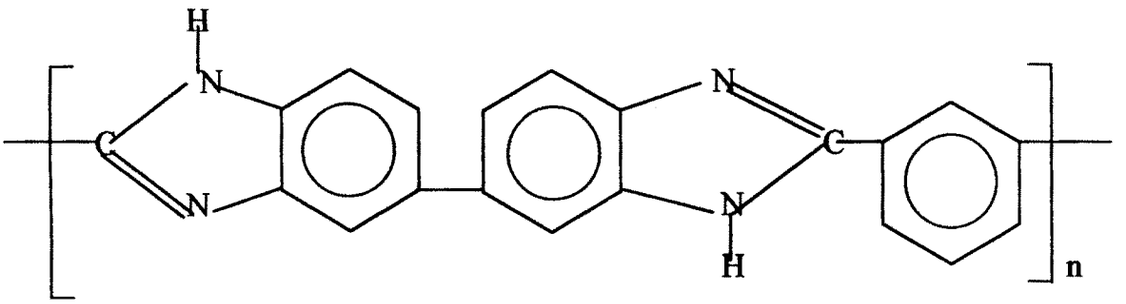
In laboratories number of approaches have been made to synthesise polyetherimides. The repeating aromatic imide units in the molecule are connected by aromatic ether units, yielding a polymer with flexible linkages for good heat flow characteristics, while retaining sufficient stiffness for good engineering properties. In addition, designing the polymer backbone with highly aromatic character combined with ether and imide connecting units leads itself to good thermal stability, and flame retardancy.

1.1.4.3 Polybenzimidazoles : -

Many other heterocyclic structures offer excellent thermal and thermooxidative stability. Among the leading high performance materials the class of polybenzimidazoles (PBI), due to their outstanding engineering properties, flame resistance, radioactive stability, excellent mechanical and dielectric strength and strength retention over a wide range of temperature as well as toughness, chemical inertness and adhesion etc. find good applications in aerospace and defence industries.

The polybenzimidazoles were first claimed in the U.S. patent in 1959 and then published as scientific report by H.Vogel and C.S. Marvel in 1961 with anticipation that the polybenzimidazole polymers would have exceptional thermal and oxidative stability[32]. An outstanding feature of the polybenzimidazole is that although the final polybenzimidazoles are insoluble and infusible, precursor of PBI could be processed in the prepolymer stage and brought into desired shape and size which is ultimately converted to PBI of

desired form. Levine[33] proficiently reviewed polybenzimidazoles. Typically PBI are synthesized by condensation of aromatic bis (*o* – diamine) with diacids or diesters or dialdehydes. The structure of poly (2,2' – *m* – phenylene –5, 5 dibenzimidazoles) is as below.

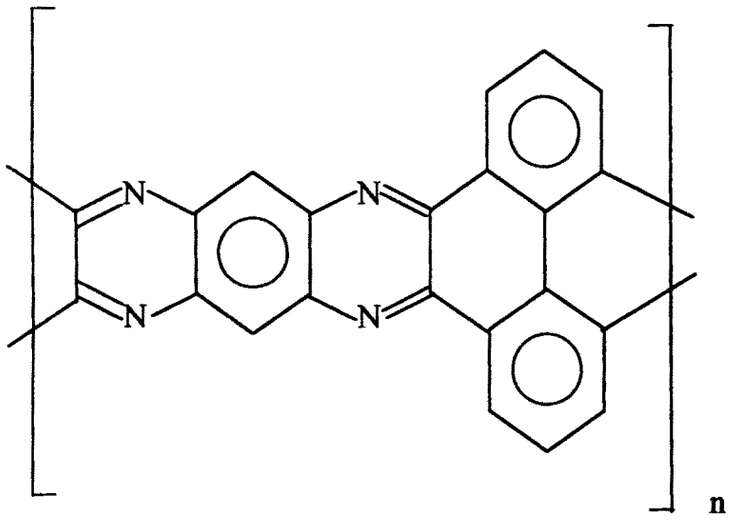


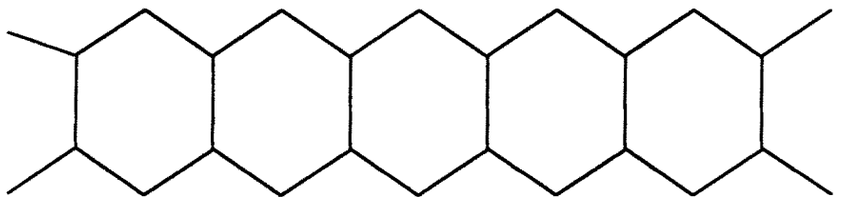
The use of high temperature solution polymerization using polyphosphoric acid was introduced in 1964 by Iwakara[34]. PBI containing N – phenylated and flexibilizing spacers into polymer backbone[35], thioxanthones, phenoxanthiandiyl[36] halogen[37], amide – imide[38] and hexafluoroisopropyl units, have been reported.

