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Synthesis and characterization of polyamideimides from diamino-benzophenone-3,3',4,4'-tetracarboxylic diimides and aromatic dicarboxylic acid— terephthalic acid (TPA)

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ABSTRACT

Four polyamideimides have been synthesized by direct polycondensation of imide containing diamines with dicarboxylic acid- terephthalic (TPA). The diimide-diamines were synthesized from benzophenone-3,3',4,4'-tetracarboxylic dianhydride with aromatic diamines — *p*-phenylene diamine(5a); benzidine(5b); 4,4'-diaminodiphenylmethane (5c) and 4,4'-diaminodiphenylsulphone(5d) respectively. The polycondensation reaction were done using triphenylphosphite(TPP)/pyridine(Py) in *N*-methyl-2-pyrrolidone(NMP) in the presence of calcium chloride and lithium chloride via. Phosphorylation method. The polyamideimides have been characterized by IR and ¹H NMR spectroscopy and elemental analysis. The solubility and intrinsic viscosity of the polymers have been determined. Thermal stability of the polymers was checked by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG).

Keywords: Diamines, benzophenone-3,3',4,4'-tetracarboxylic diimide, Phosphorylation, Polycondensation, Triphenylphosphite.

INTRODUCTION

The high reliable properties as well as excellent thermal stability, solvent resistance and superior electrical and insulating properties of polyimides^[1,2] have attracted a great deal of interest from polymer scientist over the last three decades. Although polyimides are highly thermostable, their widespread use is limited due to their poor flow characteristics, high glass transition temperature, high melting point and poor solubility^[3,4]. Several approaches have been tried to introduce the processability of polyimides without much loss of thermal stability. To overcome these difficulties various copolyimides have been developed. Polyamideimides^[5] are an important member of thermostable processable polymers that are commercially important. For polyamide synthesis

direct polycondensation reaction using triphenylphosphite (TPP)/Pyridine in the presence of metal salts (Yamazaki's phosphorylation reaction) is known to be a facile method.

In the present paper, we report the synthesis and characterization of four polyamideimides from imide containing diamines and aromatic dicarboxylic acid. Imide-diamine (6a-d) were synthesized from benzophenone-3,3',4,4'-tetracarboxylic dianhydride with aromatic diamines (5a-d) which is then polycondensed with the dicarboxylic acid(7a) via the phosphorylation method.

EXPERIMENT

Materials

Benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) (Fluka) was recrystallized from

boiling acetic anhydride. Anhydrous LiCl and CaCl₂ were dried under vacuum at 150°C for 6 h and 180°C for 10 h, respectively. N-methyl-2-pyrrolidone (NMP)(Merck), N,N'-dimethylformamide (DMF) and pyridine were purified by distillation under reduced pressure and stored under 4Å molecular sieves. Triphenylphosphite (TPP)(Merck) was purified by vacuum distillation. All the diamines were used without further purification.

PREPARATION OF DIAMINO-BENZOPHENONE-3,3',4,4'-TETRACARBOXYLIC DIIMIDE (IMIDE-DIAMINE):

Diimide-diamine (6a-d) were prepared from BTDA (II) and diamines(5a-d) by condensation reaction. BTDA (0.2mol) and the diamines (0.4mol) were heated in 250-300ml of dry DMF to 60°C for 1h. About 80ml of toluene was then added and the mixture was then refluxed for about 4h until about 7.2 ml of water distilled off azeotropically. Thereafter, the mixture was poured into cold water and the precipitated diimide-diamines were isolated by filtration and

recrystallized from hot DMF by dropwise addition of water.

