

## Synthesis and Characterization of Novel Organosoluble and Thermally Stable Polyesters Derived from Bis-[(4'-hydroxybenzyl)-4-benzamide] ether

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**Abstract:** A novel bisphenol, containing preformed aromatic-aliphatic amide, ether and methylene linkages; Bis-[(4'-hydroxybenzyl)-4-benzamide] ether (BHBE) was synthesized by the reaction of 4-hydroxy phenyl acetic acid with Bis-(4-aminophenyl) ether (ODA). The bisphenol (BHBE) was characterized by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectrometry. A new series of polyesters was prepared by low temperature interfacial polycondensation of BHBE with different mole proportions of isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC). The resulting polyesters were characterized by FT-IR spectroscopy, inherent viscosity [ $\eta_{inh}$ ], solubility, differential scanning calorimetry [DSC], thermo gravimetric analysis [TGA] and X-ray diffraction [XRD]. All these polyesters showed good solubility and easily dissolved in polar aprotic solvents like NMP, DMSO, DMAC, DMF etc. The viscosity of polyesters was in the range of 0.49 to 0.79 dL/g. Polyesters were semicrystalline in nature; as evidenced by XRD patterns; and exhibited glass transition temperatures between 237-299°C, no weight loss upto 300°C and char yields of 19-33% at 800°C under nitrogen atmosphere. These polyesters have potential applications as spin coating materials.

**Keywords:** Bisphenol, interfacial polycondensation, Polyesters, semicrystalline, solubility.

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Date of Submission: 10-07-2017

Date of acceptance: 20-07-2017

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### I. Introduction

Polyesters (PE)s is an important class of high performance and engineering polymers, which find diverse applications [1-5]. Polyester can be used as a staple fiber which is commonly used with cotton, wool, and rayon to get blended yarns having desired tailor-made properties. They are usually prepared by the solution or interfacial polymerization from dicarboxylic acid chloride and diol or ester exchange method [6,7]. Thermally stable polyesters from isophthalic and terephthalic acids with bisphenol-A have been commercialized [8].

The properties of aromatic polyesters depend on the substitution at the central carbon atom of Bisphenol. Polyesters with rigid backbone due to totally aromatic or heterocyclic repeat units generally exhibit high thermal stability, higher softening temperature and poor solubility characteristics [9]. Various efforts have been made to explain the structure-property relationship of thermally stable polyesters [10-13]. Chen et al. reported high molecular weight Polyesters with aryl-ether group, by solution polycondensation [14]. These polyesters exhibited good solubility; 5 % weight loss at about 400 °C in N<sub>2</sub> atmosphere. Polyester with amide-ester groups having good solubility were studied by Einollahi et al [15].

The present investigation aims at developing engineering polyesters with good organosolubility and thermal stability. For the purpose of increasing the solubility of resulting polymers approach of, i) Synthesis of bisphenol with preformed ether, methylene linkages and amide group [16,17], ii) Use of co-polymerization technique for random arrangement was utilized.

In order to understand the structure property correlations the type and content of substituent groups; has been varied. Thus we have synthesized a new series of polyesters from a new bisphenol with preformed ether, methylene linkages and amide group viz; Bis-[(4'-hydroxybenzyl)-4-benzamide] ether (BHBE) by using interfacial polycondensation method. The polymerization was performed at the interface of two immiscible solvents-namely water and dichloroethane (DCM), using benzyl triethyl ammonium chloride as a Phase transfer catalyst. These polyesters were characterized by FT-IR, inherent viscosity, solubility, thermal properties (DSC and TGA) and X-ray diffraction, to investigate the effect of introduction of preformed amide, flexible methylene and ether linkage into the polymer backbone on properties of these aromatic polymers.

## II. Experimental

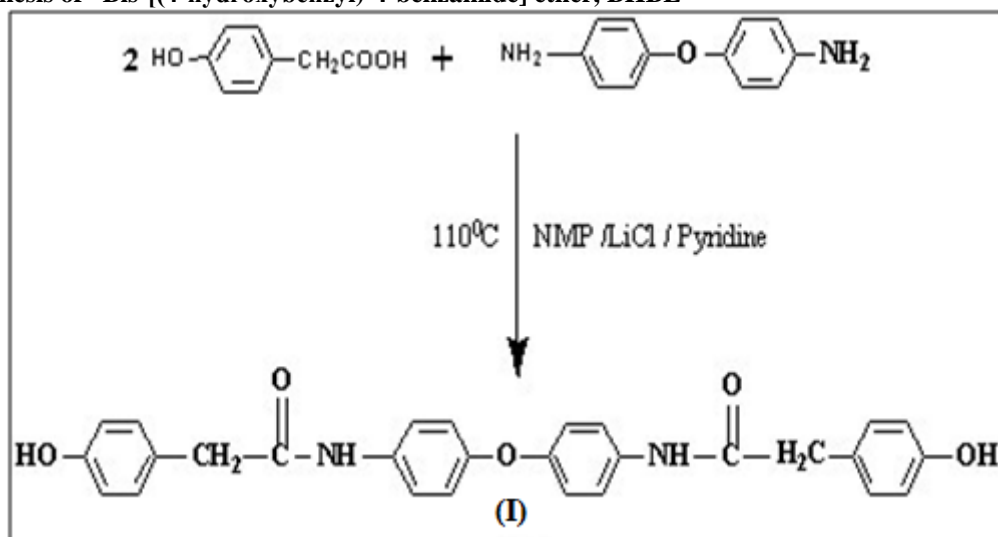
### 2.1 Materials

Potassium carbonate was dried at 180°C for 8h. Hexane, DCM was distilled and dried over metallic sodium pieces. N-methyl pyrrolidone (NMP) was purified by azeotropic distillation with toluene followed by distillation under reduced pressure and stored over 4A° molecular sieves. LiCl, Triphenyl phosphite, Bis-(4-aminophenyl) ether (ODA), 4-hydroxy phenyl acetic acid, benzyl triethyl ammonium chloride and other reagents were used as received.

