Synthesis of poly(ester-imide)s from bis(4-amino-3,5-dimethyl phenyl) 4' bromophenyl methane and 2,6-diaminopyridine

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ABSTRACT

A series of thermally stable and organosoluble poly(ester-imide)s were synthesized by polycondensation of tetrimide dicarboxylic acid chlorides containing an internal imide group with 1,4-dihydroxy benzene. The tetrimide dicarboxylic acid chlorides were synthesized by reacting the commercially available monomer 2,6-diaminopyridine and a newly synthesized monomer bis(4-amino-3,5-dimethyl phenyl) 4′ bromophenyl methane with two different dianhydrides, pyromellitic dianhydride (PMDA) and 3,3′4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and p-amino benzoic acid followed by refluxing with thionyl chloride. The synthesized polymers were characterized by elemental analysis, FTIR, ^{1}H NMR and UV-visible spectroscopy TGA, DSC and XRD studies. Thermal stability and the weight-loss behavior of poly(ester-imide)s were studied by TGA. $T_{10\%}$ temperature of the polymers ranged from 380–471° C in nitrogen atmosphere. The glass transition temperatures (T_g) of the polymers ranged from 245–306° C. All the poly(ester-imide)s synthesized are amorphous in nature. The synthesized polymers showed excellent solubility in common organic solvents, such as pyridine, chloroform, tetrahydrofuran, and m-cresol, as well as in polar organic solvents, such as N-methyl-2-pyrrolidone, N,N-dimethyl acetamide, N,N-dimethylformamide, and dimethyl sulfoxide.

Keywords: 2, 6-diaminopyridine, 1,4-dihydroxy benzene, pyromellitic dianhydride, tetrimide- diacid chlorides, thermal stability, UV-visible spectroscopy, BTDA.

I. INTRODUCTION

Aromatic polyimides are high performance polymers due to their excellent thermo-oxidative stability[1,2]. However, high crystallinity and high stiffness of the polymer backbones result in high glass transition (T_g) or melting temperature and limited solubility in most organic solvents. Thus, they are difficult to be cast into articles and their applications are restricted in many fields. There are many successful approaches to enhance the solubility and processability of polyimides without sacrificing their thermal stability. One of the best approaches to increase the solubility and processability of polyimides is the introduction of hetero aromatic ring such as pyridine, flexible linking unit like ester linkage and bulky pendant groups in the polymer backbone [3,4]. Aromatic poly(ester-imide)s (PEIs) are an important class of high performance polymers. With excellent resistance to high temperatures, better processing characteristics and favourable balance of other physical and chemical properties having both ester and rigid heterocyclic imide unit in the polymer backbone, and having the merits of both the functional groups (ester and imide) such as high thermal stability, good mechanical properties better solubility, easy processability and greater tractability. The present paper, reports the synthesis of poly(ester-imide)s from new dicarboxylic acid chlorides containing four imide rings with two aromatic diols by solution

polycondensation in nitrobenzene using pyridine as hydrogen chloride trap [5,6].

II. MATERIALS AND METHODS

2,6-dimethyl aniline, pyromellitic dianhydride (PMDA), 3,3'4,4'-benzophenone tetracarboxylic dianhydride (BTDA) 2,6-diamino pyridine, 4-bromobenzaldehyde, *p*-amino benzoic acid, 1,4-dihydroxy benzene, concentrated hydrochloric acid, N,N-dimethyl acetamide (DMAc), N,N-dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), N-methyl pyrrolidone (NMP), tetrahydrofuron (THF) toluene, acetone and chloroform were purchased from Sigma Aldrich. The solvents used for polymerization were purified according to standard methods.