POLYMERIZATION

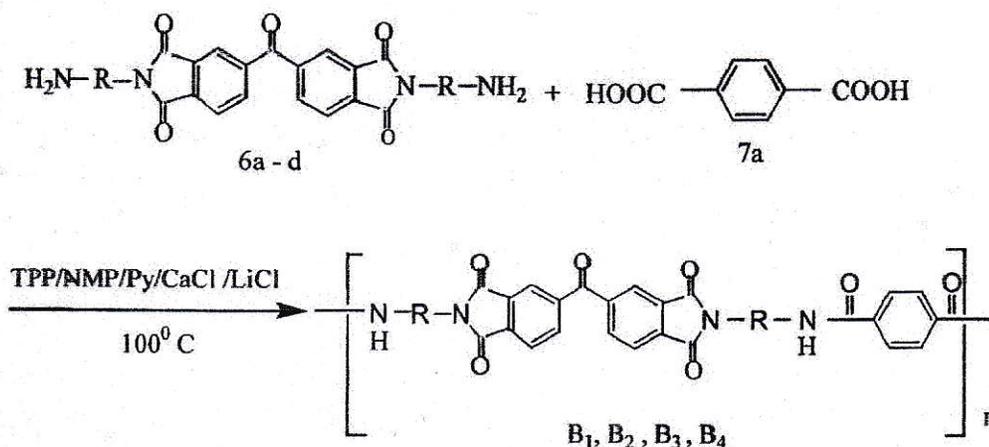
A mixture of diimide-diamine(6a-d) (1.25 mmol), terephthalic acid(7a) (1.25 mmol), 0.3 g of CaCl₂, 0.6 g LiCl, 0.8 ml of TPP, 1.6 ml of pyridine and 7 ml of NMP was heated with stirring at 100°C for 8 h under nitrogen. The obtained polymer solution was trickled on 500 ml of methanol, collected by filtration and dried.

Measurements

The IR spectra of the polymers were recorded with a Perkin-Elmer spectrophotometer on KBr pellets. ¹H spectra were recorded in DMSO-d₆. TGA and DTG were performed with a Perkin-Elmer thermal analyzer in air at a heating rate of 10°C/min. Viscosity was measured on a concentration of 0.5 g/dl in conc. H₂SO₄ at 30°C using an Ubbelohde viscometer. The solubility behavior of the polymers was determined by dissolving the polymer sample (0.002 g) in different solvents (2 ml) with thorough shaking and to stand overnight and then checked.

RESULTS AND DISCUSSION

POLYMER SYNTHESIS



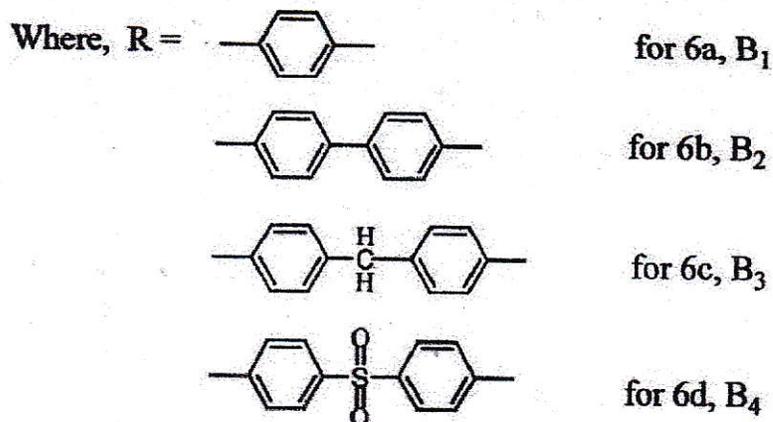


Table 1: Characterization Of Diamino-Benzophenone-3,3',4,4'-Tetracarboxylic Diimide (Diimide-Diamine):

Monomer	Time (hr)	Precipitation medium	Yield (%)	Colour
6a	5	water	72	Chocolate
6b	4	Water	81	Light green
6c	4 ¹ / ₂	Water	78.3	Brown
6d	6	water	86	Dark yellow

POLYMER CHARACTERIZATION

Characteristic properties of the polymers are shown in Table 1.