### 2.2 Measurements

Inherent viscosity measurements were made with a 0.5% (w/v) polyester solution in NMP at 30°C using suspended type Ubbelohde viscometer. The solubility of polymers was determined at 2% concentration in various solvents. The FT-IR spectra of bisphenol and polymers were recorded on FT-IR spectrophotometer (Nicolet iS 10, Thermo Scientific, USA.). <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker AV 400 MHz NMR spectrometer in DMSO-d<sub>6</sub>. Mass spectra were recorded on IIMS 30 double beam mass spectrometer. The glass transition temperature was obtained from DSC curves on Mettler Toledo DSC Instrument at a heating rate of 20°C/min. Thermogravimetric analysis (TGA) was performed on Mettler Toledo STAR TGA Instrument at a heating rate of 10°C/min under a flow of nitrogen gas. Wide angle X-ray diffraction (WAXD) pattern measurements were made with powder polyamides on a Rigaku X-ray diffractometer.

### 2.3 Synthesis of Bis-[(4'-hydroxybenzyl)-4-benzamide] ether, BHBE



**Scheme 1: Synthesis of Bis-[(4'-hydroxybenzyl)-4-benzamide] ether (I) (BHBE)**

In 250 mL flame dried three neck round bottom flask equipped with a reflux condenser, a calcium chloride guard tube, a magnetic stirrer, a nitrogen gas inlet and a thermo well; NMP 20mL, pyridine 5 mL, LiCl 2g, Bis-(4-aminophenyl) ether (ODA) 2 g (0.01 mol) and 4-hydroxy phenyl acetic acid 3.04 g (0.02 mol) were charged. Triphenyl phosphite (TPP) 6.7 mL was added and the reaction mixture was heated to 110 °C under stirring for 12 h. The reaction mixture was then allowed to cool and poured into excess methanol. The precipitated product was filtered, washed with hot water and then with cold methanol. Thus obtained bisphenol (BHBE) was recrystallized from alcohol and dried under vacuum at 80 °C.

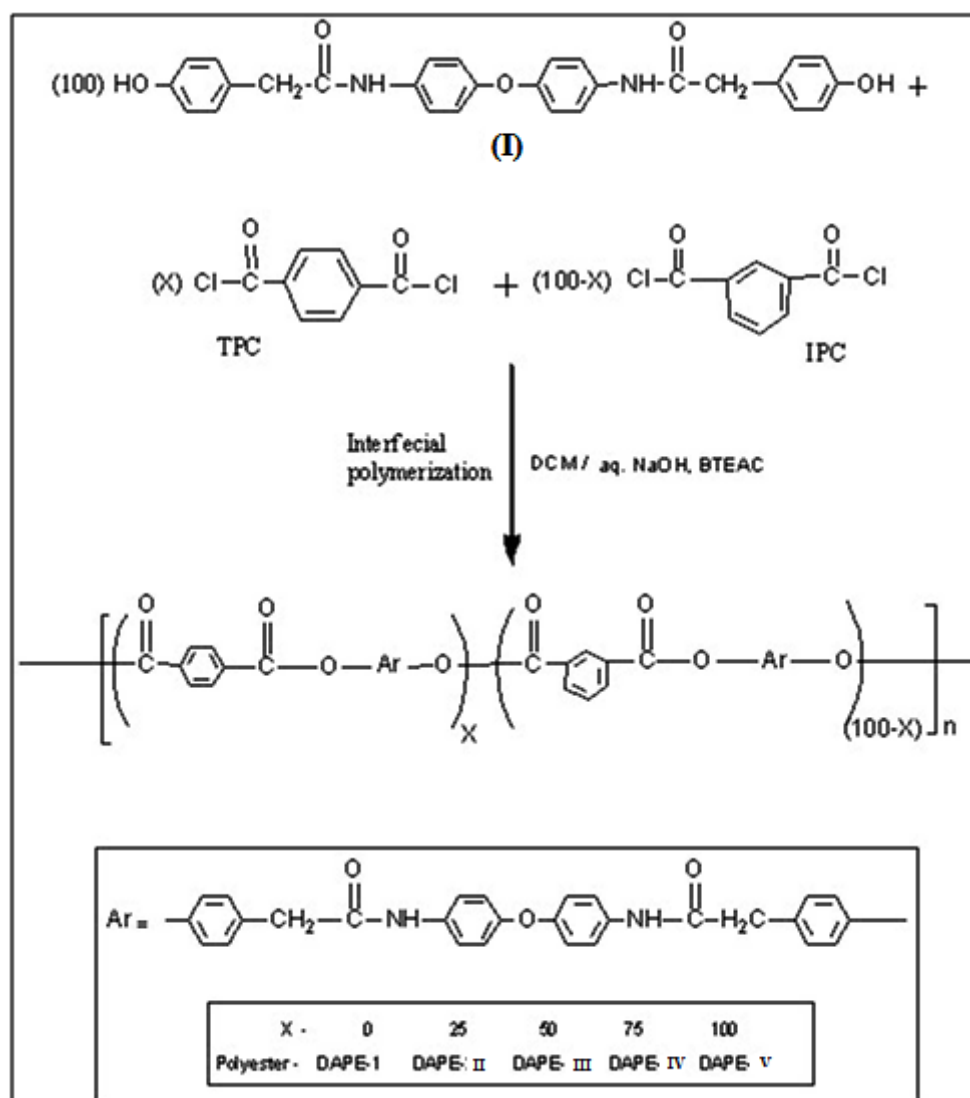
Yield = 3.88 g (83%), M.P. = 260 °C.

