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# Synthesis and Characterization of Polyetherimides Derived from AB Monomers

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Four novel imides group containing AB monomers, N-(4-hydroxyphenyl)-4-nitrophthalimide, N-(3-hydroxyphenyl)-4-nitrophthalimide, N-(5-hydroxy naphthyl)-4-nitrophthalimide, and N-4-[2-(4-hydroxyphenyl) isopropyl phenyl]-4-nitrophthalimide (IIIa-d) were synthesized and characterized by IR, and NMR. The polyetherimides were prepared by self polycondensation reaction of AB monomers. The polymers were obtained in 84–88% yield and had inherent viscosity in the range 0.42–0.47 dL/g. The polymers were characterized by IR, X-ray, TGA, DSC and solubility. All the polymers were readily soluble in polar aprotic solvents and had 10% weight loss temperature above 396°C in nitrogen.

**Keywords:** Polyetherimides, AB monomers, structure-property relationship

## 1 Introduction

Despite the emergence of heat resistance polymers, it is the polyimides that offer outstanding promise for the high technology applications of the future. Aromatic polyimides (1–3) exhibit outstanding mechanical property and excellent thermal stability. These materials are widely used in electrical, electronics, automotive and aerospace industries (4–6). However their applications are limited due to processing difficulties like insolubility in common organic solvents and their extremely high softening or melting temperature (4, 7, 8). Therefore much effort has been made to develop structurally modified aromatic polyimides such as polyetherimides (9–11), polyamideimides (12–15) and polyesterimides (16–19) with improved processability.

The incorporation of ether linkages between aromatic rings improves the processability to a great extent. Takekoshi and coworkers (9–11) have prepared a series of polyetherimides, which exhibit excellent processability.

Polyetherimides are commonly prepared from AA-type and BB-type monomers (9–11). The present paper describes the synthesis and properties of polyetherimides obtained by self polycondensation of AB monomers containing preformed imide ring. The requirement of stoichiometric equivalence to obtain high molecular weight is easily met by using AB monomers. The main

advantage of this approach is that the monomer carries the imide ring and hence the polymers do not require any post curing at high temperatures.

## 2 Experimental

### 2.1 Measurements

IR spectra were obtained on Perkin-Elmer spectrum one and <sup>1</sup>H-NMR spectra were recorded on a Bruker 300 MHz instrument. X-ray diffractograms were obtained on a PANalytical-model: X'per PRO using CuK $\alpha$  radiation. Thermogravimetric analysis (TGA) and Differential Scanning Calorimeter (DSC) were performed on TA Instruments Model SDT Q600 at a heating rate 10°C/min. Inherent viscosities were determined at a concentration of 0.5 g/d L in DMF.

### 2.2 Monomer Preparation

Commercial 4-aminophenol, 3-aminophenol and 5-amino-1-naphthol were recrystallized before use. The compound 2-(4-aminophenyl)-2'-(4-hydroxyphenyl) propane, was prepared in the laboratory from biphenol- A and aniline hydrochloride and recrystallized before use. N-methyl-2-pyrrolidone (NMP) was dried with molecular sieves before use. All the reagents used were analytical grade.

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**N-(4-hydroxyphenyl)-4-nitrophthalimide (III a),  
N-(3-hydroxyphenyl)-4-nitrophthalimide (III b),  
N-(5-hydroxynaphthyl)-4-nitrophthalimide (III c),**

**Table 1.** Physical characteristics and spectral data of AB monomers (III a-d)<sup>a</sup>

Code	Yield %	Melting point, °C	IR (K Br), cm <sup>-1</sup>	<sup>1</sup> H-NMR chemical shifts(δ) in DMSO-d <sub>6</sub>
III a	96	230-232	1785 and 1714 (symmetrical and asymmetric stretching of imide carbonyl), 1542 and 1348 (-NO <sub>2</sub> ), 721 (imide ring), 3454 (-OH)	6.8-8.8 (m, 7H, Ar), 9.9 (s, -OH)
III b	93	218-223	1784 and 1733 (symmetrical and asymmetric stretching of imide carbonyl) 1542 and 1345 (-NO <sub>2</sub> ), 719 (imide ring) 3227 (-OH)	7.0 - 8.9 (m, 7H, Ar), 10.0 (s,-OH)
III c	95	262-263	1777 and 1721 (symmetrical and asymmetric stretching of imide carbonyl) 1536 and 1344 (-NO <sub>2</sub> ) 721 (imide ring) ,3452 (-OH)	6.9 - 8.7 (m,9H,Ar), 10.5 (s,-OH)
III d	92	195-198	1772 and 1716 (symmetrical and asymmetric stretching of imide carbonyl) 1537 and 1341 (-NO <sub>2</sub> ) 719 (imide ring) 3390 (-OH)	6.7- 8.7(m,11H,Ar), 1.6 (s,6H,-CH <sub>3</sub> ), 9.3 (s,-OH)

