

Synthesis and characterization of polyimides containing thiazole moiety

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Abstract - Thiazole containing polyimides (PI) TPI-1 and copolyimides (CTPI-2,3,4,5,6) were synthesized from *N,N'*-Bis-[4-(2-amino-thiazol-4-yl)-phenyl] isophthalamide [ATPIPA] (II) and aromatic dianhydrides via thermal or chemical imidisation method. All polyimides were characterised by IR, NMR, Mass, TGA, DSC, XRD, Viscosity, Solubility. poly (amic acid) had inherent viscosities range from 0.19 to 0.37dL/g. All PI shows good solubility. PI formed by chemical imidisation method could be dissolved in DMAC. All polyimides had glass transition temperature in the range of 250-400 °C. Thus it shows best thermal stability. The temperature of 10% weight loss (T_{10}) were above 190 °C. The residues more than 10% at 900 °C in nitrogen atmosphere. XRD data shows all polyimides have been crystalline nature.

Keywords - Polyimides, thioazole, solubility.

I. INTRODUCTION

Polyimide (PI) having a favourable combination of properties such as high glass transition temperature (T_g), excellent mechanical properties, and good dimensional stabilities have been extensively investigated with both academic and industrial viewpoints. They have been widely employed in the aerospace, microelectronics, optoelectronics, composites and so on, because of their excellent balance of thermal and mechanical properties [1]-[2]. Incorporating heterocyclic unit into Polyimide main chain by using heteroaromatic monomers is also effective to improve thermal and mechanical properties of polyimides, saving the complex procedure of mechanical stretching. Here in this experiment a diamine monomer *N,N'*-Bis-[4-(2-amino-thiazol-4-yl)-phenyl] isophthalamide [ATPIPA] (II) was prepared through two step synthesis [1]-[3]. *N,N'*-Bis-(4-acetyl phenyl) isophthalamide (I) was prepared firstly by refluxing p-aminoacetophenone in dry DMAC with isophthaloyl chloride in presence of nitrogen atmosphere, few crystals of LiCl were added. The *N,N'*-Bis-[4-(2-amino-thiazol-4-yl)-phenyl] isophthalamide [ATPIPA] (II) product was obtained by refluxing (I) with Thiourea, I_2 in presence of DMAC for 24 h.

Polyimides prepared from *N,N'*-Bis-[4-(2-amino-thiazol-4-yl)-phenyl] isophthalamide [ATPIPA] and aromatic dianhydride had best

combination of properties with the purpose of improving thermal and mechanical properties of the Polyimide by increasing polymer backbone's rigidity. The properties of the copolyimide were investigated and the composition dependence of the properties was discussed.

II. EXPERIMENTAL

MATERIALS:-

Dimethyl Acetamide (DMAC), thionyl chloride, methanol, m-aminoacetophenone Isophthaloyl chloride, Terephthaloyl chloride, PMDA, BTDA, 4,4'-diphenoxy diphenyl ether (Aldrich chemicals), m-cresol, tetrahydrofuran (THF), dichloromethane (DCM), chloroform, tetrachloromethane (TCE), ethanol (S. d.fine Chem. Ltd. Mumbai), triphenyl phosphate (Merck) and sodium hypochlorite were used as received.

Benzene, Hexane, pyridine, lithium chloride, N-methyl-2-pyrrolidone (NMP) and N-N-dimethyl acetamide (DMAC) (S.d. fine Chem. Ltd. Mumbai) were purified before by following standard procedure.

III. SYNTHESIS OF MONOMER

(i) Synthesis of *N,N'*- bis (4- acetyl phenyl) isophthalamide (I)

In 100 mL three neck round bottom flask equipped with magnetic stirrer, a nitrogen gas inlet, thermowell and $CaCl_2$ guard tube were charged with p-aminoacetophenone 0.274 g (0.002mol) and dry DMAC (6mL). The mixture was stirred under nitrogen atmosphere till the complete dissolution takes place and it was cooled to -15 °C. In a cooled reaction mixture add lotwise isophthaloyl chloride 0.203 g (0.001 mol) and few crystals of LiCl. The mixture was stirred at 0 °C for 1.5 h and then at 25 °C for 1.5 h.

