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Synthesis and Characterization of Thermally Stable Photoactive PEEK Polymers

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***ABSTRACT**: Synthesis of a new aromatic PEEKs and Co-PEEKs containing Bis (4-hydroxybenzylidene) cyclopentanone (BHBC) and Bisphenol–A (BPA). The aromatic polyamide was synthesized from condensation of difluorobenzophenone with Bis (4-Hydroxybenzylidene) cyclopentenones (BCP) and Bisphenol–A (BPA) and its equimolar mixture via high temperature polycondensation method. The resulting PEEKs and Co-PEEKs were characterized by inherent viscosity measurement, solubility, FT-IR, thermal properties and XRD. At room temperature all PEEKs were limited soluble in polar aprotic solvents. The PEEKs shows inherent viscosity in the range between 0.25-0.65 dL g^{-1} in H_2SO_4 at 30°C. The PEEKs showed useful levels of thermal stability with glass transition temperature (T_g) in the range of 149-200°C and no 10% weight-loss below 300°C and semi crystalline in nature.*

***KEYWORDS:** Bis (4-Hydroxybenzylidene) cyclopentanone (BCP), Bisphenol–A (BPA), new aromatic PEEKs, Co-PEEKs, solubility, thermal properties, XRD.*

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I. Introduction

Aromatic polyethers are a relatively new group of polymers in the field of engineering plastics. Systematic study 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 ^{0}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 ^{0}C or amorphous with T_g values upto 230 ^{0}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, polyamides 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 [1-26]

II. Experimentals

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. Potassium carbonate was dried at 180 ^{0}C for 10 h.
7. Hexane was refluxed over phosphorous pent oxide for 4h, distilled and stored over Linde type 4Å molecular sieves.

2.2 Measurements:-

Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. FTIR spectra of organic compounds and polymers were recorded as a KBr pellet on a Perkin-Elmer 883 IR spectrophotometer. ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra were recorded on a Bruker NMR spectrophotometer in DMSO-d_6. Elemental Analysis was performed with a Perkin Elmer Model 2400 C, H, N and analyzer. Inherent viscosity measurements were made at polymer concentration of 0.5 g/dL in NMP at 30 ± 0.1°C using suspended level Ubbelhode viscometer. The solubility of polymers was determined at 3 wt % concentration in various solvents at room temperature or on warming if needed. Thermo gravimetric analysis was performed on Perkin- Elmer TGA-7 at a heating rate of 10°C/min. under nitrogen. DSC analysis of the polymers was performed on Rigaku Thermo flux TG 8110 at a heating rate of 10^0C/min. under nitrogen. X-ray diffraction patterns of polymers were obtained on a Rigaku Dmax 2500 X-Ray diffractometer at a tilting rate of 2^0/minute. Dried polymer powder was used for X-ray measurements.

2.3 Synthesis of monomer:-

2.3.1 Synthesis of photoactive Bis (4-Hydroxybenzylidene) cyclopentanone (BHBC):

A photoactive diol was bis (4-Hydroxybenzylidene) cyclopentanone (BHBC) was synthesized using the new method. In this method 48.8 gm (0.4mol) of 4-Hydroxybenzaldehyde and 24.7gm (0.4mol) of boric acid was mixed in a 500 ml round bottom flask. It was cooled to 0^0C in freezing mixture of ice and salt. To this mixture 100 mL concentrated HCl was added drop wise in 1 hour. Reaction mixture was converted in to colored solution at 0^oC. To this mix 19.4 gm (0.2 mol) of cyclopentanone dissolved 50 ml in dried THF was added portion wise for 1hr. with vigorous stirring. After completion of the addition, the reaction was continued for 24 hr at room temp. The mixture was poured into ice water. The precipitated yellow product was filtered and dried. Recrystallization was performed from a methanol / water mix. (1:1V/V) and the product was finally dried at 50^0_C in a vacuum oven for 16 hr. A single product spot was confirmed by thin layer chromatography with ethyl acetate & hexane (3:1 V/V) as eluent.
Yield = 70 %
MP =130^0C.

Reaction-:

Scheme1. Synthesis of BHBC (I).

