



## Full Length Research Article

### SYNTHESIS AND CHARACTERIZATION OF ALIPHATIC-AROMATIC POLYESTERS USING INTERFACIAL POLYCONDENSATION TECHNIQUE

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#### ABSTRACT

Thirteen linear aliphatic-aromatic polyesters were synthesized by interfacial polycondensation of various diacid chlorides such as adipoyl chloride (ADCL) and sebacoyl chloride (SECL) with various 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 thermo gravimetric analysis.

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#### INTRODUCTION

Polyesters are important class of high performance and engineering polymers, which find use in a number of diverse applications (Seymour and Kirshenbaum, 1986; Han *et al.*, 1997 and Jadhav *et al.*, 1991). Polyester is a strong fiber and consequently can withstand strong and repetitive movements. Its hydrophobic property makes it ideal for garments and jackets that are to be used in wet or damp environments. Coating the fabric with a water-resistant finish intensifies this effect. Since polyester can be molded into almost any shape, certain insulating properties can be built in to the fiber. Polyester is used both as staple fiber as well as continuous filament yarns. Polyester staples are commonly used with cotton, wool, and rayon to get blended yarns. Polyester also has industrial uses as well, such as carpet, filters, synthetic artery replacements, ropes, and films. Further, they are also used as film forming, coating, and adhesive and reinforced materials. Different kinds of polyesters have been synthesized over the past decades from various types of diacid chlorides and diols.

Thermally stable polyesters derived from isophthalic and terephthalic acids with bisphenol-A have been commercialized (Cassidy, 1980). 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. There are three major processes described in the literature for the synthesis of aromatic polyesters. These are (a) an interfacial polycondensation of terephthaloyl chloride (TPCL) / isophthaloyl chloride (IPCL) with bisphenol-A (BPA) under phase transfer conditions (Mitsubishi Chemical Corporation, 1982, 1985), (b) melt polycondensation of BPA-diacetate with terephthalic acid (TPA) / isophthalic acid (IPA) in the presence of a catalyst (Berzer *et al.*, 1982, 1983 and Yu, 1984), and (c) melt polycondensation of diphenyl terephthalate (DPT) / diphenyl isophthalate (DPI) with BPA in the presence of a catalyst (Kosanovich *et al.*, 1982; Pawlak *et al.*, 1982). Because phase-transfer-catalysed polycondensation or interfacial polycondensation (IPC) is known to be useful on the synthesis of general aromatic polyesters and their analogs, this method has been employed by many investigators (Morgan *et al.*, 1965; Patil *et al.*, 1981; Cassasa *et al.*, 1981; Imai, 1981, 1982,

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1984; Rao *et al.*, 1987; Yang *et al.*, 1990; Liou *et al.*, 1992; Bhowmik *et al.*, 1993; Jadhav, 1994; Hsiao *et al.*, 1995; Vibhute *et al.*, 1997; Jegal *et al.*, 1988; Watanabe *et al.*, 1998; Hu *et al.*; 1999 and Gharbi, 2000). The polyesters so obtained are in good yield with high molecular weights. Further the range of the polymers prepared is greater. The IPC is a rapid polymerization process at the interface between water containing difunctional intermediate and an inert immiscible organic solvent containing a complementary difunctional reactant. In light of this, the IPC technique with stirring has been selected in the present work for the synthesis of polyesters formed from various types of aliphatic and aromatic diacid chlorides and different types of aromatic diols.

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.

## Experimental

### Materials

**Dicarboxylic Acids:** Adipic acid (ADA) and sebacic acid (SEA) 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 (Riddick, 1986).

**Acid Chloride Monomers:** Adipoyl chloride (ADCl) and sebacyl chloride (SECl) 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 <sup>1</sup>H-NMR (Figure 1, CDCl<sub>3</sub>, 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 (Figure 2, DMSO-d<sub>6</sub>, TMS)  $\delta$  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 (Figure 3, DMSO-d<sub>6</sub>, 90 MHz, TMS)  $\delta$  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 (Figure 4, DMSO-d<sub>6</sub>, TMS)  $\delta$  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 (Figure 5, DMSO-d<sub>6</sub>, TMS,  $\delta$  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).