The solution was stirred at room temperature for 24 h. The viscous solution was poured in methanol with stirring to get white solid. Then the product was filtered and washed with methanol.

Yield:-0.38 g (95%) Melting point :-210 °C
IR (cm^{-1}): 1667 cm^{-1} (C=O stretching of (CO-NH)), 2908 cm^{-1} (aliphatic CH stretching) and 1602 cm^{-1} (NH bending) ¹HNMR (200 MHz, DMSO:ppm): 9.8 ppm (s, 2H) amide proton. The singlet peak at 2.56 ppm (s, 6H) was due to aliphatic methyl proton. 7.28-8.55 ppm. (multiplet) aromatic protons were observed in range ¹³C NMR (50 MHz DMSO:PPM)

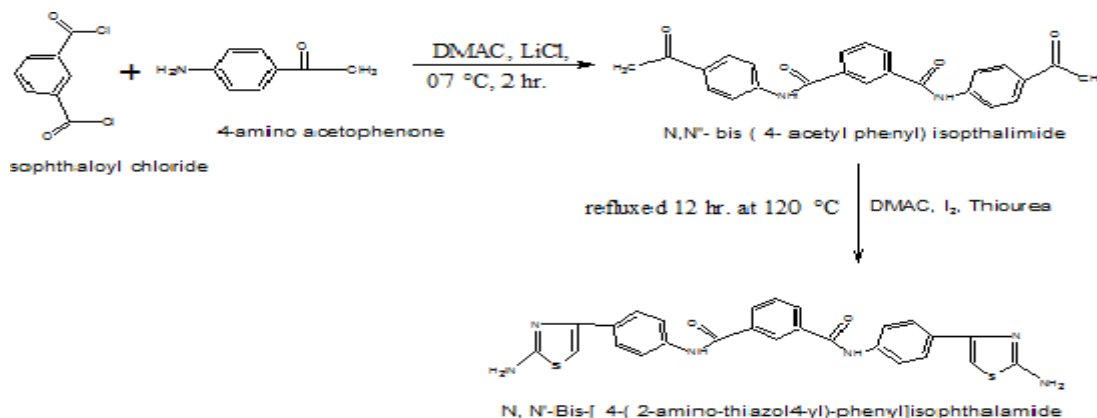
spectra showed the 16 peaks for 16 different carbon atoms. (26.71 ppm) was assigned to methyl carbon, (165.50 ppm) assigned to carbonyl carbon of amide group and at (198.03 ppm) due to carbonyl carbon of acetyl group.

(ii) Synthesis of N, N'-Bis-[4-(2-amino-thiazol-4-yl)-phenyl] isophthalamide (ATPIPA) (II)

In a 100 mL three necked round bottom flask added 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%). (IR) 1672 cm^{-1} (–C=O stretching of (CONH)) 3365 cm^{-1} (NH stretching of primary amine). ^1H NMR(200 MHz, DMSO; ppm) 10.30 ppm (s, 2H), 7.5 ppm (s, 2H) was assigned to proton of NH_2 group. The aromatic protons were exhibited peaks in range (7.55-8.55) 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



Scheme- preparation of N, N'-Bis-[4-(2-amino-thiazol-4-yl)-phenyl]isophthalamide (ATPIPA)

