Aromatic polyethers are a relatively new group of polymers in the field of engineering plastics. Systematic studies on their synthesis and properties, including the development of technically useful materials, did not start until 1950. The first technical and commercial success was the production of poly phenylene oxide (PPO) and of the polyether sulphone during the years 1960-1967. The aromatic polyethers are amorphous, transparent materials with $T_g$ in range 150-250 $^\circ$C while polyether sulphones and poly(ether ketone)s (PEK) or poly(ether ether ketone)s (PEEK) may be crystalline with melting point up to 420 $^\circ$C or amorphous with $T_g$ values upto 230 $^\circ$C. The crystalline PEK or PEEKs may possess high-distortion temperatures (HDT) as high as their melting points in particular when they were annealed or reinforced by glass and carbon fibers. Carbon fiber reinforced PEK or PEEK show good mechanical properties, which may be superior to steel and aluminium alloys on the basis of the specific weight. Poly(ether sulphone)s have found good application for membrane constructions, whereas aromatic polyethers are useful as thermo stable engineering plastics, as resins for high performance composites, as high temperature adhesive and as basic material for the production of membranes.

2.2.0 Types of polyether:-

1) Poly(phenylene oxide)s PPO  
2) Poly(ether sulphone)s PESF  
3) Poly(ether ketone)s PEK  
4) Poly(arylene ether)s PAE  
5) Special (polyether)s PE

1) Poly(phenylene oxide)s:-

The PPO polymers were prepared in various ways. Two versatile strategies were reported for the synthesis of m/p-linked polyphenylenes oxides.

a) The oxidative couplings by polycondensation of phenols  
b) The dehydrohalogenations of halogenated phenols

![Chemical Reaction Equation]
Although the reaction scheme of both condensation processes looks quite different at first glance, they have in common that the reaction mechanism involves radicals as active species, in both cases.

For the dehydrohalogenations of halophenols two different approaches were published
i) Polycondensation of alkali metal salts in the presence of an oxidizing reagent such as Cu$_2$O or Fe$_3$O complexes and
ii) Thermal polycondensation of heavy metal salts, in particular lead or silver salts. This method was first reported$^1$ in 1911.

Dehydrohalogenations of halophenols with aqueous alkali solutions potassium ferricyanide or PbO$_2$ as redox initiators$^{2,3}$. When 4-bromo 2, 6 dimethyl phenols was treated with KOH / H$_2$O / benzene and potassium ferricyanide yields upto 92% and intrinsic viscosities upto 0.58 dL/g were found. Linear structure of polyether or low degree of branching was reported.

c) Numerous copolyethers with a blocky sequence were prepared by coupling either mono functional poly (phenylene oxide)s containing one OH group or difunctional poly(phenylene oxide)s with two OH groups to various di-or multifunctional reagents, (e.g. phosgene) or oligomers or polymers with a different chain structure e.g. Triblock Copolymer.
2) Poly(ether sulphone)s:-

In addition to poly(dimethyl phenylene oxide) (PPO), poly(ether sulphone)s are the oldest class of aromatic polyether that have been commercialized successfully. They have useful properties such as high thermo stability, good chemical stability, insensitivity to hydrolysis and oxidation, high glass transition temperatures and solubility in numerous organic solvents. Their properties are partially the result of a good balance between ether and sulphone. The sulphone groups impart a high dipole moment and reduced flexibility, thereby enhancing the glass transition temperature. The ether improves the flexibility in analogy to their role in poly (ether imide)s. The random or regular sequence of bond angle (109 for sulphone and 125 for ether groups) prevents crystallization.

Synthesis Method for poly(ether sulphone)s:-

The methods of polysulfonylation are,

i) Polycondensation of diphenyl ether with aromatic bisulfonyl chlorides or polycondensation of 4- phenoxy benzyl sulfonyl chloride\(^4\).\(^7\).

ii) Polycondensation based on nucleophilic substitution of activated haloaromatics e. g. condensation of potassium salt of diphenols with 4, 4’ -dichloro diphenyl sulphone in an inert aprotic solvent.

Polycondensation in polar aprotic solvents have the advantage that both monomers and polyether sulphone are soluble in the reaction medium so that rapid and high conversions take place.
3) Poly(ether ketone)s :-

A characteristic difference between PES and PEK is the tendency of latter class of polymers to crystallize. The ability to crystallize has a strong influence on the reaction condition of the synthetic procedure and also on mechanical properties such as heat-distortion temperature.

**Synthesis Method for poly(ether ketone)s:-**

i) Fridel-Crafts polyacylation

Monomer containing acid chloride and /or phenoxy groups can be condensed in the presence of lewis acids such as AlCl₃ or BF₃. When these polycondensation are conducted in normal Fridel-Craft solvents such as carbon disulfide, dichloromethane or nitrobenzene, crystallization and precipitation of the oligomers may prevent the formation of high molecular weight polymers.

When polycondensation is conducted in HF (with BF₃ as catalyst), which is good solvent for almost all poly(ether ketone)s high molecular weight poly(ether ketone)s are obtainable that allow casting of tough films.

![Fridel-Crafts polyacylation reaction](image)

**ii) Synthesis by nucleophilic substitution:-**

The technically most successful strategy for the synthesis of poly(ether ketone)s is the polycondensation of diphenols alkali salts with dichloro or difluoroketones. The first experiment conducted with 4, 4'-dichloro or 4, 4'-difluorobenzophenone in DMSO demonstrated that dichloroketone is not reactive enough to yield high MW polymers.
When the activating effect of the two keto groups are combined in one monomer, as is true for the dichloro ketone (a) and (b). Condensation in DMSO yield poly(ether ketone)s with inherent viscosities in the range 0.6-1.0 dL/g.

![Chemical structures](image)

(a)  
(b)

4) Poly(arylene ether)s :-

Poly(arylene ether)s are well recognized high performance engineering thermoplastics. These materials have outstanding physical properties including high modulus, toughness, high thermal stability and chemical resistance. Poly(arylene ether)s are very useful in microelectronics as insulating material and are also used as membrane materials for gas separation. Poly(arylene ether)s are prepared by the step growth polymerization of activated arylhalo or dinitro monomers with bisphenoxides.

It is well known that both sulphone and ketone groups are very effective in activating aryl halides towards nucleophilic displacement Heterocyclic ring have been also used as activating groups to produce high molecular weight poly(arylene ether)s.
5) Fully aromatic polyether (Special polyether)s :-

The nitrile group is a strong electron withdrawing substituent and activates neighboring nitro groups / halogen groups so that nucleophilic substitution became feasible. The first described syntheses of poly(ether nitrile)s is based on the polycondensation of 2,4 or 2,6 –dinitro benzonitrile with alkali salts of various diphenols\textsuperscript{17,18}. The dichloro benzonitrile are more easily accessible than the corresponding dinitro compounds and the risk of side reactions is lower so that higher reaction temperatures may be utilized. It is not clear whether dinitro or dihalo benzonitrile give higher MW when reacted under identical conditions\textsuperscript{19,20}.

When polycondensation is conducted in the presence of aminophenol, telechelic oligomers with aromatic amino end group are obtained. They are useful for synthesis of multi block copolymers\textsuperscript{21}. 
2.4 Applications of PEEKs:-

The uses of PEEK cover virtually every industrial area, principally due to the combination of excellent thermal, chemical, mechanical and electrically easy processing. The wide range of PEEK have been produced or formulated to meet special requirements of easy melt flow (low viscosity-resin grades), high mechanical strength (fibre-reinforced grades), improved bearing properties, antistatic properties etc. The key application areas of PEEK and selection criteria are listed in **Table. 2.1**

**Table. 2.1 Applications of PEEKs**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Area</th>
<th>Principal criteria a</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Aerospace</td>
<td>1-3, 7, 8, 10</td>
<td>Missile connectors and randomes</td>
</tr>
<tr>
<td>2</td>
<td>Electrical</td>
<td>1, 3, 5, 7, 9</td>
<td>Cable insulation</td>
</tr>
<tr>
<td>3</td>
<td>Oil industry</td>
<td>1, 5-7</td>
<td>Data logging tools</td>
</tr>
<tr>
<td>4</td>
<td>Fluid handling</td>
<td>2, 5, 7, 10, 11</td>
<td>Acid pipelines, pump, valve parts</td>
</tr>
<tr>
<td>5</td>
<td>Bearing</td>
<td>1, 2, 5-7, 11</td>
<td>Brush bearings, thrust washers</td>
</tr>
<tr>
<td>6</td>
<td>Film</td>
<td>1, 2, 5, 7</td>
<td>Flexible circuit boards</td>
</tr>
<tr>
<td>7</td>
<td>Monofilament</td>
<td>2, 5-7, 9-11</td>
<td>Woven mat, papermaking, machinery</td>
</tr>
<tr>
<td>8</td>
<td>Coatings</td>
<td>1, 5, 7-11</td>
<td>Centrifuge components, coating, sensor</td>
</tr>
<tr>
<td>9</td>
<td>Automotive</td>
<td>1, 5-7, 11</td>
<td>Piston, skirt</td>
</tr>
<tr>
<td>10</td>
<td>Nuclear</td>
<td>3, 4, 9</td>
<td>Cable, switchgear</td>
</tr>
</tbody>
</table>

“a”:
1) Temperature resistance,
2) Mechanical resistance,
3) Electrical resistance,
4) Radiation resistance,
5) Processability,
6) Fatigue resistance,
7) Chemical resistance,
8) Environmental resistance,
9) Cut through resistance,
10) Water resistance,
11) Abrasion resistance.
2A.10 Introduction:

Poly(ether ether ketone), PEEK is an important class of industrial plastic materials developed in the 1980s which have been widely used in the various fields due to their advanced properties. Because of rigidity of imide ring, polyimides (PI) possess high thermal resistance, high tensile strength and high modules. However both PEEK and PI have limited processability and solubility in common organic solvent, therefore attempts have been made to improve processability, various functional groups have been introduced into their backbones or branched chains.

Introduction of rigid imide rings into the PEEK backbones through copolymerization could resist the inner rotations in the polymers chains, which might be an effective way to further increase the thermal stabilities of PEEK. Further in order to impart processability it was thought that, introduction of linear long alkyl flexible- C\textsubscript{15} groups may increase solubility of these modified polymers in common organic solvents.

Thus the present section describes the synthesis of new aromatic bisphenol with imide units and flexible long alkyl –C\textsubscript{15} pendant groups and its spectral characterization. Further it reports synthesis of a series of PEEK polymers from bisphenol-A, novel pendant C-15 alkyl chain containing diimide bisphenol and 4, 4’-difluorobenzophenone through copolymerization.