2.1 Synthesis of Monomer

2, 6-dimethylaniline (0.1 mol) was charged into a 250 ml three necked round bottomed flask equipped with nitrogen inlet, an additional funnel and a reflux condenser. Concentrated hydrochloric acid (8 ml) was added drop-wise to the reaction vessel for 30 minutes. The solid substance obtained was melted by heating to 100°C. To this 4-bromobezaldehyde (0.05 mol) was added. After complete addition the temperature was raised to 120°C and the reaction mixture was stirred at this temperature for 12 hrs cooled and neutralized with sodium hydroxide solution. The solid product obtained was filtered, washed with methanol, recrystallized in ethanol and finally dried in vacuum at 70°C for 12 hrs [7].(**Scheme**1)
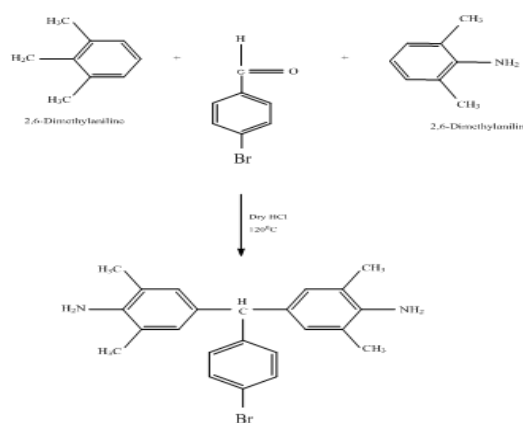
Sheme1. Synthesis of bis(4-amino-3, 5-dimethylphenyl)4'-bromo phenyl methane (BABM)

2.2. Synthesis of tetrimide dicarboxylic acids

A three necked 150 ml RB flask equipped with nitrogen inlet and a reflux condenser was charged with bis (4-amino-3,5-dimethylphenyl) 4'bromophenyl methane (BABM) (0.01 mole), *p*-amino benzoic acid (0.02 mole) and pyromellitic dianhydride(PMDA) (0.02 mole) in 10 ml DMF. The mixture was stirred at room temperature for two hrs. About 30 ml of toluene was then added and mixture was refluxed for 3 hrs. The water formed in the reaction was distilled off azeotropically using Dean-Stark trap. At the end of the reaction the residual toluene was distilled off under reduced pressure. After cooling, the obtained solution was trickled into water and the precipitated product was collected by filtration and dried in vacuum at 100°C for 12 hrs **Scheme 2**. This experiment was repeated with another monomer(2,6-diamino pyridine) and anhydride (3,3'4,4'-benzophenone tetracarboxylic dianhydride (BTDA))**Figure 1-3** represents the structure of tetimide dicarboxylic acids.
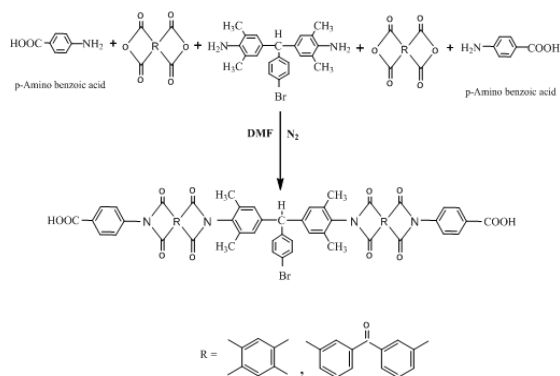
Scheme 2. Synthesis of bis [(N-carboxy phenyl) 4-pyromellitimido 3,5 dimethyl phenyl]4'-bromophenyl methane (BCPBM)
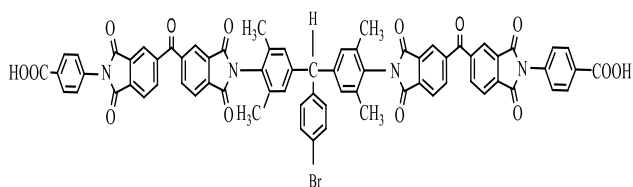

Figure 1. bis [(N-carboxy phenyl) 4-(3, 3', 4, 4'-benzophenone tetracarboximido 3,5 dimethyl phenyl]4'-bromophenyl methane (BCBBM)
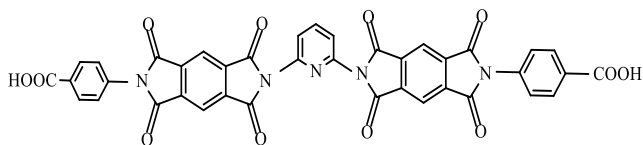

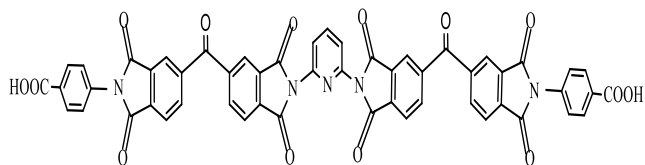**Figure 2.** bis [(N-carboxy phenyl) 2-pyromellitimido] pyridine (BCPP)

