CHAPTER 3: SYNTHESIS AND CHARACTERIZATION OF POLY(ETHERIMIDE)S VIA AROMATIC NITRO DISPLACEMENT REACTION

3.1 INTRODUCTION

Polyimides\textsuperscript{131, 132} are a class of thermally stable polymers that are based on stiff aromatic backbone. Polyimides are considered as versatile polymers with an almost unlimited spectrum of applications as speciality polymers for advanced technologies. Their extreme structural rigidity and high density of cohesive energy render them insoluble in many organic solvents\textsuperscript{133}. Thus, the processing of thermally stable polyimides is very difficult which is essential for making them into utility articles. The chemistry of polyimides has been directed to synthesize species that are soluble in common organic solvents or melt processable when fully imidized. The most important of them is poly(etherimide)s.\textsuperscript{134} The ether units inserted in the polymer chain increase the chain flexibility, solubility and good melt flow characteristics to poly(etherimide)s, while the aromatic imide units provide thermal resistance and mechanical properties.

The present work describes the synthesis of bis(nitrophthalimide)s monomers containing flexible groups (-O-, -SO\textsubscript{2}-, and -C=O). A series of poly(etherimide)s are synthesized from these bis(nitrophthalimide)s monomers and various aromatic bisphenolate ions. The main advantage of this approach is the presence of most effective activating N-substituted imide group in monomers, which favours the nitro displacement polymerization and is essentially quantitative. Another advantage of this method is the presence of flexible groups (-O-, -SO\textsubscript{2}-, and -C=O) in the polymer chain and the separation of rigid imide groups due to enlargement of repeat unit decreased the rigidity,
crystallinity and increases the flexibility of the polymer chain, and its effects on the property of the poly(etherimide)s are studied. In this approach the monomers carry the imide rings and hence the polymer is not requiring any post curing at high temperature.

Two new monomers, 4,4’-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone and 4,4’-bis(4-nitrophthalimido 4-phenoxy)benzophenone were synthesized. The poly(etherimide)s were derived from bis(nitrophthalimide)s by nucleophilic displacement of nitro group by various bisphenolate anions. The structures of monomers and poly(etherimide)s were characterized by spectroscopic analysis. The poly(etherimide)s were characterized by X-ray diffraction, thermogravimetry, differential scanning calorimetry, electrical property, inherent viscosity and solubility test.

3.2 EXPERIMENTAL

3.2.1 Materials

The commercial 4-aminophenol, 4-nitrophthalic anhydride, 1,3 dihydroxybenzene, 1,4 dihydroxybenzene, bisphenol-A and 1,5 dihydroxynaphthalene were purchased from Sigma Aldrich Chemicals. The compound 4,4’-bis(4-aminophenoxy)diphenyl sulfone and 4,4’-bis(4-aminophenoxy)benzophenone were prepared in the laboratory and recrystalised before use. Potassium carbonate was dried in vacuum at 120 °C for 24 h before use. All the reagents used were of analytical grade.

3.2.2 Measurements

FT-IR spectra were obtained on Perkin Elmer Spectrum One and \(^1\)H-NMR spectra were recorded on a Bruker 300 MHz spectrometer. X-ray diffractograms were obtained on PANalytical-model: X’per PRO using CuK\(\alpha\) radiation. Thermogravimetric analysis and
differential scanning calorimetric analysis were performed on TA Instruments Model SDT Q600 at a heating rate 10 °C / min in nitrogen atmosphere. Dielectric constant and impedance were obtained from HIOKI LCR HiTester 3532-50. Inherent viscosities were determined at a concentration of 0.5 g / d L in DMSO.

3.2.3 Synthesis of bis(nitrophthalimide)s monomer

The monomer synthesis consists of two steps, the first step was synthesis of ether containing diamines 4,4’-bis(4-aminophenoxy)diphenyl sulfone and 4,4’-bis(4-aminophenoxy)benzophenone\textsuperscript{135,136}. In the second step, two monomers 4,4’-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone and 4,4’-bis(4-nitrophthalimido 4-phenoxy) benzophenone were synthesized from 4-nitrophthalic anhydride and the corresponding ether containing diamines.\textsuperscript{137,138}

