Synthesis and Characterization of Polyamide imides from N-(P-Carboxypheny) l Trimellitimide with Aromatic Diamines

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Abstract: Four polyamide imides have been synthesized by direct polycondensation of imide containing dicarboxylic acid with aromatic diamines. — p-phenylene diamine(2a);benzidine(2b);4,4'-diaminodiphenylmethane (2c) and 4,4'-diaminodiphenylsulphone(2d) respectively The imide-diacid (IIIa) was synthesized from Trimellitic acid anhydride(TMA) and p-aminobenzoic acid (PABA).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, N-(p-carboxyphenyl)trimellitimide, Phosphorylation , Polycondensation, , acid Triphenylphosphite.

1. Introduction

Polyimides[1,2] because of their high reliable properties as well as excellent thermal stability, solvent resistance and superior electrical and insulating properties have attracted a great deal of interest from polymer scientist over the last three decades. Although polyimides are well recognized as thermally stable materials, their poor flow characteristics, high glass transition temperature , high melting point and poor solubility[3,4] made their applications limited. . To overcome these difficulties various copolyimides have been developed. Polyamideimides[2] are a class of polymers which comprise between high thermal stability and ease of processability. Direct polycondensation reaction using triphenylphosphite (TPP)/Pyridine in the presence of metal salts (Yamazaki's phosphorylation reaction) is known to be a facile method for polyamide synthesis.

In the present paper, we report the synthesis and characterization four polyamideimides from imide containing diacids and aromatic diamines. Imide-diacid (IIIa) was synthesized from trimellitic acid anhydride (*TMA)* and p-aminobenzoic acid (IIa) which is then polycondensed with the diamines(2a-d) via the phosphorylation method.

2. Experiment

2.1. Materials
Trimellitic acid anhydride (TMA) (Fluka) was recrystallized from boiling acetic anhydride. Anhydrous LiCl and $CaCl_2$ were dried under vacuum at $150^{o}c$ for 6 h and $180^{o}c$ 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. All the diamines and p-aminobenzoic acid (E. Merck) were used without further purification.

3. Preparation of N-(O-Carboxyphenyl) Trimellitimides (Imide-Diacid)

Imide-diacid (IIIa) was prepared from TMA and p-aminobenzoic acid (IIa) by condensation reaction. TMA(0.2mol) and PABA (0.2mol) were heated in 250-300ml of dry DMF to $60^{o}C$ 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. Thereafter, the mixture was poured into cold water and the precipitated diimide-diamine were isolated by filtration and recrystallized from hot DMF by drop wise addition of water.

4. Polymerization

A mixture of NPCPT (IIIa) (1.25 mmol), diamines (2a-d) (1.25 mmol), 0.3 g of $CaCl_2$, 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^oC for 8-12 h under nitrogen. The obtained polymer solution was trickled on 500 ml of methanol, collected by filtration and dried.