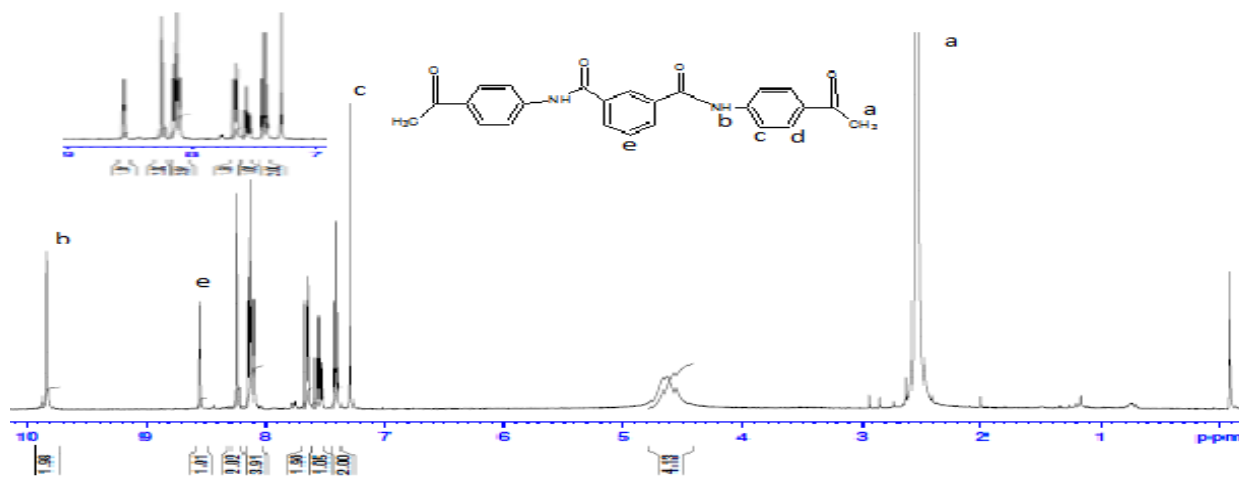


Figure 1 NMR spectra for N,N'- bis (4- acetyl phenyl) isophthalamide (I)

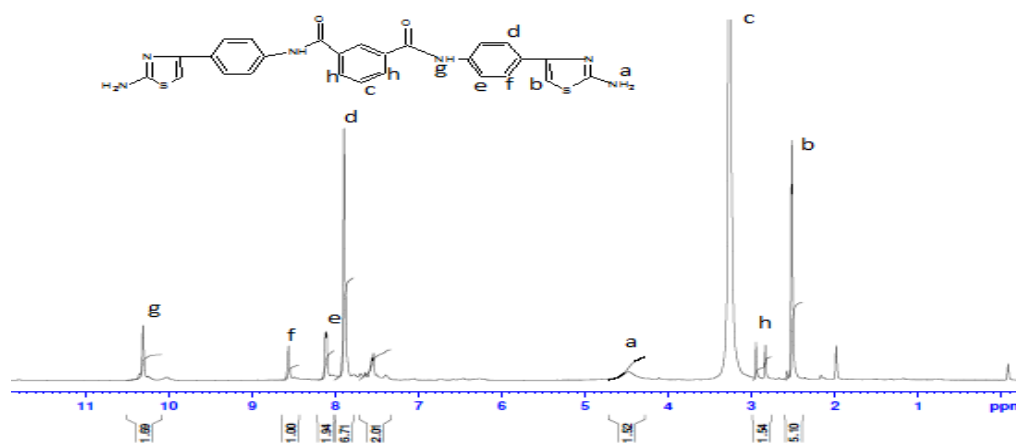


Figure 2 NMR spectra for N, N'-Bis-[4-(2-amino-thiazol-4-yl)-phenyl] isophthalamide (ATPIPA) (II)