<sup>a</sup>Ar = aromatic, s = singlet, m = multiplet

### N- 4-[2-(4-hydroxyphenyl) isopropylphenyl]-4-nitrophthalimide (III d),

The four AB hydroxy nitro monomers (III a-d) were prepared by the condensation of 4-nitrophthalic anhydride with the corresponding amino phenol/amino naphthol. A typical procedure adopted is as follows (19).

To a stirred solution of 4-aminophenol (2.18 g, 0.02 mol) in NMP (40 mL) 4- nitrophthalic anhydride (3.86 g, 0.02) was added under nitrogen atmosphere and was left stirred at room temperature for 30 min. To this, toluene (30) mL was added and the resulting mixture was heated under reflux for 6 h, while removing water azeotropically using a Dean-Stark trap. The reaction mixture was then poured into water, the precipitated N-(4-hydroxyphenyl)-4-nitrophthalimide (III a) was filtered, washed with water, and dried. The compound was recrystallized from ethanol.

The four imide containing AB monomers (IIIa-d) were characterized by melting point, IR, and <sup>1</sup>H-NMR (Table 1).

### 2.3 Polymerization

The four polyetherimides (PEI-1–PEI-4) were prepared by the self polycondensation of imide group containing AB monomers by nucleophilic displacement reaction. A typical procedure adopted is as follows.

To a stirred solution of IIIa (3.41 g, 0.012 mol) in 30 mL of DMSO, Sodium methoxide (0.65 g, 0.012 mol) was added and stirred for 30 min under nitrogen atmosphere. The methanol formed was removed by distillation. The temperature was raised to 100°C and refluxed for 10 h under N<sub>2</sub>. The reaction mixture was then poured into water and the precipitated polyetherimide (PEI-1) was filtered, washed with water and ethanol and dried.

### 3 Results and Discussion

The imide group containing AB hydroxy nitro monomers (IIIa-d) were prepared by the condensation of 4-nitrophthalic anhydride with the corresponding amino phenol/amino naphthol in N-methyl-2-pyrrolidone (NMP) (Scheme 1). The complete cyclization of the intermediate amic acid was achieved by toluene-water azeotropic distillation.

The IR spectrum of IIIa (Figure 1) showed a characteristic absorption at 1785 cm<sup>-1</sup> and 1714 cm<sup>-1</sup> (symmetrical and asymmetric stretching of imide carbonyl), 1542 cm<sup>-1</sup> and 1348 cm<sup>-1</sup> (-NO<sub>2</sub>), 721 cm<sup>-1</sup> (imide ring), and 3454 cm<sup>-1</sup> (-OH). The <sup>1</sup>H-NMR spectrum of IIIa (Figure 2) shows multiplet at δ 6.8-8.8 due to aromatic protons and singlet at δ 9.9 for phenolic proton, which disappeared on D<sub>2</sub>O treatment. The peaks at δ 2.5 and at δ 3.4 are due to DMSO and water in DMSO. The IR and NMR analysis of monomers III(a-d) are in accord with the proposed structure (Table 1).