3.2.3.1 Synthesis of 4, 4’-bis (4-aminophenoxy)diphenyl sulfone

Dry NMP (20 mL) and toluene (25 mL) were added into a mixture of 4-aminophenol (II) (10.9 g, 0.10 mol) and potassium carbonate (16.56 g, 0.12 mol). The reaction mixture was heated at 140-150 °C in nitrogen atmosphere for 10 h, while removing water azeotropically using Dean-Stark trap. After complete dehydration, the temperature was raised to 160 °C and the remaining toluene was removed. The system was cooled to 100 °C and 4,4’-dichlorodiphenyl sulfone (I) (14.35 g, 0.05 mol) was added. The mixture was stirred at 170 °C for further 6 h under nitrogen atmosphere. The mixture was allowed to cool and then poured into water and the precipitated 4,4’-bis(4-aminophenoxy) diphenyl sulfone (III) precipitated was filtered, washed with water, methanol and dried, Colour : Tan, Yield : 78 %, IR (KBr):3440 cm\(^{-1}\) (N-H, NH\(_2\)) and 1150 cm\(^{-1}\) (S=O, sulfone),
\(^1\)H-NMR (300 MHz, DMSO-d\(_6\), ppm): \(\delta\) 7.82 -7.85 (d,4H,Ar), \(\delta\) 6.95 - 6.98 (d,4H,Ar), \(\delta\) 6.78 - 6.81 (d,4H,Ar), \(\delta\) 6.58 - 6.61 (d,4H,Ar), and \(\delta\) 5.12 (s,4H,-NH\(_2\)).

3.2.3.2 Synthesis of 4,4'-bis (4-aminophenoxy)benzophenone

The compound 4,4'-bis(4-aminophenoxy)benzophenone (V) was also prepared by using the similar procedure as adopted for 4,4'-bis(4-aminophenoxy)diphenyl sulfone using 4,4'-difluorobenzophenone (IV) instead of 4,4'-dichlorodiphenyl sulfone, Colour: Tan, Yield: 85 %, IR (KBr): 3443 cm\(^{-1}\) (N-H, NH\(_2\)) and 1652 cm\(^{-1}\) (C=O, keto).

3.2.3.3 Synthesis of 4,4'-bis (4-nitrophthalimido 4-phenoxy)diphenyl sulfone

To a stirred solution of 4,4'-bis(4-aminophenoxy)diphenyl sulfone (III) (8.64 g, 0.02 mol) in NMP (30 mL), 4-nitrophthalic anhydride (VI) (7.72 g, 0.04 mol ) was added under nitrogen atmosphere and was kept stirred at room temperature for 6 h. To this, toluene (30 mL) was added and the reaction mixture was heated at 120 \(^\circ\)C in nitrogen atmosphere for 10 h, while removing water azeotropically using Dean-Stark trap. After complete dehydration, the temperature was raised to 160 \(^\circ\)C and the remaining toluene was removed. The reaction mixture was allowed to cool and then poured into water, the precipitated 4,4'-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone (VIIa) was filtered, washed with water and dried, Colour: Light yellow, Yield: 94 %, Melting point: 160 \(^\circ\)C, IR (KBr):1786 cm\(^{-1}\) and 1723 cm\(^{-1}\) (C=O, imide carbonyl), 1586 cm\(^{-1}\) (C-N stretching), 720 cm\(^{-1}\) (imide ring), 1149 cm\(^{-1}\) (S=O, sulfone), 1543 cm\(^{-1}\) and 1345 cm\(^{-1}\) (-NO\(_2\)), \(^1\)H-NMR (300 MHz, DMSO-d\(_6\),ppm): \(\delta\) 8.68 - 8.70 (d, 2H,Ar), \(\delta\) 8.59 (s, 2H,Ar), \(\delta\) 8.22 - 8.25 (d, 2H,Ar), \(\delta\) 7.97 - 8.00 (d,4H,Ar), \(\delta\) 7.55 - 7.58 (d, 4H,Ar), \(\delta\) 7.31 -7.34 (d, 4H,Ar), and \(\delta\) 7.21-7.24 (d, 4H,Ar).
3.2.3.4 Synthesis of 4,4’-bis(4-nitrophthalimido 4-phenoxy)benzophenone

The monomer 4,4’-bis(4-nitrophthalimido 4-phenoxy)benzophenone (VIIb) was also prepared by using the similar procedure as adopted for 4,4’-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone (VIIa) using 4,4’-bis(4-aminophenoxy)benzophenone instead of 4,4’-bis (4-aminophenoxy)diphenyl sulfone. Colour: Yellow, Yield: 93 %, Melting point: 283°C. IR (KBr): 1787 cm⁻¹ and 1723 cm⁻¹ (imide carbonyl), 1589 cm⁻¹ (C=N), 718 cm⁻¹ (imide ring), 1652 cm⁻¹ (C=O, keto), 1540 cm⁻¹ and 1345 cm⁻¹ (-NO₂).

¹H-NMR (300 MHz, DMSO-d₆, ppm): δ 8.68-8.71 (d, 2H, Ar), δ 8.60 (s, 2H, Ar), δ 8.22-8.25 (d, 2H, Ar), δ 7.78-7.80 (d, 4H, Ar), δ 7.55-7.58 (d, 4H, Ar), δ 7.32-7.35 (d, 4H, Ar) and δ 7.19-7.22 (d, 4H, Ar).

3.2.4 Synthesis of poly(etherimide)

Eight poly(etherimide)s (PEI-1 to PEI-8) were prepared from bis(nitrophthalimide)s by the nucleophilic displacement of nitro group by bisphenolate anions.