FT-IR spectrum (**Fig. 1**) of BHBE displayed absorption bands at 3401.96 cm<sup>-1</sup>, 3245.64 cm<sup>-1</sup>, 3131.98 cm<sup>-1</sup>, 3064.88 cm<sup>-1</sup>, 1648 cm<sup>-1</sup>, 1601.46 cm<sup>-1</sup>, 1240.1 cm<sup>-1</sup>. Its <sup>1</sup>H NMR spectrum (**Fig. 2**) exhibited doublets in the range of δ 6.67- δ 7.55 and singlet at δ 3.46. <sup>13</sup>CNMR spectrum (400, DMSO d<sub>6</sub>, TMS) (**Fig. 3**) δ ppm: 156.4, 152.9, 126.4, 135.06, 130.2, 121.17, 118.81, 115.48, 169.9 and δ 43. DEPT <sup>13</sup>C NMR spectrum (**Fig. 4**) showed a downside signal at 43 and upside signal at 130.2, 121.17, 118.81 and δ 115.48. HRMS spectrum of BHBE (**Fig. 5**) showed molecular ion peak at 468 and (m+1) peak at m/e 469.

### 2.4 Synthesis of polyester (DAPE-II) via interfacial polycondensation method

In a 100 mL three neck round bottom flask equipped with a reflux condenser, a magnetic stirrer, and calcium chloride guard tube Bis-[(4'-hydroxybenzyl)-4-benzamide] ether (BHBE) 0.468 g (1 mmol), NaOH 0.08 g (2 mmol) and benzyl triethyl ammonium chloride (Phase transfer catalyst) 0.01 g dissolved in 12.5 mL

water were placed. To the reaction mixture, solution of IPC 0.152 g (0.75mmol) and TPC 0.051 g (0.25mmol) in DCM 8 mL was introduced all at once with rapid stirring. The vigorous stirring was continued at 30<sup>0</sup> C for one hour. The resulting solution was poured into excess of hexane to precipitate the polyester. The precipitated polyester was filtered, washed with methanol, water and dried under vacuum at 100 °C for 8 h. The yield was 0.589 g (98.6 %) and the inherent viscosity of polymer in NMP was 0.53 dL/g. By using similar procedure **DAPE-I** and **DAPE-III to V** were synthesized.



Scheme 2: Synthesis of Polyesters from Bis-[(4'-hydroxybenzyl)-4-benzamide] ether (BHBE).

### III. Result And Discussion

#### 3.1 Monomer Synthesis:

The novel bisphenol viz, Bis-[(4'-hydroxybenzyl)-4-benzamide] ether (**BHBE**) was synthesized (Scheme 1) by reacting 4-hydroxy phenyl acetic acid with Bis-(4-aminophenyl) ether (ODA) in presence of LiCl, pyridine and NMP at 110<sup>0</sup> C. After completion of the reaction, the reaction mixture was poured in-to ice cold water to precipitate bisphenol, which was further purified by recrystallization from alcohol .

#### 3.2 Spectral characterization of monomer:

The structure of (**BHBE**) was confirmed by FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and mass (HRMS) spectrometry. The spectral data is consistent with its assigned structure.

##### 3.2.1 Infrared Spectroscopy:

Infrared (IR) spectral study of compounds provides useful information about their structural features as it gives the information about the nature of functional groups and the skeletal structure.