4.1. Measurements

The IR spectra of the polymers were recorded with a Perkin-Elmer spectrophotometer on KBr pellets.1H spectra were recorded in DMSO-d_6. TGA and DTG were performed with a Perkin- Elmer thermal analyzer in air at a heating rate of 10^oC/min. Viscosity was measured on a concentration of 0.5 g/dl in conc. H_2SO_4 at 30^oC using an Ubbelohde viscometer. The solubility behavior of the polymes 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.
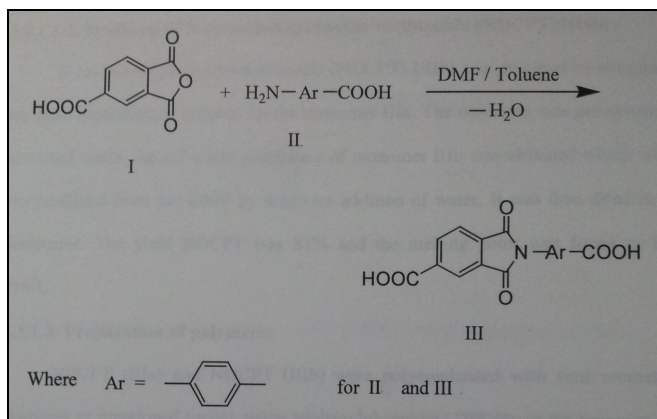
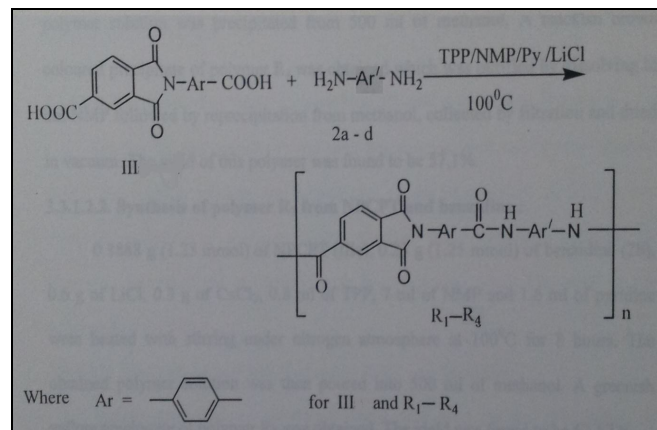## 5. Results and Discussion

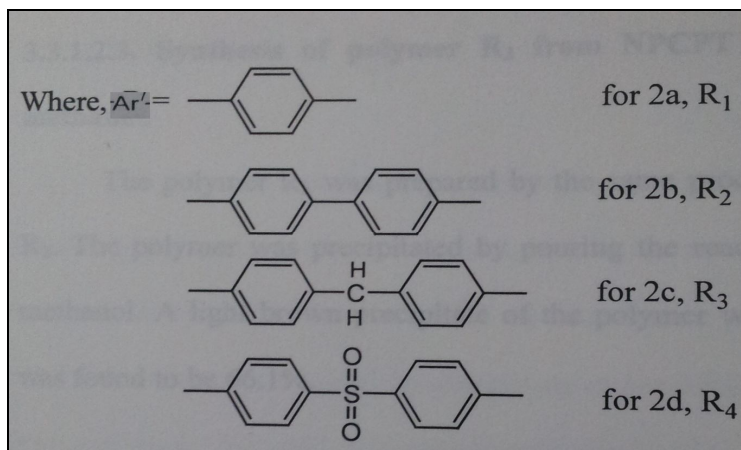Figure 1: Polymer Synthesis

Figure 2: Polymer Synthesis

Figure 3: Polymer Synthesis

6. Polymer Characterization

Characteristic properties of the polymers are shown in Table 1.

Polymer	Precipitation medium	Colour	Yield	[ŋ] dl/g	Nitrogen	
					Cald	Found
R_1	Methanol	Blackish brown	57.1	0.246	10.97	10.86
R_2	Methanol	Blackish brown	63.57	0.22	9.15	9.0
R_3	Methanol	Light brown	66.1	0.21	8.88	8.79
R_4	Methanol	Light yellow	72.03	0.23	8.52	8.46

Table 1: Reaction conditions and physical properties of polymers

Polymer R_4 have 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.

7. Solubility

The solubilities of polyamideimides are listed in Table 2. All the polymers are practically insoluble in common organic solvents such as benzene, acetone, methanol, chloroform, hexane, etc.; however they are all soluble in common organic solvents. The polymer R_4 shows better solubility than the other polymers. This is due the fact that incorporation of sulfonyl groups [5] into the polymer backbones is effective in increasing the solubility of these polymers in H_2SO_4.

Solvents	R_1	R_2	R_3	R_4
m-cresol	±	±	+	+
DMF	±	±	±	±
Chloroform	-	-	-	-
Ethyl alcohol	-	-	-	-
Dimethylether	-	-	-	-
Acetone	-	-	-	-
DMSO	±	±	±	±
Benzene	-	-	-	-
NMP	+	+	+	+
n-Hexane	-	-	-	-
Toluene	-	-	-	-
Conc.H_2SO_4	±	±	±	+
Water	-	-	-	-
Dimethylacetamide	-	-	-	+
pyridine	±	±	±	±

Table 2

8. Spectroscopy

The IR spectra of imide-dicid are shown in fig. 1.

