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Synthesis and Characterisation of Linear Aromatic Polyesterimide Containing Heterocyclic Moiety

Y. Christabel Shaji, G. Leema Rose, M. Anitha Malbi, Department of Chemistry, Holy Cross College (Autonomous), Nagercoil.

Abstract

A novel thermally stable polyesterimide was synthesised with 1,4-dihydroxy benzene and tetrimide-diacid chloride by polycondensation. The tetrimide diacid chloride containing heterocyclic moiety was synthesised by treating 2,6-diaminopyridine with pyromellitic dianhydride followed by refluxing with thionyl chloride. The synthesised polymer was characterized by FT-IR and elemental analysis. The properties of the synthesised polyesterimide were also studied. It exhibits high thermal stability, good solubility and processability.

Keywords: Pyromellitic dianhydride, tetrimide-diacid chloride, polycondensation, thermal stability

1. INTRODUCTION

Polyimides are one of the high-performance materials with excellent thermal stability, dimensional stability and high electronic property. They are mainly used in aerospace and electronic industries in the form of films and mouldings.[1,2] Poor thermoplastic fluidity and solubility are major problems for wide application of polyimides. There are two successful approaches exist for increase in solubility and processability of polyimides without sacrificing their thermal stability. First approach is the synthesis of copolyimides such as polyesterimides[3], polysiloxaneimides, polyurethaneimides and polyamideimides. Second approach is the introduction of flexible ether linkages, non-planar asymmetric units and bulky pendent groups along the polymer backbone chain[4].

Aromatic polyesterimides (PEIs) are thermally stable polymers and they have various commercial applications. The main applications of PEIs are in coatings for enameled wires, high strength fibres, hot melt adhesives, heat resistant films and printed circuit boards[5]. Several methods have been reported for the synthesis of PEIs. In the 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-diamino pyridine and all other chemicals such as Pyromellitic dianhydride (PMDA). N,N-dimethyl acetamide (DMAc), N,N-dimethyl formamide (DMF), *p*-amino benzoic acid. 1,4-dihydroxy benzene, toluene, acetone, chloroform, tetrahydrofuron (THF) were purchased from Sigma Aldrich. The solvents used for polymerization were purified according to standard methods.

Elemental analysis was carried out as VarioELII 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 10^0C/min. FTIR spectroscopy was performed on a Bruker Vertex 70 at frequencies ranging from 400-4000cm^{-1}.

2.1. Synthesis of tetrimide diacid

A three necked 150 ml RB flask equipped with nitrogen inlet and a reflux condenser was charged with 2,6-diamino pyridine (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

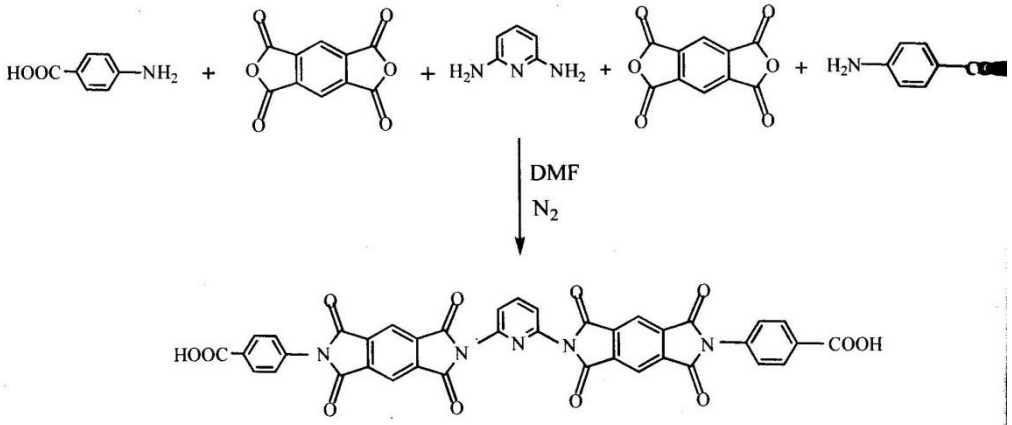
trickled into water and the precipitated product was collected by filtration and dried in vacuum at 100°C for 12 hrs (**Scheme 1**).