The purpose of investigation is an attempt to improve some properties of the PEEK polymers containing imide in main chain and pendant C-15 alkyl chain as side groups.

2A.2.0 Experimental:

2A.2.1 Materials:

1. Potassium carbonate was dried at 180\textdegree\mathrm{C} for 10 h.
2. DMSO was dried over molecular sieves and distilled under reduced pressure.
3. DMF was dried by azeotropic distillation with toluene and then distilled under reduced pressure.
4. PMDA was purified by crystallization from acetic anhydride and then subsequent vacuum sublimation.
5. Toluene was dried over metallic sodium and fractionally distilled.
6. 4, 4’-Difluorobenzophenone (Spectrochem) was used as received.
2A.2.2 Synthesis of monomer:-

2.2.1 Synthesis of 4-Amino -3-pentadecyl phenol, (4-Amino tetrahydro anacardol)

4ATHA:--

1) Cashew nut shell liquid (CNSL):-

   The refined cashew nut shell liquid was used throughout the work of present investigation. Specifications for cashew nut 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: 0.20% (max)
   5) Iodine Value: 234.0
   6) Polymerization test: a) Gel time 10 min and 6 sec, b) Oven test (viscosity) 10.21 cp

2) 3- Pentadecenyl phenol (Anacardol):-

   Raw commercial cashew nut shell liquid (heat extracted) (900g) was distilled from a 2 liter round bottom flask, under vacuum. The flask was slowly heated till the initial frothing subsided and distillate was collected between 190-200 / 2-4 mm of Hg. Yield-450 g (50 %).
   BP :190-200 C /2 mm

The elemental analysis calculated for C<sub>21</sub>H<sub>32</sub>O: C 83.80; H 10.56 %
   Found: C 83.94; H 10.76 %

3) Pentadecyl phenol (Tetra hydro anacardol) (THA):-

   Cardanol (anacardol), 300 g dissolved in ethanol 600 mL was hydrogenated at 70 C in a 2 lit autoclave under hydrogen pressure 600 psi in the presence of Raney nickel 3-5 g catalyst, which was prepared, according to the W-2 method. When no more absorption was noticed the reaction was stopped, the product filtered and solvent distilled out. Crystallization from petroleum ether (40-60 C) gave white waxy solid 3-pentadecyl phenol.
   Yield-270 g (90%)
   MP: 50-51 C.

4) 4-Amino -3-pentadecyl phenol:--

   3-Pentadecyl phenol 7.5 g (0.025 mole), NaOH 3.9 g (0.0687 mole) and 95% ethyl alcohol 50 mL were placed in one liter 3 neck round bottom flask fitted with a stirrer, thermometer and reflux condenser and cooled to -5 C. To this diazonium salt, prepared as below, was added.

   In 250 mL beaker sulphanilic acid 2.5 g, water 50 mL were placed and to this anhydrous Na<sub>2</sub>CO<sub>3</sub> 2.65 g, was added stirring with glass rod till effervescence disappear.
The mixture was warmed to get clear solution and it was then cooled to 0 °C. In another beaker sodium nitrite (NaNO₂) 3.7 g solution made in water 10 mL was cool to 0 °C. Then sodium nitrite solution was added to sulphanilic acid solution stirred and this mixed solution was immediately added to beaker containing conc. HCl 50.5 mL in 30 g ice. Light pink solid precipitated out. It was allowed to settle and liquid was drain out slowly leaving solid behind. To this salt 50 mL cold ethanol was added to get suspension. The resulting red-dye solution was stirred for 2 h in ice bath and then stirred at room temperature for 1 h.

The red solution was heated to 60-65 °C with stirring and a solution of sodium dithionite (11.25 g in 25 mL water) was added dropwise over a period of 20 min. Color of reaction mixture slowly changed from dark red to pale tan, indicating completion of reduction. A solution of glacial acetic acid 4 mL in water 30 mL was added and refluxed for another 1 h. The reduced solution was cooled, when crude 4-amino 3-pentadecyl phenol separated. The product was filtered off and washed with plenty of water till filtrate became colorless and the product was recrystallized from ethanol.

Yield- 5 g (67%).

MP. 105-106°C

The elemental analysis calculated for C₂₁H₃₇NO: C 78.77; H 11.82; N 04.33 %

Found: C 78.94; H 11.67; N 04.38 %

2.2.2 Synthesis of N, N’-Bis (4-hydroxy 2-pentadecyl phenyl) pyromellitimide (HPI) (I):-

PMDA 0.218 g (1 mmol), 4ATHA 0.638 g (2 mmol) and DMF 15 mL were placed in a dry three necked 100 mL round bottom flask equipped with a magnetic stirrer, an oil bath, a reflux condenser, a nitrogen gas inlet and a thermowell. The reaction mixture was stirred at room temperature for 0.5 h. 25 mL dry toluene was added and then heated to reflux under the nitrogen gas flow at 120 °C for 5 h. Toluene was used to remove water produced in polycondensation. After removing the calculated amount of water produced, toluene was distilled out; the reaction temperature was raised to 140 °C and kept for 6 h. Then the reaction mixture was cooled to room temperature, poured in water. The solid produced was filtered, thoroughly washed with hot water and then with hexane. The product was dried at 80 °C for 10 h under vacuum. Purification of HPI was performed by washing with hot absolute ethanol (3x 40 mL) and recrystallization of the residue from a mixture of THF and methanol (50:50).

Yield- 0.765 g (93.29%).

MP. 193-194°C

The elemental analysis calculated for C₁₅H₇₂N₂O₆: C- 76.09; H- 08.78; N-03.41 %

Found: C-76.64; H- 09.09; N-03.04 %

2A.2.3 Synthesis of the polymer (BPAPI-2) :-

To a dry three necked 100 mL round bottom flask equipped with a magnetic stirrer, an oil bath, a reflux condenser, a nitrogen gas inlet and a thermowell bisphenol-A 0.216 g (0.75 mmol), (I) 0.205 g (0.25 mmol) 4, 4’ -difluorobenzophenone 0.275 g (1 mmol), K₂CO₃ 0.276 g (2 mmol), dry DMSO 5mL, and dry toluene 15 mL were charged and stirred at 140 °C for 4 h. Then toluene was distilled out, the reaction mixture was
heated at 160 °C for 6 h, cooled to room temperature and then poured into distilled water. Precipitated polymer BPAPI-2 was filtered, washed with hot water and dried under vacuum at 80 °C for 6 h. Yield - 0.550 g (96 %).

By using similar procedure BPAPI-1 and BPAPI-3 to 5 were synthesized.

2A.3.0 Results and discussion:-

The PEEK is a semicrystalline polymer first marketed by ICI. It has a glass transition temperature \((T_g)\) of 145 °C and a melting temperature \((Tm)\) of 345 °C. It has become one of the most attractive polymer materials widely used in aerospace electronics and nuclear industrial because of its excellent resistance to heat, wear and chemical as well as friction reduction and good mechanical properties\(^{12}\).

In the present work synthesis of a new bisphenol monomer HPI (I) from 4-ATHA and PMDA were undertaken and it was used as building block for PEEK. Copolymerization is an effective approach to the synthesis of new polymer materials, which could enhance the properties of the homopolymers and produce various polymer materials with new structure. Therefore a series of PEEKs polymers through copolymerization was prepared from (I), BPA and DFB.

2A.3.1 Monomer synthesis and characterization:-

The novel N, N’–bis (4-hydroxy 2-pentadecyl phenyl) pyromellitimide (HPI) (I) was synthesized by nucleophilic substitution condensation of PMDA and 4ATHA in the DMF / toluene solvent system as shown in (Scheme 2A.1, 2A.2). The structure of the HPI monomer was confirmed by elemental analysis, IR, and NMR spectroscopy.

Elemental analysis of (I) for C, H, and N was in good agreement, with theoretical values.
Scheme 2A.1. Synthesis of 4-amino-3-pentadecylphenol (4-ATHA) from CSNL
Scheme 2A.2. Synthesis of N, N’–Bis (4-hydroxy 2-pentadecyl phenyl) pyromellitimide (HPI) (I)
FTIR:-

The FTIR spectrum of (I) (Fig. 2A.1) showed characteristic absorption bands at 1770, 1720, (imide-I), 1384 (imide-II), 1103 (imide III) and 715 cm\(^{-1}\) (imide IV). The absence of bands at 1670-1650 (amide I) and 1530-1520 cm\(^{-1}\) (amide II), 1410, 1312 and 885 cm\(^{-1}\) in the spectrum indicated the complete imidization of intermediate (amic acid). The bands at the 1616, 1582 and 1500 cm\(^{-1}\) are for aromatic moiety; where as phenolic hydroxy group appeared as broad absorption at 3560 to 3222 cm\(^{-1}\).

Fig. 2A.1. FTIR spectrum (KBr) of N, N’–Bis (4-hydroxy 2-pentadecyl phenyl) pyromellitimide (HPI) (I)
$^1$H NMR:–

The $^1$H NMR spectrum of (I) (Fig 2A.2) supported the structure proposed. Aromatic protons appeared in the range of 6.2 to 9.0, where in proton of PMDA moiety appeared at 8.95 ppm as a singlet (2H). The signals at 6.5 to 7.4 ppm were assignable to aromatic protons of phenolic ring. Signals at 0.8 to 1.53 ppm were due to aliphatic alkyl group (-C$_{15}$H$_{31}$); of which the signal (triplet) at 0.85 ppm was due to terminal -CH$_3$ and signal at 1.51 ppm was due to benzylic protons. Other (-CH$_2$)$_{13}$ protons appeared at 1.2 ppm. The signal at 4.95 ppm was assigned to hydroxyl protons.

Fig. 2A.2. $^1$H NMR spectrum of N, N’-Bis (4-hydroxy 2-pentadecyl phenyl) pyromellitimide (HPI) (I)
$^{13}$C NMR:

The $^{13}$C NMR spectrum of (I) (Fig. 2A.3) indicated nine signals for imide carbonyl and aromatic carbons in the range 113.3-167.1 ppm, aliphatic carbon due to pentadecyl substituents appeared in range 14-33 ppm. Only one signal for imide CO at 167.1 ppm indicated that all carbonyls were equivalent and carbonyl due to -CONH and –COOH groups were absent suggesting complete imidization of intermediate (amic acid).