1.1.4.4 Ladder (double strand) polymers : -

Ladder polymers are defined as those consisting of uninterrupted series of rings connected by links around which rotation cannot occur except by bond breaking. Compared to single strand analogues these polymers have exceedingly rigid chains and hence high softening points, and any chain scission through oxidation would require cleavage twice in the same ring structure, which is statistically very unlikely until massive oxidation has occurred.

In principle even higher temperature resistance may be obtained with fused ring chain polymers (double strand or ladder polymers) with the following schematic structure or their heterocyclic analogues.





These ladder polymers possess exceptionally high thermal and thermo oxidative stability up to 500°C. However no such polymers have been commercialized.

1.2 Limitations of polyamides and polyimides : -

Wholly aromatic polyamides and polyimides are widely used and belong to the class of high performance polymers, and occupy an important place among the other polymers. For example, Kevlar [poly (*p*-phenylene) terephthalamide] and Nomex [poly (*m*-phenylene) isophthalamide] are commercially marketed as high performance polymers and are usually provided in fiber form. Both polyamides exhibit good mechanical strength and thermal resistance, and are suitable materials for composites. However the versatile applications of these polyamides have generally been reduced by the high crystalllinity and limited solubility in common solvents [39].

Polyimides which are thermally stable, have excellent mechanical strength, high thermooxidative stability, and superior electrical insulating properties, but also have two major shortcomings. Unless carefully designed, they have inferior solubility in most organic solvents and processing diffeiculties due to the high melting points and / or glass transition temperatures[40 – 41].

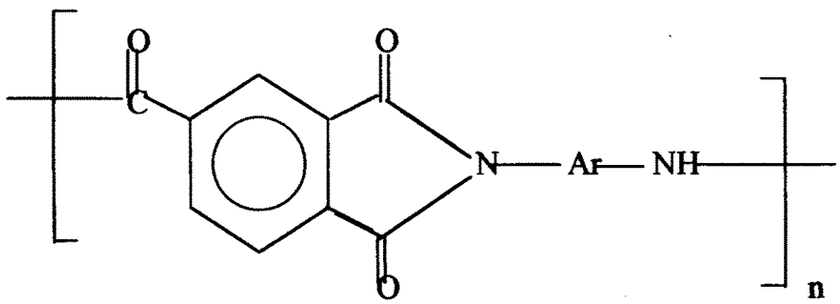
1.3 Poly (amide – imide)s : -

The present investigation is focused on the special combination of aromatic polyamides (1.1.3.8.2) and polyimides (1.1.4.1) to yield polymers with interesting properties, characteristic of both these classes of polymers resulting into poly (amide – imide)s.

Heterocyclic structures in the polymer chain provide another type of ring structure to stiffen the chain and raise Tg, Tm and softening point. In the early days of the research for high temperature resistant polymers, many such polymers (PI, PBI etc.) were synthesized and their thermal stability was studied[42-43]. However, hardly any of these materials were ever commercialized

despite the much greater variety of thermally stable heterocyclic polymers potentially available.

In order to obtain more tractable and sometimes melt processable polyimides, various copolymers have been introduced commercially. Among the better known materials is Torlon, a poly (amide – imide) of structure,



It is an injection mouldable material giving products with a continuous use temperature of up to 260°C. The material also has exceptional stiffness and creep resistance. Mouldings do require extensive annealing at high temperature to develop the best mechanical performance.

A number of poly (amide – imide) s were reported in the literature [44 - 45] and they constitute a polymer class with average properties between aromatic polyamide and aromatic polyimides. Aromatic poly (amide imide)s are easier to prepare and to process than both aromatic polyimides and polyamides because the copolymers are usually more soluble in polar solvents than the corresponding aromatic polyamides or aromatic polyimides.