### Measurements

Elemental analysis for all polyesters, C, H and N were estimated by "Carlo Erba Elemental Analyzer". FT-IR spectra of all polymer samples have been scanned in KBr pellet on Perkin-Elmer RX2, IR spectrometer by KBr pellet technique. The <sup>1</sup>H-NMR spectra were taken in DMSO-d<sub>6</sub> as a solvent on Bruker DPX-200 Spectrometer at 200 MHz (RSIC, CDRI,

Lucknow) with a sweep time of 10 minutes at room temperature. The internal reference used was TMS. The  $^{13}\text{C}$ -NMR spectra were also taken in  $\text{DMSO-d}_6$  solvent using Bruker DRX-300 Spectrometer at 300 MHz (RSIC, CDRI, Lucknow). The viscosity measurements were carried out in DMF at  $30 \pm 0.2^\circ\text{C}$ , using an Ubbelohde suspended-level viscometer. The thermogravimetric analysis was made with the Mettler TA-4000 system, incorporating TG-50 thermobalance and TA-11 microprocessor. The measurements were recorded in air at a heating rate  $10^\circ\text{C}/\text{min}$ . in  $\text{N}_2$  atmosphere.

### Conditions for polyester synthesis

In the present investigation interfacial polycondensation of diacid chloride with aromatic diol is used. It has been observed (Morgan, 1965; Cassasa *et al.*, 1981; Imai, 1981, 1982 and 1984) that the polymerization reaction is influenced by solvent system and catalytic and surfactant additives. 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 (Morgan, 1965) Chloroform/water interface system has been employed for similar polymerization of this type (Cassasa, 1981; Korshak *et al.*, 1965). 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.<sup>15</sup> 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.

### Effect of 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 (Morgan, 1965; Cassasa, 1981; Imai, 1984 and Korshak *t-et al.*, 1965). Sometimes IPC, as type of nucleophilic displacement, are carried out with phase transfer catalyst (Starks *et al.*, 1971; Docky, 1973 and Makosza, 1975). generally small symmetric quaternary ammonium cations (Cassasa, 1981; Imai, 1982 and Conix, 1959). 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 (Cassasa, 1981; Imai, 1981). In the present case we have used citramide as a cationic

surfactant and phase transfer catalyst. Considering the experience of previous investigators (Cassasa, 1981; Imai, 1981), 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  $30^\circ\text{C}$ . These are summarized in Table 1.

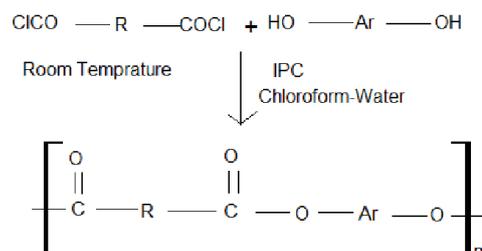
**Table 1. Reaction conditions for the synthesis of polyester from ADCl and BPA**

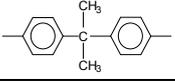
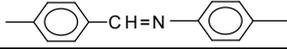
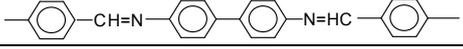
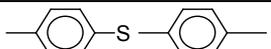
Interface System	Chloroform/Water:
Phase volume ratio	35 ml/ 85 ml
Reactants	ADCl = 0.0125 mol BPA = 0.0125 mol
Acid acceptor	: 0.025 mol NaOH
Additive	Citramide
Temperature	$30^\circ\text{C}$
Time	5 min.
Stirring	Vigorous and continuous

### Polymerization

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 min 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 (Pawlak, 1982). 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  $40^\circ\text{C}$ . 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:



Where, R =	
ADCL	$\text{---}(\text{CH}_2)_4\text{---}$
SECL	$\text{---}(\text{CH}_2)_8\text{---}$
Where, Ar =	
BPA	
15DHN	
RES	
BHBA	
BHBB	
BHBP	
BHBPT	

## RESULTS AND DISCUSSION

Thirteen linear aliphatic-aromatic polyesters were synthesized by stirred interfacial polycondensations of various 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

Yields of the different polymer samples involving a dipoyl moiety are in the range from 20 to 67% while those of sebacyl moiety are from 32 to 86% (Table 2). All the polyesters are solid powders and coloured depending upon the types of aromatic diol involved. The polyesters PAD3, PAD4, PSE3 and PSE4 are black powders while other polyesters are either brown to dark brown powders.

