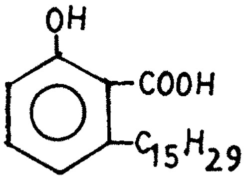
1 INTRODUCTION

The rapid growth in the production of synthetic polymers, plastics, man made fibers, films, rubbers and coatings which continued unabated for many years, suffered a severe set back for the first time in 1973-74, followed by another in 1980. A major cause of these reverse was the changed situation with respect to raw materials and energy. Currently the production of polymers is almost exclusively based on hydrocarbons as raw material [1,2,3]. The main source for the polymer industry today is petroleum and taking into account the situation created by "Gulf-war crisis", there is a need to follow new paths which would reduce dependance on petroleum as the basic raw material for polymer industry , because it is foreseeable that the fossil reserves, petroleum and natural gas would be exhausted in the not too distant future. This necessitates a look at the renewable natural resource that can serve as alternative feedstock of monomers for polymer industry. Tall, Linseed and castor oil [4] are few materials of alternate choice.

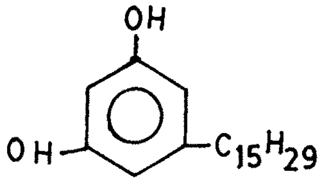
1.1 Cashewnut shell liquid (CNSL) :

Cashewnut shell liquid (CNSL) is another byproduct traditionally obtained during the isolation of the kernals from cashewnuts. CNSL is viscous resinous an abundant agricultural byproduct, the potential availability of which in India is about 55,000 tons per annum [5]. It holds considerable promise as a source of unsaturated phenol, an excellent monomer for polymer production. The chemistry of CNSL is briefly reviewed below [6].

Stadler [7] has studied the ether extraction of cashewnuts and reported that 90% of it consisted of an acid which is called ‘anacardic acid' and the rest 10% being a dihydroxy phenol known as ‘cardol'. It is now established that anacardic acid and cardol have the structure as shown below.



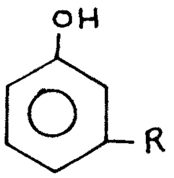
ANACARDIC ACID



CARDOL

Harvey and Caplon [8] distilled the commercial CNSL under vacuum and 70% of the total distillate was found to be single phenolic component with an unsaturated side chain in the meta position. This substance they termed as 3-pentadecenylphenol (cardanol) and is presumably formed by the decarboxylation of anacardic acid.

Dawson and coworkers [9] have studied the chemistry of cardanol in detail and established a structure for cardanol as follows :



$R = C_{15}H_{27}$,
$C_{15}H_{29}$,
$C_{15}H_{31}$.

Specifications for cashewnut shell liquid (CNSL) of export variety (Kerala state Govt, India) are ;

1.	Specific gravity	0.985
2.	Viscosity	434.1 cp.
3.	Moisture	1.17% (max.)
4.	Matter insoluble in toluene	0.29% (max.)
5.	Volatiles	5.20% (max.)
6.	Iodine value	234.0
7.	Polymerisation test	
	(a) Gel time	10 min. and 6 sec.
	(b) Oven test (viscosity)	10.21 cp.

Cardanol which is structurally similar to m-cresol behaves as a phenol and these structural features have been utilised for various commercial applications, particularly as polymeric materials [10].

Polyamides are polymers that contain recurring amide groups as integral parts of the polymer main chain. These can be prepared by many routes, however, only melt polycondensation, ring opening polymerisation and low temperature solution polymerisation have gained commercial importance. Aromatic polyamides are formed by reactions of aromatic diamines and aromatic diacid chlorides leading to formation of amide linkages between aromatic rings. The generic trade name, aramid was applied to synthetic polyamide in which atleast 85% of the amide (-CONH) linkages are attached directly to two aromatic rings.

In the past few years interest has been centred on the synthesis and characterisation of aromatic polyamides for use as high temperature materials and for their liquid crystal properties. It was the discovery in 1965 of liquid crystalline solutions of synthetic aromatic polyamides and high-strength / high modulus fibers therefrom [11] that has led to the production of high performance Kevlar^{R} aramid fibers and has served as a catalyst for the present day high level of interest in this field. Kevlar^{R} aramid fibers have a combination of outstanding properties : high melting temperature and high thermal stability, low combustibility, low density compared with glass or steel, non conductivity, good dielectric properties, high strength and modulus, high tensile fatigue resistance, high cut-resistance, good flex resistance, textile processibility, and good stability in sea water, oils, solvents, steam (pH 4-8) and other environments [12].