2.4. Synthesis of polymers (Co-PEEK-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 thermo well, Diol 0.183 g (0.25 mmol), Bisphenol-A 0.228 g (0.75 mmol), 4, 4 -difluorobenzophenone 0.218 g (1 mmol), K_2CO_3 0.276 g (2 mmol), dry DMSO 4 mL, and dry toluene 15 mL were charged and stirred at 140 ^{0}C for 4 h. Then toluene was distilled out, the reaction mixture was heated at 160 ^{0}C for 8h, cooled to room temperature and then poured into distilled water. Precipitated polymer Co-PEEK-2 was filtered, washed with hot water and dried under vacuum at 80 ^{0}C for 6 h.
Yield – 0.529 g (84 %).

By using similar procedure **PEEK- 1, 5 and Co-PEEK-3 to 4** were synthesized.

Scheme.2. PEEK, Co-PEEK using BHBC (I), BPA and DFB

III. Results And Discussion

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

Hence, in the present work synthesis of new bisphenol monomer BHBC (I) from Cyclopentanone, 4-Hydroxybenzaldehyde, THF as solvents, Boric acid and concentrated HCl at 0^0C then room temperature for 24 hrs with starring and PEEK polymers through copolymerization are required.

3.1. Monomer synthesis and characterization:-

New bisphenol monomer BHBC (I) was synthesized from Cyclopentanone, 4-Hydroxybenzaldehyde, THF as solvent , Boric acid and concentrated HCl at 0^0C in ice bath and then room temperature for 24 hrs with starring (**Scheme.1**). The composition and structure of the monomer (I) were confirmed by IR, NMR ^{1}H and ^{13} CMR.

3.1.1. FT-IR spectrum of BHBC:

The FTIR spectrum of BHBC (I) **(Fig.1)** showed characteristic absorption bands at 3297 cm^{-1} (-OH groups), 3109 cm^{-1} (=CH group), 1667 cm^{-1} (CO group), 1562 cm^{-1} aromatic -CH moiety

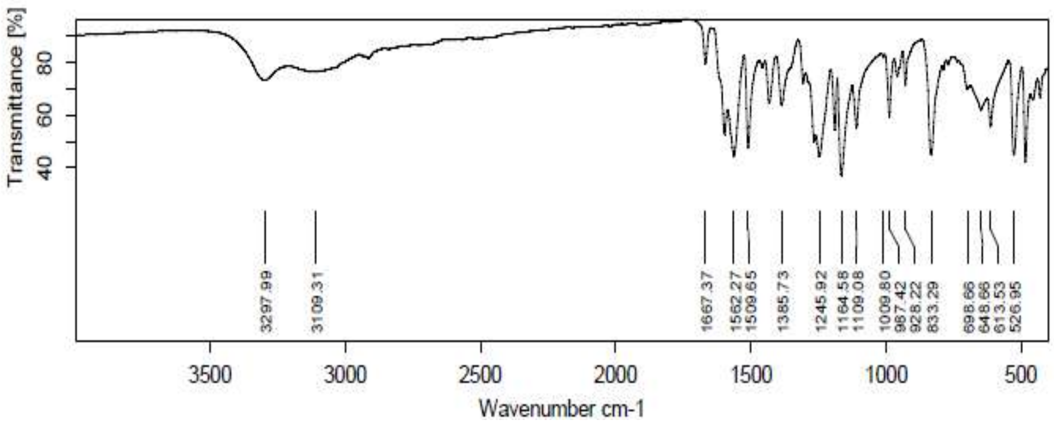

Fig.1 FT-IR spectrum (KBr) of Bis (4-Hydroxybenzylidene) cyclopentanone BHBC (I)

3.1.2. ^{1}H NMR spectrum of BHBC:-

The ^{1}H-NMR spectrum of (I) (**Fig.2**) supported the structure proposed. Hydroxy group (-OH) showed signal at 4.27 ppm, -CH_2- groups of cyclopentanone at 3.92 ppm, Aromatic protons appeared in the range of 6.56 to 7.29 ppm. The aliphatic =CH at 6.56 ppm

3.1.3. ^{13}C NMR spectrum of BHBC:-

The ^{13}C NMR spectrum of (I) (**Fig.3**) showed eight of signals corresponding to eleven different types of carbons. The carbonyl (CO) carbon appeared at (196.09 ppm), where as quaternary carbon showed signals at 159, 135, 127 ppm, the =CH carbons appeared at 133, 115 ppm. The -CH_2 carbons appeared at 26.94 ppm.