Figure 3. bis [(N-carboxy phenyl) 2-(3,3', 4,4') benzophenone tetracarboximido] pyridine(BCBP)

2.3. Synthesis of tetrimide diacid chlorides

The synthesized tetrimide dicarboxylic acids were refluxed with an excess of thionyl chloride using DMF as a solvent [8]. The viscous solution obtained was cooled and trickled into excess methanol with vigorous stirring. The precipitate was filtered off. Washed several times with hot methanol and dried in vacuum oven at 100°C for 7 hrs. The yield of the reaction was 83% (**Scheme 3**).
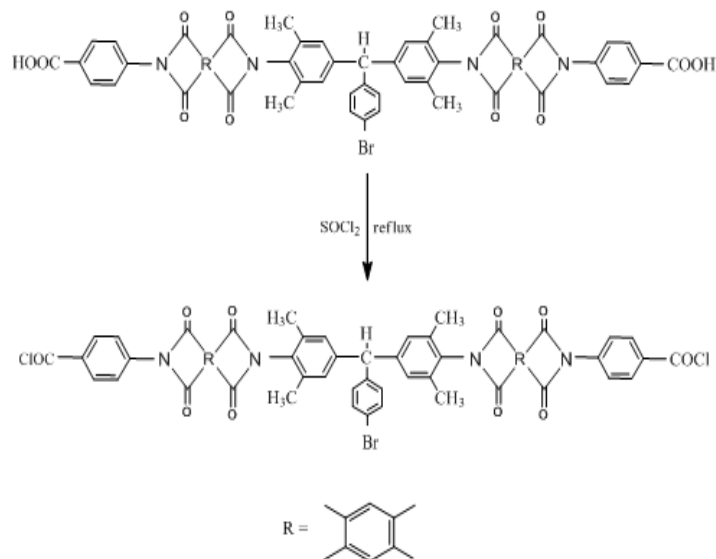
Scheme 3. Synthesis of of bis [(N- benzoyl chloro) 4-pyromellitimido 3,5 dimethyl phenyl] 4'-bromophenyl methane (BBCPBM)
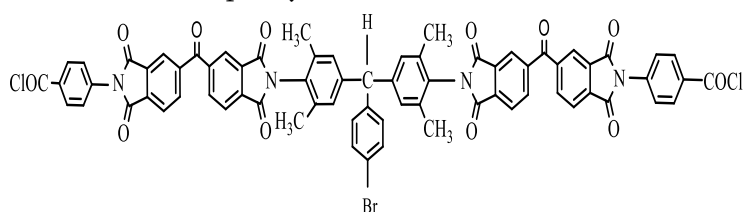

Figure 4. bis [(N- benzoyl chloro) 4-(3, 3', 4, 4'-benzophenone tetracarboximido 3,5 dimethyl phenyl]4'-bromophenyl methane (BBCBBM)
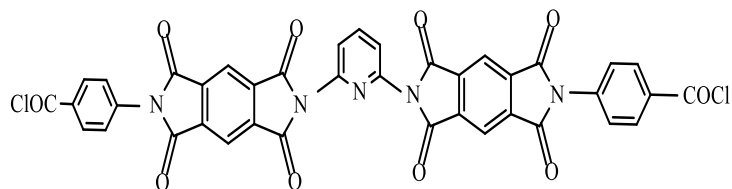

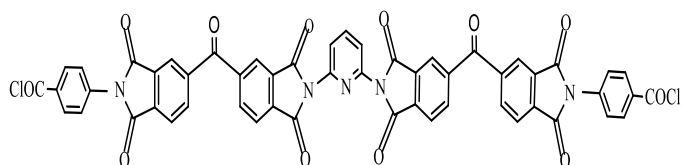**Figure 5.** bis [(N-benzoyl chloro) 2-pyromellitimido] pyridine (BBCPP)

Figure 6. bis [(N-benzoyl chloro) 2-(3,3',4,4') benzophenone tetracarboximido] pyridine (BBCBP)

