

Wholly Aromatic Polyester-Amides Containing Amide Linkages as A Processable Thermally Stable Polymers

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ABSTRACT: Polyester-amides are well known as high-performance polymeric materials because of their excellent thermal stability as well as the balanced mechanical and electrical properties and have been applied widely in the aviation, automobile and electronic industries, adhesives, composites, fibers, films. Replacement of the conventional monomers with heterocyclic moiety and introduction of flexible linkages in the main chain increases processability. Aromatic polyester-amides (PEAs) have been synthesized by interfacial polycondensation of aliphatic and aromatic diacid chlorides with aromatic diol in a chloroform /water system employing phase transfer catalyst. These polymers were characterized by IR, ¹HNMR, ¹³CNMR, solubility, inherent viscosity and TGA analysis. These polyester-amides exhibited solubility in solvents like chloroform, NMP and DMAc, DMF. Thermal analysis showed that polymers possess good thermal stability exhibited glass transition temperature (T_g) in the range 150-230°C. Percentage of char yield about 40 -50% at 900°C showed good thermal stability. Synthesised polyamides showed the inherent viscosity in the range 0.3 - 0.6 dLg⁻¹.

Keywords: chloroform-water interphase system, diacid chlorides, high performance materials, interfacial polycondensation, Polyester-amide.

I. INTRODUCTION

Aromatic amides (polyaramides) are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties [1-5] therefore essential for various technical application that require operation at increased temperatures while maintaining their structural integrity. However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful forms because of their high melting or glass-transition temperatures (T_g's) and their limited solubility in organic solvents [6-8]. These undesired properties are caused by strong interchain interaction forces, inherent macromolecular rigidity or semicrystallinity. Therefore, a great deal of effort has been expended to improve the processing characteristics of the relatively intractable polymers [9-10]. These studies include introducing flexible segments into the polymer chain; replacing symmetrical aromatic rings with unsymmetrical ones, which leads to a reduction in crystallinity; introducing bulky pendant groups to minimize crystallization; and forming a noncoplanar structure, thereby making crystallization impossible. Conventionally, it is convenient to synthesize modified aramids via the incorporation of bulky pendant groups into diamine or dicarboxylic acid monomers, followed by polycondensation [11-13]. The development of processable high-performance polymers with increased thermal stability, heat resistance and good mechanical properties has become an important problem [14]. In an attempt to prepare polymers of high glass transition temperature, T_g, Imai et al. [15] synthesized the polyester-amides of high molecular weight and investigated their properties in detail. Insertion of ester, ether or other flexible groups in main chain has been found to be effective approach towards improving processability [16-20]. The PEAs have special structure due to the regular enhancement of ester and amide groups in the same polymer.

These chain, which give them the properties intermediate between the polyester and the polyamide [21]. The rigidity due to the double bond character of the amide group coupled with extensive hydrogen bonding influences the ordering of PEA [22]. Thus, the growth and expansion of aromatic-aliphatic polyester-amides work, both basic and applied over the past few decades has been enormous [23-24]. Apart from high thermal stability, the many PEAs also exhibit liquid crystalline properties [25]. The polyester-amides have potential applications as high modulus fibres and engineering polymers [26]. Considering all these important aspects it was decided to undertake the synthesis of new PEAs from polycondensation of aminophenols and diacid chlorides by interfacial method and to evaluate their properties in detail. In this context the aim of this article is the synthesis and characterization of new polyesteramides with substantially improved solubility. These poly(amide-ester)s were synthesised by the polycondensation reaction of different aromatic diamine containing heterocyclic moiety with diacid chloride. These polymers were characterized by solubility, inherent viscosity, IR, ¹H, ¹³C NMR, and TGA-DSC analysis.

II. EXPERIMENTAL

2.1 Materials

Sulphur, benzyl chloride, 4-hydroxy benzoic acid, 4,4'-aminophenoxyoxy diphenyl ether (ODA), 4,4'-diamino diphenyl sulphone (SDA) and p-phenylenediamine, m-aminoacetophenone from (S.d.Fine chemicals Ltd.) Thionyl chloride, pyridine, ethanol, chloroform, methanol, acetone, sodium hydroxide, sodium bicarbonate, sulphuric acid, hydrochloric acid, benzyl chloride etc. were good quality laboratory reagents and used after appropriate purification and distillation if required. 4,4'-difluorobenzophenone (S.d.Fine chem.Ltd.) recrystallised using methanol. K_2CO_3 used after prior purification as per standard procedure and drying in oven. Toluene, DMF (N,N Dimethyl formamide), DMAc (N,N Dimethyl acetamide) used after distillation. All these solvents dried over 4A molecular sieves.