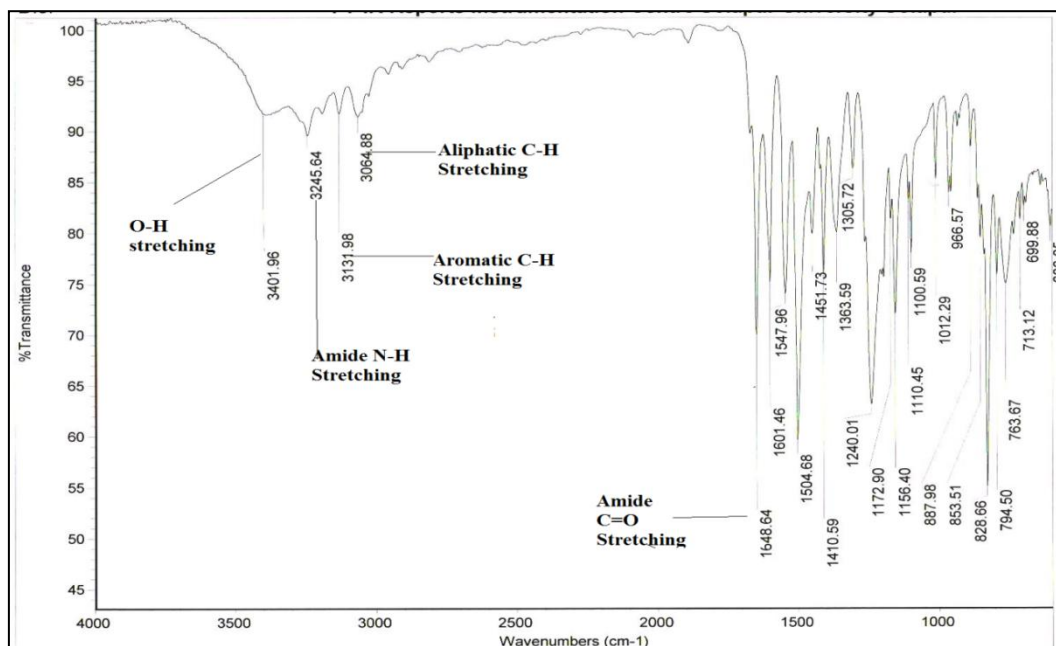


Figure 1 FT-IR spectrum of BHBE

Table I: FT-IR Characterization of synthesized bisphenol BHBE

No.	Absorption bond (cm <sup>-1</sup> )	Functional Group
A	1648.64	amide >C=O stretching
B	3131.98	CH Stretching, aromatic
C	3064.88	CH Stretching, aliphatic
D	1305.72	C-C bond stretching, alkane
E	1601.46	C-C multiple bend stretching, aromatic
F	1451.73	Hydrocarbon Alkane, -CH <sub>2</sub>
G	3401.96	Phenolic O-H bond stretching
H	1240.01	Phenolic C-O bond stretching
I	3245.64	Amide N-H bond stretching
J	794.50	CH bending, aromatic ring (p-disubstituted)

### 3.2.2 <sup>1</sup>H NMR

The <sup>1</sup>H NMR spectrum of (BHBE) showed a singlet at 9.99 corresponding to phenolic proton, singlet at 9.2 due to amide proton (-NH), methylene protons showed singlet at 3.46 where as doublets due to aromatic protons were observed in the range of δ 6.67 to 7.55 (Fig. 2).

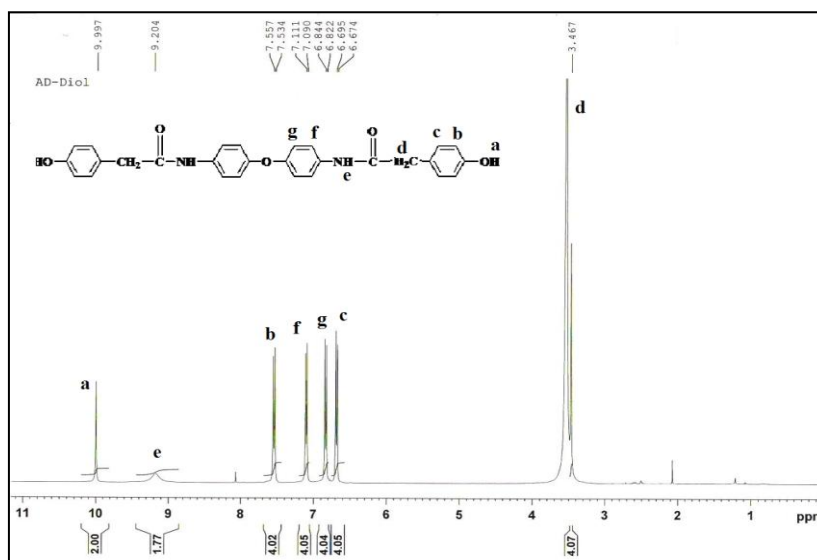
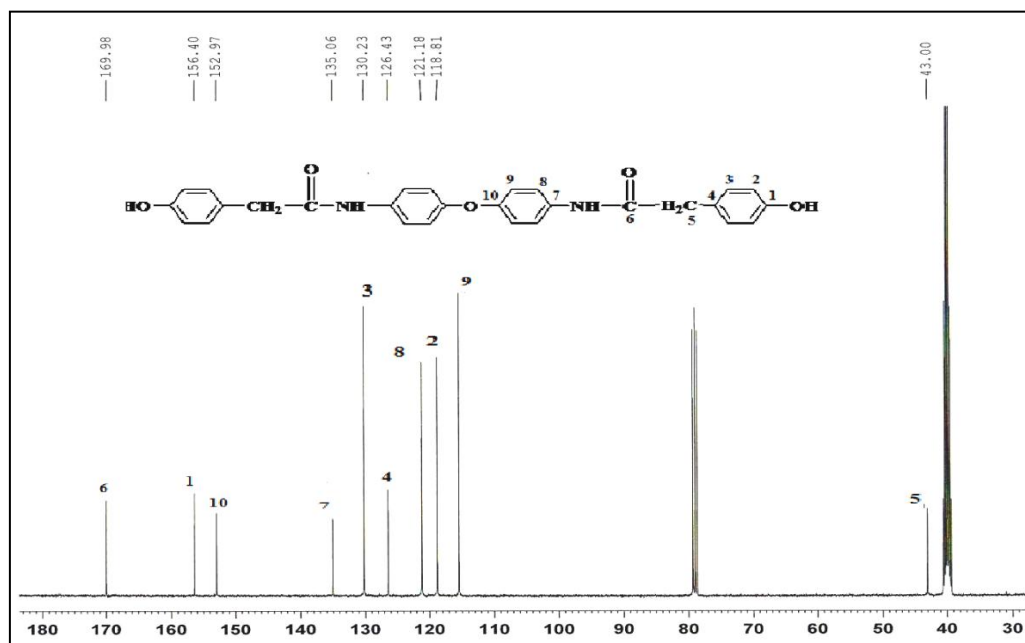