3.2.4.1 Synthesis of poly(etherimide) PEI-1

Dry NMP (20 mL) and toluene (25 mL) were added into a mixture of 1,3 dihydroxybenzene (VIII) (0.49 g, 0.0045 mol) and potassium carbonate (1.23 g, 0.009 mol). The reaction mixture was heated at 140-150 °C in nitrogen atmosphere for 10 h, while removing water azeotropically using Dean-Stark trap. After complete dehydration, the temperature was raised to 160 °C and the remaining toluene was removed. The system was cooled to 100 °C and 4,4’-bis(4-nitrophthalimido 4-phenoxy) diphenyl sulfone VIIa (3.5 g, 0.0045 mol) was added. The mixture was stirred at 100 °C for further
6 h under nitrogen atmosphere. The mixture was allowed to cool and then poured into water and the precipitated poly(etherimide) PEI–1 was filtered, washed with water, methanol and dried, Colour: Brown, Yield: 86 %, IR (KBr): 1770 cm\(^{-1}\) and 1711 cm\(^{-1}\) (C=O, imide ring).

### 3.2.4.2 Synthesis of poly(etherimide) PEI-2

Poly(etherimide) PEI-2 was synthesized from 1,4 dihydroxy benzene (IX) and 4,4’-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone using the same procedure as adopted for PEI-1. The poly(etherimide) PEI-2 was obtained as a brown coloured material, Yield: 84 %, IR (KBr): 1774 cm\(^{-1}\) and 1708 cm\(^{-1}\) (C=O, imide ring), \(^1\)H-NMR (300 MHz, DMSO-d\(_6\), ppm): \(\delta 7.60-7.91\) (br, 10H, Ar), \(\delta 7.46-7.57\) (br, 4H, Ar) and \(\delta 6.6-7.25\) (br, 12H, Ar).

### 3.2.4.3 Synthesis of poly(etherimide) PEI-3

Poly(etherimide) PEI-3 was synthesized from bisphenol-A (X) and 4,4’-bis (4-nitrophthalimido 4-phenoxy)diphenyl sulfone using the same procedure as adopted for PEI-1. The poly(etherimide) PEI-3 was obtained as a light brown coloured material, Yield: 88 %, IR (KBr): 1771 cm\(^{-1}\) and 1709 cm\(^{-1}\) (C=O, imide ring).

### 3.2.4.4 Synthesis of poly(etherimide) PEI-4

Poly(etherimide) PEI-4 was synthesized from 1,5 dihydroxynaphthalene (XI) and 4,4’-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone using the same procedure as adopted for PEI-1. The poly(etherimide) PEI-4 was obtained as a dark brown coloured material, Yield: 84 %, IR (KBr): 1771 cm\(^{-1}\) and 1711 cm\(^{-1}\) (C=O, imide ring).
3.2.4.5 Synthesis of poly(etherimide) PEI-5

Poly(etherimide) PEI-5 was synthesized from 1,3 dihydroxy benzene (VIII) and 4,4’-bis(4-nitrophthalimido 4-phenoxy)benzophenone using the same procedure as adopted for PEI-1. The poly(etherimide) PEI-5 was obtained as a brown coloured materials, Yield: 88 %, IR (KBr): 1771 cm\(^{-1}\) and 1707 cm\(^{-1}\)(C=O, imide ring).

3.2.4.6 Synthesis of poly(etherimide) PEI-6

Poly(etherimide) PEI-6 was synthesized from 1,4 dihydroxy benzene (IX) and 4,4’-bis(4-nitrophthalimido 4-phenoxy)benzophenone using the same procedure as adopted for PEI-1. The poly(etherimide) PEI-6 was obtained as a dark brown coloured materials, Yield: 84 %, IR (KBr): 1772 cm\(^{-1}\) and 1714 cm\(^{-1}\)(C=O, imide ring).

3.2.4.7 Synthesis of poly(etherimide) PEI-7

Poly(etherimide) PEI-7 was synthesized from bisphenol-A (X) and 4,4’-bis (4-nitrophthalimido 4-phenoxy)benzophenone using the same procedure as adopted for PEI-1. The poly(etherimide) PEI-7 was obtained as a light brown colour materials, Yield: 85 %, IR (KBr): 1771 cm\(^{-1}\) and 1711 cm\(^{-1}\)(C=O, imide ring).\(^1\)H-NMR (300 MHz, DMSO-d\(_6\), ppm): \(\delta\) 7.48-7.93 (br,10H,Ar), \(\delta\) 6.62-7.25 (br,20H,Ar) and \(\delta\) 1.61-1.68 (s,6H,aliphatic).