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1770-1780 cm^{-1} and 1715-1730 cm^{-1}	symmetrical and asymmetrical C=O stretching of five membered cyclic imides
720-725 cm^{-1} and 1100-1130 cm^{-1}	ring carbonyl deformation of imides[6]
1630-1680 cm^{-1} and 1550-1590 cm^{-1}	C=O stretching of the amido groups of polyamideimides
1100±10 cm^{-1}	Strong peak due to C-N-C stretching vibration
900-675 cm^{-1}	multiple absorption bands due to out of plane bending of the aromatic C-H bonds in all the monomers and polymers.
1407 cm^{-1} and 1143 cm^{-1}	sulfonyl groups in case of imide-diacd 3a and the polymer R_4

Table 3
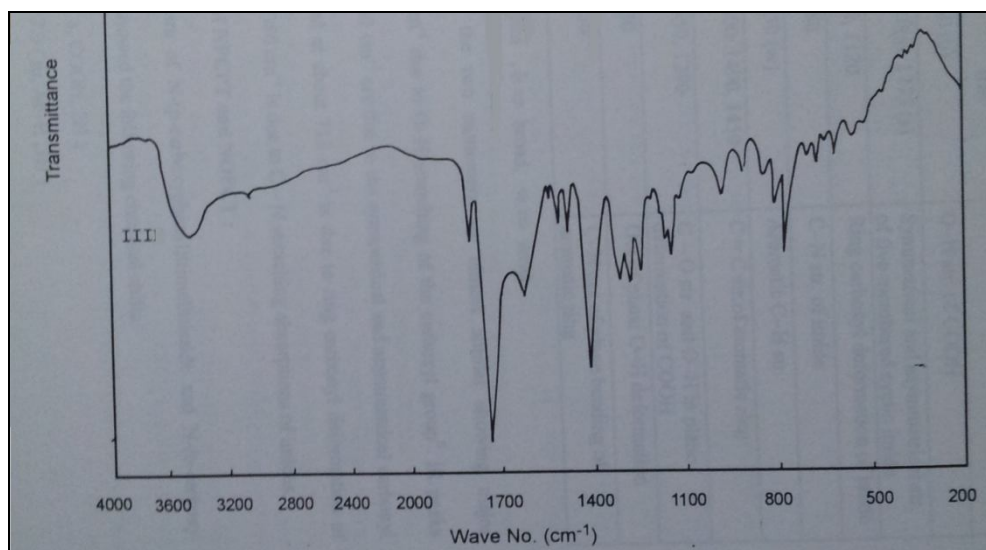
Figure 4: Fig: 1 IR Spectra of III

The spectra of all the polymers exhibited peaks at around 1770 cm^{-1} and 1720 cm^{-1} characteristics of five membered cyclic imides.a strong peak at around 1380 cm^{-1} due to C-N stretching absorption and multiple absorption bands and multiple absorption bands in the region 900-675 cm^{-1} due to out of plane bending of the aromatic C-H bonds were observed in the spectra of all the polymers. A comparative study of the IR bands monomers and the corresponding polymers reveal that band due O-H stretching at around 3420 cm^{-1} and peak at 1440 cm^{-1} due to O-H in plane deformation of the carboxyl group in the spectra of the monomers are absent in the spectra of the polymers. Two peaks at 1650 ± 10 cm^{-1} and 1560 ± 20 cm^{-1} in the spectra of the polymers confirms the presence of amido groups in the polymer molecule.

9. ^{1}H NMR Data for Polyamideimides
^{1}H NMR spectra of polyamideimides showed the following chemical shifts.