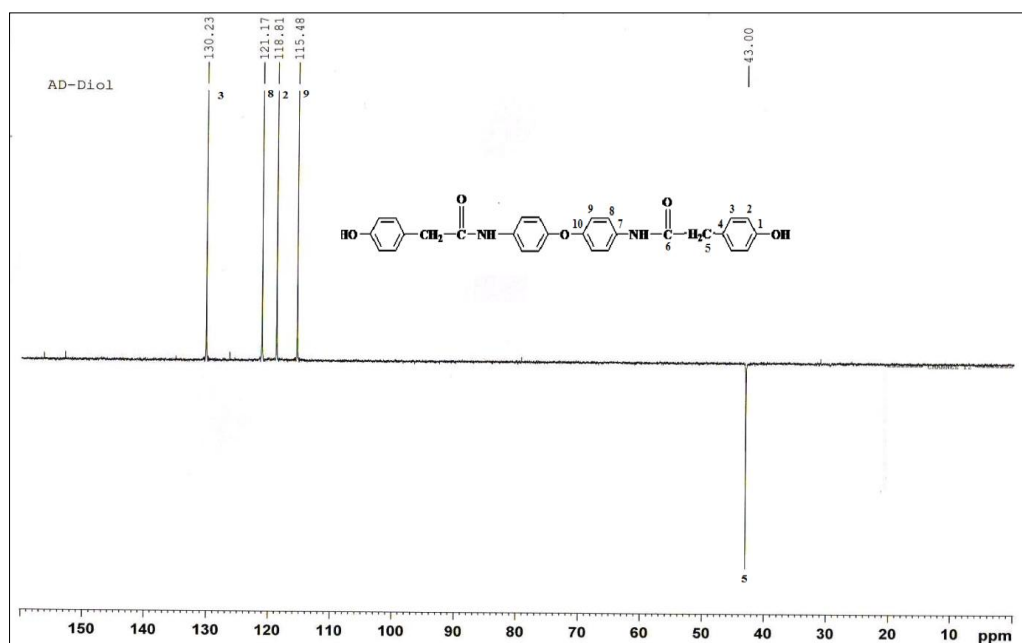
Figure 2: <sup>1</sup>H NMR spectrum of BHBE in d<sub>6</sub>-DMSO

### 3.2.3 $^{13}\text{C}$ NMR

$^{13}\text{C}$  NMR of (BHBE) (Fig. 3) showed 10 different peaks corresponding to 10 non-equivalent carbons; of which signal at 169.9 is due to amide carbonyl carbon, where as methylene carbon appeared at  $\delta$  43. All aromatic carbons were in the range of 115.4-156.4; of which tertiary carbons appeared at 156.4 (C-OH), 152.9 (C-O-C), 126.4 (C- $\text{CH}_2$ ) and 135.06 (C-NH) where as CH aromatic were at 130.2, 121.17, 118.81 and  $\delta$  115.48. This was confirmed by DEPT  $^{13}\text{C}$  NMR of (BHBE) (Fig. 4), wherein peak of  $-\text{CH}_2-$  appeared downside at 43,  $-\text{CH}-$  carbons remained upside at 130.2, 121.17, 118.81 and  $\delta$  115.48 and tertiary carbon peaks disappeared.



**Figure 3:**  $^{13}\text{C}$  NMR spectrum of BHBE in  $\text{d}_6$ -DMSO



**Figure 4:** DEPT  $^{13}\text{C}$  spectrum of BHBE in  $\text{d}_6$ -DMSO

### 3.2.4 Mass spectrometry

(HRMS) spectrum of (BHBE) (Fig. 5) showed molecular ion peak at 468 and (m+1) peak at m/e 469 which clearly indicates that molecular mass of BHBE is **468**; as expected from assigned chemical structure.