### Elemental Analysis

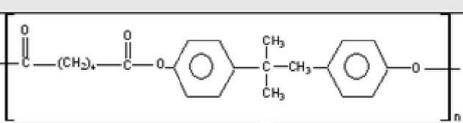
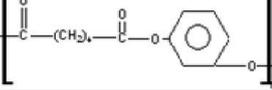
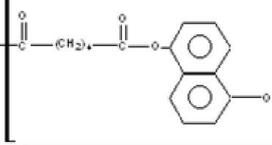
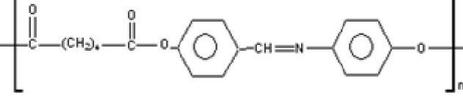
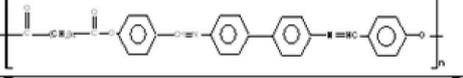
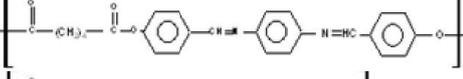
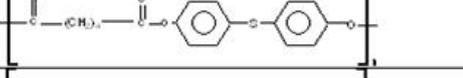
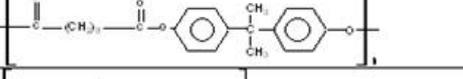
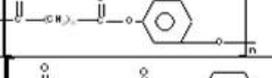
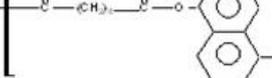
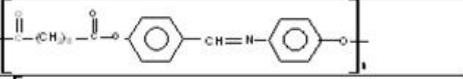
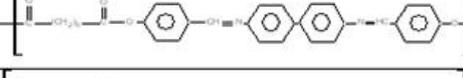
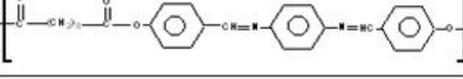
The results of elemental analysis of present polyesters are given in Table 3. The observed percentage of C, H, and N contents in present polyesters are fairly in good agreement with those theoretically calculated based on the repeat units in the chain. This suggests that both monomers join alternatively in 1:1 mole ratio.

### Solubility Behaviors

A study of solubility of polymers in different types of solvents is of great importance, both for processing the polymers and for the service of article made from them. Many films and synthetic fibers are produced from the solutions. The solubility behavior also provides additional information about polymer-polymer and polymer-solvent interactions.<sup>38,39</sup> Relative solubilities in different solvents are summarized in Table 4. The polyesters PAD1, PAD2, PAD3, PAD4, PAD5, PAD6, PAD7 are soluble in DMF and THF at room temperature while in DMSO they dissolve only on heating. They are partially soluble in nitrobenzene (NB) and insoluble in chlorobenzene

(CB), dimethylacetamide (DMA), dichloroethane (DCE), ethylacetoacetate (EAA), ethyl chloroacetate (ECA), methanol, ethanol, and petroleum ether.

**Table 2.** Polyesters obtained by the interfacial polycondensation technique from different aliphatic diacid chlorides with aromatic diols

Code	Repeat Unit	Appearance	Yield (%)
PAD1		Dark brown Powder	20
PAD2		Dark brown Powder	28
PAD3		Black Powder	45
PAD4		Black Powder	67
PAD5		Dark brown Powder	48
PAD6		Dark brown Powder	45
PAD7		Brown Powder	40
PSE1		Dark brown Powder	32
PSE2		Dark brown Powder	35
PSE3		Black Powder	75
PSE4		Black powder	43
PSE5		Dark brown Powder	33
PSE6		Brown Powder	34

The polyesters involving sebacic acid moiety PSE1, PSE2, PSE4, PSE5, and PSE7 are soluble in THF and in DMF except PSE6, which is only partially soluble in DMF on heating (Table 4). These all polyesters are only partially soluble in DMSO and NB even on heating except PSE4 and PSE7, which get dissolved in DMSO on heating.

### Solution Viscosity

Intrinsic viscosity  $[\eta]$  is a measure of hydrodynamic volume and depends on molecular weight as well as on the size of the

polymer coil in a given solution. There are number of methods which have been used to calculate the intrinsic viscosity  $[\eta]$  of polymer solutions.