Table 1: Reaction conditions and physical properties of polymers

Polymer	Precipitation medium	Colour	Yield (%)	[η] dl/g
Nitrogen Cald. Found				
B ₁ 11.0	Methanol	Blackish brown	70.2	0.322
B ₂ 8.52	Methanol	Greenish yellow	69.46	0.30
B ₃ 7.98	Methanol	Brown	72.3	0.276
B ₄ 7.02	Methanol	Light yellow	77.5	0.25

Polymer B₄ has lower intrinsic viscosity because of the presence of electron withdrawing sulfonyl group which decreases the basicity of the amines and therefore leads to lower reactivity of polymerization.

SOLUBILITY

All the polymers are practically insoluble in common organic solvents such as acetone, methanol, benzene, chloroform, hexane, etc.; however they are all soluble in common organic solvents. The polymer B₄ show better solubility than the other polymers. The incorporation of sulfonyl groups^[5] in the polymer B₄ into the polymer backbones is effective in increasing the solubility of these polymers in H₂SO₄.

Table 2

SOLVENTS	B ₁	B ₂	B ₃	B ₄
DMF	-	-	-	±h
acetone	-	-	-	-
Chloroform	-	-	-	-
Ethyl alcohol	-	-	-	-
Dimethylether	-	-	-	-
m-cresol	±	±	±	+
DMSO	±	±	±h	±h
Benzene	-	-	-	-
NMP	+	+	+	+
n-Hexane	-	-	-	-
Toluene	-	-	-	-
Conc.H ₂ SO ₄	+	+	+	+
Water	-	-	-	-
pyridine	-	-	±	±
Dimethylacetamide	±	-	±	±h

±h= partly soluble on heating

SPECTROSCOPY

Characteristics IR absorption bands of polymers (in cm⁻¹)

1770-1785 cm ⁻¹ and 1710-1735 cm ⁻¹	symmetrical and asymmetrical C=O stretching of five membered cyclic imides
710-725 cm ⁻¹ and 1105-1125 cm ⁻¹	ring carbonyl deformation of imides ^[6]
3350, 1650 and 1540 cm ⁻¹	Bands of amido group of polyamideimides
1100±10 cm ⁻¹	Strong peak due to C-N-C stretching vibration
900-675 cm ⁻¹	out of plane bending of the aromatic C-H bonds of the polymers.
1140 cm ⁻¹ and 1405 cm ⁻¹	sulfonyl groups in case of dimide-diamine 6d and the polymer B ₄

A comparative study of the IR bands diamino-benzophenone-3,3',4,4'-tetracarboxylic diimide and their polyamideimides reveals that absorption due N-H stretching of amino groups (two bands

between 3360-3480 cm⁻¹) are absent in the spectra of the polymers. Instead a band in the range of 3320-3390 cm⁻¹ appears due to N-H stretching of the amido groups.

¹H NMR DATA FOR POLYAMIDEIMIDES

¹H NMR spectra of polyamideimides showed the following chemical shifts.

B ₁	δ 6.0-6.6 (m, Ar-H, 8H);	δ 7.1-7.5 (m, Ar-H, 4H), δ 7.8-8.2 (m, Ar-H, 6H)	δ 11.4 (s, amide N-H, 2H)
B ₂	δ 6.8-7.4 (m, Ar-H, 16H)	δ 7.5-7.8 m, Ar-H, 4H), δ 8.0-8.3 (m, Ar-H, 6H)	δ 10.7 (s, amide N-H, 2H)
B ₃	δ 3.8 (s, methylene, 4H), δ 7.2-7.5 (m, Ar-H, 16H); δ 7.6-8.0 (m, Ar-H, 4H)	δ 8.1-8.4 (s, Ar-H, 6H)	δ 11.2 (s, amide N-H, 2H);
B ₄	δ 6.1-6.8 (m, Ar-H, 16H), δ 7.1-7.6 (m, Ar-H, 4H)	δ 7.8-8.3 (m, Ar-H, 6H)	δ 11.0 (s, amide N-H, 2H)

A careful examination of the ^1H NMR spectra for the monomers and the polymers reveal that the peak at about δ 5.5 for amino protons in the

spectra of the monomers disappears in the spectra of the polymers. Instead a peak in the range of 11.0-11.2 is seen in the spectra of the polymers.