3.2.4.8 Synthesis of poly(etherimide) PEI-8

Poly(etherimide) PEI-8 was synthesized from 1,5 dihydroxynaphthalene (XI) and 4,4’-bis(4-nitrophthalimido 4-phenoxy)benzophenone using the same procedure as adopted for PEI-1. The poly(etherimide) PEI-8 was obtained as a dark brown coloured materials, yield: 83 %, IR (KBr): 1770 cm\(^{-1}\) and 1710 cm\(^{-1}\)(C=O, imide ring).
3.3 RESULT AND DISCUSSION

3.3.1 Synthesis of diamine containing flexible groups

The 4,4'-bis(4-aminophenoxy)diphenyl sulfone (III) and 4,4'-bis(4-aminophenoxy) benzophenone (V) were prepared by the nucleophilic displacement reaction of 4-aminophenol with the corresponding 4,4'-dichlorodiphenyl sulfone / 4,4'-difluoro benzophenone in NMP (Scheme 3.1). The diamines synthesized were used for the synthesis of bis(nitrophthalimide)s monomers.

\[
\begin{align*}
\text{Cl} & \quad \text{S} & \quad \text{O} & \quad \text{Cl} \\
\text{I} & & & & + & \text{HO} & \quad \text{NH}_2 & \quad \text{II} \\
\text{H}_2\text{N} & \quad \text{O} & \quad \text{S} & \quad \text{O} & \quad \text{NH}_2 \\
\text{III} & & & & & & & \\
\text{4,4'}-\text{bis}(4\text{-aminophenoxy})\text{diphenyl sulfone} \\
\end{align*}
\]

\[
\begin{align*}
\text{F} & \quad \text{C} & \quad \text{F} & \quad + & \text{2HO} & \quad \text{NH}_2 & \quad \text{II} \\
\text{IV} & & & & & & & \\
\text{H}_2\text{N} & \quad \text{O} & \quad \text{C} & \quad \text{O} & \quad \text{O} & \quad \text{NH}_2 & \quad \text{V} \\
\text{4,4'}-\text{bis}(4\text{-aminophenoxy})\text{benzophenone} \\
\end{align*}
\]

Scheme 3.1: Synthesis of diamines
3.3.1.1 FT-IR spectroscopic analysis of diamine

The IR spectrum of the diamine 4,4’-bis(4-aminophenoxy)diphenyl sulfone (III) showed a characteristic absorption at 3300 cm\(^{-1}\) (NH stretching of amino group), and 1149 cm\(^{-1}\) (S=O, sulfone). Similarly the diamine 4,4’-bis(4-aminophenoxy)benzophenone (V) showed characteristic absorption at 3300 cm\(^{-1}\) (NH stretching of amino group) and 1652 cm\(^{-1}\) (C=O, keto).

3.3.1.2 \(^1\)H-NMR spectroscopic analysis of diamine

The \(^1\)H-NMR of 4,4’-bis(4-aminophenoxy)diphenyl sulfone is given in Figure 3.1. The aromatic proton ortho and meta to the sulfone group appeared as a doublet at 7.82-7.85 δ ppm and 6.95-6.98 δ ppm respectively. The aromatic protons meta and ortho to the amino group appeared as a doublet at 6.78-6.81 δ ppm and 6.58-6.61 δ ppm respectively. The amino proton appeared as a singlet at 5.12 δ ppm. The IR and \(^1\)H-NMR analysis supported the structures proposed for new diamines III and V.
3.3.2 Synthesis of bis(nitrophthalimide)s monomers

The bis(nitrophthalimide)s monomers 4,4’-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone (VIIa) and 4,4’-bis(4-nitrophthalimido 4-phenoxy)benzophenone (VIIb) were synthesized by the condensation of 4-nitrophthalic anhydride with the corresponding 4,4’-bis(4-aminophenoxy)diphenyl sulfone / 4,4’-bis(4-aminophenoxy)benzophenone in NMP in two-step method (Scheme 3.2).

In the first step a soluble polyamic acid was prepared at room temperature. In the second step complete cyclization of the intermediate amic acid was achieved by solution
imidization. The water formed was removed by toluene-water azeotropic distillation at 120 °C.

![Scheme 3.2: Synthesis of bis(nitrophthalimide)s monomers](image-url)

**Scheme 3.2: Synthesis of bis(nitrophthalimide)s monomers**
3.3.2.1 FT-IR spectroscopic analysis of bis(nitrophthalimide)s monomers

The IR spectra of the monomers 4,4’-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone (VIIa) and 4,4’-bis(4-nitrophthalimido 4-phenoxy)benzophenone (VIIb) are given in Figure 3.2.

![Figure 3.2: IR spectra of bis(nitrophthalimide)s monomers](image)

The IR spectrum of monomer 4,4’-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone (VIIa) showed a characteristic absorption at 1786 cm\(^{-1}\) (symmetric stretching of imide carbonyl), 1723 cm\(^{-1}\) (asymmetric stretching of imide carbonyl), 1586 cm\(^{-1}\) (C-N
stretching), 720 cm\(^{-1}\) (imide ring), 1149 cm\(^{-1}\) (S=O, sulfone), 1543 cm\(^{-1}\) and 1345 cm\(^{-1}\) (-NO\(_2\)). These data indicated the formation of imide ring from the 4-nitrophthalic anhydride and 4,4\(^{''}\)-bis (4-aminophenoxy)diphenyl sulfone.