2.2 Instrument

1H NMR spectra were recorded with either a Bruker 400 MHz and 50 MHz for ^{13}C measurements using $CDCl_3$ or DMSO solvent. IR spectra were recorded at a resolution of 4 cm^{-1} with co-addition of 32 scans using a Thermo-scientific Nicolet iS10 smart IR. Different scanning calorimeter (DSC) scans were obtained using in a nitrogen atmosphere at a heating rate $10^\circ\text{C}/\text{min}$. DSC was conducted on a Mettler Toledo DSC at a heating rate of $10^\circ\text{C}/\text{min}$ over a temperature range of $50\text{--}350^\circ\text{C}$ under a nitrogen flowing atmosphere. The thermogravimetric analysis (TGA) was performed with Perkin Elmer TGA-7 system at a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere from 60 to 1000°C . XRD WAXD patterns. XRD patterns of polymer were obtained with a Rigaku Micromax-007 X-ray diffractometer operating at 40 kV and 30 Ma

III. SYNTHESIS OF MONOMERS

3.1 Synthesis of diamino 2,3,4,5 tetraphenyl thiophene used as a starting material for synthesis was prepared as per procedure reported by N .N. Maldar et.al.[3]

3.2 Synthesis of N, N'-Bis-[3-(2-amino-thiazol-4-yl)-phenyl]isophthalamide (ATPIPA)(I)

In a 100 mL three neck round bottom flask added diacetyl compound (I) 0.4 g (0.001mol) and iodine 0.252 g (0.002mol) and thiourea 1.2 g (0.004 mol) and stirred the mixture in DMAc at 120°C for 24 h. Then poured the solution with stirring in water, the yellow solid was obtained. The precipitate was washed successively with water and then by ethanol. Recrystallised the product in acetone. Yield: 0.460 (90%).

Compound (I) was assigned by, (IR) 1672 cm^{-1} ($-C=O$ stretching of (CONH)) 3365 cm^{-1} (NH stretching of primary amine). 1H NMR(200 MHz, DMSO; ppm) 10.38 ppm (s, 2H), 6.97 ppm (s, 2H) was assigned to proton of NH_2 group. The aromatic protons were exhibited peaks in range (7.33-8.60 ppm. (multiplet)) ^{13}C NMR(50 MHz, DMSO; PPM) showed the 15 peaks for 15 different carbon atoms. The peak at 165 ppm was assigned to carbonyl carbon of amide group. Mass: The molecular ion peak at 512 m/e^+ was assigned as a base peak. This confirmed the Thiazole diamine structure

3.3 Synthesis of bis N-(4-Hydroxy-phenyl)4-(3-phenyl-thiophene-2-yl)benzamide(DPTB)(II)

In a 100 mL three neck round bottom flask equipped with reflux condenser, magnetic stirrer and calcium guard tube and nitrogen gas inlet were placed 0.418 g (1mmol) TPTP diamine, 0.276 g (2mmol) p-hydroxybenzoic acid, 0.200g lithium chloride (8 wt%) based on solvent (N-methyl pyrrolidine (NMP) and Pyridine mixture) and 0.744g (0.63 mL (2.4 mmol) triphenyl phosphate (TPP), 0.5 mL Pyridine and 2 mL NMP. The mixture was stirred well and temperature was slowly raised to 100°C and refluxed at 100°C for 3h. under nitrogen. After cooling the resulting viscous mixture was poured into rapidly stirred 200 mL methanol. The precipitated product was filtered, washed with methanol and air dried. The monomer was purified by dissolving in N,N-dimethylacetamide (DMAc) and reprecipitated by methanol. It was filtered washed dried under vacuum at 100°C for 8h.