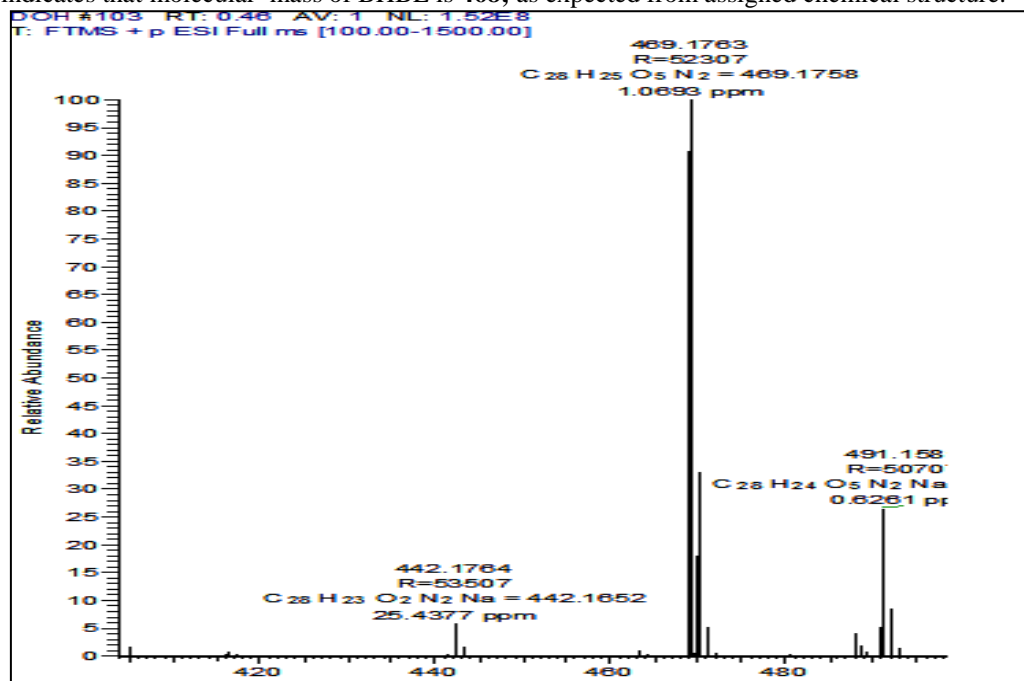


Figure 5: Mass spectrum of BHBE

### 3.3 Polymer synthesis

A series of aromatic polyesters (DAPE-I to DAPE-V) was synthesized by low-temperature Interfacial polycondensation of (BHBE) with isomeric aromatic diacid chlorides, namely IPC or TPC in DCM (Scheme 2). Benzyl triethyl ammonium chloride was used as phase transfer catalyst. The polymerization was carried out at 30°C for one hour. The resulting polyesters were precipitated by pouring the viscous reaction mixture in excess of hexane. The data on yield and viscosity of polyesters is given in **Table II**. All polyesters were obtained in almost quantitative yields.

Table II: Yield, inherent viscosity of Polyesters from BHBE<sup>a</sup>

Polymer	(mol %)			Yield (%)	$\eta_{inh}^b$ (dL/g)
	BHBE	IPC	TPC		
DAPE I	100	100	00	99.3	0.79
DAPE II	100	75	25	98.2	0.53
DAPE III	100	50	50	98.6	0.57
DAPE IV	100	25	75	97.9	0.52
DAPE V	100	00	100	98.7	0.49

a. BHBE, Bis-[(4'-hydroxybenzyl)-4-benzamide] ether

b. Measured with a 0.5 % (w/v) polymer solution in NMP at 30 ± 0.1 °C.

### 3.4 Characterization of polymers:

All the polyesters were characterized by various techniques namely:

1. Solubility
2. Viscosity Studies
3. FT-IR Spectroscopy
4. Thermal Studies (TGA and DSC)
5. XRD Studies

#### 3.4.1. Solubility

The present series of polyesters exhibited good solubility in a variety of solvents, not only in polar aprotic organic solvents (NMP, DMA and DMF) but also in m-cresol, and dimethyl sulfoxide (DMSO), pyridine and partially in THF. This demonstrated that the polymers displayed enhanced solubility, which may be attributed to increased flexibility caused by the introduction of ether and methylene linkages, and increased free

volume caused by the random arrangement m/p catenation in the repeating unit of copolymers. The chain packing of the polymers is disturbed, and consequently the solvent molecules can easily penetrate to solubilize the polymer chain [18-20]. The good solubility makes these polyesters potential candidates for applications in spin coating processes.

**Table III:** Solubility of Polyesters from BHBE

Polymer Solvent	DAPE-I	DAPE-II	DAPE-III	DAPE-IV	DAPE-V
NMP	++	++	++	++	++
DMAc	++	++	++	++	++
DMSO	++	++	++	++	++
DMF	++	++	++	++	++
m-Cresol	++	++	++	++	++
Pyridine	++	++	++	++	++
THF	+ -	+ -	+ -	+ -	+ -
DCM	--	--	--	--	--
CHCl <sub>3</sub>	--	--	--	--	--
Conc.H <sub>2</sub> SO <sub>4</sub>	++	++	++	++	++