2.4. Synthesis of poly(ester-imide)s

1,4-dihydroxy benzene (0.01 mol), tetrimide diacid chlorides (0.01 mol), pyridine and nitrobenzene were homogenized at room temperature and subjected to a

heating temperature of 170°C for 10 hrs. After the completion of the reaction, the mixture was allowed to cool down, filtered and washed several times with water. The products were filtered off and dried at 100°C for 8 hrs in a vacuum oven. The yield of the reaction was 80% (**Scheme 4**).
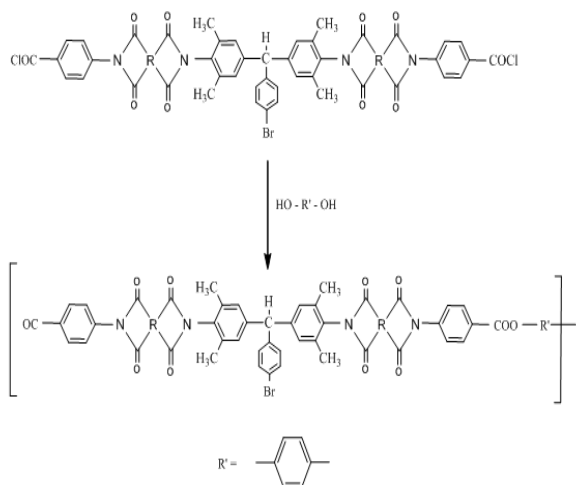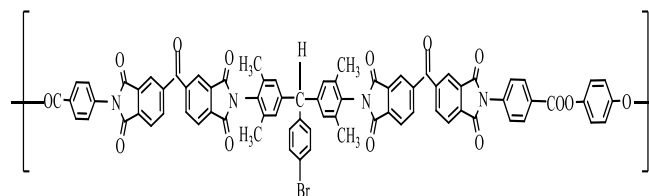

Scheme 4. Synthesis of poly(ester-imide) (PEI-1)

Figure 7. poly(ester-imide) PEI-2
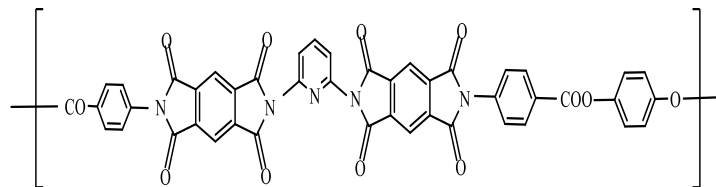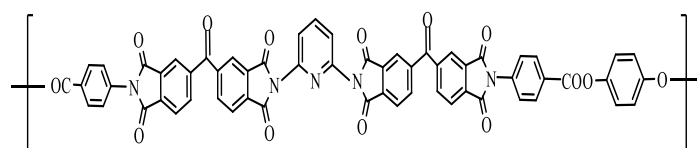

Figure 8. poly(ester-imide) PEI-3

Figure 9. poly(ester-imide) PEI-4

III. CHARECTERIZATION TECHNIQUIES

3.1 Elemental Analysis

The elemental analysis data of poly(ester-imide)s are in good agreement with the calculated values. The values are given in **Table 1.**

Table 1. Physico-chemical characteristics of poly(ester-imi de)s

S. No.	Polymer code	Molecular Formula	% Yield	Elemental analysis (wt %)					
				Carbon		Hydrogen		Nitrogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
1.	PEI-1	$(C_{63} H_{37} O_{12} N_4 Br)_n$	83	67.44	66.22	3.30	3.44	4.99	5.28
2.	PEI-2	$(C_{77} H_{45} O_{14} N_4 Br)_n$	81	69.53	68.15	3.38	3.53	4.21	4.54
3.	PEI-2	$(C_{45} H_{19} O_{12} N_5)_n$	81	65.77	65.10	2.31	2.70	8.52	9.12
4.	PEI-4	$(C_{59} H_{27} O_{14} N_5)_n$	82	68.80	68.40	2.62	2.33	6.80	6.88

3.2 IR Spectral Studies

Figures 10-12 are the IR spectra of the diamine monomer and polymers. The diamine monomer (BABM) shows absorption band around 3463-3337cm^{-1} due to N-H symmetric and asymmetric stretching of NH$_2$ groups and the absorption band around 1620-1606 due to N-H bending vibration [9]. BABM shows absorption band around 2970-2867cm^{-1} is due to the

