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## Synthesis and characterization of wholly aromatic polyesters using interfacial polycondensation technique

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### ABSTRACT

Eleven wholly-aromatic polyesters were synthesized by interfacial polycondensation of various aromatic diacid chlorides such as terephthaloyl chloride (TPCL) and isophthaloyl chloride (IPCL) with various aromatic diols such as bisphenol-A (BPA), resorcinol (RES), 1,5-dihydroxy naphthalene (15DHN), 4,4'-bis(hydroxyl)benzilidine aniline (BHBA), 4,4'-bis(hydroxybenzilidine) benzidine (BHBB), 4,4'-bis(hydroxybenzilidine)-p-phenylenediamine (BHBP), 4,4'-bishydroxy biphenyl thioether (BHBPT) using chloroform-water interphase system, alkali as an acid acceptor and citramide as phase transfer catalyst at ambient temperature. The resulting polyesters were characterized by solubility test, elemental analysis, intrinsic viscosity measurements, FT-IR, and <sup>1</sup>H-NMR spectral analysis, and thermogravimetric analysis.

**Keywords:** Wholly-aromatic polyesters, interfacial polycondensation, diacid chlorides, diols, chloroform-water interphase system, citramide, solubility test, elemental analysis, intrinsic viscosity measurements, FT-IR, and <sup>1</sup>H-NMR spectral analysis, and thermogravimetric analysis.

### INTRODUCTION

A large amount of research work and activities has been undertaken to synthesize new polyesters[1,2] and copolyesters[3,4] and to modify them for desired properties and applications. A great many aromatic polyesters have been synthesized from various types of bisphenol, and polyesters derived from bisphenol-A and isophthaloyl chloride (IPCL) / terephthaloyl chloride (TPCL) have been commercialized. However, polyesters are generally difficult to process because of their limited solubility in organic solvents and their high melting temperature or high glass-transition temperature by virtue of their rigid structures.

#### Prepared linear polyester have been codified as

- |        |                |      |
|--------|----------------|------|
| (i)    | PE(TPCL+BPA)   | PTP1 |
| (ii)   | PE(TPCL+RES)   | PTP2 |
| (iii)  | PE(TPCL+15DHN) | PTP3 |
| (iv)   | PE(TPCL+BHBA)  | PTP4 |
| (v)    | PE(TPCL+BHBB)  | PTP5 |
| (vi)   | PE(TPCL+BHBP)  | PTP6 |
| (vii)  | PE(TPCL+BHBPT) | PTP7 |
| (viii) | PE(IPCL+BPA)   | PIP1 |
| (ix)   | PE(IPCL+RES)   | PIP2 |
| (x)    | PE(IPCL+15DHN) | PIP3 |
| (xi)   | PE(IPCL+BHBPT) | PIP7 |

## MATERIALS AND METHODS

A large amount of research work and activities has been undertaken to synthesize new polyesters and copolyesters and to modify them for desired properties and applications. A great many aromatic polyesters[5,6] have been synthesized from various types of bisphenol, and polyesters derived from bisphenol-A and isophthaloyl chloride (IPCI) / terephthaloyl chloride (TPCI) have been commercialized.

Polyethylene terephthalate (PET) is widely used as a material for synthetic fibers, packaging films, recording and photographic tapes, bottles for beverage and food and engineering plastic components, because of its excellent thermal and mechanical properties, high chemical resistance, and low gas permeability. However, PET polymer has some undesirable properties: for example, poor dye ability, pilling, low moisture regain, generation of static charges, poor adhesion to metals, and poor process ability due to the high melting temperature. In general, copolymerization affords a facile means of modifying the crystallinity, morphology, melting point ( $T_m$ ), glass transition temperature ( $T_g$ ), solubility, and permeability. Poly(ethylene isophthalate-co-terephthalate) (PEIT) exemplifies copolyesters possessing a crystallizing and a poorly or non-crystallizing component. Random PEIT copolyester is known to be formed by the conventional bulk polymerization of ethylene glycol (EG), with dimethyl isophthalate (DMI) or isophthalic acid (IPA) and dimethyl terephthalate (DMT) or terephthalic acid (TPA). The incorporation of DMI changes morphology (crystallinity and crystal size), and properties ( $T_m$ ,  $T_g$ , thermal expansivity and mechanical properties) of PET homopolymer. PEIT copolyesters are currently used in industry as thermally shrinkable package films as well as heat-seal able laminating films for steel cans and metal and ceramic sheets.