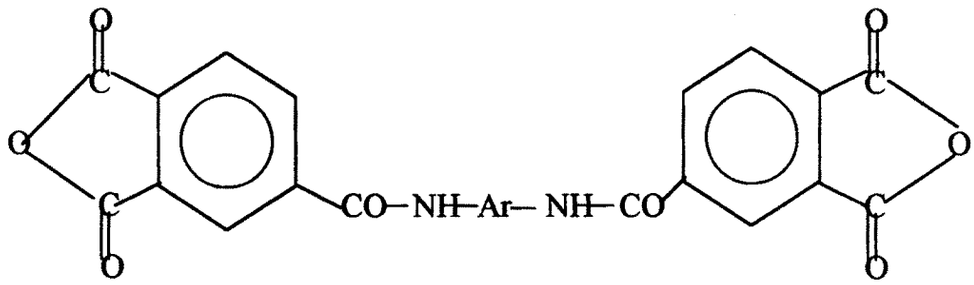
1.4 Synthetic methods for poly (amide - imide)s : -

The general methods to synthesize poly (amide-imide)s are rather simple and include those monomers and reactions to polyamides or polyimides.

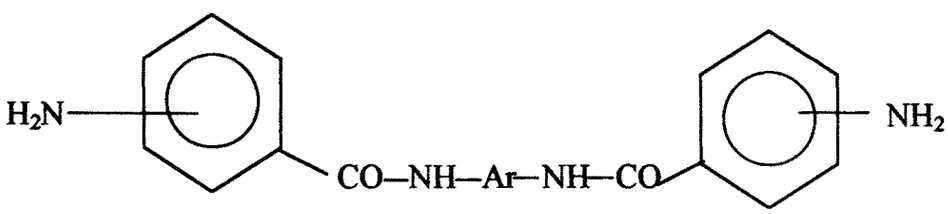
Consequently, the number and variety of chemical structure and methods reported are countless, few of them are as given below:

1.4.1 From amide containing monomers: -

The amide containing diamines or dianhydrides are suitable monomers[31,46-47] for the synthesis of poly (amide – imide)s by the general process via the corresponding intermediate poly (amide – amicacid). Solution polycondensation is the preferred procedure for these reactions.



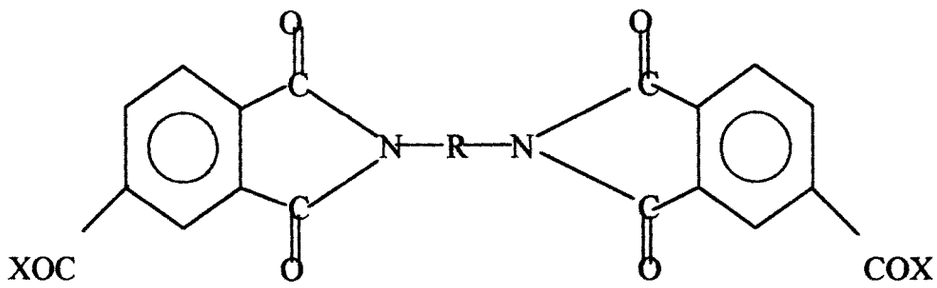
Amide containing dianhydride



Amide containing diamine

1.4.2 From imide containing monomers : -

The methods used to prepare polyamides have readily been employed to prepare poly(amide – imide)s from diamines or diamine derivatives and imide containing dicarboxylic acid or acids derivatives.



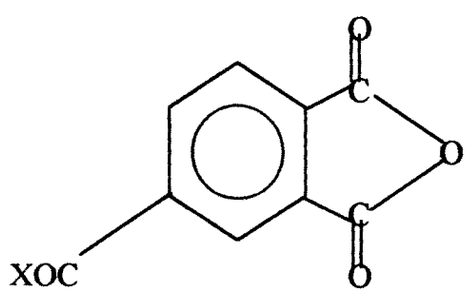
X = - OH, - Cl, - o -alkyl, - o – aryl, etc.

Since poly(amide–imide)s are polymers with high transition temperature synthetic methods involving low temperature or mild conditions, have mostly used for these reactions, although melt polymerization has also been used for aliphatic - aromatic species.

Hsiao et. al [48-53] synthesized, poly(amide–imide)s by direct polycondensation method using triphenyl phosphite as the condensing agent. The diimide containing diacids were directly polycondensed with various aromatic diamines to obtain aliphatic – aromatic poly(amide – imide)s.