Yield :- 0.493 g (75%)

M.P. :- 230°C

The resulted (DPTB) was characterized by IR, 1H NMR, ^{13}C NMR and MASS spectroscopically. IR spectrum data of diol shown below. The formation of diol from TPTP diamine and p-hydroxybenzoic acid is confirmed from the typical OH characteristic bands observed around 3277 to 3024 cm^{-1} broad band and 1640 cm^{-1} ($-C=O$ stretch of CONH linkage), 1288 cm^{-1} , 1070 cm^{-1} and 1059 cm^{-1} and (C-O-C symmetric and asymmetric stretch). 1H NMR spectra confirmed the amide linkage formation by presence of peak at 9.64 ppm. The peak present between the 7 to 7.89 ppm shows aromatic proton. ^{13}C NMR spectra give 14 different signals. The peak at 166 ppm assigned a carbon which is in amide linkage. 12 different peaks in the range between 115 ppm to 139 ppm assigned to aromatic carbon. The peak present at 160 ppm assigned to aromatic carbon which is attached to directly OH functional group. The structure of TPTP diol also confirmed by mass spectroscopically. The molecular ion peak at 659 m/e^+ as a base peak.

3.4 Synthesis of N,N'-Bis [3-2-amino-thiazol-4-yl]-phenyl isophthalamide (DATPI) (III)

In a 100 mL three neck round bottom flask equipped with reflux condenser, magnetic stirrer and calcium guard tube and nitrogen gas inlet were placed 0.512 (1mmol) N, N'-bis-[3-(2-amino-thiazol-4-yl)-phenyl]isophthalamide (ATPIPA), 0.276 g (2mmol) p-hydroxybenzoic acid, 0.200g lithium chloride (8 wt% based on solvent N-methyl pyrrolidine (NMP) and Pyridine mixture) and 0.744g (0.63 mL, 2.4 mmol) triphenyl phosphate (TPP), 0.5 ml Pyridine and 2 mL NMP. The mixture was stirred well and temperature was slowly raised to 100°C and refluxed at 100°C for 3h. under nitrogen. After cooling the resulting viscous mixture was poured into rapidly stirred 200 mL methanol. The precipitated polymer was filtered, washed with methanol and air dried. The monomer was purified by dissolving in N,N-dimethylacetamide (DMAc) and reprecipitated by methanol. It was filtered washed dried under vacuum at 100°C for 8h.

Yield :- 0.47g (60%)

The formation of diol from Thiazole diamine and p-hydroxybenzoic acid is confirmed from the typical OH characteristic bands observed around 3277 to 3024 cm^{-1} broad band and 1640 cm^{-1} (-C=O stretch of CONH linkage), 1288 cm^{-1} , 1070 \pm 4 cm^{-1} and 1059 \pm 7 cm^{-1} and (C-O-C symmetric and asymmetric stretch).

3.3 Synthesis of other diols using, ODA, SDA, 1,4 Phenylene diamine Synthesized using above similar procedure.

IV. 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/Dichloromethane phase is an excellent solvent for diacid chloride 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 diacid chloride 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.

V. SYNTHESIS OF POLYESTER

The reactants diacid chloride (ADCl) and Amide containing diol were taken in equimolar ratio, using Dichloromethane-water interphase system. 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: Dichloromethane/Water
Phase volume ratio : 35 ml/ 85 ml
Reactants : IPC= 0.001 mmol
BPA = 0.001 mmol
Acid acceptor : 0.025 mol NaOH
Temperature : 30°C
Time : 5 min.
Stirring : Vigorous and continuous

VI. RESULT AND DISCUSSION

In the view of above aim the unsaturated poly (ester-amide) s were synthesized by the addition reaction of unsaturated acid chloride with amide containing diols. These diols having amide linkage synthesized by Yamazaki high temperature solution method. Thus, the growth and expansion of aromatic-aliphatic polyester-amides work, both basic and applied over the past few decades has been enormous [28]. Apart from high thermal stability, the many PEAs also exhibit liquid crystalline properties [29-30]. The polyester-amides have potential applications as high modulus fibers and engineering polymers [31]. Considering all these important aspects it was decided to undertake the synthesis of new PEAs from polycondensation of aminophenols and diacid chlorides by interfacial method and to evaluate their properties in detail [32]. Interfacial polycondensation of aromatic diacid chlorides (terephthaloyl chloride, isophthaloyl chloride,) with diols ((ODA diol, SDA diol, TPTP diol, Thiazole diol, 1,4 Phenylene diol, Bisphenol -A) and their characterization through solubility studies, intrinsic viscosity, IR, ^1H NMR, ^{13}C NMR and TGA-DSC analysis.