Alternatively, in an attempt to increase the  $T_g$  of the PET polyester and its flame resistance and to impart unusual physical properties, the aromatic character of the polyester was increased, by modifying PET with p-hydroxy benzoic acid. Non-crystalline and liquid crystalline polyesters, poly(ester-carbonate)s, poly(ester-amide)s have been developed as high performance polymers, which have specific properties. These polymers have potential applications as high modulus fibers and engineering polymer.

Thus, the growth and expansion of polyester work, both basic and applied over the past few decades has been enormous. In an attempt to synthesize new polyesters by condensation of aliphatic and aromatic diacids or diacid chloride with aromatic diols with or without liquid crystalline structure, the present work was undertaken.

### Materials

**Dicarboxylic Acids:** Terephthalic acid (TPA) and Isophthalic acid (IPA) from SRL, Mumbai were used as received. Cyanuric chloride was obtained from ATUL, Valsad, having purity better than 98 mol% and was further purified by crystallization from pure benzene (mp 146°C).  $\beta$ -Naphthylamine was obtained from Polypharm and p-hydroxybenzaldehyde, p-aminophenol, benzidine, and p-phenylenediamine from SRL, Mumbai of purity better than 99% were used as received. Citramide (cetyltriethylammoniumbromide) (SRL, Mumbai, extra-pure 99%) was used as received.

Thionyl chloride, pyridine, ethanol, chloroform, methanol, acetone, sodium hydroxide, sodium bicarbonate, sulphuric acid, hydrochloric acid, etc. were good quality laboratory reagents and used after appropriate purification and distillation if required.

### Aromatic Acid Chloride Monomers:

**Terephthaloyl chloride (TPCI)** and **Isophthaloyl chloride (IPCI)** were synthesized from the condensation reaction of their corresponding dicarboxylic acids with excess of thionyl chloride, in the presence of few drops of pyridine as a catalyst. They were purified by crystallization with n-hexane.

### Aromatic Diol Monomers:

**Bisphenol-A (BPA)** was obtained from Fluka, Switzerland, puris having purity > 97%. It was repeatedly crystallized from 50% aqueous acetic acid. The crystals were filtered thoroughly, washed with water and dried. It was used after recrystallization from benzene (mp 156°C).

**Resorcinol (RES)** was obtained from SRL, Mumbai having purity better than 99%. It was purified by recrystallization from rectified spirit.

**4,4'-Bishydroxy biphenyl thio ether (BHBPT)** was obtained from United Phosphorous Ltd., Vapi, having purity better than 98% was used as received. The  $^1\text{H-NMR}$ ,  $\text{CDCl}_3$ , 250 MHz, TMS,  $\delta$  ppm) for BHBPT:  $\delta$  6.70-6.74 (d, 4H, ortho- to -OH), 7.10-7.13 (d, 4H, ortho- to -S-), 9.39 (s, 2H, -OH).

**1,5-Dihydroxynaphthalene (15DHN)** was obtained from ATIC, Valsad, having a purity > 92% and was further purified by crystallization from ethanol (mp 195°C).