The intrinsic viscosities of present polymer samples determined in DMF at 30°C using Huggins equation [41], Kraemer equation [42], Schulz-Blaschke equation 43 and

**Table 3. Elemental analysis C, H, and N % contents in the polyesters**

Polyester	C%		H%		N%	
	calc.	obs.	Calc.	obs.	calc.	obs.
PAD1	74.55	74.51	6.50	6.41	-	-
PAD2	62.88	62.78	5.24	5.14	-	-
PAD3	71.11	71.03	5.18	5.08	-	-
PAD4	70.58	70.29	5.30	5.19	4.33	4.03
PAD5	76.49	76.31	5.17	5.02	5.57	5.25
PAD6	73.23	72.92	5.20	5.11	6.57	6.28
PAD7	65.45	65.31	5.45	5.35	-	-
PSE1	78.12	78.03	5.20	5.08	-	-
PSE2	69.56	69.36	7.24	7.14	-	-
PSE3	71.87	71.59	7.81	7.58	-	-
PSE4	72.80	72.56	6.64	6.59	3.69	3.58
PSE5	77.41	77.21	6.09	5.98	6.01	5.84
PSE6	74.67	74.54	6.27	6.19	5.80	5.63

**Table 4. Relative solubilities of Polyesters in different solvents at 30°C**

Solvent	polyesters of ADCl + aromatic diol							polyesters of SECl + aromatic diols						
	PAD 1	PAD2	PAD3	PAD4	PAD 5	PAD 6	PAD 7	PSE1	PSE2	PSE4	PSE5	PAD6	PAD7	PSE1
THF	S	S	S	S	S	S	S	S	S	S	S	S	S	S
DMF	S	S	S	S	S	S	S	S	S	S	S	S	S	S
DMSO	SH	SH	SH	SH	SH	SH	SH	PS	PS	SH	PS	PS	SH	PS
Nitrobenzene	PS	PS	PS	PS	PS	PS	PS	PS	PS	PS	PS	PS	PS	PS
Chlorobenzene	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
a	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
DMA	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Dichloroethane	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
a	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Chloroform	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
ECA	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
EAA	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Methanol	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Ethanol	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Petroleum ether														
Water														

**Table 5. Intrinsic viscosity in dl/g and Huggins KH, Kraemer KK, SchulzBlaschke KSB and Martin KM constants for polyesters in DMF at 30°C**

COD	Eq (1)		Eq (2)		Eq (3)		Eq (4)		< $\eta$ >
	$[\eta]$	$K_H$	$[\eta]$	$-K_K$	$[\eta]$	$K_{SB}$	$[\eta]$	$K_M$	
PAD 1	0.136	0.261	0.346	0.228	0.136	0.250	0.135	0.255	0.188
PAD 4	0.229	0.313	0.229	0.182	0.230	0.289	0.230	0.300	0.229
PAD 5	0.207	0.220	0.206	0.253	0.207	0.209	0.207	0.215	0.206
PAD 6	0.218	0.245	0.217	0.234	0.218	0.230	0.218	0.237	0.218
PAD 7	0.207	0.223	0.206	0.252	0.207	0.211	0.207	0.217	0.206
PSE1 2	0.224	0.254	0.221	0.226	0.222	0.238	0.222	0.246	0.222
PSE2 1	0.221	0.329	0.221	0.168	0.221	0.305	0.221	0.315	0.221
PSE3 2	0.178	0.238	0.172	0.244	0.172	0.227	0.172	0.232	0.172
PSE4 9	0.179	0.272	0.179	0.215	0.179	0.256	0.179	0.264	0.179
PSE5 0	0.169	0.259	0.160	0.228	0.160	0.247	0.160	0.253	0.160

Martin equation 44 are given Table 5 along with Huggins KH, Kraemer KK, Schulz-Blaschke KSB and Martin KM constants. Study of Table 5 shows that in general, the values of  $[\eta]$  in DMF at 30°C obtained by using the Schulz-Blaschke equation (3) are slightly higher than those of other three equations. Since, the difference between  $[\eta]$  obtained by the various equations is not large, we have taken an average value of all the four equations, which is given, in the last column of the Table 5. An examination of intrinsic viscosities (Table 5) of given polyesters reveals that PAD4 has the highest solution viscosity and PSE5 has the lowest. The intrinsic viscosities of the investigated polyesters are in the range from 0.160 to 0.229 dl/g and follows the sequence,

$$\text{PAD4} > \text{PSE1} = \text{PSE2} > \text{PAD6} > \text{PAD5} = \text{PAD7} > \text{PAD1} > \text{PSE4} > \text{PSE3} > \text{PSE5}.$$

For the present polymer samples, the values of KH-KK are in the range 0.47 to 0.50, with an average value of 0.48±0.01. This average value of  $K_H-K_K$  is in excellent agreement with the theoretically predicted value of 0.5. Further, generally the values of  $K_H$  (hydrodynamic constant) are > 0.30, indicating chloroform to be a good solvent for these polymers.