THERMAL ANALYSIS

Polymers	IDT($^{\circ}\text{C}$)	DT _{max} ($^{\circ}\text{C}$)	T _g ($^{\circ}\text{C}$)	IPDT($^{\circ}\text{C}$)
B ₁	405	525	90	447.0
B ₂	401	521	88	445.2
B ₃	392	511	84	439.3
B ₄	397	518	85	441.1

The DSC curve of polymer B₁ is presented in fig 1.

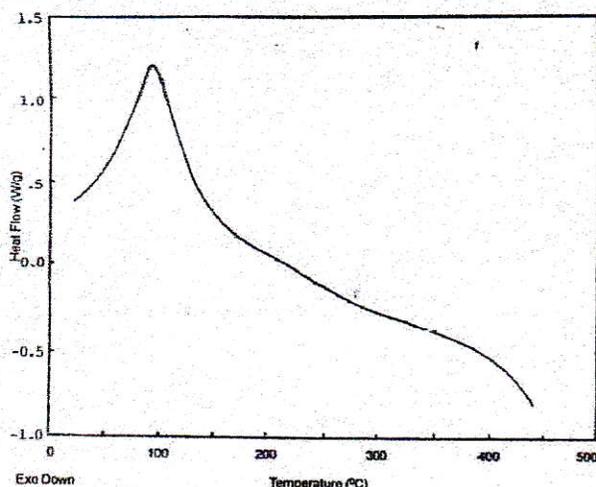


Fig: 1 DSC curve of B₁

Thermogravimetric analysis shows that an initial weight loss of about 3- 6% occurs upto 75 – 85 $^{\circ}\text{C}$ which is due to loss of moisture or entrapped solvent in the polymer. Subsequently there is only 3-4% weight loss upto to 290 $^{\circ}\text{C}$. The maximum weight loss occurs around 390-650 $^{\circ}\text{C}$. The IPDT values of the polymers B₁ and B₂ are almost same having p-phenylene and 4,4'- diphenylene rings respectively in the polymer backbone. In case of B₄ this value is slightly higher than that of B₃ as expected from the literature.^{6,7}

CONCLUSION

The successful polycondensation of imide-diamine with the diacid support the view that Yamazaki's phosphorylation method is a convenient method for synthesizing polyamideimides and TPP is a good condensing

agent for the purpose. Further work may be initiated on the basis of these studies for preparing other commercially important polyamideimides.

ACKNOWLEDGEMENT

RSIC, Punjab university; RRL Jorhat; IIT, Guwahati and NEHU, Shillong is acknowledged for recording spectral, thermal and elemental analysis of the samples.

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Synthesis And Characterization Of Polyesterimides From N-(p-Carboxyphenyl) Trimellitimide With Diols

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Abstract: Three polyesterimides have been synthesized by direct polycondensation of imide containing diacids with diols- ethylene glycol(4a), bisphenol-A (4b), and hydroquinone(4c) respectively. The imide-diacid were synthesized from trimellitic acid anhydride with p-aminobenzoic acid (PABA). The polycondensation reaction were done using triphenylphosphite(TPP)/pyridine(Py) in N-methyl-2-pyrrolidone(NMP) in the presence of lithium chloride via. Phosphorylation method. The polyesterimides have been characterized by IR and ¹H NMR spectroscopy and elemental analysis. The solubility and intrinsic viscosity of the polymers have been determined. Thermal stability of the polymers was checked by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG).