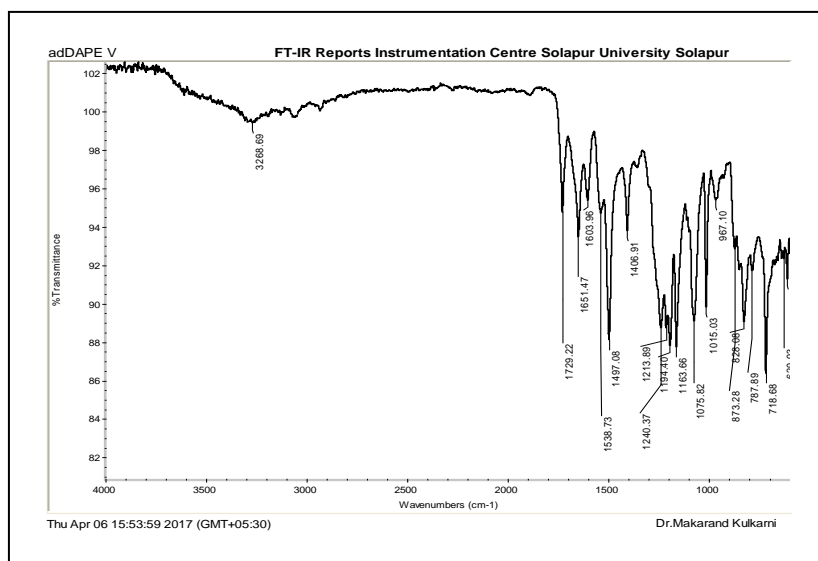
Soluble at R.T. ++, Partly soluble + -, Insoluble --.

### 3.4.2 Viscosity

Inherent viscosities of polyesters (DAPE-I to DAPE-V) were in the range 0.49 to 0.79 dL/g at 30°C in NMP (Table II) indicating built-up of moderate to high molecular weights. It was observed that the polymer DAPE-I has high viscosity among the series. It was also observed that, the polymer containing TPC had low viscosity. This may be attributed to the more solubility of IPC derived polymer in the reaction solvent allowing high molecular weight built up of polyesters.

### 3.4.3 FT-Infrared Spectroscopy

The structure of polymers was confirmed by FT-IR spectroscopy. The FT-IR spectrum of DAPE-V (Fig. 6) showed absorption band at 1729.22 corresponding to ester carbonyl (C=O stretching), 3268.69 cm<sup>-1</sup> (Amide N-H bond stretching). Disappearance of absorption band at 3401.96 cm<sup>-1</sup> indicated the complete conversion of -OH into ester.



**Figure 6:** IR spectrum of polyester (DAPE-V)



### 3.4.4 Thermal Studies

Thermal properties of polymers were evaluated by DSC (Fig. 7) to obtain the glass transition temperatures ( $T_g$ ) of the polyesters, which were in the range of 237 to 299 °C. TGA curves of polyesters (Fig. 8) showed initial decomposition temperatures in the range of 301-362 °C and  $T_{10}$  values were in the range of 335-387 °C where as the residual weight at 800 °C was between 24 to 43 % (Table IV) indicating that the polymers were thermally stable.

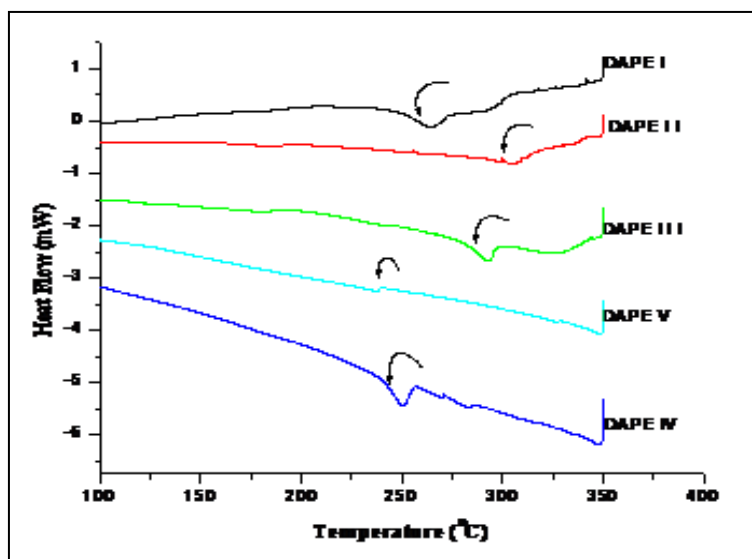


Figure 7: DSC curves of polyesters (DAPE I to DAPE V)