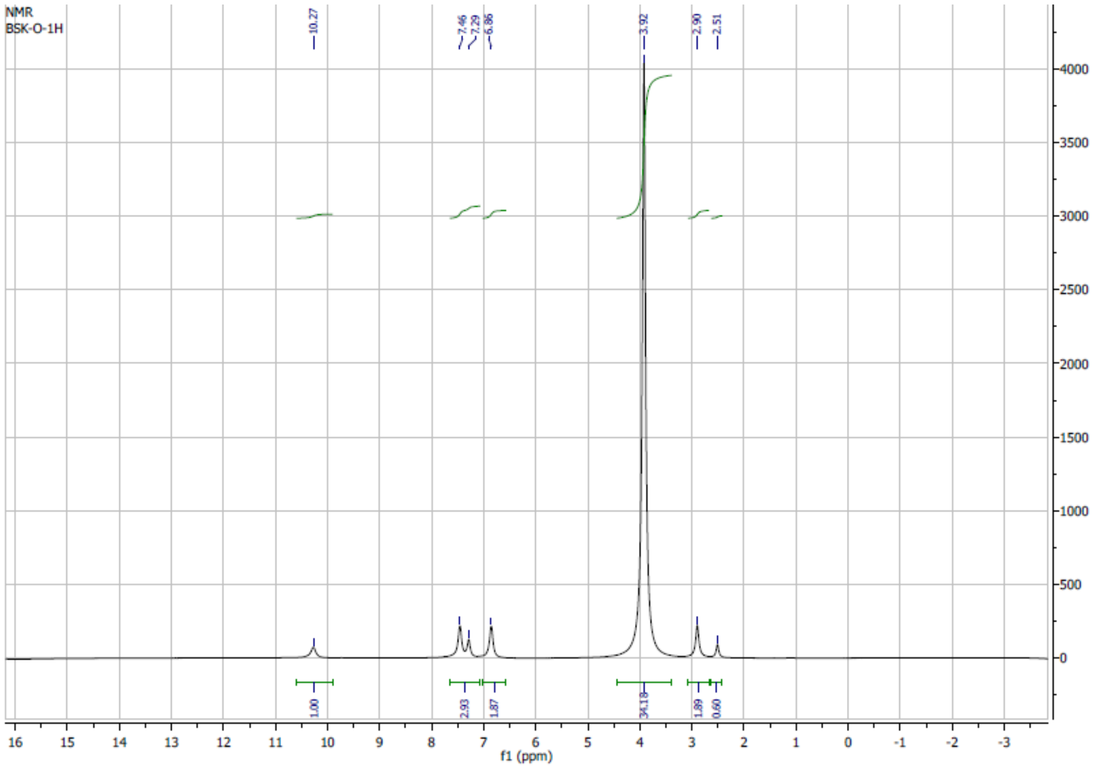

Fig.2. ^{1}H NMR spectrum of Bis (4-Hydroxybenzylidene) cyclopentanone BHBC (I)