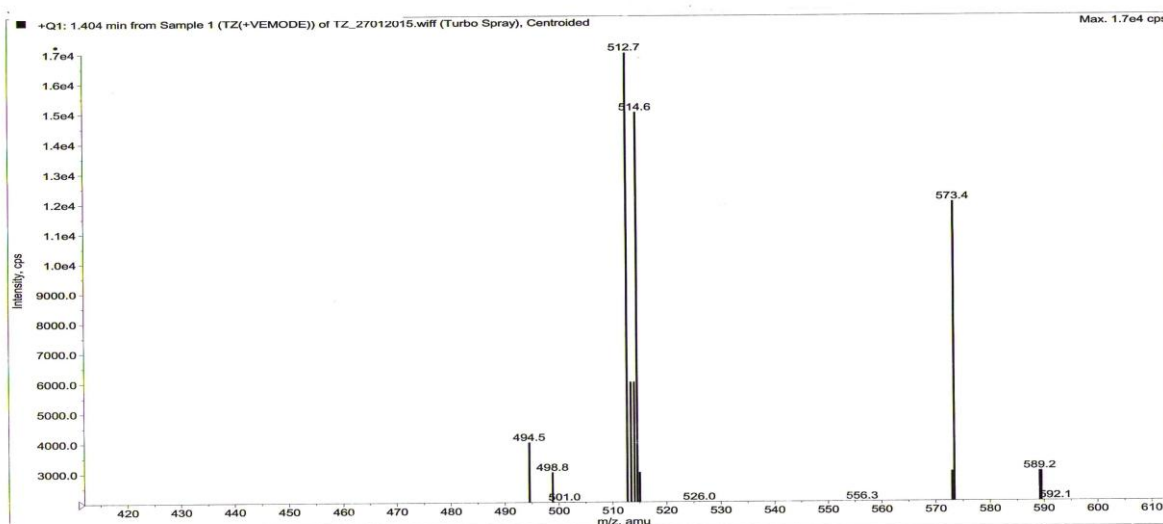


Figure 3 Mass spectra for N, N'-Bis-[4-(2-amino-thiazol-4-yl)-phenyl]isophthalamide (ATPIPA)

IV. POLYMERISATION

Aromatic polyimides were synthesized by two step polycondensation of aromatic diamine and aromatic anhydride at low temperature to form linear open chain poly(amic acid). In the second step-II the conversion of polyamic acid to polyimides was performed by chemical process initially and subsequent thermal, viz. acetic anhydride, pyridine, benzene and successive heating upto 300°C, for cyclodehydration to form polyimides. During imidisation the color of poly amic acid changed from yellow to brown as imidisation proceeded. The poly (amic-acid) and polyimide were characterised by IR, 1H NMR, TGA-DSC and XRD analysis. [4]-[7].

- **Synthesis of Polyimides via chemical cyclodehydration**

In three necked round bottom flask equipped with magnetic stirrer N₂ inlet ,

thermowell, CaCl₂ guard tube, 0.512 g (0.001 mol) thiazole diamine (I) and 4 ml dry DMAC were placed. The reaction mixture was stirred under N₂ atmosphere at low temperature till the complete dissolution occurs. Solid aromatic anhydride (0.001 mol) was added to mixture and stirring was continued for 1.5 h. at 25 °C. The solution was stirred at room temperature for 24 h. The viscous solution of poly(amic acid) PAA was obtained, which is stirred in methanol for 30 min. product was filtered and washed by methanol.

- **Characterisation:-**

FT-IR spectra of polyimide as deposited onto KBr pellets were recorded by Bruker Vector-22 FT-IR spectrometer at a resolution of 4 cm⁻¹ and were signal averaged for 128 scans. Inherent viscosities of the PAA were measured at 0.5 g dL⁻¹ in DMAC with a Ubbelohde capillary viscometer at 25 °C. NMR of monomer was measured by Bruker. Thermogravimetric analysis (TGA) was conducted

using a TA instrument, Temperature at which 10% weight loss and char yield can be calculated. DSC were performed with a TA instrument DSC Q100 system with a heating rate of 10 °C min⁻¹. Solubilities were measured with various solvents like, DMF, DMSO, Pyridine, NMP, Nitrobenzene, DCM. XRD were studied on Rigaku wide angle X-ray-diffractometer.

Result and discussion:-

Preparation of Polyimide:-

A series of Polyimide and copolyimide with different composition were prepared as shown in table-1 solution polycondensation [17]-[21] between the three monomers led to homogeneous PAA solution followed by thermal cyclodehydration to obtained yellow coloured polyimide polymer. The complete transformation to polyimide from PAA was proved by IR analysis. All spectra demonstrated characteristic band of imide ring at 1780 and 1720 cm⁻¹ and 360 cm⁻¹(C-N), which confirm the formation of polyimide. The absorption band at 3300, 1600 cm⁻¹ were absent suggesting total cyclisation of poly(amicacid).