**4,4'-Bis(hydroxy)benzilidene aniline (BHBA)** was synthesized from reaction of p-hydroxybenzaldehyde and p-aminophenol. Ethanolic solution of p-hydroxybenzaldehyde (1.2 g, 0.01 mol) mixed with ethanolic solution of p-amino phenol (1.09 g, 0.01 mol) was refluxed in water-bath for 2-3 hrs. The reaction mixture was poured in to crushed ice. The yellow precipitate separates out; it was filtered, washed with methanol and distilled water and dried (mp 194°C). **FTIR** (KBr, cm<sup>-1</sup>) 3426 (broad O-H), 1615 (-CH=N), 1588 and 1510 (-C=C aromatic). **<sup>13</sup>C-NMR** (DMSO-d<sub>6</sub>, TMS) δ ppm: 155.4-157.9 (C1, -C-OH), 115.2-117 (C2 & C8, ortho- to -OH), 128.4-128.7 (C3, ortho- to -CH=N), 130.1-132 (C4, -C-CH=N), 160-163.2 (C5, -CH=N), 122-122.4 (C6, -C-N=HC), 125.4 (C7, ortho- to -N=CH), 143.1-148.4 (C9, -C-OH).

**4,4'-Bis(hydroxybenzilidene) benzidine (BHBB)** was synthesized from reaction of p-hydroxybenzaldehyde and benzidine. Ethanolic solution of p-hydroxybenzaldehyde (2.4 g, 0.02 mol) mixed with ethanolic solution of benzidine (1.84 g, 0.01 mol) was refluxed in water-bath for 2-3 hrs. The reaction mixture was poured in crushed ice. The yellow precipitate separates out. It was filtered, washed with methanol and distilled water and dried. **FTIR** (KBr, cm<sup>-1</sup>) 3426 (broad O-H stretch), 1606 (-CH=N), 1594, 1510 and 1451 (-C=C- aromatic). **<sup>1</sup>H-NMR** (DMSO-d<sub>6</sub>, 90 MHz, TMS) δ ppm 8.4 (d, 2H, 2CH=N), 6.60-6.95 (m, 4Ar-H, ortho to -OH), 7.15-7.50 (m, 4Ar-H, ortho to phenyl), 7.65-7.85 (m, 8Ar-H, ortho to azomethine and amino). **<sup>13</sup>C-NMR**, (DMSO-d<sub>6</sub>, TMS) δ ppm: 146.7-150.9 (C1, -C-OH), 114.2-115.5 (C2, ortho- to -OH), 127-127.6 (C3, ortho- to -CH=N), 130.5-130.6 (C4, -C-CH=N), 158.9-160.6 (C5, -CH=N), 128.7 (C6, -C-N=HC), 121.3-121.5 (C7, ortho- to -N=CH), 125.8-126.8 (C8, ortho- to -Ph), 136.6-137.9 (C9, -C-Ph).

**4,4'-Bis(hydroxy benzilidene) p-phenylenediamine (BHBP)** was synthesized from reaction of p-hydroxybenzaldehyde and p-phenylenediamine. Ethanolic solution of 2.44 g (0.02 mol) p-hydroxybenzaldehyde and ethanolic solution of 1.10 g (0.01 mol) p-phenylenediamine were mixed and refluxed in water-bath for 2-3 hrs. The reaction mixture was poured in crushed ice. The yellow precipitate separates; it was filtered, washed with methanol and distilled water and dried. The product was purified by reprecipitations from chloroform-methanol (Yield 81%, mp 260°C). The FT-IR: 3426 (broad O-H stretch), 1602 (-CH=N), 1591, 1513 and 1444 (-C=C aromatic). **<sup>13</sup>C-NMR** (DMSO-d<sub>6</sub>, TMS, δ ppm): 149.2 (C1, -C-OH), 114.5-115.6 (C2, ortho- to -OH), 129.7-130.5 (C3, ortho- to -CH=N), 132 (C4, -C-CH=N), 159 - 160.5 (C5, -CH=N), 121.7 (C6, -C -N=HC), 127.6-128.1 (C7, ortho- to -N=CH).

#### Conditions for polyester synthesis

In the present investigation interfacial polycondensation of diacid chloride with aromatic diol is used. It has been observed that the polymerization reaction is influenced by solvent system, and catalytic and surfactant additives.