C-H stretching vibrations of CH$_3$. The peak corresponding to C- Br bond in the monomer appeared in the region around 1072 cm^{-1}. In the polymers, the absorption peaks around 1726 and 1779 cm^{-1} correspond to symmetric and asymmetric stretching of the imide carbonyl group [10]. The peak at 1364cm^{-1} is due to the C-N-C stretching vibration of the imide ring. The peaks at 1115 and 731cm^{-1} correspond to the imide ring deformation. The absorption band at 2922 cm^1 corresponds to C-H stretching of the methyl group. A strong characteristic absorption peak around 1730-1740cm^{-1} corresponds to aryl ester carbonyl stretching vibration [11].

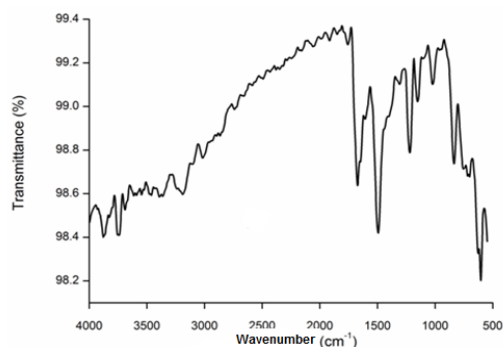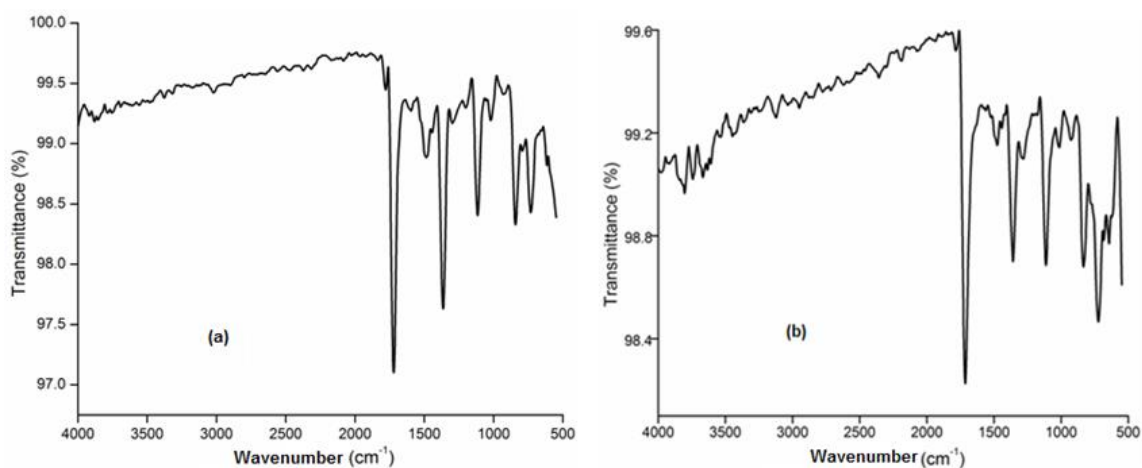**Figure 10**. FTIR spectrum of BABM

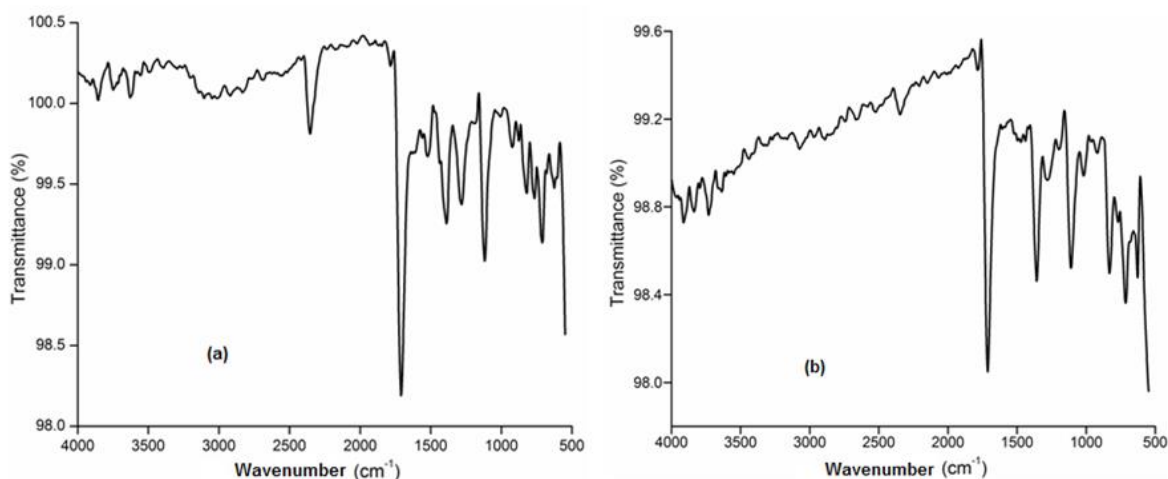**Figure 11**. FTIR spectra of a) PEI-1 b) PEI-2