1.4.3 From trimellitic anhydride and its asymmetrical derivatives : -

An acid anhydride such as trimellitic anhydride can be considered as an ideal monomer since both anhydride and carboxylic acid groups may react with diamine to make up poly (amide – imide)s[54-56].

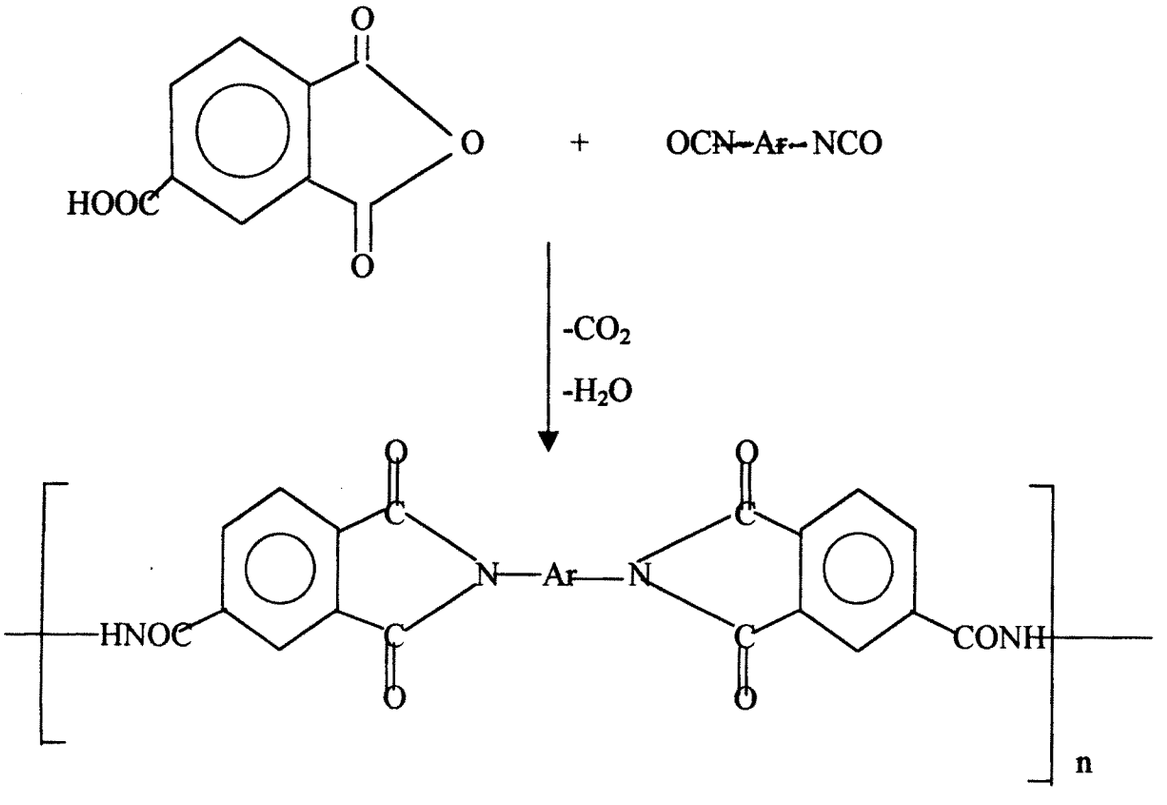


X = - OH, - Cl, - o – alkyl, - o – aryl etc.

As usual the first product formed in this reaction is poly (amic acid), which eventually is converted into poly (amide – imide) at high temperature.

1.4.4 From diisocyanates : -

Diisocyanate can react with both acid and anhydride groups in trimellitic anhydride to produce high molecular weight poly (amide – imide)s that have found practical application as high temperature varnishes[57] and fibers[58].