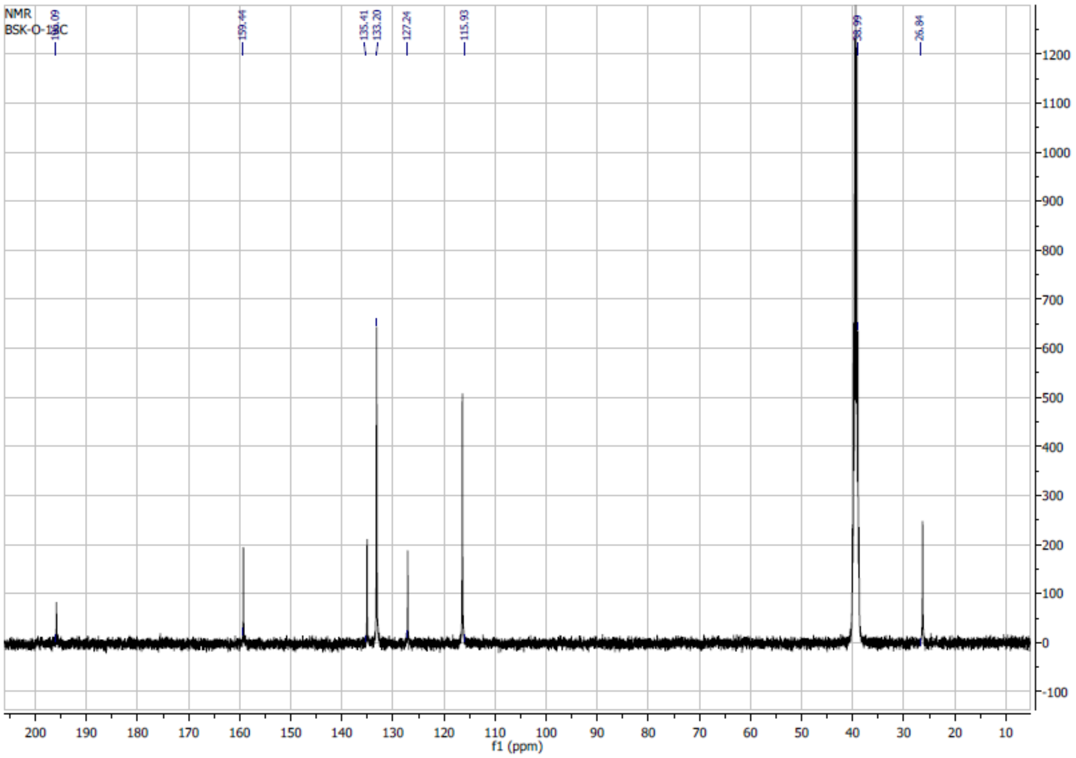

Fig.3. ^{13}C NMR spectrum of Bis (4-Hydroxybenzylidene) cyclopentanone BHBC (I)

3.2. Synthesis and characterization of the polymers:-

PEEK polymers were obtained through copolymerization of 4, 4'- difluorobenzophenone and various mol % ratios of bisphenols i.e. BPA and BHBC (I), by nucleophilic substitution reactions in DMSO. K_2CO_3 was used as the salifying reagent and toluene was used to azeotropically distill out water produced during the reaction (**Scheme .2**).

3.2.1. FTIR spectrum of polymers:- (Co-PEEK-4)

FTIR spectrum of control **PEEK-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.

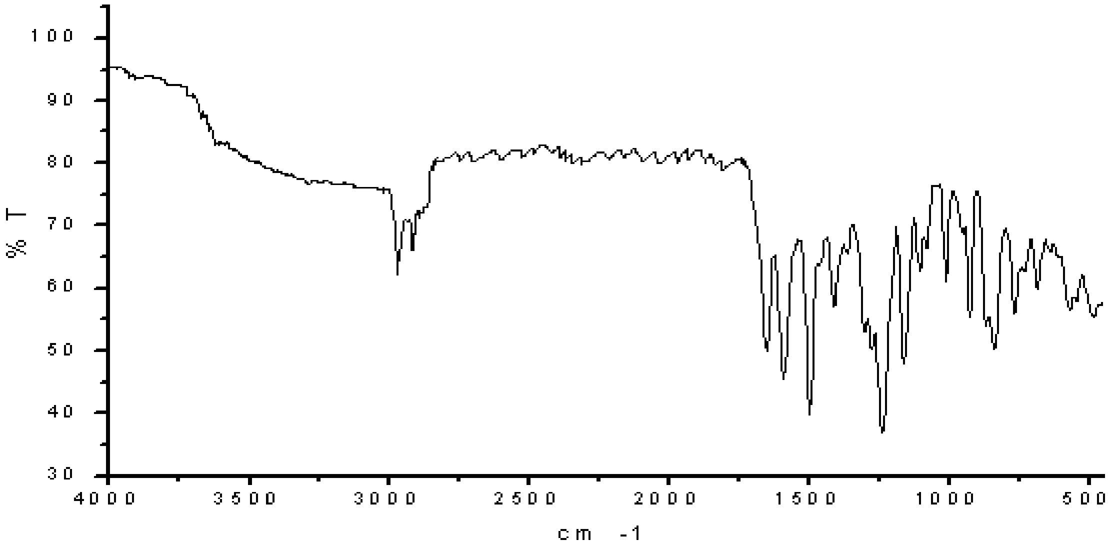

Fig.4. FTIR spectrum (KBr) of Co-PEEK-(P-1)