Similarly the IR spectrum of monomer 4,4\(^{''}\)-bis(4-nitrophthalimido 4-phenoxy) benzophenone (VIIb) showed a characteristic absorption at 1787 cm\(^{-1}\) (symmetric stretching of imide carbonyl) 1723 cm\(^{-1}\) (asymmetric stretching of imide carbonyl), 1589 cm\(^{-1}\) (C-N), 718 cm\(^{-1}\) (imide ring), 1652 cm\(^{-1}\) (C=O, keto), 1540 cm\(^{-1}\) and 1345 cm\(^{-1}\) (-NO\(_2\)). These data indicated the formation of imide ring between 4-nitrophthalic anhydride and 4,4\(^{''}\)-bis (4-aminophenoxy)benzophenone.

### 3.3.2.2 \(^1\)H-NMR spectroscopic analysis of bis(nitrophthalimide)s monomers

The \(^1\)H-NMR spectrum of 4,4\(^{''}\)-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone (VIIa) is given in Figure 3.3. The aromatic proton flanked by imide carbonyl and nitro group appeared as a singlet at 8.59 δ ppm. The two aromatic proton ortho and meta to the nitro group and flanked between by imide carbonyl and nitro group appeared as a doublet at 8.68-8.70 δ ppm and 8.22-8.25 δ ppm respectively. The aromatic protons ortho and meta to the imide nitrogen and flanked between imide nitrogen and aromatic ether groups appeared at 7.31-7.34 δ ppm and 7.21-7.24 δ ppm respectively. The aromatic protons meta to the sulfone group appeared as a doublet at 7.55-7.58 δ ppm. The aromatic protons ortho to the sulfone group appeared as a doublet at 7.97-8.00 δ ppm. The protons designated in Figure 3.3 as “a”, “b” and “c” appeared in the farthest downfield in the range 8.22-8.70 δ ppm because of the electron withdrawing –NO\(_2\) and imide groups.
The peaks at 2.5 δ ppm and at 3.4 δ ppm are due to DMSO and water in DMSO. 

$^1$H-NMR spectrum supported the formation of imide ring from the 4-nitrophthalic anhydride and 4,4’-bis(4-aminophenoxy)diphenyl sulfone.

![Figure 3.3: $^1$H-NMR spectrum of monomer 4,4’-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone](image)

The $^1$H-NMR data of 4,4’-bis(4-nitrophthalimido 4-phenoxy)benzophenone (VIIb) presented in Table 3.1 supported the formation of imide ring from the 4-nitrophthalic anhydride and 4,4’-bis(4-aminophenoxy)benzophenone. The IR and
$^1$H-NMR analysis of monomers VIIa and VIIb were accordance with the proposed structure and the spectral data are summarized in **Table 3.1**

**Table 3.1: Physical characteristics and spectral data of bis(nitrophthalimide)s monomers**

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Yield %</th>
<th>Melting point °C</th>
<th>IR (KBr) cm$^{-1}$</th>
<th>$^1$H-NMR in DMSO-d$_6$ δ ppm$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIIa</td>
<td>94</td>
<td>160</td>
<td>1786, 1723, 720</td>
<td>8.68-8.70 (d, 2H, Ar) (imide ring), 8.59 (s, 2H, Ar) 1586 (C-N), 8.22-8.25 (d, 2H, Ar) 1149 (S=O, sulfone) 7.97-8.00 (d, 4H, Ar) 1543, 1345 (-NO$_2$) 7.55-7.58 (d, 4H, Ar)</td>
</tr>
<tr>
<td>VIIb</td>
<td>93</td>
<td>283</td>
<td>1787, 1723, 718</td>
<td>8.68-8.71 (d, 2H, Ar) (imide ring), 8.60 (s, 2H, Ar) 1589 (C-N), 8.22-8.25 (d, 2H, Ar) 1652 (C=O, keto) 7.78-7.80 (d, 4H, Ar) 1540, 1345 (-NO$_2$) 7.55-7.58 (d, 4H, Ar)</td>
</tr>
</tbody>
</table>

$^a$ Ar = aromatic, s = singlet, d = doublet
3.3.3 Synthesis of poly(etherimide)s from bis(nitrophthalimide)s

Poly(etherimide)s (PEI-1 to PEI-8) were prepared from bis(nitrophthalimide)s monomers by the nucleophilic displacement of nitro group by bisphenolate ions (Scheme 3.3).

Scheme 3.3: Synthesis of poly(etherimide)s PEI-1 to PEI-8
The inherent viscosities of the poly(etherimide)s measured in DMSO at 30°C were in the range 0.40-0.78 dL/g indicating formation of reasonably high molecular weight polymers. The various characteristics of the polymerized products are given in Table 3.2.