### Spectral Characterization

FTIR spectrums all the present thirteen polyesters are shown in Figures 6 to 9 The formation of polyester is confirmed from the typical characteristic bands observed at 1726±16 cm<sup>-1</sup> (>C=O stretch in ester) and 1035±32 and 1246±43 cm<sup>-1</sup> (C-O-C symmetric and asymmetric stretch) in all the presently investigated polyesters (Silverstein *et al.*, 1981; Patil, 1981; Jeong *et al.*, 1991 and Liaw, 1996). In adipic acid or sebacic acid, >C=O stretch was observed at 1690 cm<sup>-1</sup> which on esterification has shifted to 1726±16 cm<sup>-1</sup> as expected. In all the polyesters the absorption band at 1473±13 cm<sup>-1</sup> indicates incorporation of -(CH<sub>2</sub>)<sub>n</sub>- of adipic or sebacic carboxylate moiety (Silverstein *et al.*, 1981). The different types of polyesters can be distinguished from each other by a few other characteristic absorption frequencies of involved aromatic diols.

Table 6. Thermal behavior of polyesters in air

Polymer	Step	T <sub>i</sub> °C	T <sub>max</sub> °C	T <sub>f</sub> °C	T <sub>10</sub> °C	T <sub>50</sub> °C	IPDT °C	Residue %
PAD1	I	174	192	319	234	379	338	14.8
	II	319	395	496				
PSE1	I	161	268	331	234	407	356	7.6
	II	331	388	490				
	III	490	550	635				

The involvement of BPA moiety in PAD1 and PSE1 is indicated by a band at 1384 cm<sup>-1</sup> (isopropyl group (Silverstein *et al.*, 1981 and Naik, 1986), and bands at 1612 and 1510 cm<sup>-1</sup> (aromatic C=C stretch). The presence of resorcinol moiety in PAD2 and PSE2 is confirmed due to bands at 1610±10 cm<sup>-1</sup> and 1500±10 cm<sup>-1</sup> (aromatic C=C stretch) and 900, 765, 683 cm<sup>-1</sup> (1,3- disubstituted benzene (Silverstein *et al.*, 1981). The 15DHN moiety in PAD3 can be identified due to bands at 1675-1600 cm<sup>-1</sup> and 1575 cm<sup>-1</sup> because of ring stretching vibration of substituted naphthalene (Desai *et al.*, 1995) It is difficult to separately identify BHBA, BHBB and BHBP as all these diols contain same aromatic or -CH=N- groups in one

another. The presence of characteristic band for -CH=N- at 1610-1580 cm<sup>-1</sup> confirms the presence of benzilidine group.<sup>51,52</sup> It may be noted that intensity of band varies as the number of -CH=N- are different in these polyesters. A weak band at 730 cm<sup>-1</sup> (C-S-C) and band at 1599 cm<sup>-1</sup> (C=C aromatic) show involvement of BHBPT in polyester (Silverstein, *et al.*, 1981).