It reveals that polyesters PS₁, PS₂, PS₃, PS₄, PS₆ are soluble in DMAc, DMF, NMP, DMSO at room temperature while PS₅ is insoluble in all solvents and partially soluble in nitrobenzene, m-cresol and Pyridine.

Further, all the polyesters containing isophthaloyl moiety are totally insoluble in dichloromethane, Toluene, and ethanol.

Yield and Appearance

The yield and appearance are summarized in Table 1. Yields of the different polymer samples involving isophthaloyl moiety are in quantitative yield. All the polyesters are solid powders with different colours depending upon the types of aromatic diol involved. The polyesters PS₁, PS₂, PS₃, PS₄, PS₅, PS₆, are white powders while other polyesters are either light to dark brown or pale yellow powders.

Spectral Studies

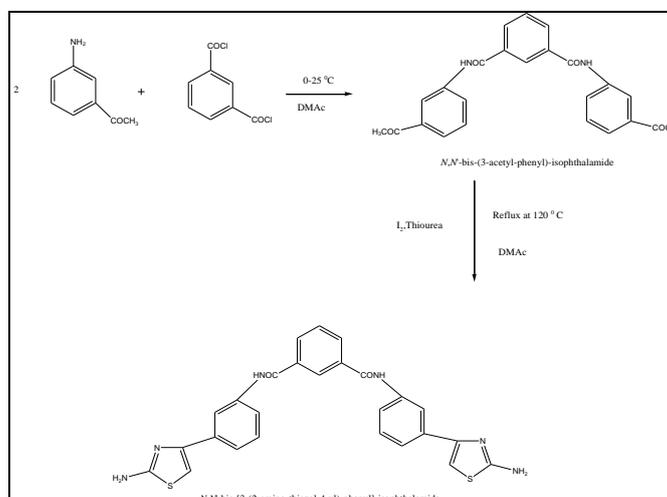
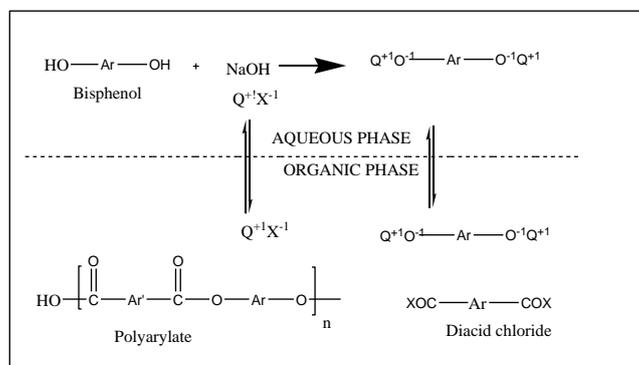
Fig-4:- IR Spectra of (DPTB)(II)

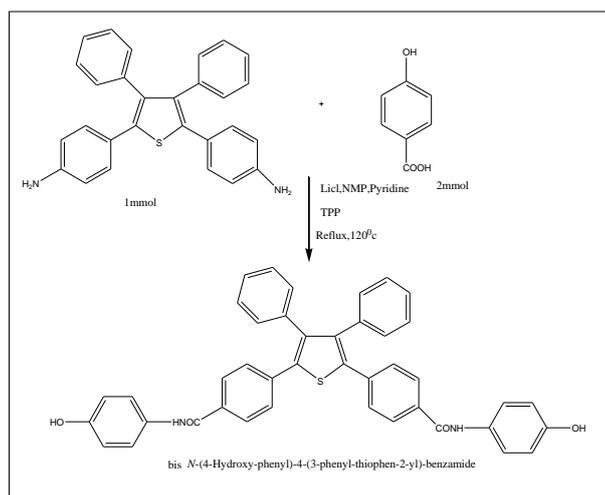
The formation of polyester from Isophthaloyl chloride and DPTB(IV) is confirmed from the typical characteristic band at 1741 cm⁻¹ (>C=O Stretch band in ester) and 1652 cm⁻¹ (-C=O stretch of CONH linkage), 1288 cm⁻¹ and 1058 cm⁻¹ and (C-O-C symmetric and asymmetric stretch).