Keywords: Diols, N-(p-carboxyphenyl)trimellitimide, Phosphorylation, Polycondensation, Triphenylphosphite

I. INTRODUCTION

One of the major limitation of the versatile applications of synthetic polymers is their poor thermal stability. To overcome the poor heat stability of organic polymers, a new generation of polymers capable of withstanding high temperatures has been prepared during the last three decades. It has long been recognized that the intrinsic thermal and oxidative stability of aromatic and/or heterocyclic rings may be exploited to develop new thermostable polymers by linking them with stable groups such as ester and imide. Aromatic polyimides¹ are well recognized as an important class of engineering plastics. However the major limitation for widespread use of these resins is their difficulty in processing². In order to overcome the processing difficulty of polyimides, attempts have been made to develop various copolymers of imides. One of the most successful commercial thermostable copolymer is polyesterimides. The

polycondensation reaction has been done by condensation of imido- dicarboxylic acids and diols using triphenylphosphite (TPP) and N-methyl pyrrolidone/Pyridine in the presence of LiCl (Yamazaki's phosphorylation reaction).

In the present paper, polycondensation of N-(p-carboxyphenyl)trimellitimide (IIIa) with diols (4a-c) – ethylene glycol, bisphenol-A and hydroquinone has been reported.

II. EXPERIMENT

MATERIALS

Trimellitic acid anhydride (TMA)(Fluka) was recrystallized from boiling acetic anhydride. Anhydrous LiCl was dried under vacuum at 150°C for 6 h and 180°C for 10 h respectively. N-methyl-2-pyrrolidone (NMP) (Merck), N, N'-dimethyl formamide (DMF) and pyridine were purified by distillation under reduced pressure and stored under 4Å molecular sieves. Triphenylphosphite (TPP) (Merck) was purified by vacuum distillation.

PREPARATION OF N-(P-CARBOXYPHENYL) TRIMELLITIMIDE (NPCPT) (IMIDE-DIACID)

TMA (0.2 mol) and p-aminobenzoic acid (PABA) (0.2 mol) (IIa) were dissolved in 290 ml of dry DMF and the reaction mixture was heated at 60°C for 1h. About 80ml of toluene was then added and the mixture was then refluxed for about 4h until about 3.6 ml of water distilled off azeotropically. The mixture was poured into cold water. A dark brown precipitate of NPCPT(IIIa) was obtained. The precipitated imide-diacid was isolated by filtration and recrystallized from hot DMF by dropwise addition of water and dried.

III. POLYMERIZATION

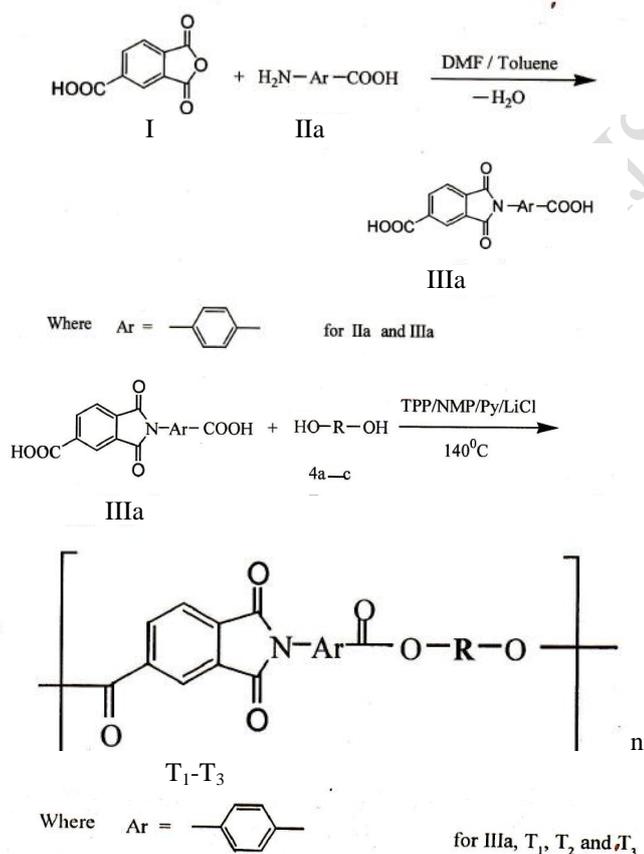
A mixture of NPCPT(IIIa) (0.005 mol), diol (4a-c) (0.005 mol), 0.385 g (0.01 mol) LiCl, 2.62 ml (0.01) of TPP, 10 ml of pyridine and 15 ml of NMP was heated with stirring at 140°C for 10 h under nitrogen. The obtained polymer solution was trickled on 500 ml of toluene, collected by filtration and dried.