**Solvent system:** The choice of the organic solvent is critical since it affects several other polymerization factors such as the potential partition of reactants between the two phases, the diffusion of the reactants, reaction rate and the solubility, swelling or permeability of the growing polymer. Chloroform/water interface system has been employed for similar polymerization of this type. The polar aqueous phase contains enough NaOH to dissolve BPA completely as the active phenolate ion, leaving as little as possible undissociated BPA, which could be extracted by the organic phase. The non-polar chloroform phase is an excellent solvent for ADCl and oligomer formed in reaction, although not for polymer of high molecular weight two possible side reactions are the alkaline hydrolysis of -OH and dichlorocarbene formation by the action of aqueous NaOH/chloroform. The low solubility of ADCl in water serves to prevent it from hydrolysis by the alkali. Moreover, very slow rate of the side reactions, as compared to the polycondensation insure that neither the course of polymerization nor the hydrolysis are adversely affected.

#### Catalytic and Surfactant Additives

The surface-active agent is known to enhance the degree of polymerization in the interfacial production of polymer. This enhancement is brought about by improved mechanical mixing, increased interfacial area and consequently increased contact of the reactants, the degree of enhancement is expected to depend on the nature of the additive and indeed the use of emulsifier has been the subject of optimization of studies. Sometimes IPC, as type of nucleophilic displacement, are carried out with phase transfer catalyst generally small symmetric quaternary ammonium cations. It has been suggested that both surfactant and catalytic functions could be combined through the use of cationic surfactants, which as quaternary ammonium compounds, could also used in transfer of monomer between phases. Earlier work has indicated a higher molecular weight of the product when amount of cationic surfactant was used. In the present case we have used citramide as a cationic surfactant and phase transfer catalyst.

**Synthesis of polyester**

Considering the experience of previous investigators, the reactants ADCl and BPA were taken in equimolar ratio, using chloroform-water interphase system and citramide as phase transfer catalyst. The stirring was vigorous and continuous and the duration of reaction was 5 min. at 30°C. These are summarized in Table 1.

**Table 1 Reaction conditions for the synthesis of polyester from ADCl and BPA**

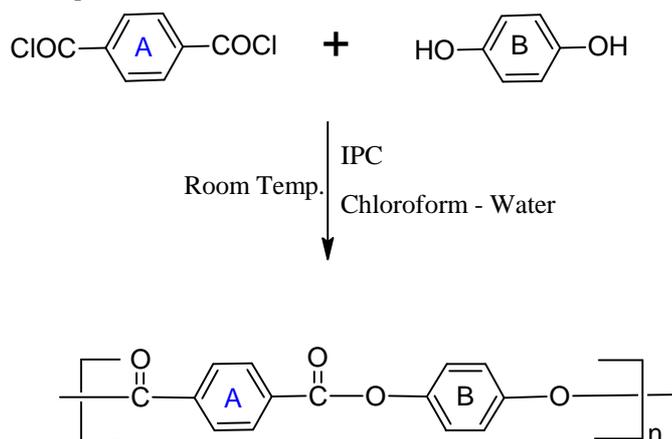
Interface System	:	Chloroform/Water
Phase volume ratio	:	35 ml/ 85 ml
Reactants	:	ADCl = 0.0125 mol BPA = 0.0125 mol
Acid acceptor	:	0.025 mol NaOH
Additive	:	Citramide
Temperature	:	30°C
Time	:	5 min.
Stirring	:	Vigorous and continuous

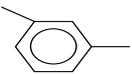
The reaction was carried out using mechanical stirrer with a switch to control the speed in a 250 ml beaker. An initial charge of 0.025 mol of NaOH dissolved in a total of 75 ml of water was stirred at a moderate speed with 0.0125 mol of BPA. 0.25 mg of additive, citramide (phase transfer catalyst) dissolved in 10 ml of water was added. The organic phase was prepared by dissolving 0.0125 mol ADCl in 35 ml of chloroform. The speed of the stirrer was raised to the maximum value, and the organic phase was introduced rapidly. Mixing was continued thereafter for 5 minutes even though the reaction mass turned to a semisolid paste and adhered to the walls of the container. Total of 5 min. was allowed to elapse so that the reaction presumably could continue for full time, as is known to occur in precipitates in mixed systems. At the end of the 5 min period stirring (which still in progress) was interrupted and acetone added to the beaker. After one minute of gentle stirring the polymer was filtered off and washed with acetone to remove unreacted monomers and chloroform. The moist product was returned to the container, stirred with distilled water to wash out excess alkali and salts, and then filtered. The water washing was repeated twice or more till it is free from impurities. The polymerized product was dried to constant weight in a vacuum oven at 40°C.