¹HNMR spectra gives peak at 10.22 ppm confirmed the amide linkage formation. In the range 6.97 to 8.89 ppm peaks were aromatic proton. ¹³CNMR gives different peak which confirms the structure of polyester formation. The peak at 165 ppm for amide linkage.

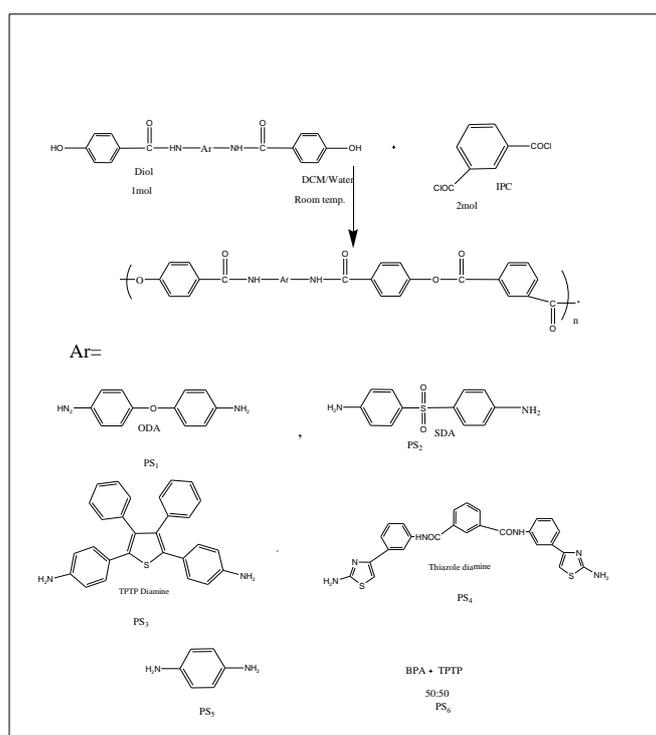
IR spectra of (DATPI) (III)

The formation of polyester from Isophthaloyl chloride and DATPI (V) is confirmed from the typical characteristic band at 1741 cm⁻¹ (>C=O Stretch band in ester) and 1644 cm⁻¹ (-C=O stretch of CONH linkage), 1285 cm⁻¹ and 1043 cm⁻¹ and (C-O-C symmetric and asymmetric stretching). From thermogravimetric analysis all polymers were stable. The glass transition temperature in range between 160 -240°C indicates highly processable. All polymers show % of char yield about 20-52 % showed high thermal stability. From XRD it was confirmed that all polyesters are semi crystalline in nature.





Scheme 3.3:-Synthesis of bis N-(4-Hydroxy-phenyl)4-(3-phenyl-thiophene-2-yl)benzamide (II)



Scheme 3.4:-Synthesis of polyester from (II) and IPC

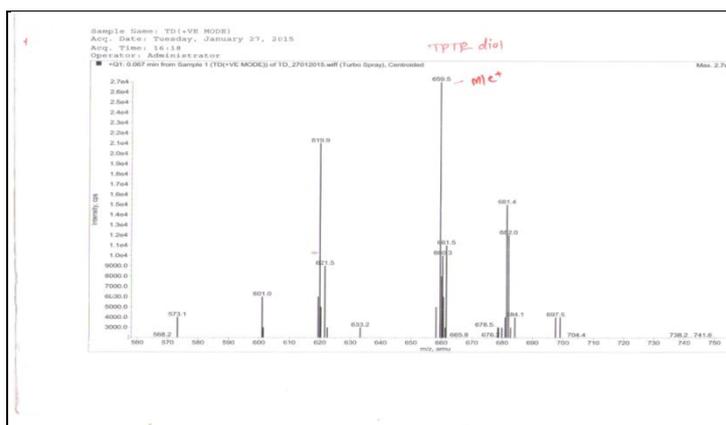


FIG.1 MASS spectra of (II)