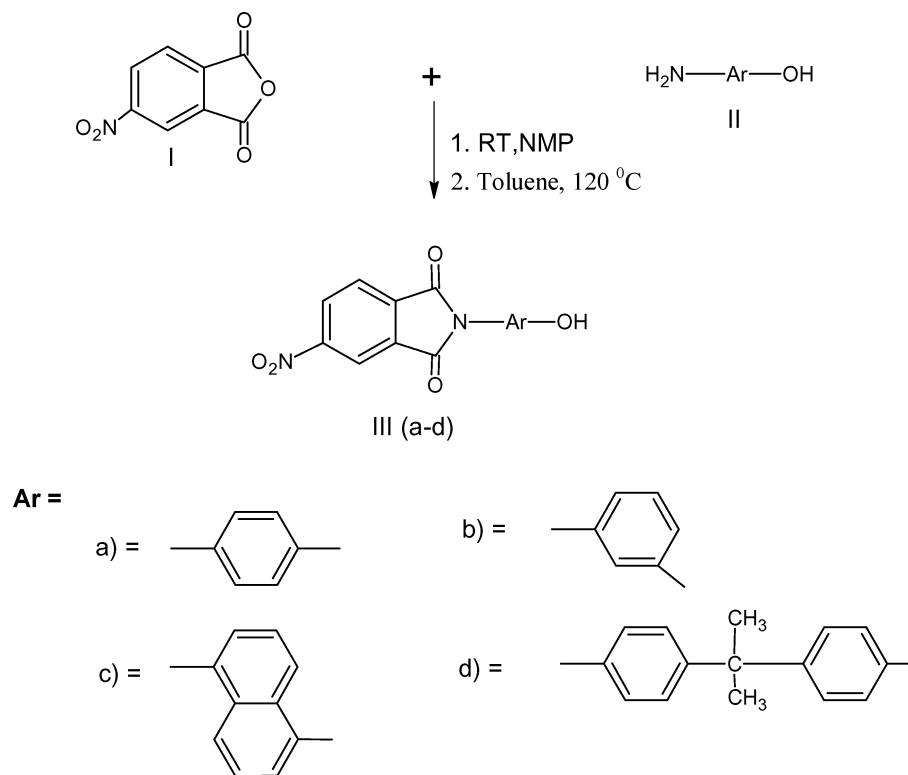
Polyetherimides (PEI-1-PEI-4) were prepared using imide containing AB monomers (III a-d) (Scheme 2). The polymerization reaction was carried at 100°C for 10 h. The results of polymerization are given in Table 2.

The IR spectrum of PEI-3 (Figure 3) shows absorption at 1774 cm<sup>-1</sup>, and 1716 cm<sup>-1</sup> associated with the imide structure. The disappearance of strong absorption due to nitro

**Table 2.** Preparation of polyetherimides

Polymer Code	AB monomer	Yield %	η <sub>inh</sub> <sup>a</sup> dL/g	γ (Imide group) cm <sup>-1</sup>
PEI-1	III a	88	0.47	1774, 1715
PEI-2	III b	84	0.42	1776, 1716
PEI-3	III c	84	0.46	1774, 1716
PEI-4	III d	85	0.43	1774, 1715

<sup>a</sup>Measured in DMF at 30°C, C = 0.5 g/dL



Sch. 1. Preparation of monomers.