Nowadays, it is accepted that, the preferred method of determining the relative short-term thermal or thermoxidative stability of high-temperature polymers is dynamic thermogravimetric analysis (TGA). Longer term stabilities are most conveniently defined by isothermal gravimetric analysis (IGA) if the temperature is properly chosen. If these tests are combined with thermomechanical analysis (TMA), which provides data on the glass transition temperature and softening behaviour, the thermal limitations of most polymers can be fairly well defined. In laboratory analysis, TGA and IGA provide the best measure of inherent thermal stability of polymeric materials. Few important heat resistant polymers available commercially are presented in Table I.

1.2 Methods for aromatic polyamide preparation

The wholly aromatic polyamides cannot be prepared by melt polycondensation. The potential polyamides either donot melt or melt at high temperatures with decomposition. Many aromatic acids will decarboxylate and the aromatic diamines are readily oxidised and have a tendency to sublime [11,12]. Consequently use is made of low temperature polymerisation methods. Since the reactivity of aromatic diamines and aromatic dicarboxylic acids is too low, it is generally necessary to employ aromatic carboxylic acid chlorides.

$$\mathrm{ArNH_2} + \mathrm{Ar'}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{-Cl} \longrightarrow \mathrm{Ar{\cdot}NH{\cdot}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{-Ar'} + \mathrm{HCl}$$

An acid acceptor is needed to bind the hydrochloric acid evolved. Usually, the polymerisation proceeds very rapidly. Two methods are in use viz. the interfacial polymerisation method (a two-phase process) and the solution polymerisation method (a single-phase process).

Table I : Commercial High Temperature Polymers

Trade Name	Generic Name	Manufacturer	Typical Uses
Kapton	polyimide	Dupont	Wire and cable insulation, flexible printed circuits, pressure sensitive tapes.
Vespel	polyimide	Dupont	Low friction bearings, bushings, cams, ratchets and pawls.
NR-150	polyimide	Dupont	Laminates, adhesives, radomes, ablative heatshields, syntactic foams, brake linings.
Kinel	polyimide	Rhodia	High temperature molding compounds.
Keramid	polyimide	Rhodia	Void free laminates & composites, adhesives.
Polyimide 2080	polyimide	Upjohn	Films for wire and cable wrap, flexible printed circuits, laminating varnish, molding compound.

Trade Name	Generic Name	Manufacturer	Typical Uses
Ryton PPS	polyphenylene sulfide	Phillips- - petroleum	Molding,bearings,bushings,seals, pump impeller,coating, pipe wire, cables,cookware.
Astrel 360	polyaryl sulfone	3M	Structural parts,fuel tanks,exhaust pipes housings for heating units, connectors, relay terminals.
Polyether sulfone 100p,200p,300p	polyaryl sulfone	ICI	Airplane cabin interiors, radomes,adhesive
Radel	polyphenyl sulfone	Union Carbide	Medical hardware, structural foam,electrical parts.
Ekkcel	Aromatic polyester	Carborundum	Self lubricating parts, molded parts, dispersion coatings.
Noryl PPO	polyarylether	General Electric	Structural parts for appliances,electrical parts.
Lexan	polycarbonate	General Electric	Crash helmets, store windows,explosion shields.

Trade Name	Generic Name	Manufacturer	Typical Uses
Torlon	polyimide Amide	AMOCO	Structural electronic components, valves, gears, bearings, pumps.
Teflon Teflon PFA Teflon FEP	Fluoro polymer	Dupont	Cookware, structural electronic parts, anti friction coatings, cable and wire insulator gaskets, tubing.
Tefzel	Fluoro polymer	Dupont	Wire and cable insulator, pump components, printed circuit boards, bearings electronic components.
Kevlar	Aromatic polyamide	Dupont	High strength fiber for parachutes, reinforcement for composites, filament around rocket cases pressure vessels.
Kalrez	Fluoro elastomer	Dupont	Seals, gaskets, O-rings in chemical plants and oil well drilling components.