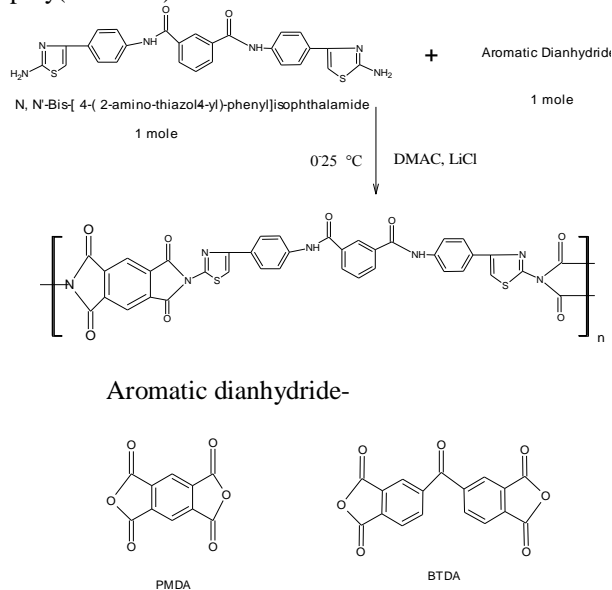


Table-1 Ratio used for preparation of polyimides

Thiazole Polyimide	PMDA (%)	Weight (gm)	BTDA (%)	Weight (gm)	Thiazole diamine (gm)
TPI-1	100	0.218	0	-	(0.512)
CTPI-2	90	0.196	10	0.032	(0.512)
CTPI-3	80	0.174	20	0.064	(0.512)
CTPI-4	70	0.152	30	0.096	(0.512)
CTPI-5	60	0.130	40	0.128	(0.512)
CTPI-6	50	0.109	50	0.161	(0.512)

Table-2 Synthesis and properties of polyimides from Thiazole diamine and aromatic dianhydrides polymer

PI code	Dianhydride	Yield(%)	$\eta_{inh}(dL/g)^a$	$T_0(^{\circ}C)^b$	$T_{10} (^{\circ}C)^c$	$T_{50} (^{\circ}C)^c$	$T_g (^{\circ}C)^e$
TPI-1	PMDA+BTDA (10:0)	80	0.19	40	100	400	280
CTPI-2	PMDA+BTDA (90:10)	85	0.33	40	200	620	300
CTPI-3	PMDA+BTDA (80:20)	80	0.22	35	210	650	310
CTPI-4	PMDA+BTDA (70:30)	75	0.26	35	190	500	340
CTPI-5	PMDA+BTDA (60:40)	75	0.37	35	100	450	390
CTPI-6	PMDA+BTDA (50:50)	85	0.4	40	200	550	400

^a η_{inh} was measured with 0.5% (w/v) solution of polyimides at 30±0.1°C in DMAC.

^b Initial decomposition temperature.

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

^d Temperature at which 50% weight loss is observed

^e Glass transition temperature measured on DSC at a heating rate of 10°C/min in N₂

The data in Table-2 shows that reaction of thiazole diamine with the two dianhydride monomers led to high molecular weight PAA's as evidenced from the high viscosity values.

Table-3: Solubilities of Polyimides

Sr.No.	Solvents							
	DM Ac	DMSO	DMF	NMP	PYRIDINE	cresol	Nitrobenzene	DCM
TPI-1	++	++	++	++	++	+-	+-	--
CTPI-2	++	++	++	++	++	+-	+-	--
CTPI-3	++	++	++	++	++	+-	+-	--
CTPI-4	++	++	++	++	++	+-	+-	--
CTPI-5	++	++	++	++	++	+-	+-	--
CTPI-6	++	++	++	++	++	+-	+-	--

Thermal properties of copolyimides:-

Thermal properties of polyimides examined by, TGA (fig.4), DSC and results were summarised in Table 2.