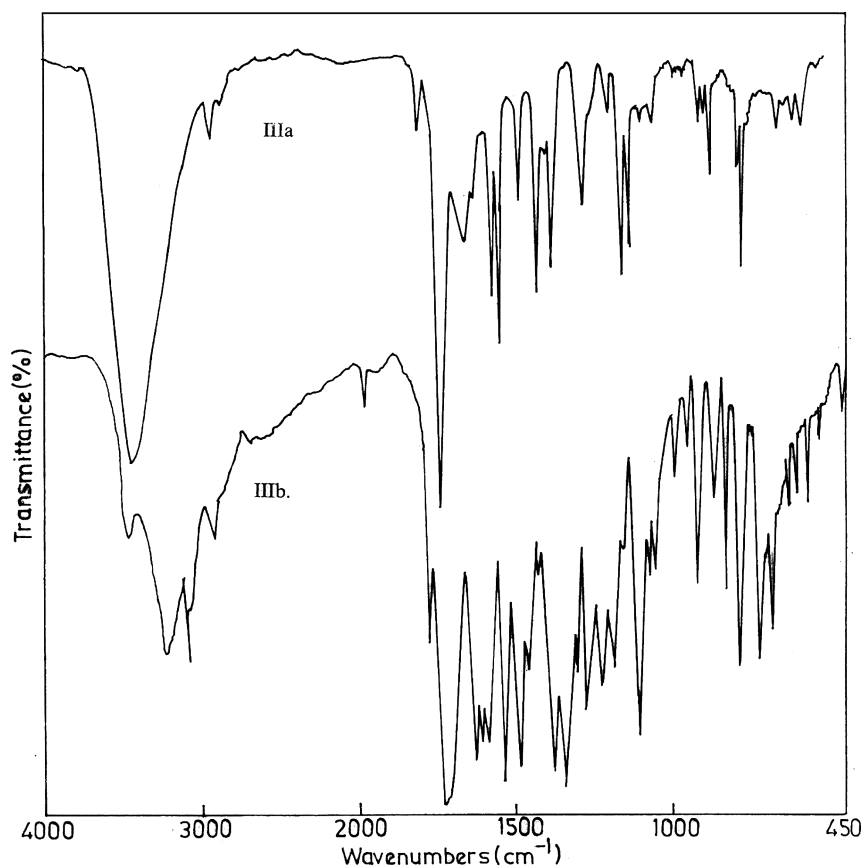
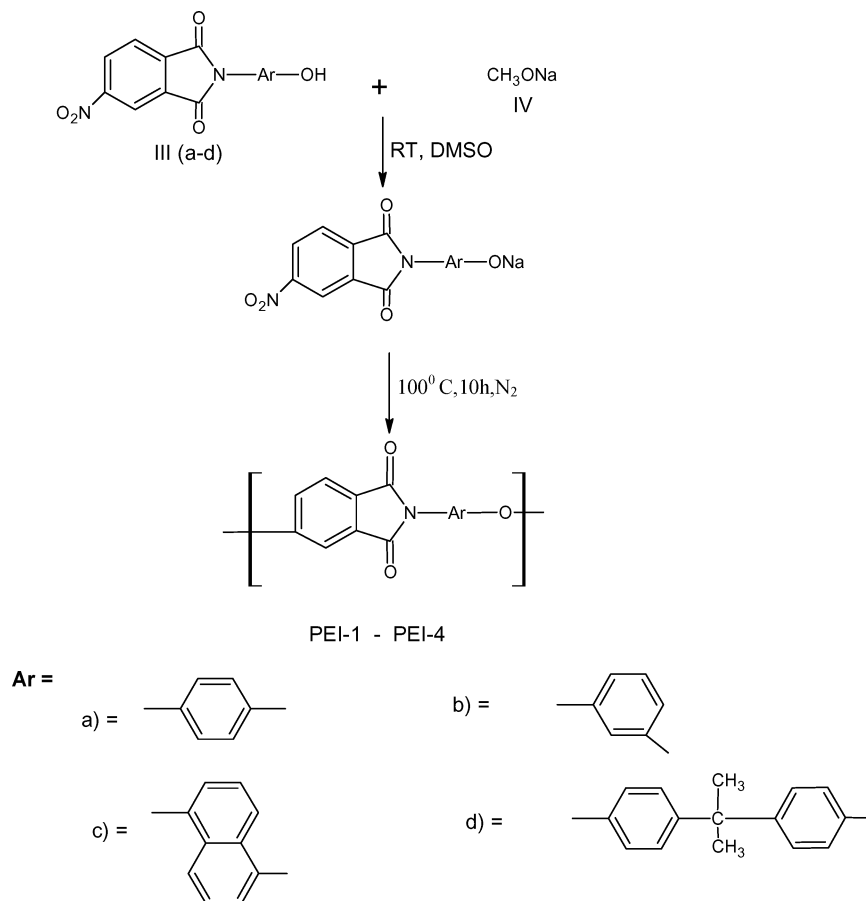


Fig. 1. IR spectra of AB monomer IIIa and IIIb.



Sch. 2. Preparation of polyetherimides.