![13C NMR Spectrum](image)

**Fig. 2A.3.** $^{13}$C NMR Spectrum N, N’-Bis (4-hydroxy 2-pentadecyl phenyl) pyromellitimide (HPI) (I)
DEPT $^{13}$C NMR:-

DEPT $^{13}$C NMR spectrum of (I) (Fig 2A.4) also confirmed the structure. Only four methine carbons (-CH-), (125.3, 122.70, 114 and 113.30 ppm) appeared as downside signals; whereas the five quaternary carbons were absent. Among the carbon signals due to aliphatic pentadecyl substituents; -CH$_3$ was distinct downside at 14.13 ppm, whereas benzylic -CH$_2$ and (-CH$_2$ -)$_3$ appeared at 33.30, 31.90, 29.67, 28.59, 26.48 and 22.69 ppm.

![DEPT $^{13}$C NMR spectrum](image)

Fig. 2A.4. DEPT $^{13}$C NMR spectrum of N, N’–Bis (4-hydroxy 2-pentadecyl phenyl) pyromellitimide (HPI) (I)

2A.3.2 Polymer synthesis and characterization:-

Novel PEEK polymer was obtained when stoichiometric amounts of HPI (I) and DBF were polycondensed in dry DMSO. K$_2$CO$_3$ was used as the salifying reagent and toluene was used to azeotropically distill out the water produced during the reaction.
Similarly numbers of new Co-PEEK polymers were obtained through polymerization of DFB and various mol % ratios (I) and BPA (Scheme-2A.3).

$$\begin{align*}
(X) \text{HO-} & \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{OH} + (100-X) \text{HO-} \begin{array}{c} \text{N} \\ \text{N} \end{array} \text{R} \text{R} \text{O} \text{O} \text{O} \text{O} \text{R} \text{R} \\
+ (100) \text{F-C=O-C-} \text{F}
\end{align*}$$

$$\xrightarrow{\Delta}$$

DMSO / $\text{K}_2\text{CO}_3$ / dry Toluene

$$\begin{align*}
\text{O-} \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{O-C=O} / (100-X) \\
\text{R = C}_{15}\text{H}_{31}
\end{align*}$$

$$\begin{align*}
\text{PEEK-BPAPI :} & 1 & 2 & 3 & 4 & 5 \\
X & 100 & 75 & 50 & 25 & 0
\end{align*}$$

Scheme 2A.3. Synthesis of PEEK-BPAPI from [BPA+HPI (I)] and DFB
Inherent viscosity:-

Inherent viscosity and % yield data on polymers from HPI (I) is presented in (Table-2A-1). All polymers were obtained in good yields. The inherent viscosity of polymers ranged from 0.45 to 0.65 dL/g in NMP indicating the formation of moderate to high molecular weight polymers.

Table 2A.1. Synthesis of BPAPI\(^{(a)}\) from [BPA+HPI (I)]\(^{c}\) and 4, 4’-difluorobenzophenone

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Diols (mol %)</th>
<th>Yield (%)</th>
<th>(\eta_{\text{inh}})(^{b}) (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPAPI -1</td>
<td>100 00</td>
<td>97</td>
<td>0.65</td>
</tr>
<tr>
<td>BPAPI -2</td>
<td>75 25</td>
<td>97</td>
<td>0.46</td>
</tr>
<tr>
<td>BPAPI -3</td>
<td>50 50</td>
<td>96</td>
<td>0.56</td>
</tr>
<tr>
<td>BPAPI -4</td>
<td>25 75</td>
<td>97</td>
<td>0.45</td>
</tr>
<tr>
<td>BPAPI -5</td>
<td>00 100</td>
<td>96</td>
<td>0.49</td>
</tr>
</tbody>
</table>

\(a\) Polymerization was carried out with 1mmol each of [BPA+HPI (I)] and DFB.

\(b\) Measured at concentration of 0.5 g/dL in NMP at 30 ± 0.1°C.

\(c\) BPA=bisphenol-A and HPI (I)=N, N’-Bis (4-hydroxy 2-pentadecyl phenyl) pyromellitimide.

FTIR of polymers:-

FTIR of BPAPI-3 and BPAPI-5 showed characteristic bands at 1780, 1720 (imide-I), 1370 (imide-II), 1120 (imide III) and 720 cm\(^{-1}\) (imide IV) indicating incorporation of the structural imide moiety from (I). Polymers showed the absorption bands at 1716, 1235 cm\(^{-1}\) corresponding to ketone (-CO-) and ether (-C-O-C-) vibration respectively. Absorption bands at 2970 and 2830 cm\(^{-1}\) were assigned to -CH\(_2\) and -CH\(_3\), vibration of aliphatic CH stretching, of -C\(_{15}\)H\(_{31}\) pendant group.

FTIR spectrum of control BPAPI-1 derived from only BPA, showed absorption bands at 2968, 1716 and 1235 cm\(^{-1}\) which corresponded to vibrations of aliphatic CH of -CH\(_3\) group, ketone and ether linkages respectively. Absorption peaks at 1780, 1370, 1120 and 720 cm\(^{-1}\) were absent as PEEK-BPAPI-1 did not contain imide bisphenol (I).
Fig. 2A.5. FTIR spectrum (KBr) of BPAPI-1

Fig. 2A.6. FTIR spectrum (KBr) of BPAPI-3
Fig. 2A.7. FTIR spectrum of BPAPI-5
Solubility of polymers:

The solubility of the polymers is represented in (Table 2A.2). It was expected that the polymers containing higher % of (I) would show good solubility in organic solvent due to pendant alkyl groups. However these PEEKS containing pendant C-15 alkyl also contained rigid heterocyclic imide rings. Therefore imide heterocyclic groups containing PEEKS showed limited solubility probably due to presence of rigid imide moieties in main chain polymer and contribution of imide structures over weighed the effect of pendant alkyl groups. BPAPI-2 to 4 were soluble in a polar aprotic solvent (NMP), THF completely, and in hot m-Cresol this is partly due to copolymerization effect and presence of BPA moiety. Copolymer BPAPI-2 containing only 25% (I) was soluble in DMAc also in addition to NMP and THF. The PEEK based on BPA was soluble in DMAc, DMSO, NMP, even dissolved in DCM, THF, CHCl₃ and pyridine.

Table 2A.2:- Solubility of BPAPI from [BPA+HPI (I)] and 4, 4’-difluorobenzophenone

<table>
<thead>
<tr>
<th>Polymer →</th>
<th>BPAPI-1</th>
<th>BPAPI-2</th>
<th>BPAPI-3</th>
<th>BPAPI-4</th>
<th>BPAPI-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent ↓</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMF</td>
<td>++</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>DMAc</td>
<td>++</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>DMSO</td>
<td>++</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>NMP</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>++</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>+</td>
</tr>
<tr>
<td>THF</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>--</td>
</tr>
<tr>
<td>pyridine</td>
<td>++</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>--</td>
</tr>
<tr>
<td>DCM</td>
<td>++</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>+</td>
</tr>
<tr>
<td>Conc. H₂SO₄</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

Soluble at R.T. ++ Soluble on heating +
Partly soluble + - Insoluble –

Thermal analysis of polymers: - [TGA, DSC]

Thermal behavior of polymers was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

The DSC curves (Fig. 2A.8) illustrate the T₉ of the BPAPI-1 to BPAPI-5 from HPI (I) and the copolymers. The T₉ of the PEEK copolymers are in the range of 146 to 248°C. The glass transition temperature of the copolymer, increased with increase in the content of HPI (I), but there is simultaneous plasticizing effect of long C-15 alkyl chain. The copolymerization broke the ordered arrangement of the backbones, which caused the T₉ of the copolymers lying between the homopolymers.
Fig. 2A.8. DSC thermograms of BPAPI-1 to BPAPI-5

The thermogravimetric curves of BPAPI-1 to BPAPI-5 are given in (Fig.2A.9), whereas the data about $T_i$, $T_{10}$ is given in (Table 2A.3). The temperatures of 10% weight loss were in the range 360 to 470°C. Initial decomposition temperatures ranged 320 to 412°C. The stability of the copolymer increased with the increase in content of imide rings, at the same time pendant alkyl groups helped in lowering the processing temperature.
Fig. 2A.9. TGA thermograms of BPAPI-1 to BPAPI-5

Table 2A.3. Thermal analysis of BPAPI\textsuperscript{a} polymers from [BPA+HPI (I)] and 4, 4’-difluorobenzophenone

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Temperature for various % Decomposition (°C)</th>
<th>Residual wt. (%) at 900 °C</th>
<th>(T_g) (°C)\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T_i)\textsuperscript{b}</td>
<td>(T_{10})\textsuperscript{c}</td>
<td>(T_{\text{max}})\textsuperscript{d}</td>
</tr>
<tr>
<td>BPAPI – 1</td>
<td>412</td>
<td>470</td>
<td>530</td>
</tr>
<tr>
<td>BPAPI – 2</td>
<td>390</td>
<td>410</td>
<td>490</td>
</tr>
<tr>
<td>BPAPI – 3</td>
<td>350</td>
<td>370</td>
<td>499</td>
</tr>
<tr>
<td>BPAPI – 4</td>
<td>355</td>
<td>365</td>
<td>420</td>
</tr>
<tr>
<td>BPAPI – 5</td>
<td>320</td>
<td>360</td>
<td>470</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Thermogravimetric analysis at a heating rate of 10 °C/min under nitrogen.
\textsuperscript{b} Temperature at which initial loss of mass was observed.
\textsuperscript{c} Temperature at which 10 % weight loss was observed.
\textsuperscript{d} Temperature at which “maximum rate of weight loss” was observed.
\textsuperscript{e} Determined by DSC.
Crystalinity of the polymers:-[XRD]

The XRD pattern of the PEEK and Co-PEEK polymers from (I) is presented in Fig. 2A.10. All the polymers exhibited partially crystalline nature; the insertion of rigid heterocyclic imide rings into the repeating units of polymer resulted in a significant increase in the crystalline nature of the polymers and the polymers exhibited overall semicrystalline behavior.

Fig. 2A.10. XRD curves of BPAPI-1 to BPAPI-5

2A.4.0 Summary and conclusions:-

Based on results presented, following summary and conclusions have been drawn.

1. Synthesis of new N, N’–Bis (4-hydroxy 2-pentadecyl phenyl) pyromellitimide (HPI) (I) was successfully accomplished and it was characterized by elemental analysis, FTIR and NMR techniques.

2. A series of PEEK-BPAPI polymers has synthesized from HPI (I), bisphenol-A and 4, 4’-difluorobenzophenone.
3. Inherent viscosity values of the polymers were in the range of 0.45 to 0.65 dL/g indicating built up of a moderate to high molecular weights.

4. PEEK derived from BPA and many of the copolymers have soluble in polar aprotic solvents and in organic solvents; due to randomness imparted by copolymerization.

5. The $T_g$ of PEEK polymers in the range of 146 to 248 °C and was found depend on of BPA/HPI contents.

6. Thermal stability of PEEK polymers was evaluated by TGA under nitrogen atmosphere and all the polymers showed no weight loss below 320 °C.