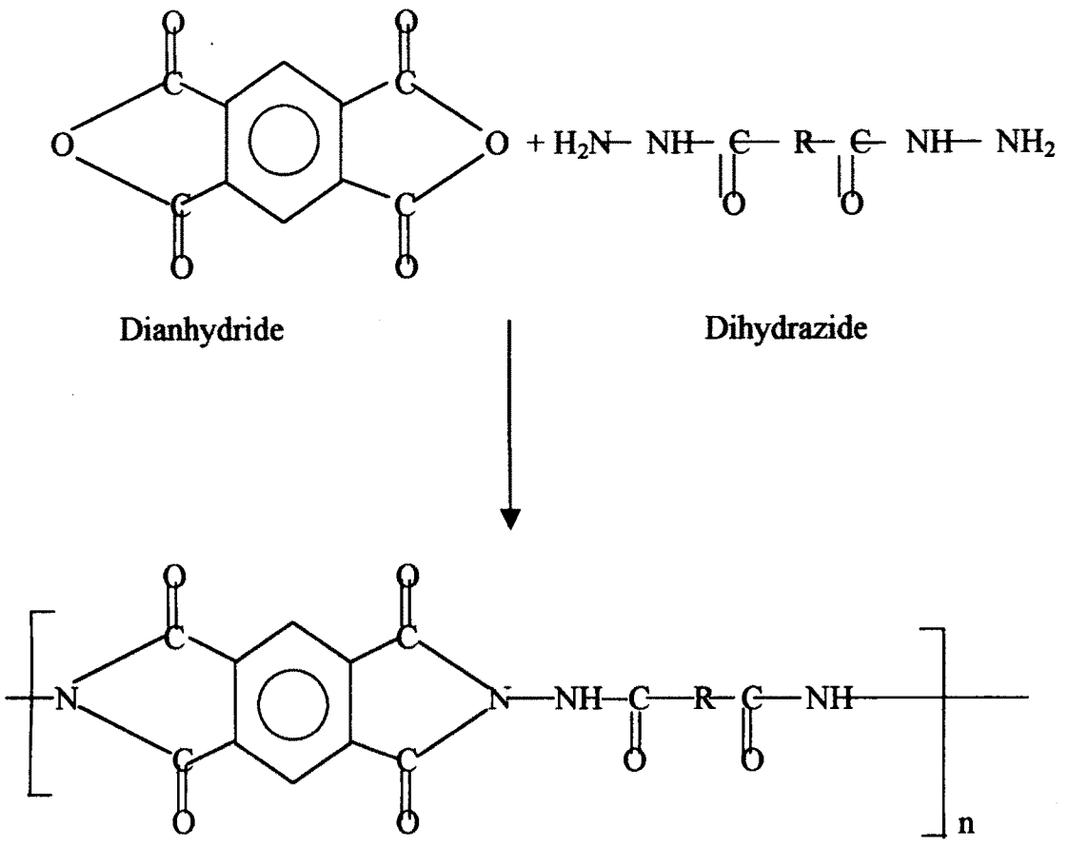


Poly(amide - imide)s

Poly (amide – imide)s from diisocyanates and trimellitic anhydride or diacid – imides are prepared preferably in solution of NMP or DMAc at relatively high temperature.

1.4.5 From dianhydrides and dihydrazides : -

The reaction of tetracarboxylic acid dianhydrides and dihydrazides[59] yields the poly (amide – imide)s as depicted below.



1.5 Soluble and / or processable polymers with thermal stability : -

Preparation of soluble and / or thermoplastic polyamides and polyimides had been a major research interest. To overcome short coming, described in (1.2) various noteworthy attempts have been made with the aim of synthetic modification of the rigid – chain structure by the introduction of flexible bridging

linkages[60-61], the distortion of molecular symmetry by meta – or ortho – oriented phenylene linkages and the introduction of bulky groups into the polymer chain.

Another way to overcome to these limitations is to synthesize poly (ester – imide)s and poly (amide – imide)s which were successfully synthesized by the direct polycondensation of imide ring – containing diacids with diols or aromatic diamines respectively. Trimellitic anhydride has been the unique monomer for the synthesis of the aforementioned imide ring containing diacids which give alternating poly(ester – imide)s or poly(amide – imide)s. Poly (amide – imide)s were also synthesized by the condensation reaction between either amide linkage containing diamine and a dianhydride[39, 62] or imide linkage containing diamine and a diacid chloride. Perfectly alternating aromatic poly(amide – imide)s have been synthesized easily with trimellitic anhydride, but, other two methods have not been utilized extensively probably due to synthetic difficulties[61].

Perfectly alternating poly(amide – imide)s prepared by Ozarslan et al[63] using N, N - bis (4' – amino – 4 – biphenylene) isophthalamide (BABPI) have been reported. They utilized an aromatic dinitro compound to synthesize a novel diamine, which contained amide units within the monomer structure. This diamine (BABPI) was then utilized to synthesize a series of perfectly alternating novel poly(amide – imide)s.