FTIR spectrum of control Co-PEEK-4 (**Fig.4**) derived from only BPA, BHBC (I), showed absorption bands at 2968, 1716 and 1235 cm^{-1} which corresponded to vibrations of aliphatic -CH group, ketone and ether linkages respectively.

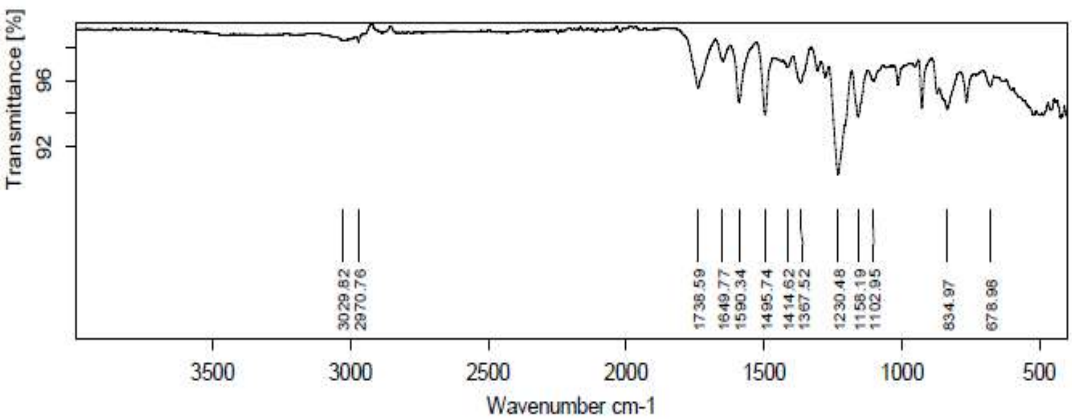

Fig.5. FTIR spectrum (KBr) of Co-PEEK-(P-4)

3.2.2. Inherent Viscosity Polymers:-

The composition and data on inherent viscosities of PEEKs from BHBC (I) is presented in **(Table.1).** All polymers were obtained in good yields. Inherent viscosity of polymers ranged from 0.26 dL/g to 0.65 dL/g in H_2SO_4 indicating moderate to high molecular weight polymers.

Table.1. Synthesis of PEEK $^{(a)}$ from [BPA+BHBC (I)]$^{(c)}$ and 4, 4'-difluorobenzophenone

Polymer Code	Diols (mol %)		Yield (%)	η_{inh}^{b} (dL/g)
	BPA	BHBC		
PEEK (P-1)	100	00	96	0.65
PEEK (P-2)	75	25	97	0.25
PEEK (P-3)	50	50	96	0.28
PEEK (P-4)	25	75	97	0.26
PEEK (P-5)	00	100	96	0.34

a) Polymerization was carried out with 1mmol each of [BPA + BHBC (I)] and DBF.
b) Measured at concentration of 0.5 g/dL in H_2SO_4 at 30 ± 0.1°C.
c) BPA=Bisphenol-A and BHBC (I) = Bis (4-Hydroxybenzylidene) cyclopentanone

3.2.3. Solubility:

The solubility of the polymers was tested in different solvent and is given in **(Table.2).** The polymers showed good solubility in Conc. H_2SO_4 and limited solubility in NMP (**PEEK-1),** DMF (**PEEK-4),** DMSO (**PEEK-2, 3, 4)**, in common organic solvent like, $CHCl_3$ (**PEEK- 3, 4 and 5)**, THF (**PEEK-1)**, DCM (**PEEK-1 and 5)** and m-Cresol (**PEEK-1and 2)** indicating moderate to high molecular weight polymers.

Table.2. Solubility of PEEK from [BPA+ BHBC (I)] and 4, 4' –difluorobenzophenone.