7. The polymers exhibited partially crystalline nature.
Chapter-2.Section 2B

2B.10 Introduction:

Poly(ether ether ketone)s are important high performance engineering thermoplastics with favorable combination of physical, chemical and mechanical properties. To increase their thermal stability and solubility in common organic solvent these polymers can be modified by introduction of appropriate flexible / functional groups in main chain or as a pendant side chain.\(^{36a,b}\)

As discussed in section 2A, in order to combine properties of both PEEKs and PI, we thought to prepare new aromatic diimide-diols from alkyl substituted aminophenol and dianhydride (BTDA). Section 2A deals with bisphenol derived from PMDA and that work was extended by adding one more ketone group in a dianhydride. This might be an effective way to increase the thermal stabilities of PEEK, whereas introduction of flexible groups in main chain and side chain might be an effective way to increase the processability of PEEK.\(^{37-42}\)

Thus the present section describes the synthesis of new aromatic bisphenol with ketone, imide units and flexible long alkyl –C\(_{15}\) pendant groups and its spectral characterization. Further it reports synthesis of a series of PEEK polymers from bisphenol-A, novel ketone containing diimide bisphenol and 4, 4’-difluorobenzophenone through copolymerization.

These polymers were characterized by inherent viscosity, FTIR, thermal properties, XRD and solubility tests. The purpose of investigation is an attempt to improve some properties.

2B.2.0 Experimental:

2B.2.1 Materials

1. Potassium carbonate was dried at 180 °C for 10 h.
2. BTDA was purified by crystallization from acetic anhydride.
3. DMF was purified by azeotropic distillation with toluene to remove traces of water; and then distilled under reduced pressure.
4. Toluene was dried over metallic sodium and fractionally distilled.
5. DMSO was dried over molecular sieves and distilled under reduced pressure.
6. 4, 4’-Difluorobenzophenone (Spectrochem) was used as received.

2B.2.2 Synthesis of N, N’-Bis (4-hydroxy 2-pentadecyl phenyl) 3, 3’, 4, 4’-benzophenone tetracarboxylicimide (HBI) (II):

BTDA 0.322 g (1 mmol), 4ATHA 0.638 g (2 mmol) and DMF 15 mL were placed a dry three necked 100 mL round bottom flask equipped with a magnetic stirrer, an oil bath, a reflux condenser, a nitrogen gas inlet and a thermowell. The reaction mixture was stirred at room temperature for 0.5 h, 25 mL dry toluene was added and then heated to reflux under the nitrogen gas flow at 120 °C for 5 h. Toluene was used to remove water produced in polycondensation. After removing the calculated amount of water produced, toluene was distilled out; the reaction temperature was raised to 140 °C.
and kept for 6 h. Then the reaction mixture was cooled to room temperature, poured in water. The solid produced was filtered, thoroughly washed with hot water and then with hexane. The product was dried at 80 °C for 10 h under vacuum. Purification of HBI was performed by washing with hot absolute ethanol (3x 40 mL) and recrystallization of the residue from a mixture of THF and methanol (50:50).
Yield- 0.795 g (94.29 %).
MP. 199-202 °C.

The elemental analysis calculated for C_{59}H_{76}N_{2}O_{7}: C 76.62; H 8.22; N 3.03 %, Found: C 76.50; H 8.44; N 3.18 %

2B.2.3 Synthesis of the Polymer (BPABI-2)

To a dry three necked 100 mL round bottom flask equipped with a magnetic stirrer, an oil bath, a reflux condenser, a nitrogen gas inlet and a thermowell bisphenol-A 0.216 g (0.75 mmol), (II) 0.231 (0.25 mmol), 4, 4’-difluorobenzophenone 0.275 g (1 mmol), K_{2}CO_{3} 0.276 g (2 mmol), dry DMSO 5 mL, and dry toluene 15 mL were charged and stirred at 140 °C for 4 h. Then toluene was distilled out, the reaction mixture was heated at 160 °C for 6 h, cooled to room temperature and then poured into distilled water. Precipitated polymer BPABI-2 was filtered washed with hot water and dried under vacuum at 80 °C for 6 h.
Yield - 0.550 g (96 %).

By using similar procedure BPABI-1 and BPABI-3 to BPABI-5 were synthesized.

2B.3.0 Results and discussion:-

To enhance the thermal stabilities of PEEKs various functional groups have been introduced into their backbones. Copolymerization is one of the effective approaches to the synthesis of polymer with enhanced properties due to new structure.

Hence, in the present work synthesis of a new bisphenol monomer HBI (II) with ketone diimide in the main chain and pendant C-15 alkyl group was performed. It was used to prepare new PEEK by reacting with DFB. Some copolymers were also prepared from DFB and a mixture of HBI (II) and BPA.

2B.3.1 Monomer synthesis and characterization:-

The novel N, N’-bis (4-hydroxy 2-pentadecyl phenyl) 3, 3’, 4, 4’-benzophenone tetracarboxylicimide (HBI) (II) was synthesized by nucleophilic substitution condensation of BTDA and 4ATHA in the DMF / toluene solvent system, (Scheme 2B.1). The structure of the bisphenol monomer was confirmed by the elemental analysis, IR, and NMR [H1 and 13C] spectroscopy.

Elemental analysis of (II) for C, H, and N was in good agreement, with theoretical values.
Scheme 2B.1. Synthesis of N, N’-Bis (4-hydroxy 2-pentadecyl phenyl 3, 3’, 4, 4’-benzophenone tetracarboxylicimide (HBI) (II))
FTIR:-

The FTIR spectrum of (II) (Fig. 2B.1) showed characteristic absorption bands at 1778, 1722, (imide-I), 1393 (imide-II), 1162 (imide- III) and 733 cm\(^{-1}\) (imide- IV). The band at 1622 cm\(^{-1}\) indicated presence of ketone group.

The absence of bands at 1670-1650 (amide I), 1530-1520 (amide II), 1410, 1310 and 885 cm\(^{-1}\) in spectrum indicated the complete imidization. The bands observed at the 1616, 1543 and 1507 cm\(^{-1}\) were due to aromatic moiety; whereas phenolic hydroxy group appeared as broad absorption band at 3560 to 3222 cm\(^{-1}\).

![FTIR spectrum (KBr) of N, N'-Bis (4-hydroxy 2-pentadecyl phenyl) 3, 3', 4, 4'-benzophenone tetracarboxylicimide (HBI) (II)](image)

Fig. 2B.1. FTIR spectrum (KBr) of N, N’-Bis (4-hydroxy 2-pentadecyl phenyl) 3, 3’, 4, 4’-benzophenone tetracarboxylicimide (HBI) (II)
$^1$H NMR:-

In $^1$H NMR spectrum of (II) (Fig. 2B.2), aromatic protons of phenolic ring appeared in the range 6.2 to 7.2, and protons of BTDA moiety appeared at 8.11 to 8.29 ppm. Aliphatic protons of $-\text{C}_{15}\text{H}_{31}$ substituents showed peaks at 0.8 to 1.53 ppm of which the signal (triplet) at 0.88 was due to terminal $-\text{CH}_3$ and signal at 1.53 ppm was due to benzylic protons. Other-$($CH$_2$)$_{13}$- protons appeared as broad signal at 1.20 ppm. The signal at 3.9 ppm was assigned to hydroxyl protons.

Fig. 2B.2. $^1$H NMR spectrum of N, N’ -Bis (4-hydroxy 2-pentadecyl phenyl) 3, 3’, 4, 4’-benzophenone tetracarboxylicimide (HBI) (II)
The $^{13}$C NMR spectrum of (II) (Fig. 2B.3) showed fourteen signals for aromatic and carbonyl carbons in the range 113.3-196, whereas aliphatic carbons due to pentadecyl substituents appeared in the range 14-33 ppm. Only one signal for imide CO at 167 ppm indicated that all imide carbonyls were equivalent and carbonyl due to -CONH and -COOH groups were absent suggesting complete imidization of intermediate (amic acid). Ketone carbonyl due to BTDA moiety appeared at 196 ppm.

Fig. 2B.3. $^{13}$C NMR spectrum of N, N’-Bis (4-hydroxy 2-pentadecyl phenyl) 3, 3’, 4, 4’-benzophenone tetracarboxylicimide (HBI) (II)
DEPT $^{13}$C NMR:-

In the DEPT $^{13}$C NMR spectrum of (II) ([Fig. 2B.4]) only six methine carbons (-CH) signals were downside (133.0, 128.0, 127.0, 122.7, 114.0 and 113.3 ppm) and remaining eight quaternary carbons (196, 167, 143.1, 135.7, 133.7 133.0, 131.7, and 127.3 ppm) were absent. Among the pentadecyl substituents -CH$_3$ was distinct downside at 14.13 ppm, whereas benzylic –CH$_2$ and (-CH$_2$)$_{13}$ appeared at 33.2, 31.54, 29.67, 28.54, 26.48, 22.7 ppm as distinct upside peaks.

![Fig. 2B.4. $^{13}$C NMR (DEPT) spectrum of N, N'-Bis (4-hydroxy 2-pentadecyl phenyl) 3, 3', 4, 4'-benzophenone tetracarboxylicimide (HBI) (II)](image)

**2B.3.2 Polymers synthesis and characterization:-**

A series of polymers were obtained through ternary co polymerization of 4, 4’-difluorobenzophenone and various mol ratios of two bisphenols i.e. HBI (II) and BPA, by nucleophilic substitution reactions in DMSO. K$_2$CO$_3$ was used as the salifying reagent and toluene was used to azeotropically remove the water produced during the polycondensation. The synthetic route is shown in (Scheme-2B.2).
Scheme 2B.2. Synthesis of PEEK-BPABI from [BPA+HBI (II)] and DFB
Inherent viscosity of Polymers:–

Inherent viscosity and % yield data on polymers from HBI (II) is presented in (Table-2B.1). All polymers were obtained in good yields. The inherent viscosity of polymers ranged from in 0.32 to 0.65 dL/g in NMP. This indicated the formation of moderate to high molecular weight polymers.