2.2. Synthesis of tetrimide diacid chloride

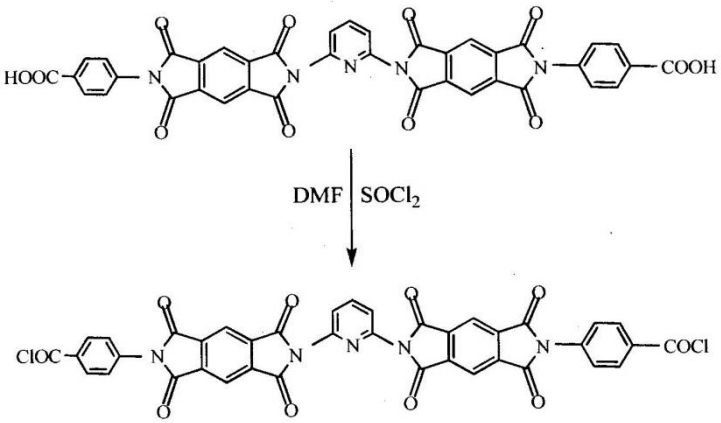
The synthesised tetrimide diacid was refluxed with an excess of thionyl chloride using DMF as a catalyst[6]. The viscous solution obtained was cooled and trickled into excess methanol with vigorous stirring. The precipitate was filtered off. Washed several times with hot methanol and dried in vacuum oven at 100°C for 7 hrs. The yield of the reaction was 85% (**Scheme 2**.

2.3. Synthesis of Polyesterimide

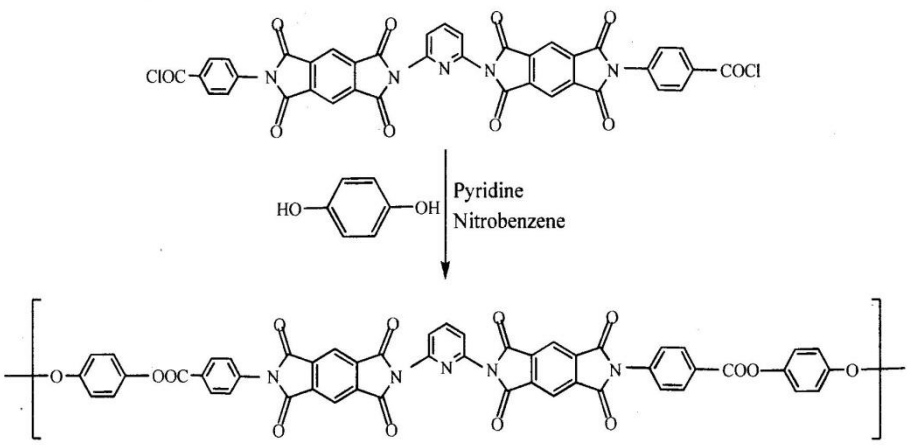
1,4-dihydroxy benzene (0.02 mole), tetrimide diacid chloride (0.01 mole), pyridine and nitrobenzene were homogenized at room temperature and subjected to a heating temperature of 170°C for 10 hrs. After the completion of the reaction, the mixture was allowed to cool down, filtered and washed several 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%. (**Scheme 3**).



Scheme 1 Synthesis of tetrimide diacid



Scheme 2 Synthesis of tetrimide diacid chloride



Scheme 3 Synthesis of polyesterimide

3. CHARECTERIZATION TECHNIQUIES

3.1 Elemental Analysis

The elemental analysis data of the tetrimide diacid chloride (precursor) and polyesterimide (polymer) are in good agreement with the calculated values. The values are given in **Table 1.**

Table 1 Physico-chemical characteristics of polymer

Compound	Mol. Formula	% Yield	Elemental Analysis wt (%)		
			Carbon	Hydrogen	Nitrogen
Precursor	$C_{39}H_{15}O_{10}N_5Cl_2$	83%	59.97 (59.68)	2.06 (1.92)	9.2 (8.9)
polyesterimide	$C_{51}H_{23}O_{14}N_5$	80%	65.57 (65.86)	2.78 (2.49)	7.69 (7.5)

3.2 IR Spectral Studies

The tetrimide diacid chloride shows absorptions band at 1395 cm^{-1} which corresponds to the imide ring axial vibration and that around 719 cm^{-1} is due to imide ring out of plane bending vibration. The band around 1726 cm^{-1} corresponds to imide ring transverse vibration. The spectrum shows an absorption peak at 1720 cm^{-1} due to C = O stretching of acid chloride[7]. The PEI shows absorption band at 1720 cm^{-1} which corresponds to the symmetric stretching vibration of the imide carbonyl group. Aromatic C = C bands are seen at 1609 and 1515 cm^{-1}, whereas aromatic C - H stretching band was found at 2300 cm^{-1}. The IR spectrum of the tetrimide diacid chloride and polyesterimide are given in **Figures 1** and **2**.