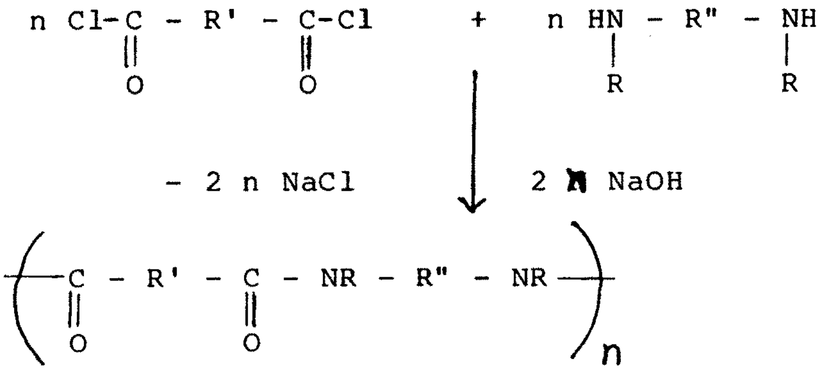
Trade Name	Generic Name	Manufacturer	Typical Uses
Parylene	Poly (Xylylene)	Union Carbide	Conformal coatings for electronic circuitry, moisture barrier.
(PBI)	polybenzimidazoles	Narmco Inc.division whittaker corp. Celanese Corp.	Fibers for astronaut's suit,ablative shields, parachute lines.
(PQ)	Polyquinoxalines	Narmco,Inc., division of whittaker corp.	Laminates,adhesives for very high temperature.
	Pyrrones	Hughes Aircraft corp.	High temperature application parts.
	Polyphenylenes	Monsanto	

1.2.1 Interfacial Polymerisation Method

In interfacial polymerisation, the reaction takes place at the interface between a solution of the diacid chloride in an organic solvent (immiscible with water under the conditions applied) and an aqueous solution of the diamine.

Interfacial polycondensation is mostly conducted at temperatures that are close to room temperature. As a rule, a rise in temperature increases the contribution of side reactions (e.g. hydrolysis) and decrease the polymer yield and molecular weight. However, in each particular case the optimum temperature of the process can differ noticeably from room temperature and the synthesis of high molecular weight polymers being a problem of major importance, a researcher always faces the task of searching for the optimum polycondensation conditions.

Polyamides are obtained by means of interfacial polycondensation of acyldichlorides and diamines or their salts.



$$n\ \mathrm{Cl{-}}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}} - R' - \underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{{-}Cl} \quad + \quad n\ \underset{\substack{|\\ R}}{\mathrm{HN}} - R'' - \underset{\substack{|\\ R}}{\mathrm{NH}} \xrightarrow[-\,2\,n\,\mathrm{NaCl}]{2\,n\,\mathrm{NaOH}} \left(\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}} - R' - \underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}} - \mathrm{NR} - R'' - \mathrm{NR} \right)_n$$

where,

R = H, Me.

Although high molecular weight polymer can be produced by interfacial polymerisation method, the molecular weight distribution, unlike that for polymer from solution polymerisation, is rather broad, with some very high and some very low molecular weight species. Therefore this method is not suitable for the preparation of fibers and films. Extraction of the polymer to remove the oligomeric species gives a polymer of better utility.

1.2.2 Solution Polymerisation Method

In the solution polymerisation method the reaction simply takes place in a homogenous solution.

In the synthesis of polyamides the role of the acceptor for the evolving acid (HCl) is often played by the amide solvent, eg. dimethylacetamide or N-methyl-2-pyrrolidone. Thus for the solution polymerisation of aromatic polyamides, it is advantageous to use aprotic polar amide solvents such as dimethylacetamide (DMAC), N-methyl-2-pyrrolidone (NMP), and hexamethylphosphoramide (HMPA). Dimethylformamide (DMF) is unsuitable because it reacts with acid chlorides, nor is dimethylsulfoxide (DMSO) of any use because of it's violent reaction with acid chlorides.