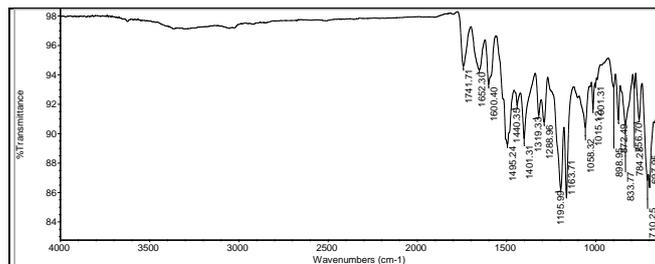


Fig. 1:- IR spectra of Polyester from (II) and IPC

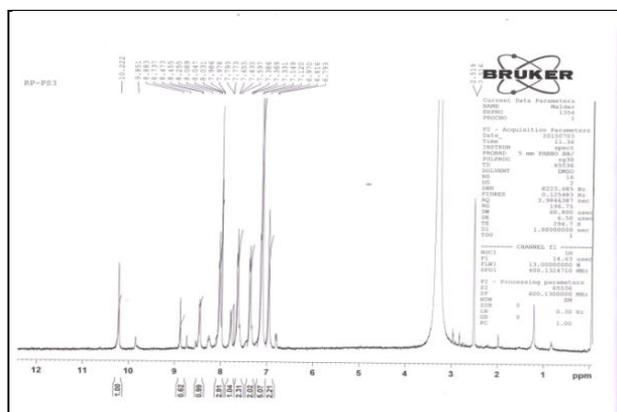


Fig. 2 :- ¹H NMR Spectra of Polyester from (II) and IPC

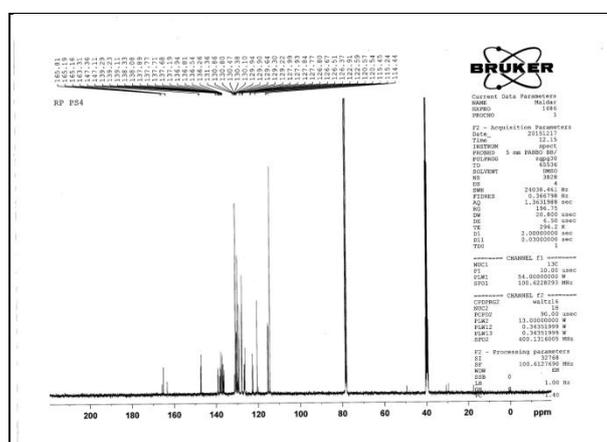


Fig. 3:- ¹³C NMR Spectra of polyester from (II) and IPC

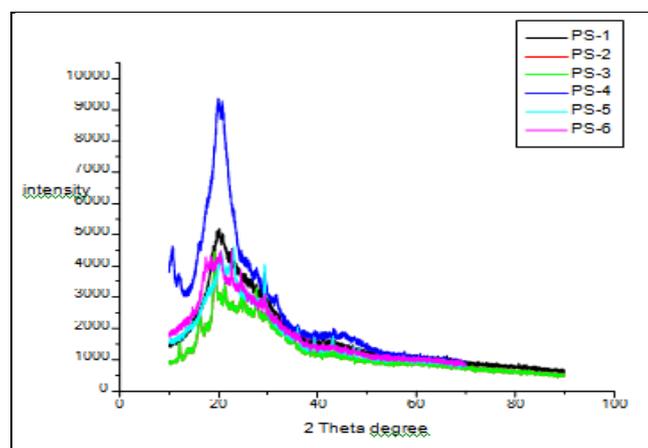


Fig.4 XRD of polyester

Fig.5:-DSC of PS-1and PS-7

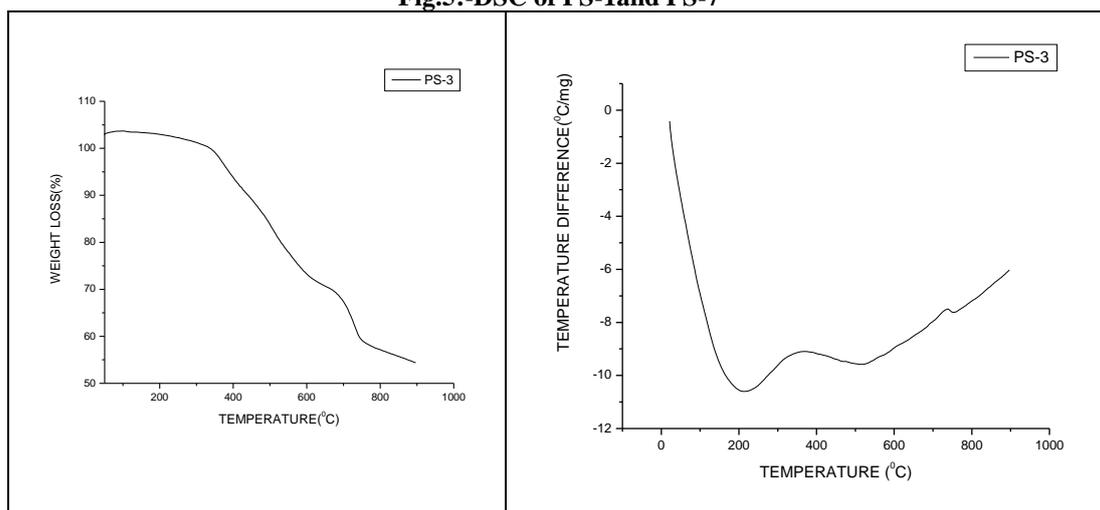


Fig. 6:-TGA of PS-3 Fig. 7:-DSC of PS-3

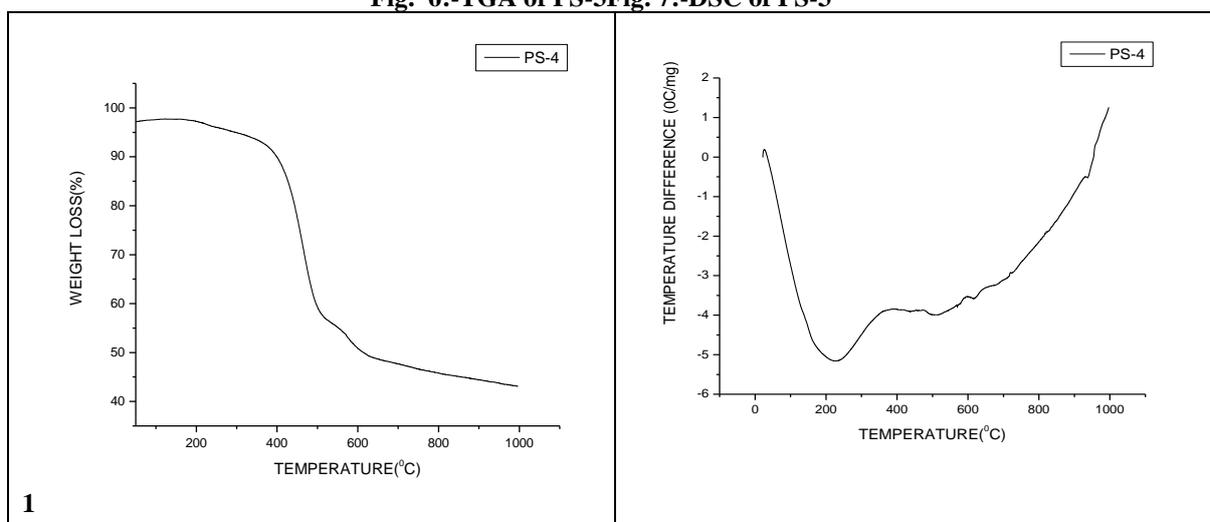


Fig. 8:-TGA of PS-4 Fig. 9:-DSC of PS-4

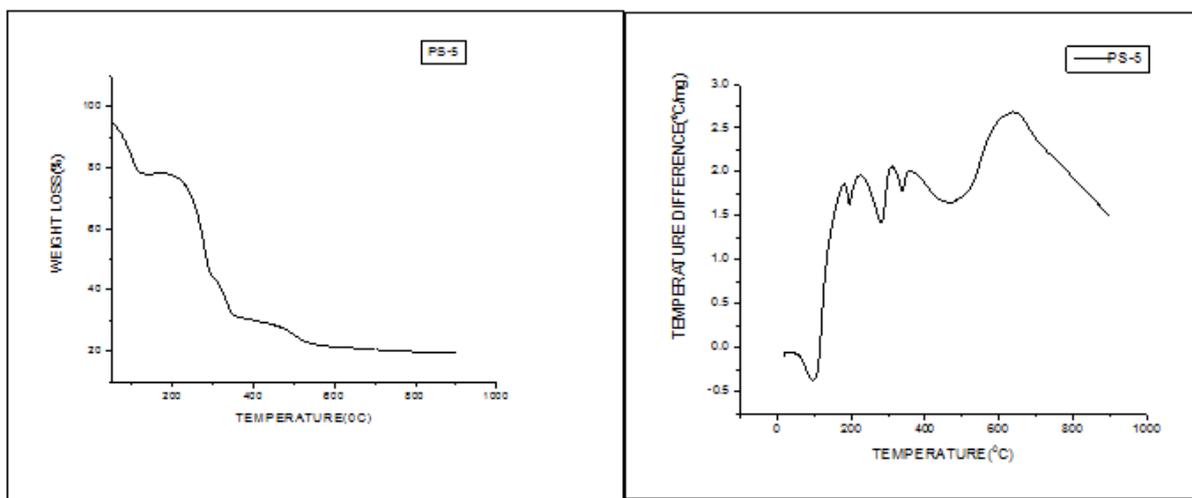


Fig. 10:-TGA of PS₅ Fig. 11:-DSC of PS₅

POLYESTERS

Table-2 synthesis and properties of polyesters from aromatic diol and Isophthoyl chloride

Polymer	Diol	Diacid chloride	Yield (%)	η_{inh} (dL/g) ^a	T _i (°C) ^b	T ₁₀ (°C) ^c	T ₅₀ (°C) ^d	Residue at 980°C (%)	T _g (°C) ^e