Table 2B.1. Synthesis of BPABI \(^{(a)}\) from \([BPA+HBI (II)]^{(c)}\) and 4, 4’-difluorobenzophenone (DFB)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Diols (mol %)</th>
<th>Yield (%)</th>
<th>(\eta_{inh}^{b}) (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BPA</td>
<td>HBI</td>
<td></td>
</tr>
<tr>
<td>BPABI-1</td>
<td>100</td>
<td>00</td>
<td>97</td>
</tr>
<tr>
<td>BPABI-2</td>
<td>75</td>
<td>25</td>
<td>96</td>
</tr>
<tr>
<td>BPABI-3</td>
<td>50</td>
<td>50</td>
<td>96</td>
</tr>
<tr>
<td>BPABI-4</td>
<td>25</td>
<td>75</td>
<td>97</td>
</tr>
<tr>
<td>BPABI-5</td>
<td>00</td>
<td>100</td>
<td>96</td>
</tr>
</tbody>
</table>

a) Polymerization was carried out with 1mmol each of [BPA+ HBI (II)] and DBF.
b) Measured at concentration of 0.5 g/dL in NMP 30 ± 0.1°C.
c) BPA=Bisphenol-A and HBI (II) =N, N’ -Bis (4-hydroxy 2- pentadecyl phenyl) 3, 3,’ 4, 4’-benzophenone tetracarboxylicimide.

FTIR of polymers:–

FTIR spectra of polymers from (II) **BPABI-2 to 5** showed characteristic absorption bands at 1716, 1235 indicating ketone and ether functional groups and at 1780 and 1720 (imide-I), 1370 (imide II), 1120 (imide III), and 720 cm\(^{-1}\) (imide IV) corresponding to imide heterocycle in polymer chain. Absorption bands at 2968, 1363 cm\(^{-1}\) corresponded to stretching vibration and bending vibration of aliphatic CH from pendant -C\(_{15}\)H\(_{31}\) alkyl group in BPABI-2 to 5; where as for BPABI-1 these absorption bands were due to -CH\(_{3}\) group
Fig. 2B.5. FTIR spectrum (KBr) of BPABI-3

Fig. 2B.6. FTIR spectrum (KBr) of BPABI-5
Solubility of polymers:-

The solubility of the polymers was tested in various solvents and is given in (Table 2B.2). It was expected heterocyclic that the polymers containing higher mol % of (II) would show good solubility in organic solvent due to pendant alkyl groups. However PEEK containing pendant C-15 alkyl and imide heterocyclic groups showed limited solubility probably due to presence of rigid imide moieties in main chain polymer and contribution of imide structures over weighed the effect of pendant alkyl groups. The BPABI-5 derived from (II) was partly soluble in NMP; whereas polymer BPABI-1 showed good solubility in NMP, DMAc, DMSO and in common organic solvent like THF, pyridine and conc. H$_2$SO$_4$.

PEEK and Co-PEEKs based on (II), BPABI-3 to 5 were insoluble in most of the solvents; except BPABI-2 which dissolved in NMP and m-Cresol. Thus BTDA derived rigid imide heterocyclic units in the polymer chain contributed to insolubility of polymers. All polymers dissolved in Conc. H$_2$SO$_4$.

Table 2B.2 Solubility of BPABI from [BPA+HBI (II)] and 4, 4’ - difluorobenzophenone:-

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent ↓</th>
<th>BPABI-1</th>
<th>BPABI-2</th>
<th>BPABI-3</th>
<th>BPABI-4</th>
<th>BPABI-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>DMAc</td>
<td>++</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>DMSO</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>NMP</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>--</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>THF</td>
<td>++</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>pyridine</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>--</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>+</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>DCM</td>
<td>+</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Conc. H$_2$SO$_4$</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

Soluble at R.T. ++ Soluble on heating +
Partly soluble + - Insoluble –

Thermal analysis of polymers: - [TGA, DSC]

Thermal behavior of polymers was evaluated by means of thermo gravimetric and differential scanning calorimetry.

The DSC curves (Fig. 2B.7) illustrates, the T$_g$ of the PEEK from HBI (II). T$_g$ of the PEEK copolymers are in the range of 146 to 248 °C and T$_g$s increased with the increase in the content of the HBI (II). The copolymerization of PEEK broke the ordered arrangement of the backbones, which caused the T$_g$ of the copolymers lying between the homopolymers.
The thermal data such as glass transition temperature ($T_g$), initial decomposition temperature ($T_i$), 10 % weight loss temperature ($T_{10}$) and residual weight at 900 °C is given in (Table 2B.3). The thermogravimetric curves of BPABI-1 to BPABI-5 are given in (Fig. 2B.8). Initial decomposition temperatures were in the range 370 to 412 °C. The temperatures of 10 % weight loss were in the range 410 to 472 °C. The stability of the copolymers increased with the increase in content of imide rings.
Fig. 2B.8. TGA thermograms of BPABI-1 to BPABI-5

Table 2B.3. Thermal analysis of BPABIa polymers from [BPA+HBI (II)] and 4, 4’ - difluorobenzophenone

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Temperature for various %</th>
<th>Residual wt. (%) at 900°C</th>
<th>Tg (°C)e</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_i^b</td>
<td>T_{10}^c</td>
<td>T_{max}^d</td>
</tr>
<tr>
<td>BPABI – 1</td>
<td>412</td>
<td>472</td>
<td>530</td>
</tr>
<tr>
<td>BPABI – 2</td>
<td>370</td>
<td>451</td>
<td>460</td>
</tr>
<tr>
<td>BPABI – 3</td>
<td>390</td>
<td>436</td>
<td>479</td>
</tr>
<tr>
<td>BPABI – 4</td>
<td>385</td>
<td>410</td>
<td>478</td>
</tr>
<tr>
<td>BPABI – 5</td>
<td>390</td>
<td>445</td>
<td>487</td>
</tr>
</tbody>
</table>

a) Thermogravimetric analysis at a heating rate of 10°C/min under nitrogen.
b) Temperature at which initial loss of mass was observed.
c) Temperature at which 10% weight loss was observed.
d) Temperature at which “maximum rate of weight loss” was observed.
e) Determined by DSC.
Crystalinity of the polymers: - [XRD]

The XRD pattern of the PEEK and Co-PEEK polymers from (II) is presented in (Fig. 2B.9). All the polymers exhibited partially crystalline nature; the insertion of rigid heterocyclic imide rings into the repeating units of polymer resulted in a significant increase in the crystalline nature of the polymers and the polymers exhibited overall semicrystalline behavior.

![XRD curves of BPABI-1 to BPABI-5](image)

**Fig. 2B.9. XRD curves of BPABI-1 to BPABI-5**

**2B.4 Summary and conclusions:-**

Based on results presented, following summary and conclusions have been drawn.

1. Synthesis of new N, N’-Bis (4’-hydroxy 2’-pentadecyl phenyl) 3, 3’, 4, 4’-benzophonone tetracarboxylimide (HBI) (II) was successfully accomplished and it was characterized by elemental analysis, FTIR and NMR techniques.

2. A series of PEEK polymers (BPABI-1 to BPABI-5) was synthesized by copolymerization of the HBI (II) and / or bisphenol-A and 4, 4’-difluorobenzophenone.
3. Viscosity values of polymers were in the range of 0.32 dL/g to 0.65 dL/g indicating built up of a moderately to high molecular weight.

4. Many of copolymers were soluble in aprotic solvents and in common organic solvent.

5. The $T_g$ of PEEK polymers was in the range of 146 to 288 $^\circ$C and $T_g$'s found depend on of BPA / HBI contents in these polymers.

6. Thermal stability of PEEK polymers was evaluated by TGA under nitrogen atmosphere and all the polymers showed no weight loss below 370 $^\circ$C.

7. The polymers exhibited partially crystalline nature.
Chapter 2. Section 2C

2C.1.0 Introduction:

PEEKs are an important class of industrial plastic materials developed in the 1980s which have been widely used in the field of traffic, aeronautics, astronautics and medicines etc due to their advance mechanical properties, solvent resistance, insulation properties, and flame retardation^43, 44^.

Polyamides are one of the most successful classes of high performance polymers due to their high thermal and chemical resistance as well as high modulus. Kevlar and Nomex are commercially marketed as high performances polymers usually in fiber form. Aromatic polyamides exhibit excellent mechanical strength and thermal stability and are suitable for composite. Some applications of these polyamides have restricted been reduced by high crystalinity and limited solubility in common organic solvents^45, 46^.

Therefore the preparation of soluble and / or processable polyamides has been a major research interest. To accomplish this goal, many attempts have been made, namely synthetic modification of flexible bridging linkages distortion of molecular symmetry by meta or ortho catenated aromatic units and introduction of bulky groups into polymer chain^47-49^.

The purpose of investigation is an attempt to improve some properties of the PEEK polymers. The copolymerization is an effective approach to the synthesis of polymers which enhance the properties of the homopolymers.

Thus the present section describes the synthesis of new aromatic bisphenol with preformed amide units and its spectral characterization. Synthesis of PEEK and Co-PEEKs from 4, 4’-difluorobenzophenone and various moles of Bisphenol-A and HIA (III) through copolymerization, is also described.

2C.2.0 Experimental:

2C.2.1 Materials:

1. NMP was refluxed over barium oxide for 4h, distilled under vacuum and stored over Linde type 4Å molecular sieves.
2. DMSO were dried over molecular sieves and distilled under reduced pressure before use.
3. DMF was purified by azeotropic distillation with toluene to remove traces of water; then distilled under reduced pressure and stored over Linde type 4Å molecular sieves.
4. Toluene was dried over metallic sodium and fractionally distilled.
5. 4, 4’-Difluorobenzophenone (Spectrochem) was used as received.
6. 3-Aminophenol was purified by crystallization from dry toluene.
7. Potassium carbonate was dried at 180 °C for 10 h.
8. Hexane was refluxed over phosphorous pentaoxide for 4h, distilled and stored over Linde type 4Å molecular sieves.
2C.2.2 Synthesis of Bis (3-hydroxy phenyl) isophthalamide (HIA) (III):-

A 100 mL three necked round bottom flask equipped with a magnetic needle, a nitrogen gas inlet, a thermowell and an air condenser with calcium chloride guard tube, was flame dried and cooled under stream of nitrogen gas. 3-aminophenol 0.218 g (2 mmol), dry NMP 4 mL, dry triethyl amine 0.28 mL were charged in to RBF and stirred at room temperature for 10 minute and cooled to 0 °C for 30 minutes. A solution of terephthaloyl chloride 0.203g (1mmol) in NMP 1mL was added drop wise over a period of 20 minutes. The reaction mixture was stirred at 0 °C for another 30 minutes and starring was continued at 25 °C for one day. The reaction mixture was poured into ice cold water; precipitated solid was filtered, washed with cold water and by hexane. Product was crystallized from ethanol and dried under vacuum at 80 °C for 6 h.
Yield- 0.82 g. (93.29%).
MP.322-325 °C.