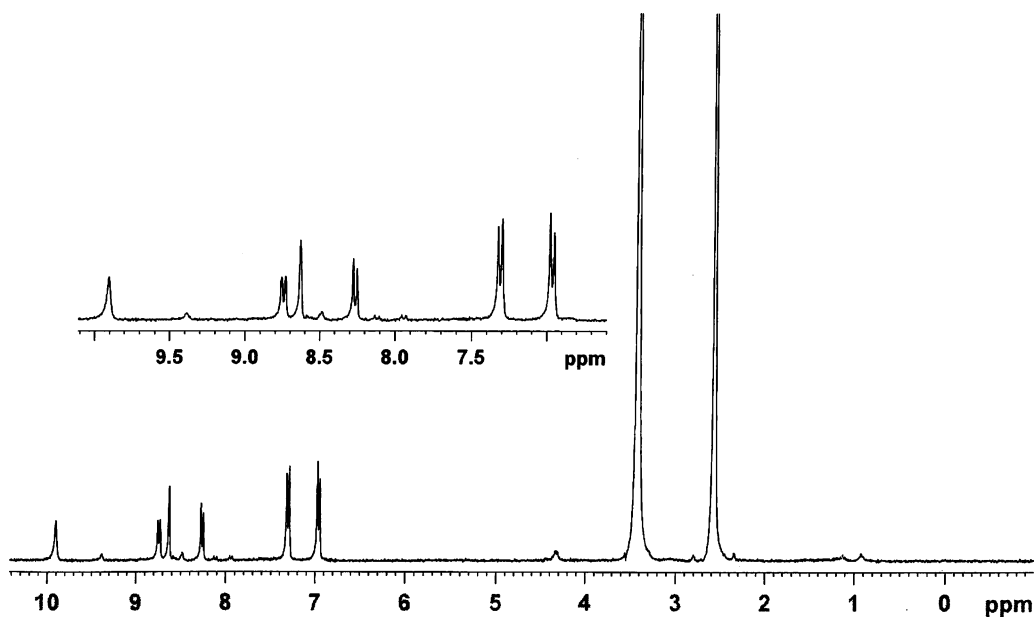
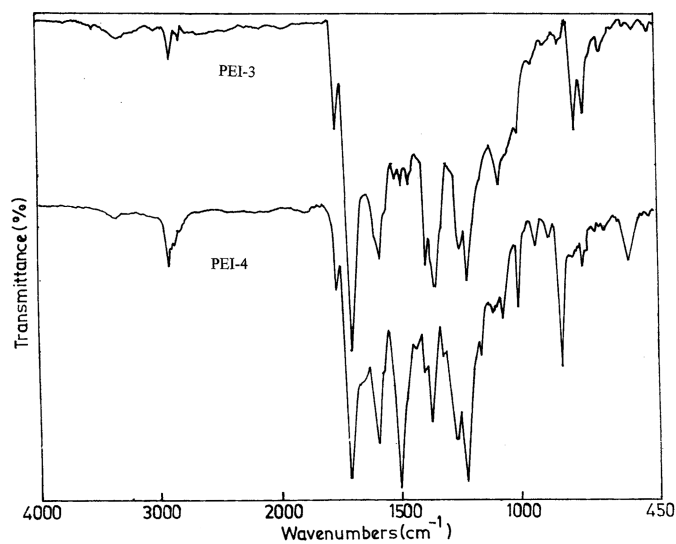
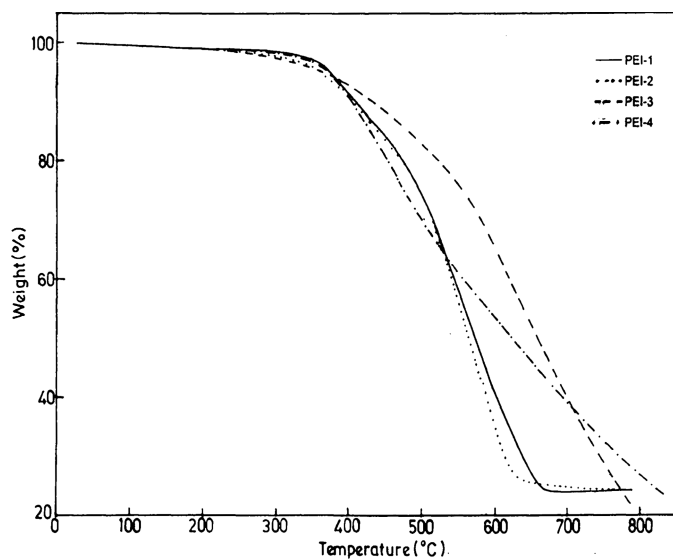
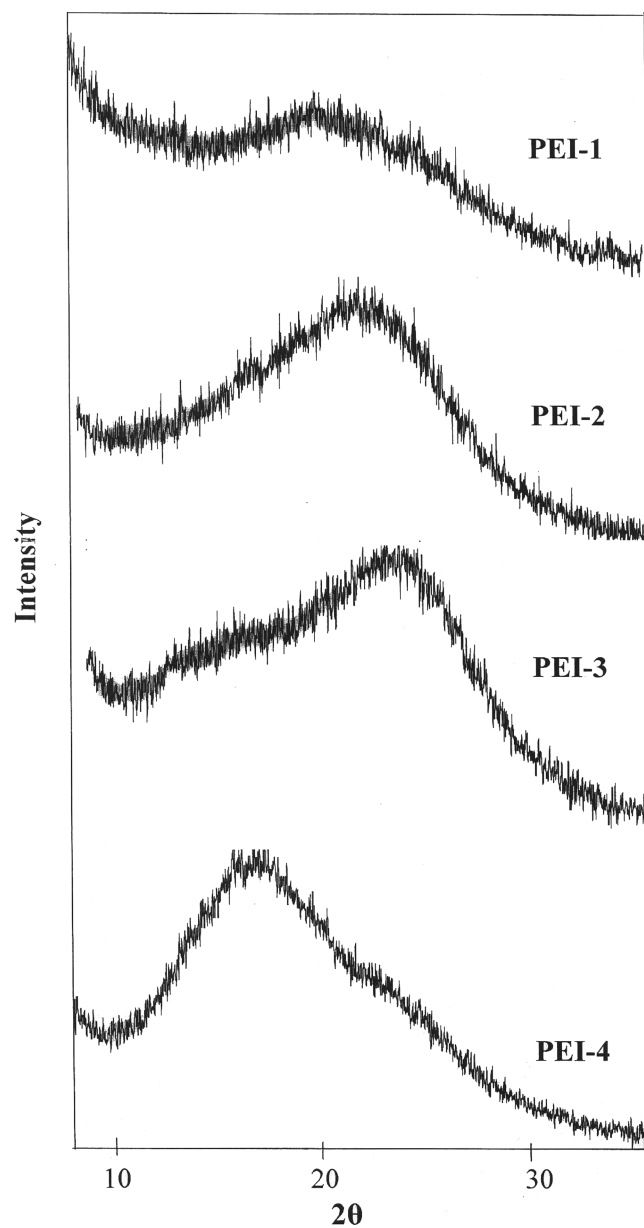