R$_1$	6.2-7.6 (m, Ar-H, 8H);	7.1-8.1 (m, Ar-H, 3H)	11.2 (s, 2H, amide N-H)
R$_2$	6.0-7.6 (m, Ar-H, 12H)	7.8-8.2 m, Ar-H, 3H)	11.0 (s, 2H, amide N-H)
R$_3$	6.8-7.8 (m, Ar-H, 15H);	8.2 (s, Ar-H, 2H)	11.1 (s, 2H, amide N-H); 3.8 (s, methylene, 2H)
R$_4$	6.8-8.4 (m, Ar-H, 15H)	8.1 (s, Ar-H, 2H)	10.6 (s, 2H, amide N-H)

Table 4

From the values of the ^{1}H NMR spectra for the polymers it is seen that a peak at 10.6-11.2 appears due to amido proton.

10. Thermal Analysis

Polymers	IDT(^{0}C)	DTmax	Tg (^{0}C)	IPDT
R$_1$	392	503	107.01	444°C
R$_2$	389	498	100.30	441°C
R$_3$	381	487	91.12	430°C
R$_4$	385	493	94.67	437°C

Table 5

The DSC curve of polymer R$_1$are presented in fig 2.
The TGA curves of all polymers show a sight inflexion upto about 70°C which is due to loss of moisture. The IDT values of the polymers R$_3$ was found to be lower than that of R$_4$. The decrease in IDT value in case of the polymer R$_3$ may be attributed to the presence of –CH$_2$- linkage into the polymer backbone. Incorporation of –CH$_2$- linkage enhances flexibility of polymer R$_3$ which in turn reduce the thermal stability. The order of thermal stability of the polymers prepared from PABA is R$_1$ >R$_2$ > R$_4$ > R .
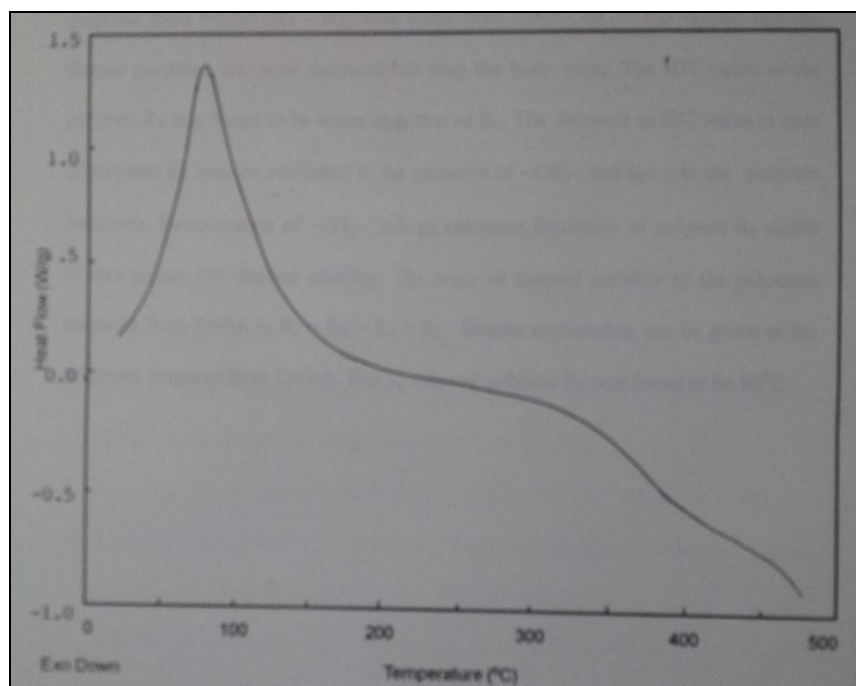
Figure 5 Fig: 2   DSC curve of R₄

11. Conclusion
The successful polycondensation of N-(o-carboxyphenyl)trimellitimides (imide-diacid) with the diamines 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. Based on these studies further work may be initiated for preparing other commercially important polyamideimides.

12. Acknowledgement

13. References
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