Polymer / Solvent	**PEEK P-1**	**Co-PEEK P-2**	**Co-PEEK P- 3**	**Co-PEEK P-4**	**PEEK P-5**
DMF	+-	--	--	+-	--
m-cresol	++	+-	--	--	--
DMAc	++	- -	+-	+-	--
DMSO	++	+-	+-	+-	--
NMP	++	--	--	--	--
$CHCl_3$	++	--	--	--	--
DCM	++	--	--	--	+h
H_2SO_4	+	++	++	++	++
THF	++	--	--	--	--

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

3.2.4. Thermogravimetric Analysis:

Thermal behaviour of polymers was evaluated by means of thermo gravimetric and differential scanning calorimetry. The thermogravimetric curves of **P-1 to P-5** are given in (**Fig.7**), whereas the data about T_i, T_{10} is given in (**Table.3**). The temperatures of 10 % weight loss were in the range 300 to 470 ^{0}C. Initial decomposition temperatures ranged 399 to 270 ^{0}C. The stability of the copolymer increased with the increase in content of cyclopentanone with conjugation.

Table.3. Thermal analysis of PEEK^a polymers from [BPA+BHBC (I)] and 4, 4' -difluorobenzophenone

PEEK code	T_i(^{o}C)	T_{10}(^{o}C)	T_g(^{o}C)	Residue at 800^{o}C
PEEK (P-1)	399	470	149	30
Co-PEEK (P-2)	235	335	215	48
Co-PEEK (P-3)	235	355	210	45
Co-PEEK (P-4)	280	340	220	45
PEEK (P-5)	270	300	200	30

a) Thermogravimetric analysis at a heating rate of 10^{0}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.

The DSC curves (**Fig.5**) illustrate the T_g of PEEK (P-1 to P-5) from BHBC (I). The T_g of the PEEK polymers were in the range 149-200 ^{0}C. T_g increases with the increase in the content of the BHBC (I). The copolymerization broke the ordered arrangement of the backbones, which caused the Tg of the copolymers lying between the homopolymers.

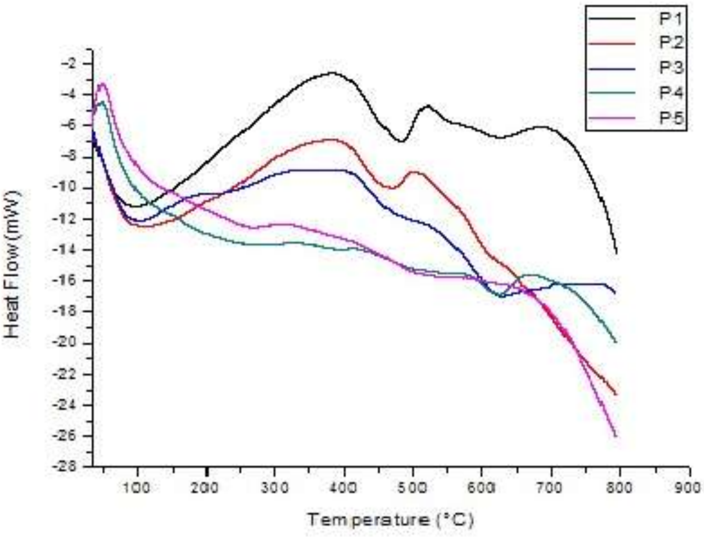

Fig.6. DSC thermograms of PEEK and Co-PEEK (P-1 to P-5)

3.2.5. XRD pattern:

The XRD pattern of the **PEEK (P-1 to P-5)** polymers is represented in (**Fig.8).** All the polymers exhibited partially crystalline nature; this result could be explained in terms of the polymer backbone which hindered packing of the polymer chains and decreased the intermolecular forces, subsequently causing a decrease in crystallinity.