The triphenyl phosphite activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides was reported by Yamazaki et at[64] and has been extended by Yang, et. al[48-52] to synthesise many series of poly(amide – imide)s in their laboratory, by the direct polycondensation of imide ring – containing diacids and aromatic diamines. They demonstrated that the incorporation of a diphenoxynaphthalene moiety into the poly (amide-imide) backbone is one effective means of enhancing the solubility with retention of

good thermal properties[65-66]. In continuation of these studies work, on the synthesis of a novel series of poly (amide –imide)s from the imide ring containing dicarboxylic acid, 2,5 bis(4 - trimellitimido phenoxy) naphthalene was reported [67].

Twisted biphenyl structures have been successfully introduced into polyimide backbone to enhance the solubility in common organic solvents while maintaining the high – temperature performance [68 - 72].

In the recent papers [73-74] 1, 1' – binaphthyl –2, 2' diyl (B N) – based aromatic poly (ether imide)s, in which the rotary axis of the two naphthylene rings is perpendicular to the backbone, were synthesized. The resulting polyimides exhibited excellent solubility in common organic solvents, high transition temperature and high thermal stability. Analogously Imai et al [75] reported the synthesis of poly (ether-imide)s containing BN units in the main chain. Some polyesters [76-77] and polyamides [78] based on BN units were also synthesized. In fact, besides the noncoplanarity and nonlinearity, there is a more interesting structural characteristic for BN containing polymers, i.e. the changeable dihedral angle between the two naphthalene rings [79 - 80]. According to different pendant groups at 2 and 2'- positions and the rigidity of the main chain, the dihedral angles may vary in order to adopt a suitable conformation. The resulting poly (amide – imide)s and poly (ether imide)s were thoroughly characterized [81].

Liaw et al [82] prepared new cardo diimide–dicarboxylic acid, 1,1–bis [4–(4–trimellitimidophenoxy) – phenyl] cyclododecane, BTPCD, containing a pendant cyclododecyl group by the condensation reaction of 1,1 – bis [4 – aminophenoxy) phenyl] cyclodecane and TMA in glacial acetic acid. A series of new cardo poly(amide – imide)s were prepared by the direct polycondensation of

BTPCD and various aromatic diamines in N – methyl –2 pyrrolidinone (NMP) with triphenyl phosphite and pyridine as condensing agents. It has been reported that the aromatic cardopolymers possessed excellent thermal and chemical stability, excellent mechanical and electric properties and excellent solubility and easy processability [83-84]. Previously new polyamides and polyimides containing a pendant cyclododecyl group[85-86] were reported however, some of the cyclododecyl – containing polyimides derived from rigid dianhydrides showed limited solubility [86].

Soluble poly(amide imide)s based on trimellitic anhydride (TMA) have been synthesized using diamines having isopropylidene[87], biphenyl[88] and naphthalene moieties. Although being more soluble in organic solvents, the glass transition temperature (Tg) of the poly(amide - imide)s containing a flexible linkage often decreased.

It has been reported that polyimides based on phenyl – substituted pyromellitic dianhydride (PMDA) have much better solubility than rigid poly (aryl pyromellitimide) s [68, 89].

Zheng et al[90] carried out synthesis and characterization of a series of novel poly (aryl-imide)s and further described amide a series of soluble, high – Tg polyimides derived from a dianhydride structurally analogous to phenylated PMDA [91]. It was found that the pendant phenyl groups impart solubility to these polyimides without sacrifying their thermal stability. Therefore, a monomer having a pendant phenyl group into TMA that lead to the preparation of soluble high–Tg poly (aryl-amide-imide)s was reported.

Option of the incorporation of specific functionalities between amide or imide groups may provide a method of controlling certain physical properties of the resulting poly (amide - imide)s. In one of the previous publication[92], a

diimide ring – containing dicarboxylic acid, or a bis(trimellitimide), was prepared via condensation of (PIDA) and TMA and a series of poly (amide-imide)s were synthesized by the TPP – Py direct polycondensation reaction of this diimide – diacid with various aromatic diamines.