In solution polymerisation method, diamine is dissolved in amide solvent and diacid chloride is added with cooling in the molten state or as a solid material (powder or flakes). Solvent systems suitable for solution polymerisation in which polymer of a sufficiently high molecular weight is obtained are hexamethylphosphoramide (HMPA) or a solvent mixture of HMPA and NMP (2:1 by volume). As HMPA has been declared to be a carcinogen, it is no longer permitted for use in commerical operations. NMP or DMAC with / without LiCl / $CaCl_2$ are preferred solvents. For the reaction of diacid chlorides with diamines, the presence of even slight concerntration of moisture (more than 0.01 %) in solution leads to a decrease in the polymer molecular weights.

The preferred process for aromatic polyamides is the low temperature polycondensation of diacid chlorides and diamines in amide solvents. It is often more convenient than interfacial polycondensation and provides a solution amenable to direct fabrication of fibers such as Nomex. Another advantage of solution polycondensation over the interfacial method results from the solubility characteristics of certain polyamides, although such polymers are soluble as made in solution by low temperature polycondensation, they often cannot be redissolved in solvents (other than strong acids, eg. sulfuric acid). Thus interfacial polymerisation gives a precipitated product that cannot be readily fabricated from solution [13].

In view of the potential high temperature uses of aromatic polyamides, it is not surprising that these materials have given rise to a number of papers. The thermal properties of wholly aromatic polyamides [14] and Kevlar-49 [poly (p-phenyleneterephthalamide)] [15] show the impressive thermal stability that these materials possess. Some polyamides with more exotic chemical structures have also come under scrutiny, often in an attempt to provide functional groups in the chain. The synthesis of polyamides containing hydrophilic groups and photosensitive moieties [16],epoxy groups [17] and azo groups [18,19] have all been described. The azo-containing polyamides prepared by interfacial polycondensation were inherently coloured.

Poly (1,4-phenyleneterephthalamide) and poly (chloro-1,4-phenyleneterephthalamide) have been synthesised in HMPA, NMP and conditions have been established for the formation of liquid crystalline solutions [20]. Krigbaum and others have studied in details the conditions of phosphorylation reaction for the preparation of aromatic polyamides using the Higashi reaction medium to establish optimum polymerisation conditions for poly (p-phenyleneterephthalamide) [21]. The procedure used for the polymerisations was the low temperature solution polycondensation technique developed for poly (p-phenyleneterephthalamide) and homologues [20,21]

The polymerisation was started at -5 to 0°C and over several hours was allowed to warm to 25°C. It was determined that heating (upto 80°C) overnight did not increase the inherent viscosity over that obtained by reaction at room temperature.

Very little information is available on polymers from toluene 2,5 diamine, where as thousands of papers appeared on p-phenylenediamine, toluene 2,4-or toluene 2,6 -diamine. This is because of commercially availability of p-phenylenediamine (BDA) and 2,4 / 2,6- toluenediamines whereas preparation of 2,5-toluenediamine by the reduction of corresponding dinitro compound is not economically feasible as explained in fig.1.

Rogers and coworkers [23] have reported very high molecular weight, highly amorphous, para linked rod like aromatic polyamides, where in trifluoromethyl, methoxy or halogen substituents were placed on the aromatic rings so as to force them into a non-coplaner conformation. The effect of this non coplanarity was to reduce the crystallinity of even highly oriented films, enhance solubility and reduce or completely eliminate absorption of visible radiation.

Summarising the literature, it was found that synthetic aromatic polyamides have been investigated mainly for high temperature applications. For example Preston [24] prepared wholly aromatic polyamides of high heat resistance from aromatic diacids and aromatic diamines. However, many such wholly aromatic polyamides are insoluble in all common organic solvents and dissolve in concentrated sulfuric acid. Sometimes properties are such that these polymers may not be processible. It was thought the processing properties may be improved if a portion of the repeat unit of these polymers is made aliphatic or aliphatic substituents are introduced on aromatic repeat units.

Therefore the present investigation was under-taken for the synthesis of aromatic polyamides based on polycondensation of isophthallic / terephthallic acid chlorides with aromatic diamines such as 2-methyl-1,4-benzenediamine (MBDA) or 2-pentadecyl-1,4-benzenediamine (PBDA) and BDA / ODA. The polycondensation was carried out in solution using DMAC as solvent and also by interfacial method. These polymers, some of which are based on CNSL, were characterised by IR spectra, viscosity measurement in concentrated sulfuric acid, solubility and by thermal analysis.