Table 3.2: Preparation of poly(etherimide)s

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Bisnitro-imide</th>
<th>Diol</th>
<th>Yield %</th>
<th>( \eta_{inh} ) a dL/g</th>
<th>IR(KBr), cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-1</td>
<td>VIIa</td>
<td>VIII</td>
<td>86</td>
<td>0.78</td>
<td>1770,1711</td>
</tr>
<tr>
<td>PEI-2</td>
<td>VIIa</td>
<td>IX</td>
<td>84</td>
<td>0.62</td>
<td>1774,1708</td>
</tr>
<tr>
<td>PEI-3</td>
<td>VIIa</td>
<td>X</td>
<td>88</td>
<td>0.58</td>
<td>1771,1709</td>
</tr>
<tr>
<td>PEI-4</td>
<td>VIIa</td>
<td>XI</td>
<td>84</td>
<td>0.50</td>
<td>1771,1711</td>
</tr>
<tr>
<td>PEI-5</td>
<td>VIIb</td>
<td>VIII</td>
<td>88</td>
<td>0.48</td>
<td>1771,1707</td>
</tr>
<tr>
<td>PEI-6</td>
<td>VIIb</td>
<td>IX</td>
<td>84</td>
<td>0.45</td>
<td>1772,1714</td>
</tr>
<tr>
<td>PEI-7</td>
<td>VIIb</td>
<td>X</td>
<td>85</td>
<td>0.44</td>
<td>1771,1711</td>
</tr>
<tr>
<td>PEI-8</td>
<td>VIIb</td>
<td>XI</td>
<td>83</td>
<td>0.40</td>
<td>1770,1710</td>
</tr>
</tbody>
</table>

a Measured with 0.5 g / dL at 30°C, in DMSO.

3.3.3.1 FT-IR spectroscopic analysis of poly(etherimide)s

Representative IR spectra of poly(etherimide)s PEI-1, PEI-5 and PEI-7 are given in Figure 3.4. The IR spectrum of poly(etherimide)s (PEI-1 to PEI-8) (Table 3.2) showed absorption band at about 1770-1774 cm\(^{-1} \) (imides C=O symmetrical stretching) and
1707-1714 cm$^{-1}$ (imides C=O asymmetrical stretching) associated with imide structure indicating that during the nucleophilic displacement polymerization the imide ring was stable.

Figure 3.4: IR spectra of poly(etherimide)s PEI-1, PEI-5 and PEI-7
The disappearance of strong absorption due to nitro group at 1543 cm\(^{-1}\) & 1540 cm\(^{-1}\) that was present in the bis(nitrophthalimide)s monomers VIIa and VIIb respectively indicated the complete displacement of nitro group by the bisphenolate ion and successive formation of aromatic ether bonds.

3.3.3.2 \(^1\)H-NMR spectroscopic analysis of poly(etherimide)s

The \(^1\)H-NMR spectrum of poly(etherimide) PEI-2 is given in Figure 3.5. The \(^1\)H-NMR spectrum of poly(etherimide) PEI-2 showed absorption at 7.60-7.95 (br, 10H, Ar) \(\delta\) ppm, 7.46-7.57(br, 4H, Ar) \(\delta\) ppm and 6.61-7.25(br, 12H, Ar) \(\delta\) ppm. The disappearance of the farthest downfield signal that was present in the monomer 4,4\(^{\prime}\)-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone (VIIa) in the range 8.70-8.22 \(\delta\) ppm (because of the electron withdrawing –NO\(_2\) and imide ring) and appearence of signal in the range 7.60-7.95 \(\delta\) ppm supported the displacement of –NO\(_2\) by hydroquinone dianion and successive formation of aromatic ether bond.
The $^1$H-NMR spectrum of poly(etherimide) of PEI-7 is given in Figure 3.6. $^1$H-NMR spectrum of PEI-7 showed absorption at 7.48-7.93 (br, 10H, Ar) $\delta$ ppm, 6.62-7.25 (br, 20H, Ar) $\delta$ ppm and 1.61-1.68 (s, 6H, aliphatic) $\delta$ ppm. The disappearance of the farthest downfield signal that was present in the monomer 4,4'-bis(4-nitrophthalimido 4-phenoxy)benzophenone (VIIb) in the range 8.71-8.22 $\delta$ ppm (because of the electron withdrawing $-\text{NO}_2$ and imide ring) and appearence of signals at 7.48-7.93 $\delta$ ppm and 1.61-1.68 $\delta$ ppm (singlet, aliphatic) farthest high field confirmed the displacement of –
NO₂ by bisphenol-A dianion. The observed ¹H-NMR spectra were fully in agreement with the chemical structure of the poly(etherimide)s.

![Chemical structure of poly(etherimide)](image)

**Figure 3.6: ¹H NMR spectrum of poly(etherimide) PEI-7**

### 3.3.4 Properties of poly(etherimide)s

#### 3.3.4.1 Solubility characteristics of poly(etherimide)s

Poly(etherimide)s were tested for solubility at 5 wt % concentration in different organic solvents and the data are summarized in Table 3.3. All these poly(etherimide)s were
soluble in NMP, DMAc, DMF, DMSO, and H$_2$SO$_4$. Most of the poly(etherimide)s were soluble in pyridine and $m$-cresol on heating.