<sup>1</sup>H-NMR spectra of four selected polyesters PAD1, PAD4 PSE1 and PSE4 obtained in DMSO-d<sub>6</sub> solvent on Bruker DPX-200 spectrometer at 200 MHz (RSIC, CDRI, Luknow) with a sweep time of 10 minutes, at room temperature are shown in Figs. 10 to 13. The internal reference used was TMS. PAD1: 4H of two -CH<sub>2</sub>- and 4H of two -CH<sub>2</sub>O- in adipoyl moiety appears at δ 1.51 ppm and at 2.26 ppm, respectively. A sharp singlet at δ 1.59 ppm is indicative of 6H of isopropyl unit 56,57 and two doublets in the range of 6.60-6.62 and 6.94-6.97 ppm corresponds to 4 Ar-H (o- to isopropyl group) and 4 Ar-H (m- to isopropyl group) in BPA segment. PAD4: 4H of two -CH<sub>2</sub>- and 4H of two -CH<sub>2</sub>O- in adipoyl moiety appear at δ 1.61 ppm and at 2.26 ppm, respectively. Multiplet in the range of 6.79 to 7.76 ppm corresponds to 8Ar-H of BHBA segment. 4Ar-H ortho- to OC=O link, and 2Ar-H ortho- to amino + 2Ar-H ortho- to benzilidine groups resonate around 7.25-7.76, and 6.90-7.1258, respectively. A singlet at δ 9.77 ppm is due to 1H of -CH=N-. small peak at 6.70-6.79 ppm is due to 2Ar-H, ortho- to residual end -OH group of BHBA moiety. PSE1: 12H (a,b) of 6 -CH<sub>2</sub>- and 4H(c) of two -CH<sub>2</sub>CO- of sebacyl moiety appear at δ 1.23-1.51 and at 2.17 ppm, respectively. A sharp singlet at δ 1.57 ppm is indicative of 6H of isopropyl unit 56,57 and two doublets in the range of 6.60-6.63 and 6.94-6.97 ppm corresponds to 4 Ar-H (o- to isopropyl group) and 4 Ar-H (m- to isopropyl group) in BPA segment. PSE4: 12H(a,b) of 6 -CH<sub>2</sub>-, 4H(c) of two -CH<sub>2</sub>C=O- of sebacyl moiety appear at δ 1.22-1.45 and at 2.14 ppm, respectively. Multiplet in the range of 6.86 to 7.73 ppm corresponds to 8Ar-H of BHBA segment. 4Ar-H ortho- OC=O (ester), and 2Ar-H ortho- to amino + 2Ar-H ortho- to benzilidine groups resonate around 7.37-7.73, 6.86-7.31 ppm, respectively. A singlet at δ 8.9 ppm is due to 1H of -CH=N-.58 A small peak at 6.66 ppm is attributed to Ar-H ortho- to residual end -OH group of BHBA moiety.

### Thermal gravimetric analysis

Thermo grams for the two investigated polyester samples: PAD1 and PSE1 thermo grams initial decomposition temperature (Ti), temperature for maximum rate of decomposition (Tmax) and half volatilization temperature T50 and integral procedural decomposition temperature (IPDT) have been summarized in Table 6. Qualitative behavior of each of these thermo grams has been described. PAD1: Thermo gram indicates the two-step degradation of PAD1. In the first step in the temperature range 174°C to 319°C only 8.5% weight loss occurred. The second step degradation from 319 to 496°C has accounted for 77.8% weight loss. The temperature at which maximum degradation of polyester PAD1 took place in this step was 395°C. The temperature at which 50% weight of polymer degraded was 379°C. At 700 °C temperature 14.8% residue was left behind. PSE1: It exhibits three-step thermal degradation.

The first step decomposition started at 161°C, which extended up to 331°C, accounting for about 33.7% weight loss. The second step degradation from 331 to 490°C has accounted for 28.8% weight loss and in the third step degradation from 490°C to 635°C about 29.6% weight was lost. The maximum rates of weight loss occurred at 268, 388 and 550°C in the first, second and third step, respectively. 50% of the polyester weight loss occurred at 407°C. The residue left behind at 700°C was 7.6%.

## Conclusion

The investigated linear aliphatic-aromatic polyesters show excellent solubility in DMF and THF at ambient temperature. They are partially soluble in DMSO and NB. However, in many cases they dissolve in DMSO on the heating. The intrinsic viscosity of linear aliphatic-aromatic polyesters varies in the range of 0.160-0.229 dl/g at 30°C. The IR spectra of polyester is confirmed in the linear aliphatic aromatic polyesters from the typical characteristic bands observed at 1726±16 (>C=O stretch in ester) and 1035±32 and 1246±43 (C-O-C symmetric and asymmetric stretch). High-resolution <sup>1</sup>H-NMR spectra of four selected aliphatic-aromatic polyesters PAD1, PAD4, PSE1 and PSE4 were consistent with the structure of repeat unit in corresponding polyesters. The thermal behavior of polyester PAD1 decomposes in two-steps and PSE1 polyester shows three-step thermal degradation. Both polyester have modest to good thermal stability. From this study it can be seen that the thermal stability is highly dependent on the type of diacid and/or diol moieties and their chemical structure. It is found that by replacing aromatic rings in place of aliphatic chain in the polyester, the thermal stability can be enhanced significantly.