The elemental analysis calculated for C_{20}H_{16}N_{2}O_{4}: C 68.96; H 04.59; N 08.05%
Found: C 68.95; H 04.65; N 08.04%

2C.2.3 Synthesis of polymer: - (BPAIA-2)

To a dry three necked 100 mL round bottom flask equipped with a magnetic stirrer, an oil bath, a reflux condenser, a nitrogen gas inlet and a thermowell, bisphenol-A 0.216 g (0.75 mmol), (III) 0.087 g (0.25 mmol), 4, 4’difluorobenzophenone 0.275 g (1 mmol), K₂CO₃ 0.276 g (2 mmol), dry DMSO 5mL, and dry toluene 15 mL were added and stirred and stirred at 140 °C for 4 h. Then toluene was distilled out, the reaction mixture was heated at 160 °C for 6 h, cooled to room temperature and then poured into distilled water. Precipitated polymer BPAPI-2 was filtered, washed with hot water and dried under vacuum at 80 °C for 6 h.
Yield – 0.467g (96.99 %).

By using similar procedure BPAIA-1 and BPAIA-3 to 5 were synthesized.

2C.3.0 Results and discussion:-

PEEKs have been synthesized via electrophilic or nucleophilic polycondensation in an effort to improve their properties. To enhance the thermal stabilities of PEEKs, various functional groups have been introduced into their backbones and branch chains.

Hence, in the present work synthesis of a preformed amide group containing new bisphenol monomer HIA (III) from 3-aminophenol and isophthaloyl chloride (IPC) and PEEK polymers through copolymerization are required.

2C.3.1 Monomer Synthesis and Characterization:-

A novel bis (4-hydroxy phenyl) isophthalamide (HIA) (III) was synthesized by condensation of IPC with 3-aminophenol in NMP solvent at 0°C in presence of triethylamine as shown in (Scheme 2C.1).

The composition and structure of the monomer (III) were confirmed by IR, NMR, Mass and elemental analysis.
Elemental analysis of (III) for C, H, and N was in good agreement, with theoretical values.

Scheme 2C.1. Synthesis of Bis (3-hydroxy) isophthalamide (HIA) (III)
FTIR:-

The FTIR spectrum of (III) (Fig. 2C.1) showed characteristic absorption bands at 3308 cm\(^{-1}\) (-NH groups), 1645-1620 (amide-I), 1562-1520 (amide II), 1402, 1305 and 885 cm\(^{-1}\) indicating presence of amide linkages. The bands observed at the 1616, 1562 and 1500 cm\(^{-1}\) were for aromatic moiety, whereas phenolic hydroxy group (-OH phenolic) appeared at 3560 to 3222 cm\(^{-1}\).

Fig. 2C.1. FTIR spectrum (KBr) of Bis (3-hydroxy phenyl) isophthalamide (HIA) (III)
$^1$H NMR:

The $^1$H-NMR spectrum of (III) (Fig. 2C.2) supported the structure proposed. Aromatic protons appeared in the range of 6.2 to 8.2 ppm. The hydroxy group (-OH) showed signal at 8.64 ppm, while amide (–NH) showed signal at 4.90 ppm.

![NMR spectrum of Bis (3-hydroxy phenyl) isophthalamide (HIA) (III)](attachment:image)

Fig. 2C.2. $^1$H NMR spectrum of Bis (3-hydroxy phenyl) isophthalamide (HIA) (III)
$^{13}$C NMR:

The $^{13}$C NMR spectrum of (III) (Fig. 2C.3) showed eleven of signals corresponding to eleven different types of carbons. The carbonyl (CO) carbon appeared at 164.8 ppm, whereas quaternary carbon showed signals at 158.7, 137, 134.5 ppm, the -CH carbons appeared at 130.9, 130.4, 129, 125, 114, 111.5 and 105.5 ppm.

Fig. 2C.3. $^{13}$C NMR spectrum of Bis (3-hydroxy phenyl) isophthalamide (HIA) (III)
DEPT $^{13}\text{C}$ NMR:-

DEPT $^{13}\text{C}$ NMR spectrum of (III) also confirmed the structure of (III) (Fig. 2C.4). In the region of low field only seven methine (-CH-) signals appeared at (130.9, 130.4, 129, 125, 114, 111.5 and 105.5 ppm), while signals for all quaternary carbons were absent.

![DEPT $^{13}\text{C}$ NMR spectrum of Bis (3-hydroxy phenyl) isophthalamide (HIA) (III)](image)

Fig. 2C.4. $^{13}\text{C}$ NMR (DEPT) spectrum of Bis (3-hydroxy phenyl) isophthalamide (HIA) (III)
Mass spectrum:-

Fig. 2C.5. Mass spectrum of Bis (3-hydroxy phenyl) isophthalamide (HIA) (III)

The mass spectrum showed molecular ion peak at 348. (Fig. 2C.5)

2C.3.2 Polymers synthesis and characterization:-

PEEK polymers were obtained through copolymerization of 4, 4’-difluorobenzophenone and various mol % ratios of bisphenols i.e. BPA and HIA (III), by nucleophilic substitution reactions in DMSO. K$_2$CO$_3$ was used as the salifying reagent and toluene was used to azeotropically distill out water produced during the reaction (Scheme 2C.2).
Scheme 2C.2. Synthesis of PEEK-BPAIA from [BPA+HIA (III)] and DFB
Inherent viscosity of Polymers:-

The composition and data on inherent viscosities of PEEKs from HIA (III) is presented in (Table-2C.1). All polymers were obtained in good yields. Inherent viscosity of polymers ranged from 0.26 dL/g to 0.65 dL/g in NMP, indicating moderate to high molecular weight polymers.

### Table 2C.1. Synthesis of BPAIA\(^{\text{(a)}}\) from [BPA+HIA (III)]\(^{\text{(c)}}\) and 4, 4’-difluorobenzophenone

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Diols (mol %)</th>
<th>Yield (%)</th>
<th>(\eta_{\text{inh}})(^{\text{b}}) (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPAIA-1</td>
<td>100 00</td>
<td>97</td>
<td>0.65</td>
</tr>
<tr>
<td>BPAIA-2</td>
<td>75 25</td>
<td>97</td>
<td>0.25</td>
</tr>
<tr>
<td>BPAIA-3</td>
<td>50 50</td>
<td>96</td>
<td>0.28</td>
</tr>
<tr>
<td>BPAIA-4</td>
<td>25 75</td>
<td>97</td>
<td>0.26</td>
</tr>
<tr>
<td>BPAIA-5</td>
<td>00 100</td>
<td>96</td>
<td>0.34</td>
</tr>
</tbody>
</table>

a) Polymerization was carried out with 1mmol each of [BPA + HIA (III)] and DBF.

b) Measured at concentration of 0.5 g/dL in NMP at 30 ± 0.1°C.

c) BPA=bisphenol-A and HIA (III)=Bis (3-hydroxy phenyl) isophthalamide

FTIR of polymers:-

FTIR spectra of polymers BPAIA-3 and BPAIA-5 (Fig. 2C.5) showed characteristic absorption bands at 3300 cm\(^{-1}\) (NH stretching), a sharp band at 1540 cm\(^{-1}\) (characteristic for –NH bending) and 1660 cm\(^{-1}\) (due to C=O in amide group). The absorption band at 3030 cm\(^{-1}\) was characteristic of aromatic CH stretching and absorption band at 1235 cm\(^{-1}\) corresponded to -C-O-C- vibration.

FTIR spectrum of control BPAIA-1 derived from only BPA, showed absorption bands at 2968, 1716 and 1235 cm\(^{-1}\) which corresponded to vibrations of aliphatic CH of -CH\(_3\) group, ketone and ether linkages respectively.
Fig. 2C.6. FTIR spectrum (KBr) of BPAIA-3

Fig. 2C.7. FTIR spectrum (KBr) of BPAIA-5
Solubility of polymers:-

The solubility of the polymers was tested in different solvent and is given in (Table 2C.2). The polymers showed good solubility in NMP and limited solubility in DMF (BPAIA-1, 4 and 5), DMSO (BPAIA-1), in common organic solvent like, CHCl₃, pyridine, (BPAIA-3, 4 and 5), THF (BPAIA-3, 4), DCM (BPAIA-3, 4 and 5) and m-Cresol (BPAIA-4 and 5).

Table 2C.2. Solubility of BPAIA from [BPA+HIA (III)] and 4, 4’ - difluorobenzophenone

<table>
<thead>
<tr>
<th>Polymer→</th>
<th>BPAIA-1</th>
<th>BPAIA-2</th>
<th>BPAIA-3</th>
<th>BPAIA-4</th>
<th>BPAIA-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent ↓</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMP</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>DMAc</td>
<td>++</td>
<td>--</td>
<td>+</td>
<td>++</td>
<td>+-</td>
</tr>
<tr>
<td>pyridine</td>
<td>++</td>
<td>--</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>THF</td>
<td>++</td>
<td>--</td>
<td>+</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>++</td>
<td>--</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>+</td>
<td>--</td>
<td>++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>DMF</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>DCM</td>
<td>++</td>
<td>--</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>DMSO</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Conc. H₂SO₄</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

Soluble at R.T. ++ Soluble on heating + Partly soluble + Insoluble –

Thermal analysis of polymers: - [TGA, DSC]

Thermal behavior of polymers was evaluated by means of thermo gravimetric and differential scanning calorimetry.

The DSC curves (Fig. 2C.8) illustrate the Tₙ of PEEK from HIA (III). The Tₙ of the PEEK polymers are in the range of 146 to 270 °C, Tₙ increased with the increase in the content of the HIA (III). The copolymerization broke the ordered arrangement of the backbones, which caused the Tₙ of the copolymers lying between the homopolymers.
The thermogravimetric curves of BPAIA–1 to BPAIA-5 are given in (Fig. 2C.9), whereas the data about $T_i$, $T_{10}$ is given in (Table 2C.3). The temperatures of 10 % weight loss were all above 454 °C; whereas polymers did not show any weight loss below 316 °C. The stability of the copolymers increased with the increase in content of imide rings.
Fig. 2C.9. TGA thermograms of BPAIA-1 to BPAIA-5

Table 2C.3. Thermal analysis of BPAIA\textsuperscript{a} polymers from [BPA+HIA (III)] and 4, 4’ - difluorobenzophenone

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Temperature for various % Decomposition (\textdegree{}C)</th>
<th>Residual wt. (%) at 900 \textdegree{}C</th>
<th>Tg (\textdegree{}C)\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$\textsuperscript{b}</td>
<td>$T_{10}$\textsuperscript{c}</td>
<td>$T_{\text{max}}$\textsuperscript{d}</td>
</tr>
<tr>
<td>BPAIA – 1</td>
<td>412</td>
<td>470</td>
<td>530</td>
</tr>
<tr>
<td>BPAIA – 2</td>
<td>316</td>
<td>478</td>
<td>533</td>
</tr>
<tr>
<td>BPAIA – 3</td>
<td>320</td>
<td>482</td>
<td>535</td>
</tr>
<tr>
<td>BPAIA – 4</td>
<td>324</td>
<td>479</td>
<td>513</td>
</tr>
<tr>
<td>BPAIA – 5</td>
<td>369</td>
<td>454</td>
<td>476</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Thermogravimetric analysis at a heating rate of 10 \textdegree{}C/min under nitrogen.
\textsuperscript{b} Temperature at which initial loss of mass was observed.
\textsuperscript{c} Temperature at which 10 % weight loss was observed.
\textsuperscript{d} Temperature at which “maximum rate of weight loss” was observed.
\textsuperscript{e} Determined by DSC.
Crystalinity of the polymers: - [XRD]

The XRD pattern of the **BPAIA-1 to BPAIA-5** polymers from (III) is presented in (Fig. 2C.10). All the polymers exhibited partially crystalline nature; introduction of amide groups with meta catenation may have disturbed the chain regularity to some degrees and packing thereby leading to semicrystalline behavior.