In the similar manner other polyesters were prepared adopting the same procedure outlined above selecting appropriate acid chloride and diol. Thirteen polyesters of, ADCl or SECl with aromatic diols BPA, RES, 15DHN, BHBA, BHBB, BHBP, and BHBPT reported in the present investigation have been synthesized by the above IPC technique and reaction conditions.

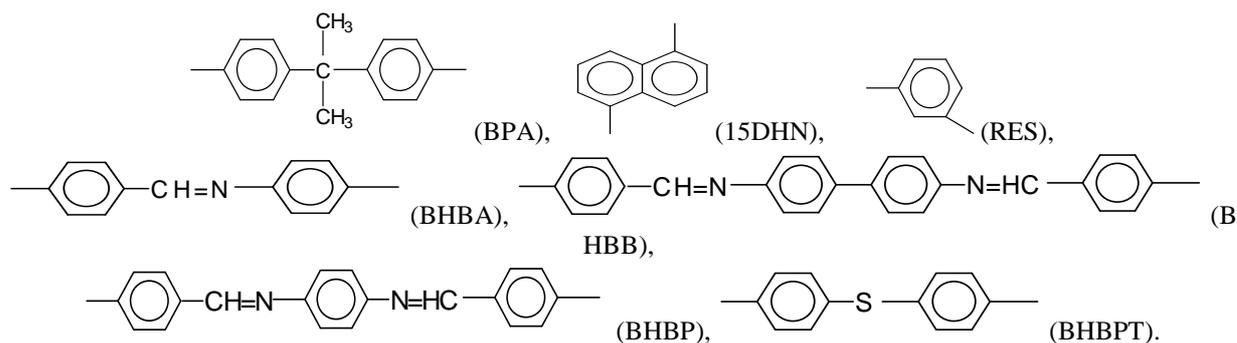
The polymerization reaction is representing as follows:

The polymerization reaction is represent as follows:



Where, Ar (A)=  (TPCl),  (IPCl), and

Ar (B)=



## RESULTS AND DISCUSSION

Eleven wholly aromatic polyesters were synthesized by stirred interfacial polycondensations of various aromatic diacid chlorides and aromatic diols using chloroform / water interphase, citramide as phase transfer catalyst at 30°C as listed in Table 2

### Yield and Appearance

The yield and appearance are summarized in Table 2. Yields of the different polymer samples involving terephthaloyl moiety are in the range from 41 to 86%, and those of isophthaloyl moiety are from 80 to 92%. All the polyesters are solid powders with different colours depending upon the types of aromatic diol involved. The polyesters PTP1, PTP5 and PIP1 are white powders while other polyesters are either light to dark brown or pale-yellow powders.

### Elemental Analysis

The results of elemental analysis of present polyesters are given in Table 2. The observed percentage of C, H and N contents in present polyesters are fairly in good agreement with those theoretically calculated based on the repeat units in the chain. This suggests that both monomers join alternatively in 1:1 mole ratio.

### Solubility Behavior

As describes in the preceding chapter that the solubility behavior provides additional information about polymer-polymer and polymer-solvent interactions and is very useful for processing industries. Therefore, solubility of present fourteen polyesters was studied in variety of solvents. Relative solubilities in different solvents are summarized in Table 2.