## REFERENCES

- Berzer, M.H., Maresca, L.M., and Steiner, U.A. 1982. *Eur. Pat. Appl. EP* 35,269 (1981) to Union Carbide Corp., USA, CA 96, 20601g.
- Berzer, M.H., Maresca, L.M., and Ulrich, A. 1983. *U.S. Pat.* 4, 374,239 (1983) to Union Carbide Corp., USA, CA 98, 161355h.
- Bhowmik, P.K., Atkins, E.D.T., and Lenz, R.W. 1993. *Macromolecules*, 26, 440.
- Bilmayer, F. W. Jr., 1994. *Text book of Polymer Science John Wiley & Sons*, New York, 3<sup>rd</sup> Ed.
- Bovey, F.A. 1972. *High Resolution NMR of Macromolecules*, Academic Press, INC, New York.
- Cassasa, E.Z., Chao, D.Y., and Henson, M. 1981. *J. Macromol. Sci. Chem. A-15(5)*, 799.
- Cassidy, P.A. 1980. *Thermally stable polymers*. New York: Dekker.
- Conix, A. 1959. *Ind. Eng. Chem.*, 51, 147.
- Crompton T.R., 1989. *Analysis of Polymers An Introduction*, Pergamon Press, New York.
- Desai, D.R. 1995. *Ph. D. Thesis*, South Gujarat University, Surat.
- Docky J., 1973. *Synthesis*, 441.
- Flory, P.J., 1962. *Principle of Polymer Chemistry*, Cornell University Press, Ithaca, New York.
- Gharbi S., Andreolety J.P., and Gandini A., 2000. *Eur. Polym. J.*, 36(3), 463.
- Han, H., Bhowmik P.K. 1997. *Prog Polym Sci*; 22:1431–502.
- Hatt, H.H. 1943. *Organic Synthesis II*, 395.
- Hildebrand, J.H., and Scott R.L. 1950. *The Solubility of Nonelectrolyte*, 3<sup>rd</sup> Ed. Reinhold, New York.
- Hsiao, S.H. and Chang H.Y. 1995. *J. Polym. Res.*, 2(2), 99.
- Hu, X., and Li, X. 1999. *J. Polym. Sci. Part B: Polym. Phys.*, 37, 965.
- Huggins, M.L. 1942. *J. Am. Chem. Soc.*, 64, 2716.
- Idage, S.B., Idage, B.B., and Vernekar, S.P., 1992. *J. Polym. Sci. Part A Polym. Chem.* 30, 513.
- Imai, Y., Abe S., and Ueda M. 1981. *J. Polym. Sci., Polym. Chem. Edn.*, 19, 3285.
- Imai, Y., Abe S., Takahashi, T. and Ueda, M. 1982. *J. Polym. Sci., Polym. Chem. Edn.*, 20, 683.
- Imai, Y., and Tassavori, S. 1984. *J. Polym. Sci., Polym. Chem. Edn.*, 22, 1319.
- Jadhav, A.S., Wadgaonkar, P.P., and Varnekar, S.P., 1994. *Polym. Sci.*, 1, 349.
- Jadhav, J.Y., Kantor, S.W. 1991. In: *Kroschwitz II, editor. High performance polymers and composites*. New York: Wiley.
- Jegal, J., and Blumstein, A., 1988. *J. Appl. Polym. Sci.*, 68, 387.
- Jeong, H.J., Kakimoto, M.A., and Imai, Y. 1991. *J. Polym. Sci, Part A. Polym. Chem.* 29, 1293.
- Kim, S. G., Han, Y. K., Gong, M. S. 1995. *Bull. Korean Chem. Soc.*, 16, 326.
- Kim, S.G., Han, Y.K., and Gong, M.S., 1995. *Bull. Korean Chem. Soc.* 16, 326.
- Korshak V.V., and Vinogradova S.V. 1965. *Polyesters*, Transform from Russian by Hazzard B.J., Pergamon Press, Oxford.
- Kosanovich, G.M., and Salee, G. 1981. *Eur. Pat. Appl. EP* 35,895 (1981) to Hooker Chem. and Plastic Corp., USA, CA 102, 52927j.
- Kraemer, E.O. 1938. *Ind. Eng. Chem.*, 30, 1200.
- Liaw, D.J., and Chen P.S., 1996. *J. Polym. Sci. Part A Polym. Chem.* 34, 885.
- Liou, G.S., Kakimoto, M., and Imai, Y. 1992. *J. Polym. Sci. Part A: Polym. Chem.*, 28, 2195.
- Mahajan S.S., Idage B.B., Chavan N.N., and Sivaram S. 1996. *J. Appl. Polym. Sci.*, 61(13), 2297.
- Makosza, M. 1975. *Pure & Appl. Chem.*, 43, 439.
- Martin A. F. 1951. *Tappi*, 34, 363.
- Mitsubishi Chemical Corporation Ltd. Japan, *Jpn. Kokai Tokkyo Koho JP* 82, 96,017 (1980), CA 97, 163706b (1982).
- Mitsubishi Chemical Corporation Ltd. Japan, *Jpn. Kokai Tokkyo Koho JP* 59, 223,721, 59, 223722 (1983), CA 102, 204497b, 204498c (1985).
- Mitsubishi Chemical Corporation Ltd. Japan, *Jpn. Kokai Tokkyo Koho JP* 60, 23,420 (1983), CA 103, 6875f (1985).
- Morgan, P.W., 1965. *Condensation Polymer by Interfacial and Solution Methods*, John Wiley And Sons, Inc., New York.
- Naik, R. B., and Shah, P. P. 1989. *Eur. Polym. J.*, 25(2), 193.
- Patil, A.O., Deshpande D.D., Talwar S.S., and Biswas A.B. 1981. *J. Polym. Sci., Polym. Chem. Ed.*, 19, 1155.
- Patil, A.O., Deshpande, D.D., Talwar, S.S., and Biswas, A.B. 1981. *J. Polym. Sci, Polym. Chem. Ed.*, 19, 1155.