![XRD curves of BPAIA–1 to BPAIA-5](image)

**Fig.2C.10 XRD curves of BPAIA–1 to BPAIA-5**

2C.3.0. Summary and Conclusions:-

Based on results presented, following summary and conclusions have been drawn.

1. Synthesis of new bis (3-hydroxy phenyl) isophthalamide (HIA) (III) is successfully accomplished and it was characterized by elemental analysis, FTIR, NMR techniques.

2. A series of PEEK polymers (**BPAIA-1 to BPAIA-5**) was synthesized by copolymerization of the HIA (III), bisphenol-A and 4, 4’-difluorobenzophenone.
3. Inherent viscosity values of polymers were in the range of 0.26 to 0.65 dL/g indicating built up of a moderately to high molecular weight.

4. Many of the copolymers were soluble in polar aprotic solvent and in some organic solvents.

5. The $T_g$ of these amide group containing PEEK polymers were in the range of 146 to 270 $^\circ$C. $T_g$s was found depend on of BPA / HIA contents in the polymer.

6. Thermal stability of PEEK polymers was evaluated by TGA under nitrogen atmosphere and all the polymers showed no weight loss below 316 $^\circ$C.

7. The polymers exhibited partially crystalline nature.
Chapter-2. Section 2D

2D.10 Introduction:-

Poly(ether ketone) and poly(ether ether ketone) are an important class of industrial plastic materials which have been widely used in the various fields due to their advanced properties\textsuperscript{50,51}. However, due to their semicrystalline property, these polymers are insoluble in organic solvents at ambient temperature, except for strong acid. Therefore, they cannot be processed by the casting method and require a high molding temperature due to their high melting temperature (around 340\textdegree C). At the same time, the glass transition temperature (\(T_g\)) of these polymers is low (around 140\textdegree C) which leads to a low dimensional stability. Considerable efforts have been devoted for improving the processability and glass transition temperature (\(T_g\)) of PEEKs. It has been suggested the introduction of heterocyclic moieties, pendant groups, and asymmetry structure onto the molecular chains of PEEKs could improve the processability and / or glass transition temperature (\(T_g\)) and solubility in organic solvents\textsuperscript{52-54}.

To increase their thermal stability and solubility\textsuperscript{55} in common organic solvent, again various functional groups have been introduced into their backbones chains through further copolymerization. Introduction of rigid amide groups into the PEEK backbones through copolymerization could resist the inner rotations in the polymers chains, which might be an effective way to further increase the thermal stabilities of PEEK. Further in order to processability it was thought that, introduction of linear long alkyl flexible C-15 groups may increase solubility of this modified polymers\textsuperscript{56-58}.

Thus the present section describes the synthesis of new aromatic bisphenol with preformed amide units and flexible long alkyl –C\textsubscript{15} pendant groups and its spectral characterization. Further it reports synthesis of a series of PEEK polymers from bisphenol-A, novel alkyl –C\textsubscript{15} pendant group containing diamide bisphenol and 4, 4’-difluorobenzophenone through copolymerization.

The purpose of investigation is an attempt to improve some properties of the PEEK polymers.

2D.2.0 Experimental:-

2D.2.1 Materials:-

1. NMP was refluxed over barium oxide for four h, distilled under vacuum and stored over Linde type 4Å molecular sieves.
2. DMSO was dried over molecular sieves and distilled under reduced pressure.
3. Triethyl amine was dried over Linde type 4Å molecular sieves, then distilled from phosphorous pentaoxide and distillate was stored over Linde type 4Å molecular sieves.
4. Toluene was dried over metallic sodium and fractionally distilled.
5. 4, 4’-Difluorobenzophenone (Spectrochem) was used as received.
6. Potassium carbonate was dried at 180 \textdegree C for 10 h.
6. Hexane was refluxed over phosphorous pentaoxide for 4 h, distilled and stored over Linde type 4Å molecular sieves.

2D.2.2 Synthesis of monomers:-

a) Synthesis of 4ATHA:-
Preparation of 4ATHA is described in Section-2A.2.2

b) Synthesis of Bis (4-hydroxy 2-pentadecyl phenyl) isophthalamide (HPIA) (IV):-

A 100 mL three necked round bottom flask equipped with a magnetic needle, a gas inlet, a thermowell and an air condenser with calcium chloride guard tube, was flame, dried and cooled under stream of nitrogen gas. 4ATHA 0.638 g (2mmol), dry NMP 4 mL and triethyl amine 0.28 mL were placed and stirred at room temperature for 10 minute and cooled to 0°C for 30 minutes. A solution of terephthaloyl chloride 0.203g (1mmol) in 1mL NMP was added drop wise over a period of 20 minutes.

The reaction mixture was stirred at 0°C for another 30 minutes, stalling was continued at 25°C for one day. Reaction mixture was poured into ice water; precipitated solid was filtered, washed with water, followed by hexane. Product was dried and crystallized from ethanol.

Yield- 0.680 g (88.43 %).

MP.135-140°C.

The elemental analysis calculated for C_{50}H_{76}N_{2}O_{4}: C 78.13; H 0.98; N 0.36 %

Found: C 78.15; H 0.68; N 0.36 %

2D.2.3 Synthesis of polymer: - (BPA15IA -2)

To a dry three necked 100 mL round bottom flask equipped with a magnetic stirrer, an oil bath, a reflux condenser, a nitrogen gas inlet and a thermowell bisphenol-A 0.216 g (0.75 mmol), (IV) 0.192 g (0.25 mmol), 4, 4’-difluorobenzophenone 0.218 g (1 mmol), K_{2}CO_{3} 0.276 g (2 mmol), dry DMSO 5mL, and dry toluene 15mL were added and stirred at 140°C for 4 h. Then toluene was distilled out, the reaction mixture was heated at 160°C for 6 h, cooled to room temperature and then poured into distilled water. Precipitated polymer BPAPI-2 was filtered, washed with hot water and dried under vacuum at 80°C for 6 h.

Yield - 0.568 g (96.92 %).

By using similar procedure BPA15IA-1 and BPA15IA-3 to BPA15IA-5 were synthesized.

2D.3.0 Results and discussion:-

To enhance the thermal stabilities and solubility of PEEKs, various functional groups have been introduced into their backbones and side chains. Copolymerization is an effective approach to the synthesis of polymer materials which enhance some of the
properties of the homopolymers and produce various polymeric materials with new structure.

Hence, in the present work synthesis and characterization of a new bisphenol monomer HPIA (IV) with amide groups from 4-ATHA and isophthaloyl chloride (IPC) and further a series of PEEKs from preformed bisphenol-A, 4, 4’-difluorobenzophenone and HPIA (IV) is described.

2D.3.1 Monomer synthesis and characterization:-

The novel Bis (4-hydroxy 2-pentadecyl phenyl) isophthalamide (HPIA) (IV) was synthesized by condensation of IPC with 4-aminophenol in NMP solvent at 0 °C in presence of triethylamine as shown in (Scheme 2D.1).

Scheme 2D.1. Synthesis of Bis (4-hydroxy 2-pentadecyl phenyl) isophthalamide (HPIA) (IV)
The composition and structure of the resulted bisphenol monomer were confirmed by FTIR, NMR, Mass and elemental analysis.

Elemental analysis of (IV) for C, H, and N was in good agreement, with theoretical values.

**FTIR:**

FTIR spectrum of HPIA (IV) (Fig. 2D.1) showed characteristic absorption bands at 3307 cm\(^{-1}\) (-NH groups), 1723-1665 (amide-I), 1530-1520 (amide II), 1410, 1371 and 885 cm\(^{-1}\) indicating presence of amide linkages and absorption band.

The bands at the 1616, 1582 and 1500 cm\(^{-1}\) are for aromatic moiety, where as phenolic hydroxy group (-OH phenolic) appeared as broad absorption at 3560 to 3222 cm\(^{-1}\). Alkyl groups in C-15 appeared at 2925, 2851 cm\(^{-1}\) (C-H stretching).

![Fig. 2D.1. FTIR spectrum of bis (4-hydroxy 2-pentadecyl phenyl) isophthalamide (HPIA) (IV)](image)

The bands at the 1616, 1582 and 1500 cm\(^{-1}\) are for aromatic moiety, where as phenolic hydroxy group (-OH phenolic) appeared as broad absorption at 3560 to 3222 cm\(^{-1}\). Alkyl groups in C-15 appeared at 2925, 2851 cm\(^{-1}\) (C-H stretching).
$^1$H NMR:

The $^1$H-NMR spectrum of (IV) (Fig. 2D.2) supported the structure proposed. Aromatic protons appeared in the range 6.2 to 8.2 ppm. The signals at 6.53 to 7.42 were assignable to protons substituted aromatic ring. Aliphatic protons of -C$_{15}$H$_{31}$ alkyl appeared at 1.17 to 2.50 ppm of which the signal (triplet) at 0.86 was due to terminal-CH$_3$ protons. Other -(CH$_2$)$_{13}$ which on benzylic –CH$_2$- protons appeared at 1.2 ppm. The signal at 8.85 ppm was assigned to -NH group proton. The signal at 4.90 ppm was assigned to hydroxyl group.

Fig. 2D.2. $^1$H NMR spectrum of Bis (4-hydroxy 2-pentadecyl phenyl) isophthalamide (HPIA) (IV)
$^{13}$C NMR:-

The $^{13}$C NMR spectrum of (IV) (Fig. 2D.3) indicated eighteen of signals of which eleven carbon peaks were corresponding to eleven different types of amide carbonyl and aromatic carbons. The carbonyl (CO) carbon appeared at 164.8 ppm and aromatic carbons appeared from 125.1 to 153.9.0 ppm. The signals for –CH- aromatic in pentadecyl substituted aromatic ring appeared from 113.3 to 130.0 ppm.