MEASUREMENTS

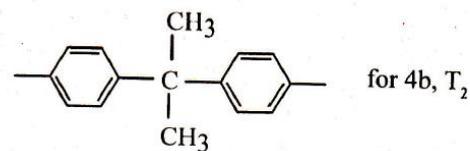
The IR spectra of the polymers were recorded with a Perkin-Elmer spectrophotometer on KBr pellets. ¹H spectra were recorded in DMSO-d₆. TGA and DTG were performed with a Perkin-Elmer thermal analyzer in air at a heating rate of 10°C/min. Viscosity was measured on a concentration of 0.5 g/dl in conc. H₂SO₄ at 30°C using an Ubbelohde viscometer. The solubility behavior of the polymers was determined by dissolving the polymer sample (0.002 g) in different solvents (2 ml) with thorough shaking and to stand overnight and then checked.

IV. RESULTS AND DISCUSSION

POLYMER SYNTHESIS



and $R = -CH_2-CH_2-$ for 4a, T₁



CHARACTERIZATION OF THE POLYMERS

To find suitable conditions for the preparation of polyesterimides with high molecular weights, the effects of monomer concentration and reaction temperatures in the preparation of polymer T₃ from NPCPT and hydroquinone were investigated in some details.

The effects of concentration of LiCl on the intrinsic viscosity in the preparation of the polymer T₃ is shown in table 4.1.

LiCl (mol)	Temperature (°C)	[η] dl/g
0	140	0.11
0.005	140	0.15
0.01	140	0.18
0.015	140	0.09
0.02	140	0.03

Table 4.1

The polymer T₃ was prepared by varying the amount of LiCl added. As reported by Higashi⁴, the addition of LiCl was effective in lowering the electronic density of N-phosphonium salts and preventing the formation of by products, phenylester compound. The amount of the salt significantly affected the molecular weight of the resulting polymer. The maximum viscosity of 0.19 dl/g was obtained at the concentration of 0.01 mol of LiCl. Further addition retarded the reaction and low intrinsic viscosity for the polymer T₃ was obtained.

The effect of reaction temperature on the intrinsic viscosity in the preparation of the polymer T₃ is shown in table 4.2.

Temperature (°C)	Yield (%)	[η] dl/g
80	21	0.03
100	32	0.09
120	49	0.12
140	51	0.19
160	30	0.11

Table 4.2

A higher reaction temperature would destroy the stability of N-phosphonium salts and a lower temperature would depress the reactivity of the monomer⁵. The highest viscosity of 0.19 dl/g was obtained at the reaction temperature of 140°C.

Reaction conditions and physical characteristics of polymers are presented in Table 4.3

Polymer	Precipitation medium	Colour	Yield (%)	[η] dl/g
T ₁	Toluene	Chocolate	52.6	0.13
T ₂	Toluene	Light brown	49.3	0.152
T ₃	Benzene	Blackish	54.1	0.18

		brown		
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Table 4.3

The polymers are found to be insoluble in common organic solvents.