The residue of diamines, PIDA, was also incorporated in other polymer systems, such as polyimides, polyamides, and bis (maleimide) resins, to enhance the processing characteristics and toughness of the resulting polymers [92-98]. As a continuation of the efforts on screening new poly(amide-imide)s Hisao et. al[87] studied the preparation and characterization of a novel series of poly(amide-imide)s based on the diamine PIDA and the bis (trimellitimide)s condensed from TMA and many other aromatic diamines. A comparative study on the properties of the two analogous series of poly (amide-imide)s was also presented.

Tullos et al[99] used a one – pot procedure for imide – acid monomer synthesis and polymerization to yield four new poly(amide – imide)s. This direct polycondensation route gave high molecular weight polymers and avoided the use of moisture – sensitive acid chlorides. Thus the DIDC was formed by the reaction of bisphenol – A dianhydride with aromatic amino acid, without isolation, the DIDC was polymerized with aromatic diamines to give high molecular weight PAI. The thermal and solubility properties of the new polymers obtained were reported.

Poly(amide – imide)s (PAI)s as a family, have deserved particular attention, as they are probably the class of copolyimides that most closely resemble the thermal properties of aromatic polyimides. Furthermore, the inclusion of an amide group into the polyimide backbone increases its processability, solubility, and moldability [100].

Liaw et al[101] described the synthesis and characterization of PAIs prepared from diamines and a new diimide – dicarboxyllic acid containing an ether linkage and tert – butyl substituent derived from 1,4 bis (4 – aminophenoxy) – 2 – tert – butylbenzene and trimellitic anhydride. It has been reported[102–103] that incorporating a flexible ether unit and bulky tert – butyl substituent into the polymer backbone effectively improved the solubility and lowered the transition temperature of the polyimides and polyamides while preserving their good thermal stability.

1.6 Outline of present investigation :-

To overcome the difficulties in processing various copolyimides such as poly (amide – imide)s, poly (imide – quinoxaline)s, poly (ester – imide)s were developed. Poly (amide – imide)s were developed as alternative materials that offer a compromise between excellent thermal stability and processability.

Imai et. al [55, 104] reported the phenylated polyimides; polyazomethines, poly(amide – imide)s with enhanced solubility compared to *p*–phenylene diamine or oxydianiline based conventional corresponding polymers.

Marvel C.S., Maldar N.N et. al [55, 104 -109] synthesized phenylated and silicon containing poly (amide – imide)s. Yang et al [110] synthesized the poly(amide – imide)s from 2, 5 – bis (4 – trimellitimidophenyl) – 3, 4 – diphenylthiophene and other aromatic diamines, however solubility of these poly (amide – imide)s was limited. Hence we thought that it will be interesting to increase the solubility of poly (amide – imide)s derived from 2,5 – bis (4 – trimellitimidophenyl) – 3, 4 –diphenylthiophene by utilizing the technique of copolymerisation i.e. copoly (amide–imide)s from 2,5–bis(4–trimellitimidophenyl) – 3, 4–diphenyl thiophene and other aromatic diamine

containing flexible ether or sulphone linkage. Thus the present work includes synthesis of novel phenylated diimide containing diacid i.e. 2, 5 – bis (4 – trimellitimidophenyl) – 3, 4 – diphenyl thiophene (IV) and it's polymerization with aromatic diamine to yield two series of copoly (amide – imide)s from oxydianiline + (o - BBA + IV) and second series from 4,4 – diaminodiphenyl sulphone + (o - BBA + IV). Few poly (amide – imide)s from (IV) and MPD, PPD, ODA and NDA under same condition of the polycondensation were repeated. These polymers and copolymers were characterized by viscosity, IR, solubility and thermal stability, to realise that solubility can be improved in copolymers without sacrifying the thermal stability as compared to the poly (amide – imide)s reported by Yang et al [110].

Thus, the present investigation aims at developing poly(amide - imide)s and copoly(amide - imide)s with enhanced solubility and high thermal stability. For the purpose of increasing the solubility of resulting poly and copoly(amide - imide)s approach of (i) reactant with pendant phenyl groups i.e. phenylated a monomer and (ii) copolymerisation technique for random arrangement, have been used. In order to understand the structure - property correlations, it was essential to vary the type and content of imide groups and hence copoly(amide - imide)s with ODA and SDA were investigated. The effect of the ratio of the diimide-diacid to diacid (viz. oxybis benzoic acid) has also been studied.