**Table 3.3: Solubility behavior of poly(etherimide)s**

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>NMP</th>
<th>DMSO</th>
<th>DMF</th>
<th>Pyridine</th>
<th>THF</th>
<th>$m$-Cresol</th>
<th>Chloroform</th>
<th>Conc. H$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-1</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>PEI-2</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>PEI-3</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>PEI-4</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>PEI-5</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>PEI-6</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>PEI-7</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>PEI-8</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

+ = Soluble at room temperature, + = Soluble on heating, - = Insoluble

Poly(etherimide)s (PEI-1 to PEI-4) derived from monomer 4,4’-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone (VIIa) showed improved solubility due to the presence of -SO$_2$- group in addition to the ether group in the polymer backbone when compared to the corresponding poly(etherimide)s (PEI-5 to PEI-8) derived from monomer 4,4’-bis(4-nitrophthalimido 4-phenoxy)benzophenone (VIIb). The poly(etherimide) PEI-1 derived from 1,3-dihydroxy benzene showed higher solubility than the corresponding poly(etherimide) PEI-2 derived from 1,4-dihydroxy benzene.
because the *meta* substituted phenyl ring lowers regularity and orderly arrangement more than *para* substituted phenyl ring. Similarly the PEI-5 with *meta* catenation showed higher solubility than the corresponding PEI-6 having *para* catenation. The improved solubility of the poly(etherimide)s may be explained by the fact that the incorporation of flexible linkages into the poly(etherimide)s backbone chain decreases chain symmetry, leading to amorphous morphology, which in turn increases solubility. Thus, the solubility was governed by the structure of both the bis(nitrophthalimides)s monomers and aromatic bisphenolate ions.

### 3.3.4.2 Thermal properties of poly(etherimide)s

The thermal properties of the poly(etherimide)s were evaluated by TG and DSC in nitrogen atmosphere at a heating rate of 10 °C /min. TG curves are given in Figure 3.7 and Figure 3.8. TG curves indicated that these poly(etherimide)s undergo rapid degradation around 482– 650 °C. The thermal stability of poly(etherimide)s PEI-2 having *para* catenation was higher than the corresponding poly(etherimide)s PEI-1 having *meta* catenation. This clearly results from the orderly arrangement of *para* disubstituted phenyl ring. Less orderly arrangement is present in PEI-1 because of *meta* disubstituted phenyl ring. Similarly the PEI-6 with *para* catenation showed higher thermal stability then the corresponding PEI-5 having *meta* catenation.
Figure 3.7: TG curves of poly(etherimide)s PEI-1 to PEI-4

Figure 3.8: TG curves of poly(etherimide)s PEI-5 to PEI-8
The percentage weight losses at various temperatures are given in Table 3.4. TG analysis indicated that these poly(etherimide)s were highly thermo stable. A 10 % weight loss occurred in the temperature range 357 - 453 °C. The percentage of char yield at 800 °C was in the range 12-19 %.

**Table 3.4: Thermal properties of poly(etherimide)s**

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>$T_{10}^a$ °C</th>
<th>$T_{20}^a$ °C</th>
<th>$T_{30}^b$ °C</th>
<th>Char $^b$ yield %</th>
<th>$T_g^c$ °C</th>
<th>$T_{ex}^c$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-1</td>
<td>419</td>
<td>486</td>
<td>550</td>
<td>13</td>
<td>201</td>
<td>756</td>
</tr>
<tr>
<td>PEI-2</td>
<td>433</td>
<td>524</td>
<td>590</td>
<td>19</td>
<td>201</td>
<td>770</td>
</tr>
<tr>
<td>PEI-3</td>
<td>433</td>
<td>514</td>
<td>562</td>
<td>13</td>
<td>200</td>
<td>595</td>
</tr>
<tr>
<td>PEI-4</td>
<td>453</td>
<td>529</td>
<td>586</td>
<td>18</td>
<td>201</td>
<td>601</td>
</tr>
<tr>
<td>PEI-5</td>
<td>367</td>
<td>471</td>
<td>562</td>
<td>12</td>
<td>201</td>
<td>603</td>
</tr>
<tr>
<td>PEI-6</td>
<td>448</td>
<td>519</td>
<td>562</td>
<td>17</td>
<td>---</td>
<td>570</td>
</tr>
<tr>
<td>PEI-7</td>
<td>357</td>
<td>429</td>
<td>481</td>
<td>12</td>
<td>---</td>
<td>550</td>
</tr>
<tr>
<td>PEI-8</td>
<td>376</td>
<td>457</td>
<td>505</td>
<td>16</td>
<td>---</td>
<td>525</td>
</tr>
</tbody>
</table>

$^a$ = Temperature at 10 %, 20 % or 30 % weight loss in N$_2$ atmosphere  
$^b$ = Percentage char yield at 800 °C  
$^c$ = Temperature at which maximum exothermic peak observed

DSC thermogram of these poly(etherimide)s showed a broad exothermic peak due to the degradation of the poly(etherimide)s in the temperature range 525 - 770 °C. The glass transition temperature was observed in the temperature range 200 - 201 °C; the low
Tg value was due to the presence of more number of flexible groups in the repeat unit leading to high amorphous characters. The amorphous character was well reflected in the X-ray diffraction patterns and in solubility.