Figure 12. FTIR spectra of a) PEI-3 b) PEI-4

3.3 ^{1}HNMR spectroscopy

The diamine monomer (BABM) shows a signal around 3.84 - 4.01 ppm (singlet) corresponding to the -NH$_2$ protons and the methyl protons resonate around 2.08 - 2.25 ppm (singlet). The diamine monomer shows a sharp signal around 5.35 ppm

(singlet) for the methyne proton [12]. The aromatic protons of the polymers resonate at varying δ values between 6.90 and 8.5 ppm depending on the polymer backbone structure The aromatic protons of PMDA containing polymers appear in the farthest downfield region (8.6-8.8 ppm) due to the presence of electron withdrawing imide C=O group [13].

3.4 Solubility

The solubility of the PEIs were tested qualitatively in various organic solvents such as N-Methyl pyrrolidone(NMP), Dimethyl sulphoxide(DMSO), Dimethyl acetamide (DMAc), Chloroform (CHCl$_3$) and Tetrahydrofuran (THF). The results are reported in Table **2.** The excellent solubility of the PEIs in the different solvents may be due to the presence of bulky pendant substituted phenyl group, which decreases inter and intra chain interactions and disturbs the co-planarity of the aromatic unit reducing the packing efficiency [14]. The PEIs containing BTDA moiety are found to be readily soluble, due to the presence of flexible C=O,-O-linkages, between the phthalimide groups.

Table 2. Solubility behavior of Poly(ester-imide)s

S.No.	Code	NMP	DMF	DMAc	DMSO	THF	CHCl$_3$
1.	PEI-1	++	++	++	++	++	++
2.	PEI-2	++	++	++	++	++	+h
3.	PEI-3	+-	++	++	+-	-	-
4.	PEI-4	++	++	++	+-	+h	-

Solubility keys: (++) soluble, ±sparingle soluble, +h soluble on heating, - insoluble.

3.5 UV –Visible studies

Using UV-Visible spectroscopy, electron conjugation in polymers can be investigated. Strong conjugation leads to absorption at higher wavelength. The PMDA based polymers have higher $λ_0$ than the BTDA based polymers which is due to the increased CTC formation by PMDA moiety [15]. The pyridine series polymers (PEI-3 and PEI-4) show higher cutoff wavelength than the other polymers because of their rigid close packed structure which increases the electronic conjugation between the polymer chains. Figure 13 is UV-visible spectra of PEIs.
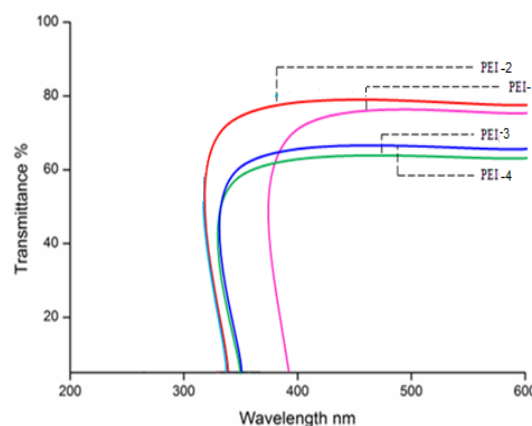

Figure 13.UV-Visible spectra of PEIs

3.6 X-ray diffraction studies

The crystallinity of the PEIs is examined by X-ray diffraction studies. Figures 14 -18 are the powder X-ray diffraction patterns of the PEIs. From diffraction pattern it has been found that the synthesized PEIs are almost amorphous. This could be attributed to the introduction of the packing disruptive bulky pendant group which resulted in increased chain distance and decreased chain to chain interactions, thereby leading

to decrease in crytallinity [16]. The pyridine series of PEIs show slightly sharp diffraction peaks, indicative of moderate level of crystallinity. This may be due to the absence of pendant group and high density of hydrogen bonding between polymer chains of highly symmetric pyridine ring.
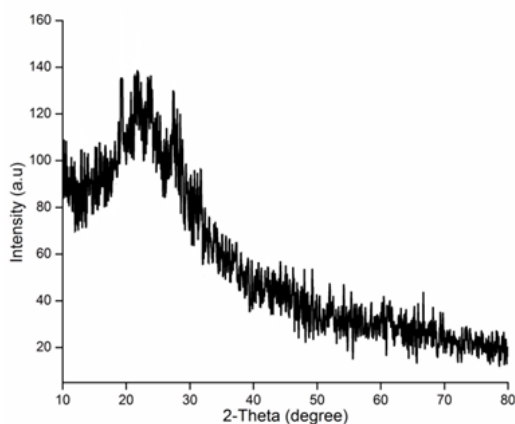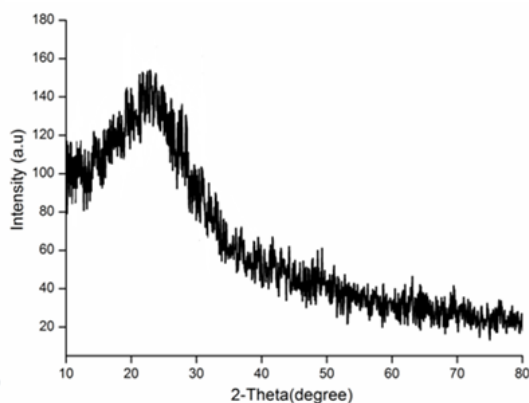