SPECTROSCOPY

T ₁	T ₂	T ₃	Assignment
1722(s) 1789(s)	1725(s) 1785(s)	1710(s) 1780(s)	symmetrical and asymmetrical C=O stretching of five membered cyclic imides
714(s)	720(s)	720(s)	ring carbonyl deformation of imides ^[6]
1393(s)	1365(s)	1381(s)	C-N stretching of imide
1260(s)	1260(s)	1250(s)	C-O stretching ester
858,820	850,810	860,810	C-H deformation of aromatic ring
3040(w)	3045(w)	3030(w)	Aromatic C-H stretching

Table 4.4: IR absorption bands of the polymers (in cm⁻¹)

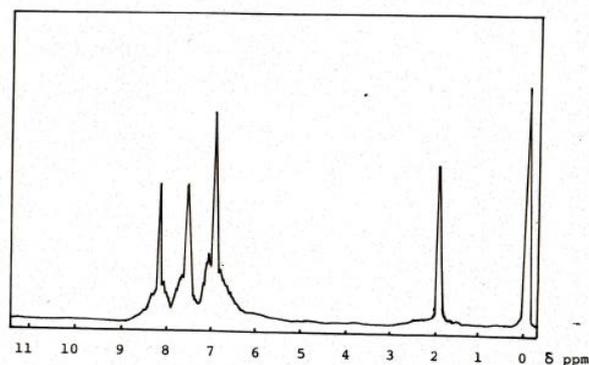
A careful look into the spectra of imide-diacid and the polymers reveals that the absorption bands due to the O-H stretching of the carboxyl group⁶ appearing at around 3460 cm⁻¹ and that due to O-H in plane deformation of the carboxyl group at around 1440 cm⁻¹ are absent in the spectra of the polymers. Peak at around 1260 cm⁻¹ which may be attributed to C-O stretching of the ester group⁷ appears in the spectra of all the polymers. The peak due to C=O stretching of the ester group coincides with the strong imide absorption at around 1720 cm⁻¹.

¹H NMR DATA FOR POLYESTERIMIDES

¹H NMR spectra of polyesterimides showed the following chemical shifts.

T ₁	δ 3.8 (s, methylene, 4H)	δ 6.8-7.4(m, Ar-H, 4H)	δ 7.6-8.2 (m, Ar-H, 3H)
T ₂	δ 2.0 (s, CH ₃ 6H) δ 6.4-7.0 (m, Ar-H, 8H)	δ 7.3-7.8 m, Ar-H, 4H)	δ 8.0-8.3 (m, Ar-H, 3H)
T ₃	δ 6.4-6.8 (m, Ar-H, 4H)	δ 7.0-7.6 (m, Ar-H, 3H)	δ 7.8-8.2 (m, Ar-H, 4H)

Table 4.5

Figure 1: ¹H NMR Spectra of T₂

A comparison of the ¹H NMR spectra for the monomers and the polymers shows that peak at δ 10.3-10.6 due to the carboxyl proton in the spectra of the monomers disappears in the spectra of all the polymers. Peaks at δ 3.8 and δ 2.0 due to the methylene and methyl proton appears in the polymers T₁ and T₂.

THERMAL ANALYSIS

Polymers	IDT(°C)	DT _{max} (°C)	T _g (°C)	IPDT(°C)
T ₁	310	332	54	324
T ₂	371	412	81	398
T ₃	375	420	89	401

The IPDT values in case of polymer T₁ may be due to the presence of —CH₂—CH₂— linkage into the polymer backbone. Incorporation of the flexible —CH₂—CH₂— linkage reduces rigidity of the polymer backbone and hence also the thermostability. The glass transition temperature (T_g) of the polymers are in the order T₃ > T₂ > T₁. This decrease in T_g values may be due to the increase in the flexibility of the polymer chain.

V. CONCLUSION

The successful polycondensation of imide-diacid with the diols support the view that Yamazaki's phosphorylation method is a convenient method for synthesizing polyesterimides and TPP is a good condensing agent for the purpose. Based on these studies further work may be initiated for preparing other commercially important polyesterimides.

ACKNOWLEDGEMENT

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