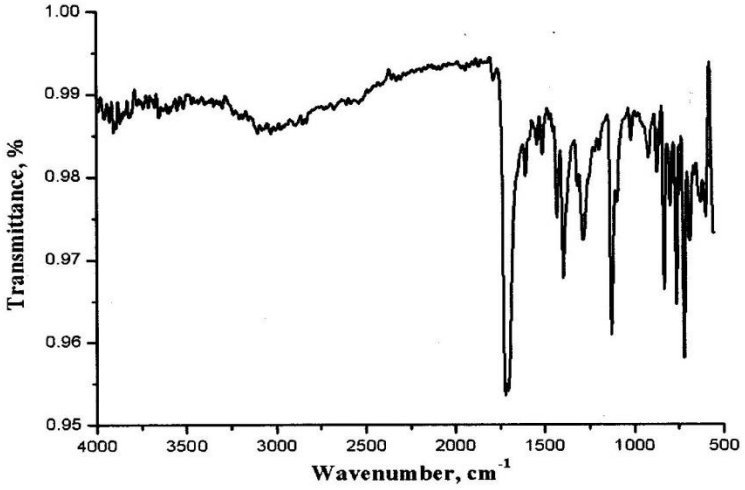


Fig.1 IR spectrum of tetrimide diacid chloride

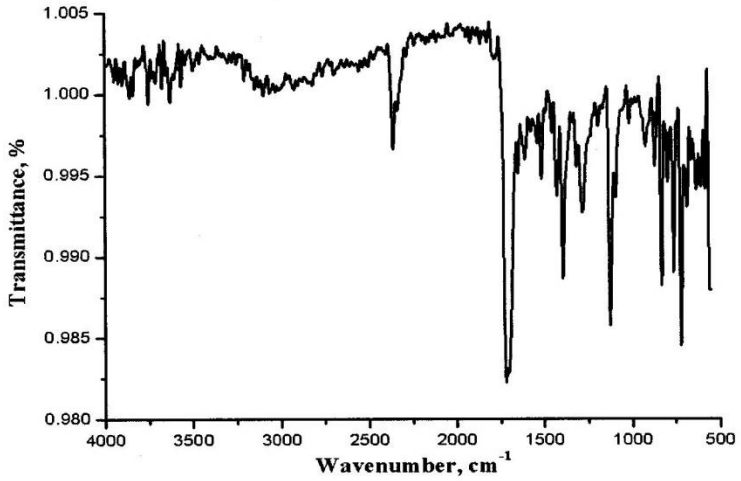


Fig.2 IR spectrum of Polyesterimide

3.3 Solubility

The solubility of the polyesterimide was tested qualitatively in various organic solvents such as N-Methyl pyrrolidone (NMP), Dimethyl sulphoxide (DMSO), Dimethyl acetamide (DMAc), Chloroform ($CHCl_3$), Tetrahydrofuran(THF), Toluene, m-cresol and Xylene. The results are reported in **Table 2**.

Table 2 Solubility of the PEI

Polymer	NMP	DMSO	DMAc	$CHCl_3$	THF	Toluene	*m*-cresol	Xylene
PEI	++	++	++	+-	+	-	++	-

Solubility keys: (++) soluble; (+) soluble on heating; (+-) partly soluble; (-) insoluble.

The new PEI shows high solubility in solvents such as NMP, DMSO, DMAc and m-cresol. This may due to the incorporation of flexible ester linkage in the polymer chain.[8] This enchanced solubility may increase the processability also.

3.4 Thermal Analysis

The newly synthesised PEI has good thermal stability. The thermal and thermoxidation stability of the polymer was evaluated by thermogravimetric analysis (TGA) in nitrogen atmosphere with the heating rate of 10°C/min. The decomposition temperature (T_d) of 10% weight loss in nitrogen atmosphere was determined from the original TGA thermogram and was found to be 400°C. The amount of carbonized residue (char yield) at 800°C in nitrogen atmosphere of the polyesterimide was found to be 35%. 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 heterocyclic ring in the polymer backbone,which may reduce chain-chain packing and lowers the rigidity of the polymer backbone[9]. The TGA of polyesterimide is given in **Figure 3**.

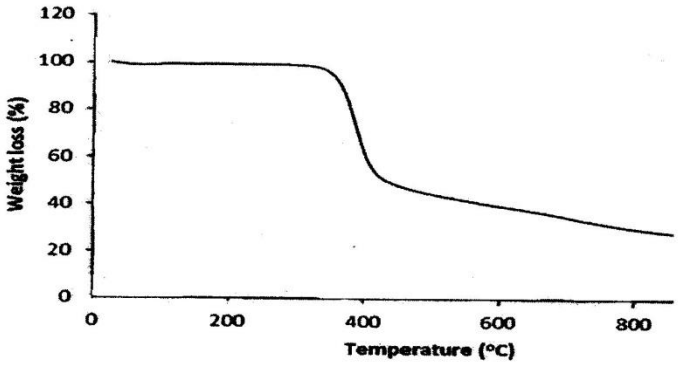


Fig. 3 TGA of polyesterimide

CONCLUSION

The new polyesterimide (PEI) was synthesized from the precursor tetrimide 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 heterocyclic moiety in the polymer backbone has effectively enhanced the thermal stability. The incorporation of the flexible ester linkage 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.

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