Table-2 Elemental analysis C, H and N % contents in the polyesters

Polyester	C%		H%		N%	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
PTP1	77.08	76.59-	5.06	4.81-	-	-
PTP2	70.00	69.12-	3.36	3.10-	-	-
PTP3	74.48	74.10-	3.47	3.40-	-	-
PTP4	73.46	73.21	3.82	3.73	4.08	3.87
PTP5	78.15	77.93	4.24	4.13	5.36	5.09
PTP6	75.33	75.06	4.06	3.97	6.28	5.99
PTP7	68.96	68.77	3.47	3.34	-	-
PIP1	77.08	76.95	5.06	4.93	-	-
PIP2	70.00	70.14	3.36	3.27	-	-
PIP3	74.48	74.35	3.47	3.31	-	-
PIP7	68.96	68.74	3.47	3.28	-	-

The examination of the Table 3 reveals that polyesters PTP4 and PTP7 are soluble in DMF while PTP1, PTP2 and PTP5 are soluble in nitrobenzene at room temperature. PTP3, PTP4, PTP5, PTP6 and PTP7 are soluble in hot DMSO on heating, but PTP1 and PTP2 even on heating dissolve only partially. All the polyesters are only partially soluble only in THF. Further, all the polyesters containing terephthaloyl moiety are totally insoluble in chlorobenzene, dimethylacetamide, dichloroethane, ethylacetoacetate, ethyl chloroacetate, methanol, ethanol, and petroleum ether.

Table 3 shows that the polyesters PIP1, PIP2 and PIP3 involving isophthaloyl carboxylate moiety are soluble in DMF at room temperature but dissolve in DMSO only on heating. The PIP7 is only partially soluble in DMF and DMSO. These polyesters dissolve only partially in THF and nitrobenzene even on heating, except PIP3, which dissolves in THF. The polyesters PIP1, PIP2, PIP3, and PIP7 are totally insoluble in chlorobenzene, dimethylacetamide, dichloroethane, ethylacetoacetate, ethyl chloroacetate, methanol, ethanol, and petroleum ether.

**Table 3 Relative solubilities of polyesters involving terephthaloyl moiety**

Solvent	PTP1	PTP2	PTP3	PTP4	PTP5	PTP6	PTP7
THF	PS						
DMF	PS	PS	PS	S	PS	PS	S
DMSO	PS	PS	SH	SH	SH	SH	SH
Nitrobenzene	S	S	PS	PS	S	PS	PS
Chlorobenzene	IS						
DMA	IS						
Dichloroethane	IS						
Chloroform	IS						
ECA	IS						
EAA	IS						
Methanol	IS						
Ethanol	IS						
Petroleum ether	IS						
Water	IS						

*S = soluble at room temperature, SH soluble on heating, PS = partially soluble on heating, IS = insoluble.*

### Solution Viscosity

Since these polyesters are not easily soluble in common solvents, the intrinsic viscosity of only two polyesters PTP4 and PIP1 was determined in DMF at 30°C using equations (1.1) to (1.4). The values of  $[\eta]$  obtained by the various equations are 0.244 and 0.231 dl/g for PTP4 and PIP1, respectively.

#### Huggins [7]

$$\eta_{rel}/C = [\eta] + K_H [\eta]^2 C \quad (1.1)$$

#### Kraemer [8]

$$\ln \eta_{rel}/C = [\eta] + K_K [\eta]^2 C \quad (1.2)$$

#### Schulz-Blaschke [9]

$$\eta_{sp}/C = [\eta] + K_{SB} [\eta_{rel}] \eta_{sp} \quad (1.3)$$

#### Martin [10]

$$\ln(\eta_{sp}/C) = \ln [\eta] + K_M [\eta] C \quad (1.4)$$

**Table 4 Intrinsic viscosity in dl/g and constants of Eqs. (3.5) to (3.8) for given polyesters in DMF at 30°C**

Code	Eq (1.1)		Eq (1.2)		Eq (1.3)		Eq (1.4)	
	$[\eta]$	$K_H$	$[\eta]$	$-K_K$	$[\eta]$	$K_{SB}$	$[\eta]$	$K_M$
PTP4	0.185	0.251	0.185	0.232	0.185	0.237	0.185	0.244
PIP1	0.241	0.239	0.241	0.236	0.241	0.223	0.241	0.231