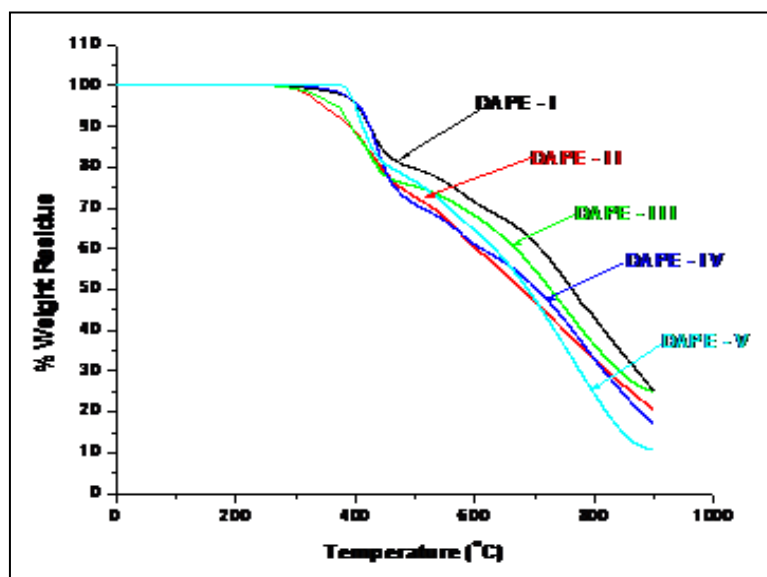


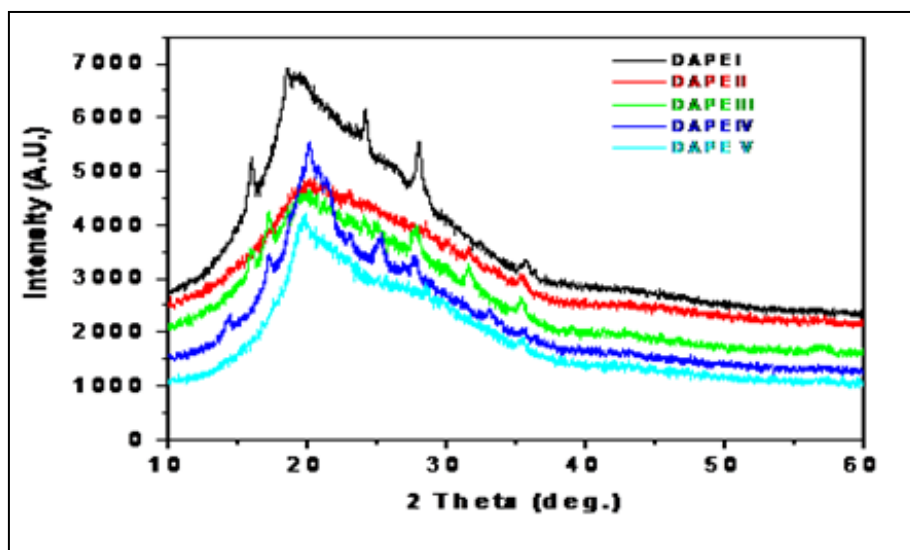
Figure 8: TG curves of polyesters (DAPE I to DAPE V)

Table 4: Thermal properties <sup>a</sup> of Polyesters from BHBE

Polymer Code	Temperature for various % Decomposition (°C)				Residual wt. (%) at 800 °C	$T_g$ (°C) <sup>f</sup>
	$T_i$ <sup>b</sup>	$T_5$ <sup>c</sup>	$T_{10}$ <sup>d</sup>	$T_{50}$ <sup>e</sup>		
DAPE I	341	402	423	762	43	258
DAPE II	300	333	391	678	32	299
DAPE III	301	309	385	726	36	286
DAPE IV	315	406	423	704	32	244
DAPE V	362	424	437	713	24	237



- Thermogravimetric analysis at a heating rate of 10°C/min under nitrogen.
- Temperature at which initial weight loss was recorded.
- Temperature at which 5 % weight loss was recorded.
- Temperature at which 10 % weight loss was recorded.
- Temperature at which 50% weight loss was recorded.
- Glass transition temperature recorded at a heating rate of 20°C/min in nitrogen by DSC.



**Figure 9:** XRD of polyesters (DAPE I to DAPE V)

#### 3.4.5 XRD Studies

All the polymers showed almost similar diffraction patterns. X-ray diffractograms of polymers DAPE-I to DAPE-V (**Fig. 9**) showed that polymers (DAPE-II to DAPE-V) were partly crystalline in nature; whereas DAPE-I exhibited lesser crystallinity which showed broad diffractogram with only two minor peaks at  $2\theta = 24.1^\circ$  and  $28^\circ$  in X-ray diffractograms. This indicated that morphology of polyesters depend on the structure of reactant components utilized.

### IV. Conclusions

Based on the above discussed results, following conclusions are drawn.

- Bisphenol; Bis-[(4'-hydroxybenzyl)-4-benzamide] ether (**BHBE**) was synthesized and was characterized by physical constant, FT-IR, NMR and Mass spectrometry.
- Using interfacial polycondensation method bisphenol; Bis-[(4'-hydroxybenzyl)-4-benzamide] ether (**BHBE**) was polymerized with different mole proportions of IPC, TPC to yield a series of polyesters and co polyesters.
- Solubility of these polyesters was tested in different organic solvents. These polymers were soluble in NMP, DMAc, DMF, DMSO, pyridine, m-cresol and conc.  $H_2SO_4$ .
- Inherent viscosities of these polyesters were in the range 0.49 to 0.79 dL/g and indicated built-up of moderately high molecular weights.
- The glass transition temperatures of the polyesters were in the range 237-299°C.
- Thermal stability of polyesters was evaluated by dynamic thermogravimetric analysis in nitrogen atmosphere. A remarkable thermal stability was observed for all polymers, as evidenced by  $T_{10}$  values above 385 °C. This is due to the considerable aromatic content, amide and ether linkages in the main polymer chains.
- X-ray diffractograms of polymers suggested that introduction of ether and methylene linkages may have imparted flexibility leading to less crystalline nature and in copolymers m/p catenation disrupted the chain regularity and packing leading to partly crystalline nature and it is supported by solubility data. As these polyesters are soluble in various organic solvents they can be used for film forming and coating materials.

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International Journal of Engineering Science Invention (IJESI) is UGC approved Journal with  
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A. V. Diwate. "Synthesis and Characterization of Novel Organosoluble and Thermally Stable  
Polyesters Derived from Bis-[(4'-hydroxybenzyl)-4-benzamide] ether." *International Journal of  
Engineering Science Invention (IJESI)* 6.7 (2017): 10-19.