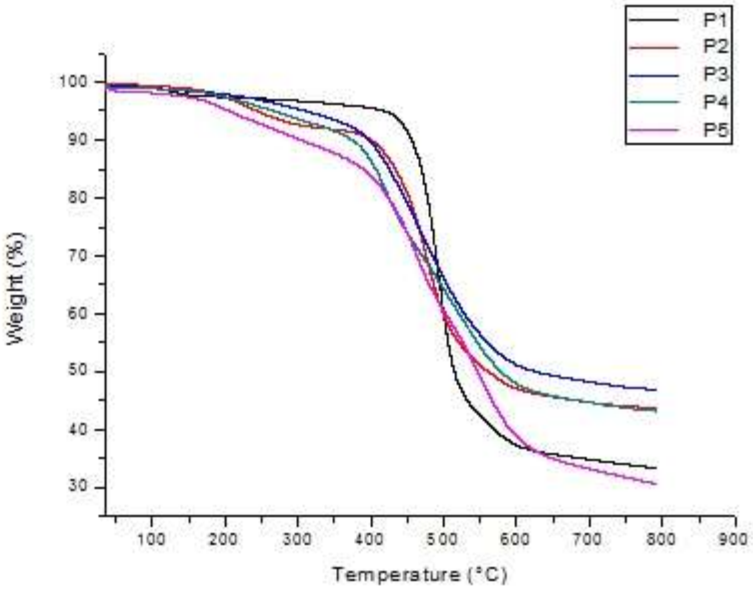

Fig.7 TGA thermograms of PEEK and Co-PEEK (P-1 to P-5)

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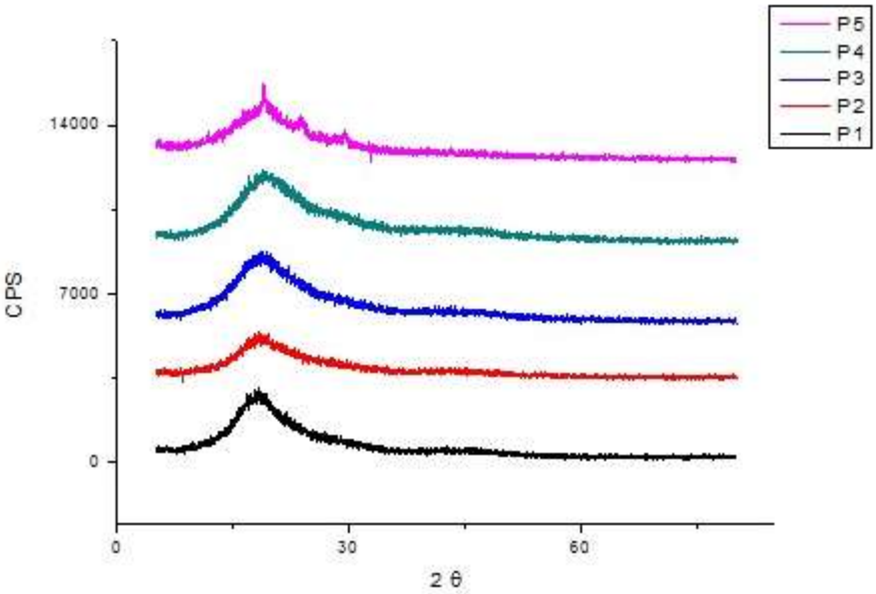

Fig.8 XRD curves of PEEK and Co-PEEK (P-1 to P-5)

IV. Conclusion

Synthesis of **BHBC (I)** using new method was successfully accomplished and characterized by FT-IR and NMR (^{1}H and ^{13}C) techniques. A series of new **PEEK, Co-PEEK (P-1 to P-5)** containing, aromatic ether ketone ether linkages and **PEEK, Co-PEEK (P-1 to P-5)** containing ether ketone ether linkages and cyclopentanone moiety substituent were synthesized from **BFB** and various mol % of BPA/ BHBC by using high temperature solution method. PEEKS were characterized by inherent viscosity, IR, solubility, DSC and TGA technique. Inherent viscosity values of polymers were in the range of 0.26 dL/g to 0.65 dL/g indicating built up of a moderately to high molecular weight. Some Co-PEEK derived from **BHBC and BPA** was limited soluble in polar aprotic solvents because of presence of presence of highly conjugated structure in polymer backbone. Thermal stability of polymers was evaluated by TGA and all the polymers showed no weight loss below 300 ^{0}C. The XRD showed partly crystalline morphology for polymers. These new polymers are expected to find applications as gas separation membranes and engineering materials in aerospace and nuclear industries as high performance films, coatings etc.

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