### Spectral Studies

#### Infrared Spectra

FT-IR spectrums data of all the present eleven polyesters are shown below. The formation of polyester from TPCl and aromatic diol is confirmed from the typical characteristic bands observed around  $1738 \pm 3 \text{ cm}^{-1}$  ( $>C=O$  stretch in ester) and  $1275 \pm 12 \text{ cm}^{-1}$ ,  $1070 \pm 4 \text{ cm}^{-1}$  and  $1009 \pm 7 \text{ cm}^{-1}$  and (C-O-C symmetric and asymmetric stretch) in all presently investigated aromatic polyesters(77-79). The relative intensities decreases in the order at  $1275 > 1070 > 1009 \text{ cm}^{-1}$ . This difference has been attributed to the rigid configuration of the terephthalate ester linkage, which further confirmed the presence of terephthaloyl moiety in the polyester. In addition, the spectra also exhibited several other absorption frequencies, which distinguish the polyesters from each other, because of the involvement of the different diols. The presence of BPA moiety in PTP1 is indicated by C-H bending vibration of isopropyl group as a typical strong doublet at  $1384\text{-}1360 \text{ cm}^{-1}$  and at  $1170 \text{ cm}^{-1}$ . The presence of resorcinol moiety in PTP2, is confirmed due to bands around  $1691$ ,  $1600$ , and  $1483 \text{ cm}^{-1}$  (aromatic C=C stretch) and  $937$ ,  $778$ ,  $677 \text{ cm}^{-1}$  (1,3-substituted benzene). 15DHN moiety in PTP3 can be identified due to bands at  $1636 \text{ cm}^{-1}$  and  $1598 \text{ cm}^{-1}$  because of ring stretching vibration of substituted naphthalene. It is difficult to separately identify BHBA, BHBB and BHBP

diol moieties in the polyesters PTP4, PTP5 and PTP6 as all these diols contain same aromatic and CH=N groups in one another. It may be noted that the intensity of band varies as number of CH=N are different in these polyesters. A weak band at  $730\text{ cm}^{-1}$  (C-S-C) and band at  $1599\text{ cm}^{-1}$  (C=C aromatic) show the involvement of BHBPT in the polyester PTP7.

Like the terephthalic polyesters just discussed, the polyesters involving isophthaloyl chloride and aromatic diol show the typical characteristic bands around  $1734\pm 7\text{ cm}^{-1}$  (>C=O stretch in ester) and  $1296\pm 3$ ,  $1070\pm 9$  and  $1009\pm 7\text{ cm}^{-1}$  and (C-O-C symmetric and asymmetric stretch) which confirms the polyester formation. As expected the relative intensities follow the sequence at  $1296 > 1070 > 1009\text{ cm}^{-1}$  because of the rigid configuration of the tere/isophthalate ester linkage. The different types of polyesters can be distinguished from each other by a few other characteristic absorption frequencies of different involved aromatic diols.

The presence of BPA moiety in PIP1 is indicated by C-H bending vibration of isopropyl group at  $1364$  and  $1171\text{ cm}^{-1}$ . The resorcinol moiety in PIP2 is recognized due to out of plane vibration of 1,3-substituted benzene at  $886$ ,  $778$ , and  $680\text{ cm}^{-1}$ . 15DHN moiety in PIP3 can be identified due to the bands at  $1690$ ,  $1600$  and  $1505\text{ cm}^{-1}$  because of ring stretching vibration of substituted naphthalene.

### Nuclear Magnetic Resonance Spectra

$^1\text{H-NMR}$  spectra of eleven selected polyesters PTP1 to PTP7, PIP1, PIP3, and PIP7 were obtained. The  $^1\text{H-NMR}$  spectra were taken in DMSO- $d_6$  solvent on Bruker DPX-200 spectrometer at 200 MHz (RSIC, CDRI, Luknow) with a sweep time of 10 min. at room temperature. The internal reference used was TMS.