PS-1	ODA Diol	IPC	90	0.36	310	390	590	38	160
PS-2	SDA Diol	IPC	95	0.30	-	-	-	-	-
PS-3	TPTP Diol	IPC	90	0.60	320	420	590	52	220
PS-4	Thiazole Diol	IPC	80	0.54	320	420	600	44	210
PS-5	TPTP+ BPA (70:25)	IPC	95	0.48	250	310	520	34	190
PS-6	TPTP+ BPA (50:50)	IPC	95	0.52	390	420	590	42	230
PS-7	BPA	IPC	90	0.5	320	400	610	20.79	170

^a η inherent was measured with 0.5%(w/v) solution of polyesters at 30±0.1°C in NMP.

^b Initial decomposition temperature.

^c Temperature at which 10% weight loss is observed.

^d Thermal data for diol derived polyesters. ^e Glass transition temperature measured on DSC at a heating rate of 10°C/min in nitrogen atmosphere.

Table 3:- Solubility data of polyesters from from various diols and Isophthoyl chloride^a

Sr. No.	Solvents										
	DMAc	DMSO	DMF	NMP	PYRIDINE	cresol	Nitrobenzene	DCM	Toluene	Ethanol	Conc. H ₂ SO ₄
PS-1	++	++	++	++	+	+-	+-	--	--	--	++
PS-2	++	++	++	++	+-	+-	+-	--	--	--	++
PS-3	++	++	++	++	+-	+-	+-	--	--	--	++
PS-4	++	++	++	++	+-	+-	+-	--	--	--	++
PS-5	++	++	++	++	+-	+-	+-	--	--	--	++
PS-6	++	++	++	++	+-	+-	+-	--	--	--	++
PS-7	++	++	++	++	+-	+-	+-	--	--	--	++
PS-8	-	--	--	--	--	--	--	--	--	--	++

Solubility of polymer: 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.

^a ++: soluble at room temperature +-:soluble on heating; --:insoluble

PS-1= ODA diol

PS-2 =SDA diol

PS-3=TPTP diol

PS-4= Thiazole diol

PS-5= BPA diol+TPTPdiol (75:25)

PS-6=BPA diol+TPTPdiol (50:50)

PS-7=BPA

PS-8=1,4 Phenylene diamine

VII. CONCLUSION

The synthesised polyesters series were synthesized from various amide linkage containing diol with IPC by interfacial polycondensation system. The polyesters show solubility in polar aprotic solvent like DMAc, DMSO, NMP etc. They showed good thermal stability

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