- Pawlak, J., Rosenfeld, J., and Salee, G. 1982. *U.K. Pat. Appl. GB 2, 085,458* (1982) to Hooker Chem. & Plastic Corp., USA, *CA* 97, 56415.
- Ramey, K.C., and Brey W. S. 1967. *J. Macromol. Sci. Rev. Macromol. Chem.*, 1, 263.
- Rao, M.V., Rajivadiya A.J., Parsania P.H., and Parekh H.H. 1990. *J. Macromol. Sci. Chem.*, A 27(1), 53.
- Rao, M.V., Rajivadia, A.J., Parsania P.H., and Parekh, H.H. 1987. *J. Ind. Chem. Soc.*, 15, 758.
- Riddick, J.A., Bunger, W.B., and Sakano, T.K. 1986. *Organic Solvents Physical Properties and Methods of Purification, Wiley Interscience*, New York.
- Schulz, G.V., and Blaschke, F., *J. Prakt. Chem.*, 158, 130, (1941).
- Seymour, R.B., Kirshenbaum G.S, 1986. editors. High performance polymers: their origin and development. New York: Elsevier.
- Silverstein, R.M., Basseler, G.C., and Marill, T.C.,1981. *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, New York, 4<sup>th</sup> edition.
- Smith, D. A. 1981. Addition polymers [formation and characterization, plenum, New York.
- Starks C.M. 1971. *J. Am. Chem. Soc.*, 93, 195.
- Vibhute, S.S., Joshi, M.D., Wadgaonkar, P.P., Patil, A.S., and Maldar, N.N. 1997. *J. Polym. Sci. Part A: Polym. Chem.*, 35, 3227.
- Watanabe, S., Murayama, H., Murata M., Masuda Y., and Tanabe, M.1998. *J. Polym. Sci. Part A: Polym. Chem.*, 36, 2229.
- Yang, C.P., Oishi, Y., Kakimoto, M. and Imai, Y., 1990. *J. Polym. Sci. Part A: Polym. Chem.*, 28, 1353.
- Yu M.C., 1985. *U.S. Pat.* 4, 485,230 (1984) to Philips Petroleum Co., USA, *CA* 102, 46468m.

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