Fig. 2D.3. $^{13}$C NMR spectrum of Bis (4-hydroxy 2-pentadecyl phenyl) isophthalamide (HPIA) (IV)
DEPT $^{13}$C:-

DEPT $^{13}$C NMR spectrum of (IV) (Fig. 2D.4) confirmed the structure of monomer. Only six methine carbons (-CH-) appeared as downside signals downside (113.3 to 130.0 ppm), whereas four quaternary carbons (153.9, 134.3, 131.7, 130.9 ppm) were absent. Among the carbon signals due to aliphatic pentadecyl substituents; -CH$_3$ was distinct downside at in at 14.1 ppm, whereas benzylic –CH$_2$ and -(CH$_2$)$_{13}$ appeared at 31.9, 31.30, 29.7, 27.20, 22.8 ppm.

![Fig. 2D.4. $^{13}$C NMR (DEPT) spectrum of Bis (4-hydroxy 2-pentadecyl phenyl) isophthalamide (HPIA) (IV)](image)

2D.3.2 Polymer synthesis and characterization:-

A series of polymers were obtained through copolymerization of 4, 4'-difluorobenzophenone and various ratios of two bisphenols i.e. BPA and HPIA (IV), by nucleophilic substitution reactions mol in DMSO. K$_2$CO$_3$ was used as the salifying reagent and toluene was used to azeotropically remove the water produced during the polycondensation. The synthetic route is shown in Scheme 2D.2.
Scheme 2D.2. Synthesis of PEEK-BPA15IA from [BPA+HPIA (IV)] and DFB
Inherent viscosity of Polymers:

The composition and data on inherent viscosities of PEEK-BPA15IA from HPIA (IV) are presented in (Table 2D.1). All polymers were obtained in good yields. The inherent viscosity of polymers ranged from 0.57 to 0.81 dL/g in NMP. This indicated formation of high molecular weight polymers.

Table 2D.1. Synthesis of BPA15IA\(^{(a)}\) from [BPA+HPIA (IV)]\(^{(c)}\) and 4, 4’-difluorobenzophenone (DFB)

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Diols mol %</th>
<th>Yield (%)</th>
<th>(\eta_{inh})(^{(b)}) (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA15IA-1</td>
<td>100 00</td>
<td>97</td>
<td>0.65</td>
</tr>
<tr>
<td>BPA15IA-2</td>
<td>75 25</td>
<td>97</td>
<td>0.78</td>
</tr>
<tr>
<td>BPA15IA-3</td>
<td>50 50</td>
<td>96</td>
<td>0.81</td>
</tr>
<tr>
<td>BPA15IA-4</td>
<td>25 75</td>
<td>97</td>
<td>0.58</td>
</tr>
<tr>
<td>BPA15IA-5</td>
<td>00 100</td>
<td>96</td>
<td>0.57</td>
</tr>
</tbody>
</table>

a) Polymerization was carried out with 1 mmol each of [BPA+ HPIA (IV)] and DBF.
b) Measured at concentration of 0.5 g/dL in NMP at 30 ± 0.1°C.
c) BPA=bisphenol-A and HPIA (IV)=Bis (4-hydroxy 2-pentadecyl phenyl) isophthalamide

FTIR of polymers:-

FTIR spectra of polymers BPA15IA-3 and BPA15IA-5, showed characteristic absorption bands at 3300-3250 (-NH stretching), 1700-1645 (amide I, C=O Stretching) 1530-1520 (amide II, interaction of -NH bending and -CN stretching) and band at 1200-1240 cm\(^{-1}\), which confirmed the presence of the amide functional group and ether group respectively. The -OH broad band at 3600 cm\(^{-1}\) was absent, indicated utilization of –OH groups in the formation of polymer. FTIR spectrum of control BPA15IA-1 derived from only BPA, showed absorption bands at 2968, 1716 and 1235 cm\(^{-1}\) which corresponded to vibrations of aliphatic CH of -CH\(_3\) group, ketone and ether linkages respectively.
Fig. 2D.5. FTIR spectrum (KBr) of BPA15IA-3

Fig. 2D.6. FTIR spectrum (KBr) of BPA15IA-5
Fig. 2D.7. $^1$H NMR spectrum of BPA15IA-3

$^1$H NMR spectrum of BPA15IA-3 (Fig. 2D.7) showed peaks in the range 0.80-2.60 ppm due to pentadecyl group, whereas the signal at 1.69 ppm due to −CH$_3$ group in BPA moiety. The aromatic protons of broads signal appeared in the region 6.9 to 8.65 ppm were for aromatic protons of both diphenols and DFB. The signal at 8.19 ppm was due to the proton of amide −NH group.

**Solubility of polymers:**

The composition and data on inherent viscosities of BPA15IA-1 to BPA15IA-5 is represented in (Table 2D.2). Polymers showed good solubility in NMP. Polymers also showed good solubility in common organic solvent like, m-Cresol (BPA15IA-2 to 5), CHCl$_3$, THF, DCM (BPA15IA-1 to 5) and partly in pyridine (BPA15IA-2 to 5) and some copolymers were partially soluble DMSO (BPA15IA-2 to 5). This indicated the polymers are semicrystalline in nature due to presence amide group and flexible ether and alkyl groups in polymer backbone.
Table 2D.2 Solubility of BPA15IA from [BPA+HPIA (IV)] and 4, 4’-difluorobenzophenone

<table>
<thead>
<tr>
<th>Polymer →</th>
<th>BPA15IA-1</th>
<th>BPA15IA-2</th>
<th>BPA15IA-3</th>
<th>BPA15IA-4</th>
<th>BPA15IA-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>THF</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Pyridine</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>DCM</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>DMF</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>DMSO</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>DMAc</td>
<td>++</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Conc. H₂SO₄</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

Soluble at R.T. ++ Soluble on heating +
Partly soluble + - Insoluble –

Thermal analysis of polymers: - [TGA, DSC]

Thermal behavior of polymers was evaluated by means of thermogravimetric and differential scanning calorimetry.

The DSC curves (Fig 2D.8) illustrated the T_ᵣ of the PEEK from HPIA (IV). The glass transition temperature of the PEEK polymer decreased with the increase in the content of the HPIA (IV). BPA15IA-1 to BPA15IA-5 showed clear transition at 146, 97, 81, 74 and 70 °C respectively. This indicated, even though polymers contained amide linkages, the flexible pentadecyl groups, played important role in the lowering the T_ᵣ values. Low T_ᵣ value and high T_i provides a wide window was in polymer processing.
Fig. 2D.8 DSC thermograms of BPA15IA-1 to BPA15IA-5

The thermogravimetric curves of BPA15IA-1 to BPA15IA-5 are given in (Fig. 2D.9). The thermal data such as glass transition temperature ($T_g$), initial decomposition temperature ($T_i$), 10% weight loss temperature ($T_{10}$) and residual weight at 900°C is given in (Table 2D.3). The temperatures of 10% weight loss were in the range 370 to 412°C. The stability of the copolymer increased with the increase in content of amide moiety, i.e. with increased content of HPIA.
Fig. 2D.9 TGA thermograms of BPA15IA-1 to BPA15IA-5

Table 2D.3. Thermal analysis of BPA15IA\textsuperscript{a} polymers from [BPA+HPIA (IV)] and 4, 4\textsuperscript{'}-difluorobenzophenone

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Temperature for Decomposition (T_i) \textsuperscript{b}</th>
<th>Temperature at which 10 % weight loss was observed (T_{10}) \textsuperscript{c}</th>
<th>Temperature at which “maximum rate of weight loss” was observed (T_{\text{max}}) \textsuperscript{d}</th>
<th>Residual wt. (%) at 900 °C</th>
<th>(T_g) (°C)\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA15IA – 1</td>
<td>412</td>
<td>468</td>
<td>530</td>
<td>45</td>
<td>146</td>
</tr>
<tr>
<td>BPA15IA – 2</td>
<td>370</td>
<td>435</td>
<td>485</td>
<td>49</td>
<td>97</td>
</tr>
<tr>
<td>BPA15IA – 3</td>
<td>380</td>
<td>432</td>
<td>475</td>
<td>09</td>
<td>81</td>
</tr>
<tr>
<td>BPA15IA – 4</td>
<td>384</td>
<td>430</td>
<td>478</td>
<td>15</td>
<td>74</td>
</tr>
<tr>
<td>BPA15IA – 5</td>
<td>390</td>
<td>431</td>
<td>474</td>
<td>10</td>
<td>70</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Thermogravimetric analysis at a heating rate of 10 °C/min under nitrogen.
\textsuperscript{b} Temperature at which initial loss of mass was observed.
\textsuperscript{c} Temperature at which 10 \% weight loss was observed.
\textsuperscript{d} Temperature at which “maximum rate of weight loss” was observed.
\textsuperscript{e} Determined by DSC.
Crystalinity of the polymers: - [XRD]

The XRD of polymers BPA15IA-1 to BPA15IA-5 are shown in (Fig. 2D.10). All the polymers exhibited partially crystalline nature. However introduction of various amounts of pendant alkyl moieties in polymer backbone may have disturbed the chain regularity and packing to different levels and therefore % crystallinity varied as the content if (IV) was varied leading to semicrystalline polyamides.

![XRD curves of BPA15IA-1 to BPA15IA-5](image)

**Fig. 2D.10. XRD curves of BPA15IA-1 to BPA15IA-5**

2D. 4.0:- Summary and Conclusions:-

Based on results presented, following summary and conclusions have been drawn.

1. Synthesis of new bis (4-hydroxy 2-pentadecyl phenyl) isophthalamide HPIA (IV) was successfully accomplished and it was characterized by elemental analysis, FTIR, NMR techniques.

2. A series of PEEK polymers (BPA15IA-1 to BPA15IA-5) was synthesized by ternary copolymerization of the HPIA (IV), bisphenol-A and 4, 4’-difluorobenzophenone.

3. Inherent viscosities values of copolymers were in the range of 0.65 to 0.81 dL/g indicating built up of a moderate to high molecular weight.
4. Polymers showed good solubility in NMP and in common organic solvent like Pyridine, CHCl₃, THF, DCM, m-Cresol etc. and some copolymers were partially soluble in DMF and DMSO.

5. The T_g of PEEK polymers were in the range of 70 to 146 °C and depend on ratio of BPA / HPIA contents.

6. Thermal stability of PEEK polymers was evaluated by TGA under nitrogen atmosphere and all the polymers showed no weight loss below 370 °C.

7. The polymers exhibited partially crystalline behavior.
References: