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Synthesis and Characterization of Novel Polyesterimide Containing Naphthalene Moiety

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Abstract:

A new thermally stable polyesterimide was synthesized by the polycondensation of Bisphenol-A and tetrimide- diacid chloride. The tetrimide- diacid chloride was synthesized by heating the monomer bis (4-amino-3,5-dimethyl phenyl) 4' methoxy naphthyl methane with pyromellitic dianhydride and p-amino benzoic acid followed by refluxing with thionyl chloride. The synthesized polymer was characterized by elemental analysis, FT-IR and ¹H-NMR spectroscopy. The properties of the polyesterimide such as thermal stability, inherent viscosity and solubility were also studied. Furthermore the crystallinity of the polymer was evaluated by means of X-ray diffraction patterns. The novel PEI exhibits high thermal stability, good solubility and processability.

Keywords: 4-methoxy naphthaldehyde, Bisphenol-A, pyromellitic dianhydride, tetrimide- diacid chloride, polyesterimide, thermal stability

1. Introduction

Aromatic polyimides are one of the high performance polymers, because of their high thermal and oxidative stabilities, high transition temperatures and outstanding mechanical, insulating and chemical resistance properties. Therefore this polyimides have been widely used in many applications such as aerospace, microelectronics, optoelectronics and information industries [1,2]. However, one of the drawbacks of the high performance polymers is the difficulty in processing due to their insoluble nature in organic solvents in addition to their high melting temperatures or glass transition temperatures[3].Therefore, the applications of the majority of polyimides are limited because of their infusibility and insolubility. Certain approaches exist for increase in solubility and processability of polyimides without sacrificing their thermal stability are synthesis of copolyimides such as poly(esterimide)s, poly(siloxane-imide)s, poly(urethane-imide)s, poly(amide-imide)s[4-6] and the introduction of flexible ether linkages, non-planar – asymmetric units and bulky pendent groups along the polymer backbone chain[7-8].

Aromatic poly(ester-imide)s (PEIs) are thermally stable polymers and they have various commercial applications. The main application of PEIs are in coatings for enameled wires, high strength fibers, hot melt adhesives, heat resistant films and printed circuit boards[9].Several methods have been reported for the synthesis of PEIs. In this present work a new polyesterimide was prepared by the reaction of tetrimide diacid chloride containing imide group with a diol.

2. Materials and Methods

2,6-dimethyl aniline and all other chemicals such as Pyromellitic dianhydride (PMDA),4-methoxy naphthaldehyde, N,N-dimethyl acetamide (DMAc), N,N-dimethyl formamide (DMF), p-amino benzoic acid, Bisphenol-A, Concentrated sulphuric acid, toluene, acetone, chloroform, m-cresol, Dimethyl sulphoxide(DMSO), N-methyl pyrrolidone (NMP), xylene, tetrahydrofuron (THF) were purchased from Sigma Aldrich. The solvents used for polymerization were purified according to standard methods.

Elemental analysis was carried out as Vario EL II elemental analyzer at CUSAT, Kochi. Thermo Gravimetric Analysis (TGA) was performed at a Mettler TA 4000 system under nitrogen atmosphere at a heating rate of 10⁰C/min. FTIR spectroscopy was performed on a Bruker Vertex 70 at frequencies ranging from 400-4000cm⁻¹. The powder X-ray diffraction (XRD) patterns were recorded on a

X-ray diffractometer Bruker AXS D8. ^1H NMR was recorded on a Bruker Advance III 400MHz instrument. Glass transition temperature (T_g) was recorded on Mettler Toledo DSC 822c.

2.1. Synthesis of Monomer

2, 6-Dimethylaniline (12.1g, 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-methoxy naphthaldehyde (8.3 g, 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 hrs⁵.(Figure-1)

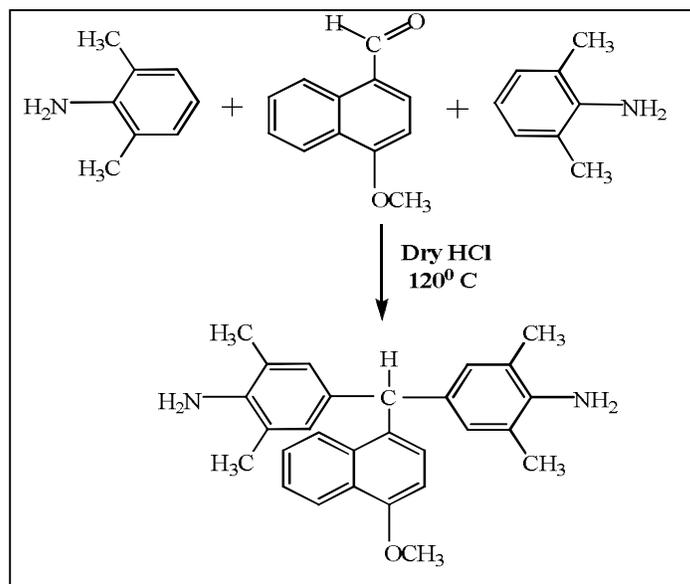


Figure 1: Synthesis of bis(4-amino-3,5-dimethylphenyl) 4-methoxy naphthyl methane(BADM)

2.2. Synthesis of Tetrimide Diacid

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-methoxy naphthyl methane(BADM) (0.01 mole), *p*-amino benzoic acid (0.02 mole) and pyromellitic dianhydride (0.02 mole) in 20 ml DMF. The mixture was stirred at room temperature for two hrs. About 25 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 (Figure 2).

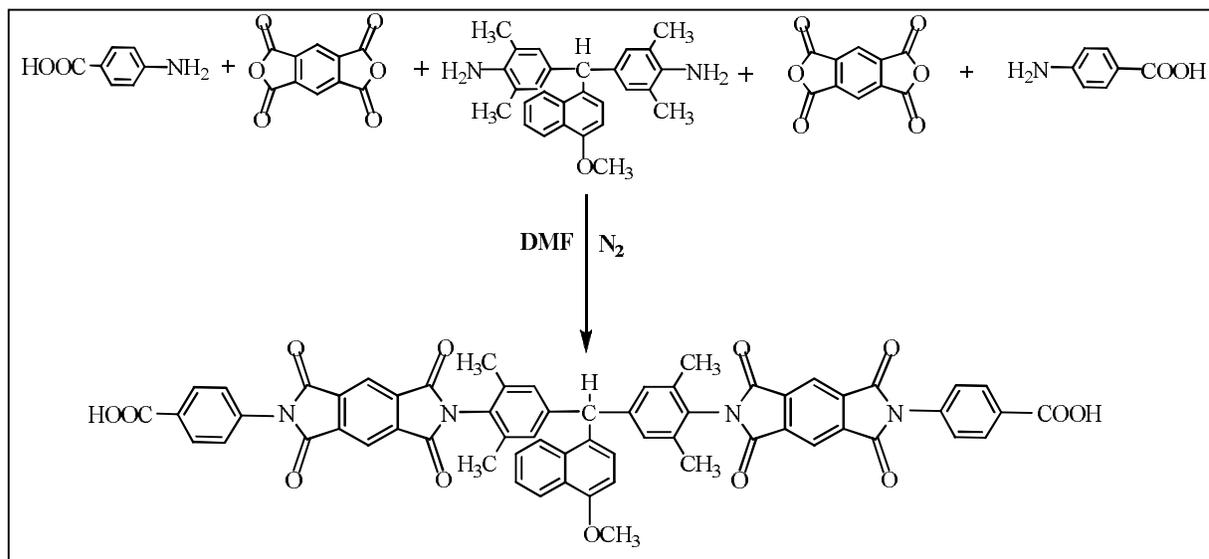


Figure 2: Synthesis of tetrimide diacid

2.3. Synthesis of Tetrimide Diacid Chloride

The synthesized tetrimide diacid was refluxed with an excess of thionyl chloride using DMF as a catalyst [10]. 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% (Figure 3).

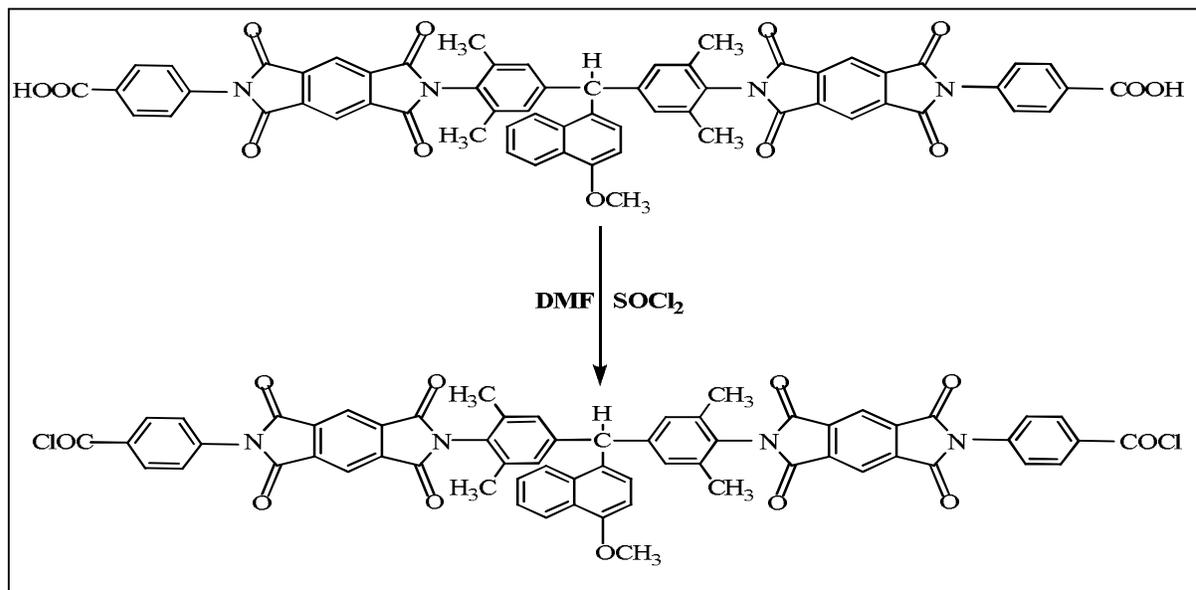


Figure 3: Synthesis of tetrimide diacid chloride

2.4. Synthesis of Polyesterimide

Bisphenol-A (0.02 mole), tetrimide diacid chloride (0.01 mole), 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 product was filtered off and dried at 100°C for 8 hrs in a vacuum oven. The yield of the reaction was 80%. (Figure 4).

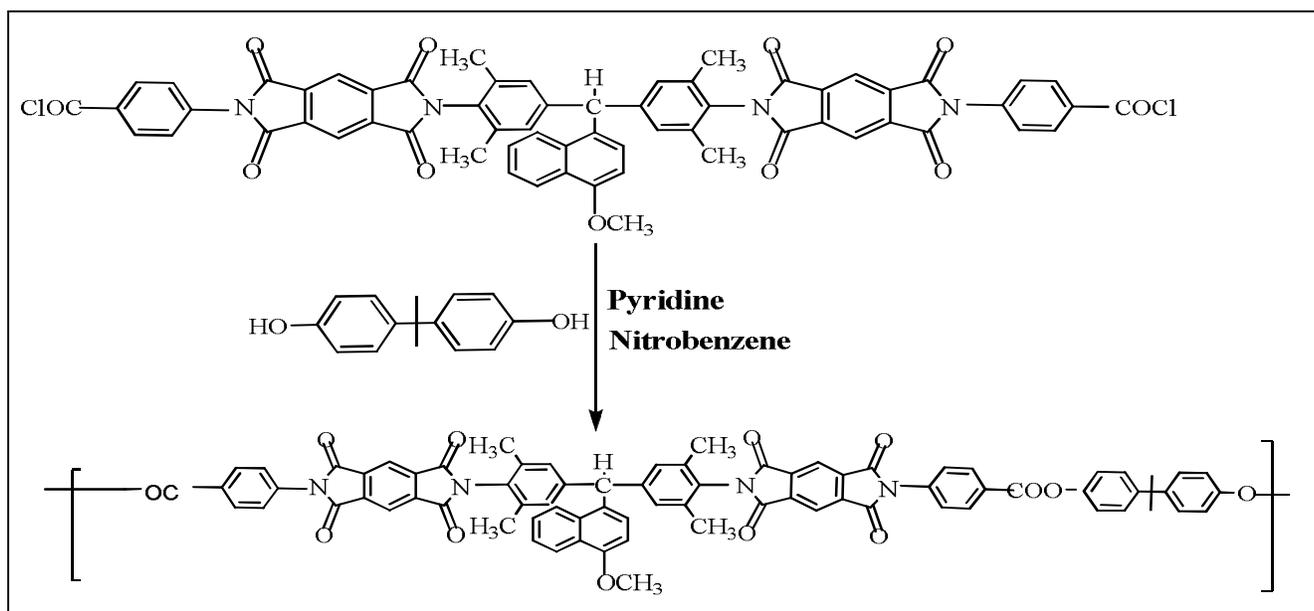


Figure 4: Synthesis of polyesterimide

3. Result and Discussion

3.1. Monomer Characterization

3.1.1. Elemental Analysis

The elemental analysis data of the monomer is in good agreement with the calculated values (Table 1).

Sl. No	Monomer code	Mol. Formula	% Yield	Elemental Analysis wt.(%)					
				Carbon		Hydrogen		Nitrogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
1	BADM	C ₂₈ H ₃₀ ON ₂	85	81.5	79.3	7.3	6.53	6.8	6.82

Table 1: Physico-chemical characteristics of diamine monomer

3.1.2. Infrared Spectroscopy

Infrared spectroscopy continues to be the prominent tool in determining the chemical structure of the product. The infrared spectrum of the monomer is shown in figure 5. The diamine monomer show absorption bands around 3340 cm⁻¹, 3381 cm⁻¹ and 3450 cm⁻¹, 3460 cm⁻¹ due to N-H symmetric and asymmetric stretching of NH₂ groups and the absorption band around 1615-1620 cm⁻¹ is due to N-H bending vibration. The monomer shows absorption around 2900-2970 cm⁻¹ due to the C-H stretching vibration of CH₃ group. In addition to these characteristic vibrations, the monomer shows absorption band around 1400-1466 cm⁻¹ corresponding to aromatic ring vibrations.

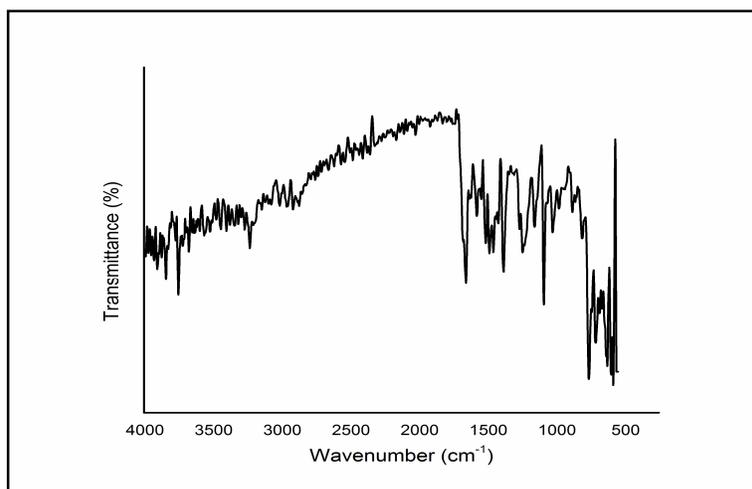


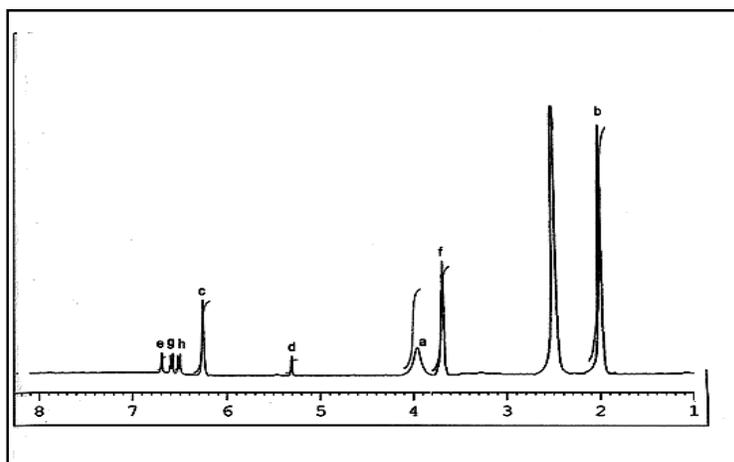
Figure 5: FT-IR of monomer

3.1.3. ¹H-NMR Spectroscopy

¹H-NMR spectrum of diamine monomer is shown in figure 6. The chemical shift values are summarized in (Table 2). The diamine monomer shows a singlet around 3.9 ppm corresponding to the NH₂ protons. The methyl protons of this monomer resonate around 2.0 to 2.1 ppm (singlet) and the aromatic protons resonate around 6.3 to 6.8 ppm. Methyne proton resonates around 5.3 ppm (singlet) and the -OCH₃ group around 3.7 ppm (singlet).

Monomer No.	Monomer Code	A	b	c	d	e	f	g	h
1	BADM	3.95 (s)	2.04 (s)	6.32 (s)	5.32 (s)	6.71 (s)	3.72 (s)	6.61 (d)	6.55 (d)

Table 2: ¹H-NMR spectral data of diamine monomer

Figure 6: ¹H-NMR Spectrum of BAMB

3.2. Characterisation of Polymer

The polymer is subjected to elemental analysis. The result of elemental analysis with molecular formula is presented in Table 3. The result obtained is good agreement with those calculated for the suggested formulae.

Sl. No	Polymer	Mol. Formula	% Yield	Elemental Analysis wt.(%)					
				Carbon		Hydrogen		Nitrogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
1	Polyesterimide	C ₇₄ H ₄₆ O ₁₅ N ₄	82	72.19	70.69	3.73	3.65	4.5	4.01

Table 3: Physico-chemical characteristics of Polyesterimide

3.2.1. Infrared Spectroscopy

The FT-IR spectroscopic technique is an important method in determining the structure of the polymer. The FT-IR spectra of polyetherimide is shown in figure 7. The adsorptions at 1760 and 1779 cm⁻¹ correspond to symmetric and asymmetric stretching of imide carbonyl group. The bands around 1364 and 731 cm⁻¹ are due to the C-N-C stretching and bending vibrations of the imide ring. The band at 1115 cm⁻¹ corresponds to the imide ring deformation. Aryl ether stretching absorption appears near 1250 cm⁻¹. In addition to these characteristic vibrations, all the polymers show absorption band around 1400-1460cm⁻¹ and 1540-1600cm⁻¹ corresponding to aromatic ring vibrations. The band at 1425cm⁻¹ corresponds to cyclic imide ring.

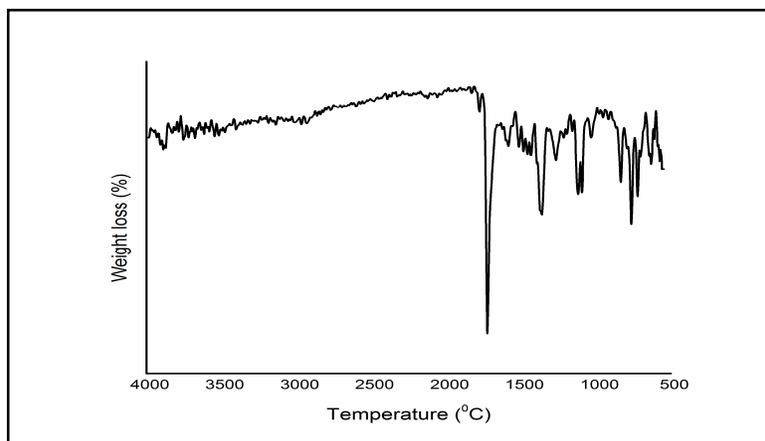


Figure 7: FT-IR spectrum of polyesterimide

3.2.2. ¹H-NMR Spectroscopy

The chemical shift values of PEI are summarized in Table 4.

No.	Polymer	a	b	c	d	e	f	g	h	i	j	k
1	PEI	6.8 (d)	7.4 (d)	7.5 (d)	8.9 (s)	2.3 (s)	6.7 (s)	5.3 (s)	6.3 (s)	3.7 (s)	6.6 (d)	6.8 (d)

Table 4: ¹H-NMR spectral data of PEI

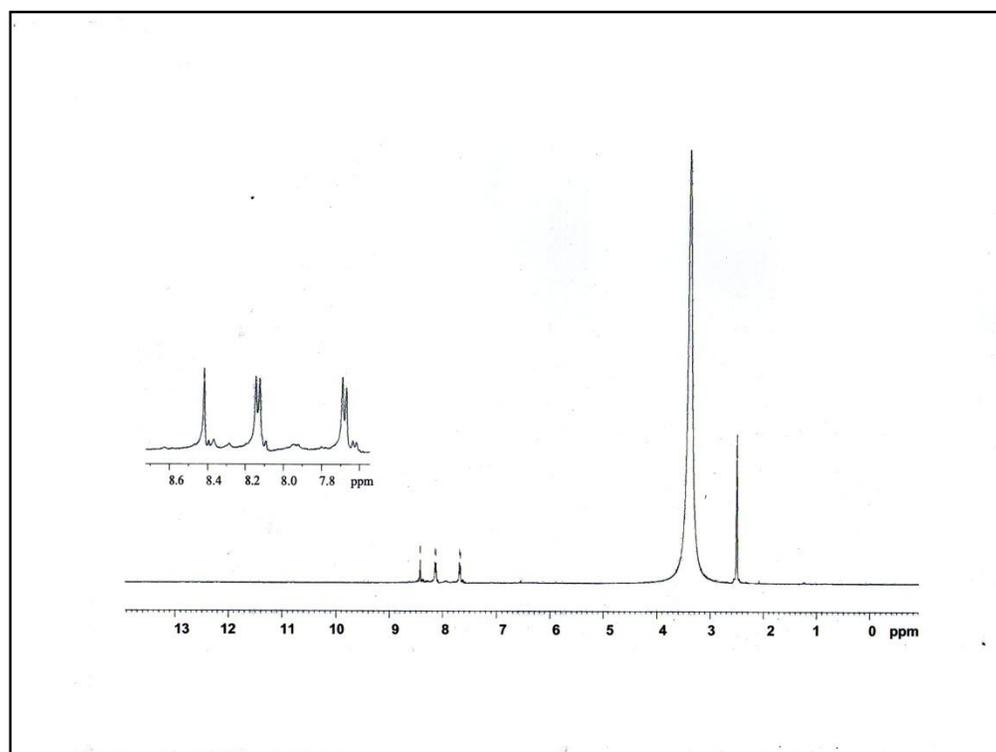


Figure 8: $^1\text{H-NMR}$ Spectrum of Polymer

4. Thermal Properties of Polyesterimide

4.1. Thermal Analysis

The thermal behavior of the PEI was evaluated by means of Differential Scanning Calorimetry(DSC) and Thermo gravimetric Analysis(TGA). The thermoxidative stability of the polymer was evaluated by TGA in nitrogen atmosphere with the heating rate of $10^\circ\text{C}/\text{min}$. The polymer did not shows any significant weight loss up to 360°C . The PEI began to decompose in the range of $370\text{-}390^\circ\text{C}$, as indicated by the temperature of 5% weight loss in TGA thermograms. The temperature of 10% weight loss was in range of $390\text{-}410^\circ\text{C}$. The amount of carbonized residue (char yield) at 800°C in nitrogen atmosphere of the polyesterimide was found to be 31%. The high char yield limits the production of combustible gases, decreases the exothermicity of the pyrolysis reactions of the polymers, inhibits the thermal conductivity of the burning materials, thus increase the flame retardancy[11]. The synthesised polymer exhibited high $T_{d10\%}$ value, showing high thermal stability and greater char yield (35%). This may be due to the introduction of flexible ester linkage in the polymer backbone. TGA suggests that the synthesized PEI could be considered as a novel processable high-performance material. The TGA of polyesterimide is given in figure 9.

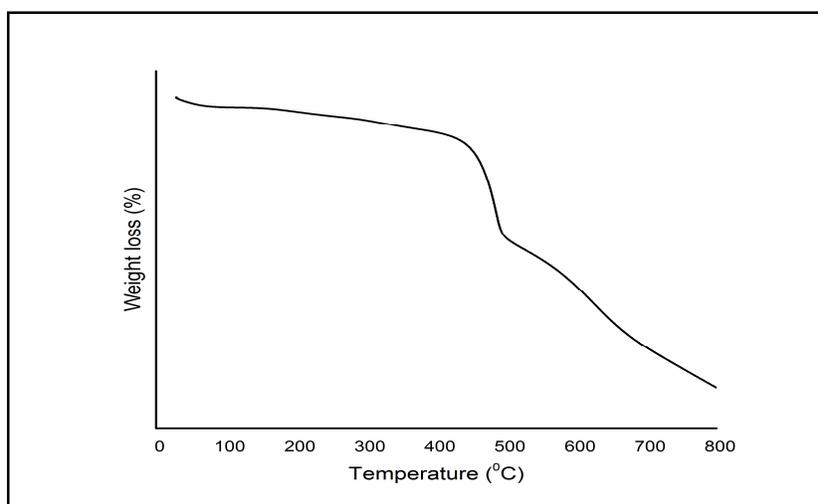


Figure 9: TGA of polyesterimide

Thermal behavior of PEI was studied by DSC technique. It was carried out at a rate of 20⁰C/min in nitrogen. Glass- transition temperature (T_g), defined by the midpoint of the baseline shift of the polymer was found in range 270- 290. The presence of bulky pendent naphthyl unit tends to enhance the T_g by restricting the segmental motion of the polymer chain. It can be noted that, PEI with flexible linkages, there is a large interval between the T_g and decomposition temperature which makes the polymers attractive for thermoforming process.

5. Crystallinity

The crystallinity of the new polyesterimide was estimated by wide- angle X-ray diffraction measurements. Polymer showed the diffraction peak which indicates the presence of a fair degree of crystalline as shown in fig 6. The polymer showed very weak crystalline absorption. The amorphous nature the polymer was reflected in their excellent solubility which is in agreement with the general rule that the solubility decreases with increasing crystallinity and this could be attributed to the introduction of the packing disruptive bulky pendent group, along the polymer backbone, which results in increased chain distances and decreased chain to chain interactions thereby leading to decrease in crystallinity[12].

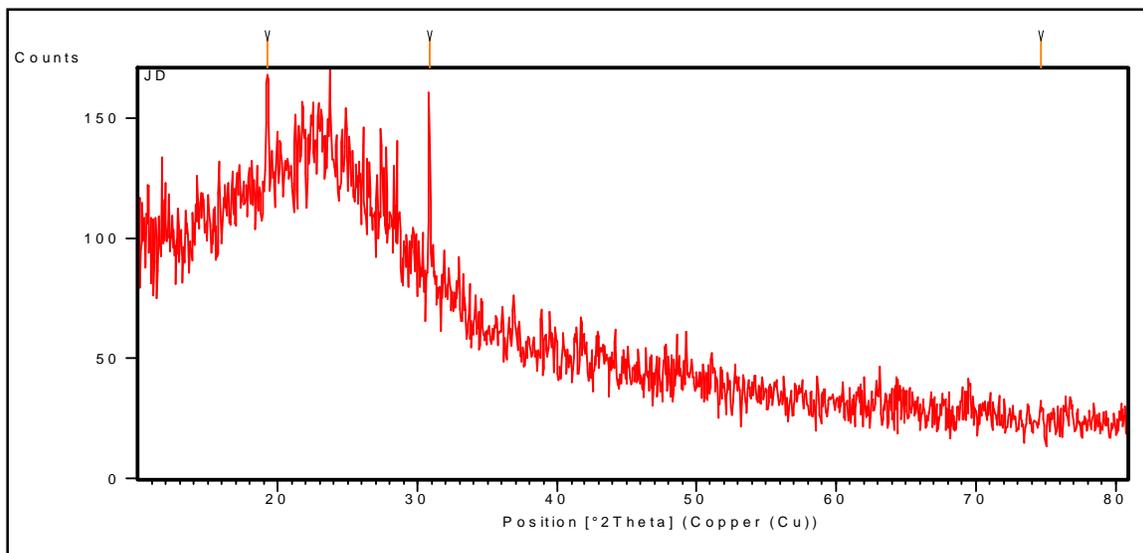


Figure 10: XRD Spectrum of Poly(ester-imide)

5.1. Solubility

The synthesized aromatic PEI is readily soluble in aprotic solvents such as NMP, DMAC, DMSO and m-cresol at room temperature as well as in common organic solvents such as THF, CHCl₃ etc is shown in table 5. The good solubility of the polymer is possibly governed by the structural modifications through the incorporation of the flexible ester linkage and bulky diamine moiety. The excellent solubility may also be due to the presence of bulky pendant substituted phenyl group, which decrease the polymer inter and intra chain interactions and disturb the co-planarity of the aromatic units to reduce the packing efficiency.

Polymer	NMP	DMSO	DMAC	Pyridine	CHCl ₃	THF	Toluene	m-cresol	Xylene
PEI	++	++	++	++	+	+	-	++	-
++ → readily soluble			+ → soluble on heating			- → insoluble			

Table 5: Solubility behavior of PEI

S. No	Polymers	Inherent Viscosity dL/g
1	PEI	0.72

Table 6: Inherent viscosity of PEI

6. Conclusion

The new polyesterimide (PEI) was synthesized from the precursor tetrimeric diacid chloride with 1,4-dihydroxy benzene in the presence of pyridine and nitrobenzene. The elemental analysis and the spectral studies confirm the structure of the polyesterimide. The introduction of bulky pendent group in the polymer backbone has effectively enhanced the thermal stability, inherent viscosity and glass transition temperature. The incorporation of the flexible ester linkage and bulky pendent phenyl group has increased the solubility of the PEI and hence, the processability may also be increased. Therefore this polyesterimide can be used as high performance polymer.

7. References

- i. Leng, W.N., Zhou, Y.M., Xu, Q. H., Liu, J.Z., *Polymer.*, (2001) 42: 9253-9259. .
- ii. Liaw, D.J., Chang, F.C., Leung, M.K., Chou, M.Y., Muellen, K., *Macromolecules.*, (2005) 38: 4024-4029.
- iii. Sroog, C.E., Endrey, A.L., Abramo, S.V., Beer, C.V., Edwards, W.M., Olivers, K.L., *J. Polym. Sci.* (1965) 3: 1373.
- iv. Simionescu, M., Marcu, M., Cazacu, M., *Eur. Polym. J.*, (2003) 39: 777 Mehdipour Alacis, Keshavarzs., *Poylm. Int.*, (2003) 52: 1487 .
- v. Banihashemi, A., Behniafar, H., *Polym. Int.*, (2003) 52: 1136 .
- vi. Mehdipour Alacis, Heidari, H., *J. Appl. Polym. Sci.* (2004), 91: 22 .
- vii. Liou, G.S., *J. Polym. Sci., Part A: Polym. Chem.*, (1998) 36: 1937.
- viii. Kricheldorf, H.R., *Adr., Polym. Sci.*, (1999) 141: 83.
- ix. Der-Jang Liaw, Chi-Cheng Lin, Kun-Li Wang., *J. Appl. Polym.* (2004) 92: 2486-2493.
- x. Xiu-Ru Li, Yue-Sheng Li, *Polym.*, (2003) 44: 3855-3863.
- xi. Der-Jang Liaw, Chung-Yu Hsu, Pei-Nan Hsu, Shu-Ling Lin., *J. polym. Sci., Part A: Polym. Chem.* (2002), 40: 2066-2072.
- xii. Yang, C.P., and Chen W.T., *J. polym. Chem.*, (1993) 32: 435-444..