Fig. 2. NMR spectra of AB monomer IIIa.

**Table 3.** Solubilities of polyetherimides<sup>a</sup>

Polymer code	NMP, DMF .DMSO, DMAc	Pyridine	THF	m-cresol	Acetone	Conc. H <sub>2</sub> SO <sub>4</sub>
PEI-1	+	+	—	—	—	+
PEI-2	+	+	—	—	—	+
PEI-3	+	—	—	—	—	+
PEI-4	+	+	+—	+—	+	+

<sup>a</sup> + = Soluble at room temperature, +— = Soluble on heating, — = Insoluble

**Fig. 3.** IR spectra of polymer PEI-3 and PEI-4.**Fig. 4.** TGA curves of polyetherimides (PEI-1-PEI-4).**Fig. 5.** X-ray diffractograms of polyetherimides (PEI-1-PEI-4).

**Table 4.** Thermal properties of polyetherimides

Polymer Code	Temperature at various Percentage decompositions, °C			Char yield %	DSC	
	10	20	30		T <sub>g</sub> °C	T <sub>exo</sub> °C
PEI-1	408	472	516	24	238	628
PEI-2	410	478	518	25	210	630
PEI-3	424	535	585	22	235	650
PEI-4	396	452	502	27	233	640

group at 1536 cm<sup>-1</sup> was observed. The IR spectrum of polymers PEI-1 to PEI-4 (Table 2) also indicates that during the nucleophilic displacement polymerization, the imide ring is stable.

The inherent viscosities of the polymers measured in DMF at 30°C were in the range 0.42-0.47 dL/g.

### 3.1 Solubility Characteristics

The solubility characteristics of the polyetherimides are shown in Table 3. A 10% solution was taken as the criteria for solubility. All these polymers were soluble in NMP, DMAc, DMF, DMSO, and H<sub>2</sub>SO<sub>4</sub>. The PEI-4 was soluble in acetone and pyridine at room temperature and on heating in THF and m-cresol. The PEI-1, PEI-2 and PEI-4 were soluble in pyridine at room temperature. The improved solubilities of the polyetherimides may be explained by the fact that the incorporation of aromatic ether linkages in to the polymer backbone chain decreases chain symmetry and consequently, the degree of crystallinity which in turn increases solubility.

### 3.2 Thermal Properties

The thermal stabilities of the polyetherimides were evaluated by TGA in nitrogen atmosphere at a heating rate of 10°C/min. TGA curves (Figure 4) indicates that these polymers undergo rapid degradation around 450–550°C. The temperature at which 10% weight loss occurs ranges from 396–424°C (Table 4). The DSC thermogram of these polymers showed a broad exothermal peak due to the degradation of the polymers in the temperature range 628 to 650°C. Endotherms corresponding to the crystalline melt temperature (T<sub>m</sub>) were not observed for any of the polymers. The glass transition temperature was observed in the temperature range 210 to 238°C (Table 4).

### 3.3 Crystallinity

The crystallinity of the polyetherimides was examined by X-ray diffraction. The X-ray diffraction pattern (Figure 5) showed that all these polymers were amorphous.

## 4 Conclusions

We have successfully synthesized four AB monomers in high yield. A series of polyetherimides were prepared. These polyetherimides were amorphous and shows excellent solubility in common organic solvents. All the polyetherimides exhibit good thermal stability.

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