Figure 14. XRD patterns of PEI-1
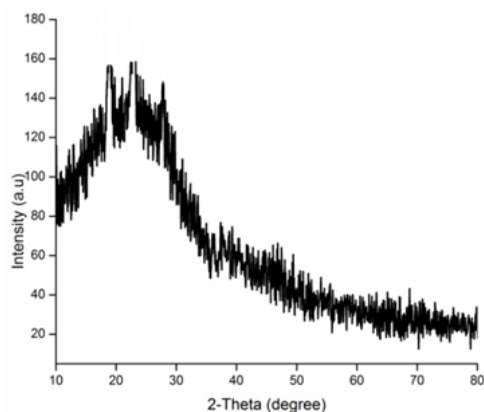

Figure 15. XRD patterns of PEI-2
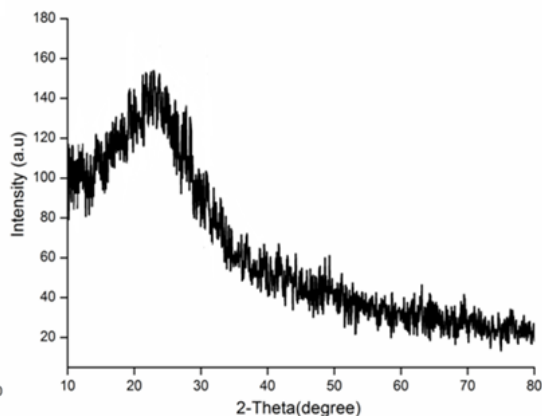

Figure 16. XRD patterns of PEI-3

Figure 17. XRD patterns of PEI-4

3.7 Thermal Analysis

In the present study the PEIs are stable up to 420^{0}C, indicating high thermal stability. The PMDA based polymers exhibit greater thermal stability in comparison with BTDA based polymers due to inherent rigidity of PMDA units. The high thermal stability of the polymers could be attributed to the incorporation of imide units, performed ester groups and phenylation of backbone [16,17]. The 10% weight loss temperatures ($T_{10\%}$) from thermogravimetric analysis curves were found to be in the range 380–471 °C in nitrogen atmosphere(Figure 19). Thermograms of all the synthesized PEIs seemed to exhibit a two stage decomposition behavior at elevated temperature. The first stage of weight loss occurs in the range of 420-450^{0}C and it might be attributed to the early degradation of less stable ester groups, and second weight loss occurring in the range 470-550^{0}Cis most probably due to the degradation of rigid imide segments[18]. The glass transition temperatures (T_g) of the polymers determined by differential scanning calorimetry thermograms were in the range 245–306 °C.
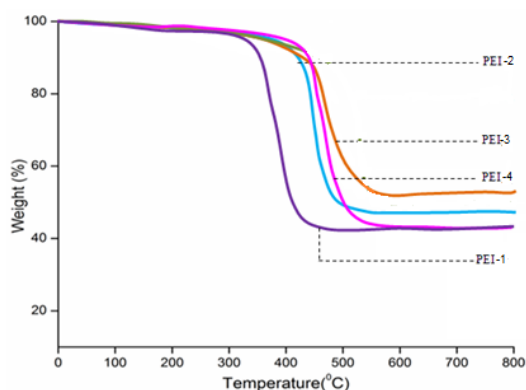
Figure 19. TGA Thermograms of PEIs

IV. CONCLUSION

The elemental analysis and the spectral studies confirm the structure of the PEIs. The introduction of heterocyclic moiety in the polymer backbone has effectively enhanced the thermal stability. The incorporation of the flexible ester linkage and the pendant group in the polymer backbone has increased the solubility of the PEIs and hence, all the observed properties like good solubility, moderate crystallinity and excellent thermal stability of the synthesized polymers make them to be used as high performance polymers with attractive practical applications.

V. REFERENCES

[1]. McGrath, J.E., Dunson, D.L., Mecham, S.J., Hedrick, J.L., Adv. Polym. Sci., 1999, 140, 61-105.

[2]. Sroog, C.E., Prog. Polym. Sci., 1991, 16, 561-594.

[3]. Manami, H., Nakazawa, M., Oishi, Y., Kakimoto, M., Imai, Y., J. Polym. Sci., Part A: Polym. Chem., 1990, 28, 465-477.

[4]. Espeso, J.F., De la Campa, J.G., Lozano, A.E., De Abajo, J., J. Polym. Sci., Part A: Polym. Chem., 2000, 38, 1014-1023.

[5]. Li, H., Lun, Y., Tang, X.L, Li, S.J., J. Macro.Mol. Sci. Pure Appl. Chem., 2002, 39, 815-824.

[6]. Shieh, J.Y., Hsu, P.H., Wang, C.S., J .Appl. Polym Sci., 2004, 94,730-738.

[7]. Hariharan, R., Bhuvana, S., Anuradha, G., Sarojadevi, M., Polym. Int., 2004, 53, 1442-1447.

[8]. Kute, V., Banerjee, S., Macromol. Chem. Phys., 2003, 204, 2105-2112.

[9]. Yin, D., Li, Y., Yang, H., Yang,H., Fas, L., Liu, J., Polym, 2005, 46, 3119-3127.

[10]. Yang, C.P., Cherng, J.J., J.Polym. Sci. Polym. Chem., 1996, 33, 31-37.

[11]. Yang, C.P., Cherng, J.J., J.Polym. Sci. Polym. Chem., 1996, 33, 31-37.

[12]. Hariharan. R., Sarojadevi, M., J. Appl.Polym. Sci., 2006, 102, 4127-4135.

[13]. Yim, K.S., Lee, S.Y., Chang, H.N., Biotechnology and Bioengineering, 1996, 49, 495-503.

[14]. Wilson, D., Slinzenberger, H.D., Hergenrother, P.M., Blackie & Son Ltd., Glascow and London, 1990.

[15]. Yang, C.P., Chen, R.S. Hung, K.S., Polym., 2001, 42, 4569-4577.

[16]. Ataei, S.M., Laleh, N,B., Amirshaghaghi, A., Polym. Degrad. Stabil., 2006, 91, 2622-2631

[17]. Shabbir, S., Zulfiqar, S., Z. Sarwar, M.I., Polym.Degrad.Stabil., 2010,95,1251-1259.

[18]. Wang, C.S., Shieh, J.Y., Polym., 1998, 39, 5819-5829.