**PTP1:** The sharp singlet at  $\delta$  1.6 ppm corresponds to 6H of isopropyl group. Polymer repeat unit has over all 12Ar-H, which appear in the range  $\delta$  6.60 to 8.30 ppm. The 8Ar-H for BPA segment resonates at  $\delta$  6.60-7.34(m) ppm while 4Ar-H of terephthaloyl group appears at  $\delta$  7.76-8.30 ppm as multiplet.

**PTP2:** Multiplet in the range  $\delta$  6.67-7.59 ppm corresponds to 4Ar-H for resorcinol segment, while the multiplet at  $\delta$  8.01-8.34 ppm is attributable to 4Ar-H of terephthaloyl segment.

**PTP3:** As expected, 4Ar-H of terephthaloyl segment appears as a multiplet at  $\delta$  8.15-8.54 ppm while multiplet in the range  $\delta$  7.16-7.99 ppm corresponds to 6Ar-H of 15DHN segment. Small peak at 6.92 ppm is due to Ar-H ortho- to residual end -OH of 15DHN moiety.

**PTP4:** The broad peak at  $\delta$  9.77 ppm is attributed to 1H of azomethine group. The Ar-H due to BHBA unit appears in the  $\delta$  range 6.90 to 7.75 ppm while for terephthalic unit in the  $\delta$  range 8.03-8.23 ppm. Small peak centered at  $\delta$  6.71 ppm may be attributed to Ar-H ortho- to residual end -OH of BHBA moiety.

**PTP5:** The singlet at  $\delta$  10.02 ppm is attributed to 2H of two azomethine groups. Multiplet in the range  $\delta$  7.56-8.06 ppm corresponds to 16Ar-H of BHBB segment while at  $\delta$  8.11-8.35 ppm for the 4Ar-H of terephthaloyl segment.

**PTP6:** The peak at  $\delta$  9.74-10.6 ppm is attributed to 2H of two-azomethine group. Multiplet in the range  $\delta$  6.87-7.78 ppm corresponds to 12Ar-H of BHBP segment while at  $\delta$  7.97-8.32 ppm for 4Ar-H of terephthaloyl moiety. Small peak at  $\delta$  6.80 ppm corresponds to Ar-H ortho- to residual end -OH of BHBP moiety.

**PTP7:** 8Ar-H in BHBPT segment appears at  $\delta$  6.83-7.49 ppm, while the 4Ar-H of terephthaloyl resonates at  $\delta$  8.00-8.32 ppm.  $\delta$  at 6.73-6.86 ppm shows Ar-H ortho- to residual end -OH.

**PIP1:** The aromatic ester substituted isophthalic unit shows Ar-H at  $\delta$  7.58-7.85, 8.13-8.46 and 8.61-8.75 ppm. The multiplet in the range  $\delta$  7.14-7.34 ppm corresponds to 4Ar-H ortho- to isopropyl in BPA. The peak at  $\delta$  6.64-7.02 ppm results from Ar-H ortho- to end -OH group of BPA moiety. A doublet at  $\delta$  1.60-1.70 ppm is indicative of aliphatic 6H of isopropyl unit in BPA segment.

**PIP3:** As expected the aromatic ester substituted isophthalic unit shows Ar-H at  $\delta$  7.57-8.00, 8.05-8.51 and 8.64-8.73 ppm. The 15 DHN is expected to resonate at  $\delta$  6.79-7.99 ppm for its 6Ar-H. The Ar-H in the range  $\delta$  7.57 to 7.99 ppm has merged with isophthalic acid protons.

**PIP7:** The aromatic ester substituted isophthalic unit shows Ar-H at  $\delta$  7.63-7.83, 8.14-8.44 and 8.61-8.75 ppm. The multiplet in the range  $\delta$  6.82-7.49 ppm is attributed to Ar-H of BHBPT segment in polyester.

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