3.3.4.3 X-ray diffraction studies of poly(etherimide)s

The crystallinity of the poly(etherimide)s was examined by X-ray diffraction. X-ray diffraction patterns are given in Figure 3.9.

![Figure 3.9: X-ray diffractograms of poly(etherimide)s (PEI-1 to PEI-6)](image)

In general the diffraction patterns were broad indicated that most of these poly(etherimide)s were amorphous. The diffraction pattern of poly(etherimide)s (PEI-1 to
PEI-4) derived from 4,4’-bis(4-nitrophthalimido 4-phenoxy)diphenyl sulfone (VIIa) was broad with no well defined peaks which indicated that these poly(etherimide)s were amorphous due to the presence of flexible ether and -SO₂- groups in the chain, which prevent the chain – chain interaction. However, the poly(etherimide)s (PEI-5 to PEI-8) derived from 4,4’-bis(4-nitrophthalimido 4-phenoxy)benzophenone (VIIb) showed some crystalline character due to the presence of carbonyl group along with rigid imide ring. The amorphous nature of these poly(etherimide)s was reflected in their solubility, which was in agreement with the general rule that the solubility increased with increasing amorphous characteristics. The solubility behavior was consistent with the results of X-ray diffraction studies.

3.4 APPLICATIONS OF POLYETHERIMIDES - HIGH TEMPERATURE INSULATION

Polyimide film is used in high temperature electrical insulation. Newer polymeric materials are being investigated to meet demand of various types. Synthetic efforts have been focused for improving the solubility of polyimides in organic solvents for easy fabrication of polyimides into film without sacrificing the thermal stability and insulation characteristics. The poly(etherimide)s PEI-1 to PEI-8 reported in this chapter were studied for possible application as high temperature electrical insulations.

3.4.1 Electrical properties of poly(etherimide)s

The dielectric constant is an important parameter for selecting electrical insulation material. The dielectric constant and impedance of the poly(etherimide)s were determined at a frequency of 10 MHz. The results are presented in Table 3.5. The dielectric constants of poly(etherimide)s were in the range 4.90–5.54.
The poly(etherimide)s have excellent electrical insulation character and the films can be used in insulation of electrical items operating at elevated temperatures.

<table>
<thead>
<tr>
<th>Poly(etherimide)</th>
<th>Dielectric constant (ε)</th>
<th>Impedance (Z) (M Ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-1</td>
<td>5.40</td>
<td>58</td>
</tr>
<tr>
<td>PEI-2</td>
<td>5.38</td>
<td>62</td>
</tr>
<tr>
<td>PEI-3</td>
<td>5.37</td>
<td>63</td>
</tr>
<tr>
<td>PEI-4</td>
<td>4.94</td>
<td>70</td>
</tr>
<tr>
<td>PEI-5</td>
<td>5.10</td>
<td>68</td>
</tr>
<tr>
<td>PEI-6</td>
<td>4.98</td>
<td>70</td>
</tr>
<tr>
<td>PEI-7</td>
<td>5.54</td>
<td>55</td>
</tr>
<tr>
<td>PEI-8</td>
<td>4.90</td>
<td>80</td>
</tr>
</tbody>
</table>

3.5 CONCLUSIONS

1. Two new bis(nitrophthalimide) monomers were successfully synthesized in high yield.
2. A series of poly(etherimide)s were prepared by the nucleophilic displacement of nitro group by bisphenolate ions.
3. The inherent viscosities of the poly(etherimide)s were in the range 0.40-0.78 dL/g, indicating formation of reasonably high molecular weight polymers.
X-ray diffraction revealed that these poly(etherimide)s were amorphous due to the presence of flexible linkages in the polymer chain. All the poly(etherimide)s exhibited high solubility in common organic solvents. The solubility behavior was consistent with the results of X-ray diffraction studies.

Poly (etherimide)s exhibited good thermal stability. A 10 % weight loss occurred in the temperature range 357 – 453 °C. The glass transition temperature was observed in the range 200-201 °C, the low Tg value was due to the presence of more number of flexible groups in the repeat unit leading to high amorphous character. The high amorphous character was well reflected in the X-ray diffraction patterns and in solubility.

The poly(etherimide)s have dielectric constant in the range 4.90 - 5.54. The poly(etherimide)s have electrical insulation character and the films can be used in insulation of electrical items operating at elevated temperatures.