TGA curves of the copolyimide under N₂ atmosphere were shown in (fig.1) weight loss temperature were detected in the range of 50 °C to 850 °C exhibiting good thermal stabilities of copolyimides. All polyimides had glass transition temperature in the range of 250-400 °C. This could be attributed to the high content of aromatic heterocyclic moieties in polymer backbone.

X-ray diffraction (Fig.6) will be performed suggest that crystalline nature of polyimide.

Conclusion:

With the purpose of enhancing thermal and mechanical properties of the polyimides based on TZD, PMDA and symmetric pyromellitic units was incorporated into homopolymer system by copolymerizing with BTDA formed the copolyimide film were all tough and flexible. The result shows that thermal and mechanical properties of copolyimides were remarkably promoted after the incorporation of BTDA component. The effect of varying the molar percentage of PMDA-BTDA on solubility, thermal properties of copolyimides were evaluated. Polyimide showed poor solubility even in Ethanol and Acetone. The reason is that the thiazole group of poly(amic acid) segments linked with terminal amino group of polymer chains during imidisation [3-5]. It was observed that chain rigidity and linearity as well as structural symmetry played crucial roles in determining the properties of polyimide films. The structure property relationship provide an opportunity for designing accurately the properties needed in specific application.

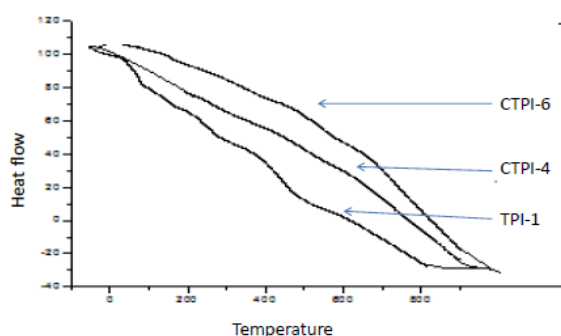


Figure 4 TGA Thermogram of polyimides

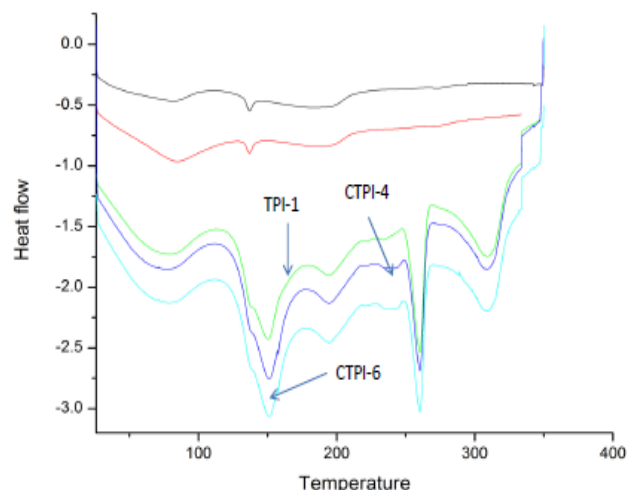


Figure 5 DSC curves of polyimides

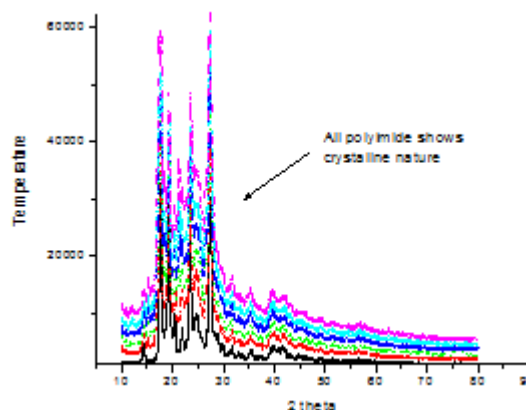


Figure 6 XRD curves of polyimides

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