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Synthesis and Characterization of Some Aromatic Polyamideimides from Diamino- Pyrromellitimidates and Dicarboxylic Acid

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Abstract:

Four polyamideimides have been synthesized by direct polycondensation of four diimide-diamines and aromatic dicarboxylic acid- terephthalic acid (TPA). The diimide-diamines (3a-d) were synthesized from pyrromellitic dianhydride and the amines— *p*-phenylene diamine(2a); benzidine(2b); 4,4'-diaminodiphenylmethane (2c) and 4,4'-diaminodiphenylsulphone(2d) 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: Phosphorylation , Polycondensation, Pyrromellitic dianhydride, Terephthalic acid Triphenylphosphite.

1. Introduction

Aromatic polyimides are highly thermostable but the poor flow characteristics, high glass transition temperature, high melting point and poor solubility^[1] of polyimides 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 diimides and aromatic dicarboxylic acid- terephthalic acid. Four diimide-diamines (3a-d) were synthesized from pyrromellitic anhydride and the amines (2a-d) respectively which are then polycondensed with terephthalic acid(TPA)(4a) via the phosphorylation method.

2. Experiment

2.1. Materials

Pyrromellitic dianhydride (PMDA) (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'*-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 were used without further purification.

3. Preparation of Diimide-Diamines (Pyrromellitimidates)

Four diimides-diamines(3a-d) were prepared from PMDA and the corresponding diamines(2a-d) by condensation reaction.PMDA (0.2mol) and diamine (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 3h until about 7.2ml 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 dropwise addition of water.

4. Polymerization

A mixture of diimide-diamine (1.25 mmol), terephthalic acid(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 8-12 h under nitrogen. The obtained polymer solution was trickled on 500 ml of methanol and hot water, collected by filtration and dried.

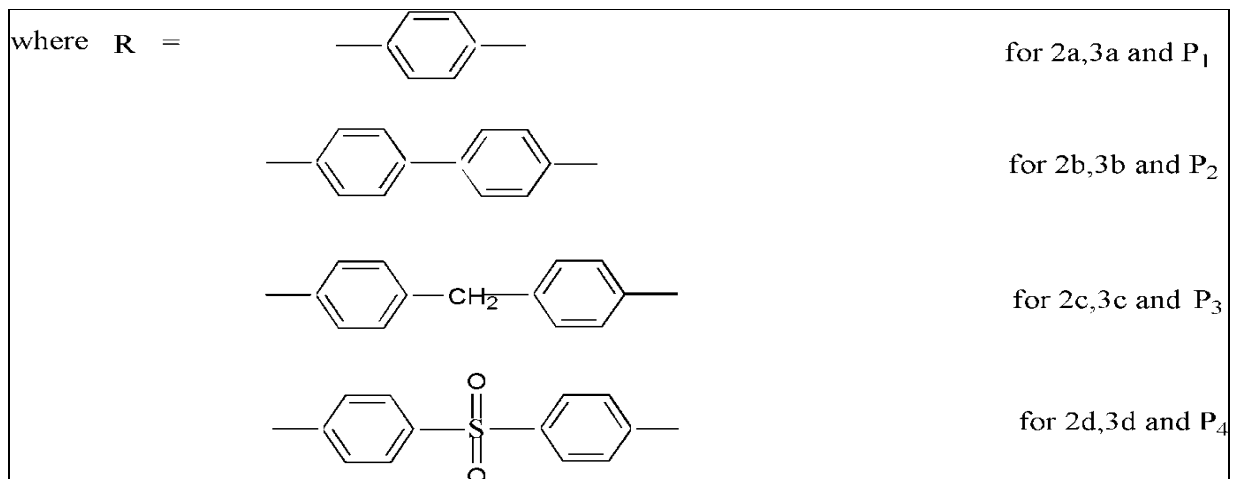
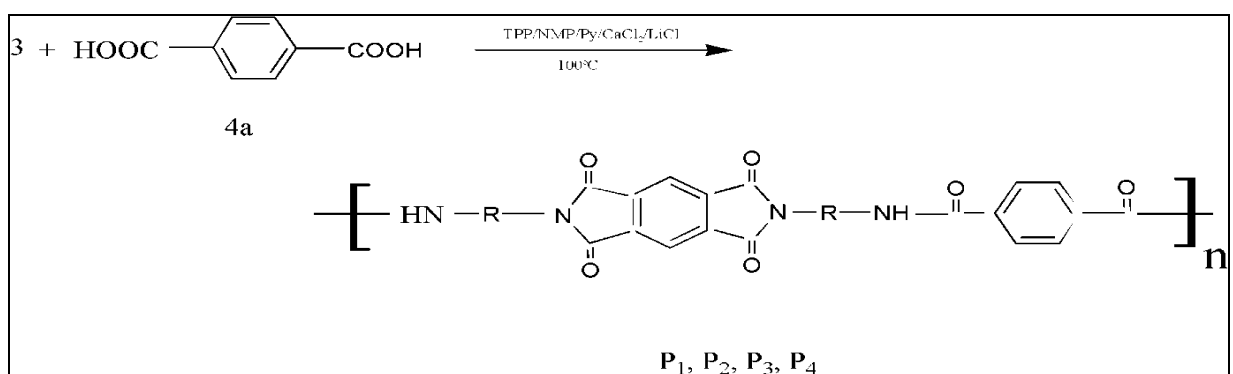
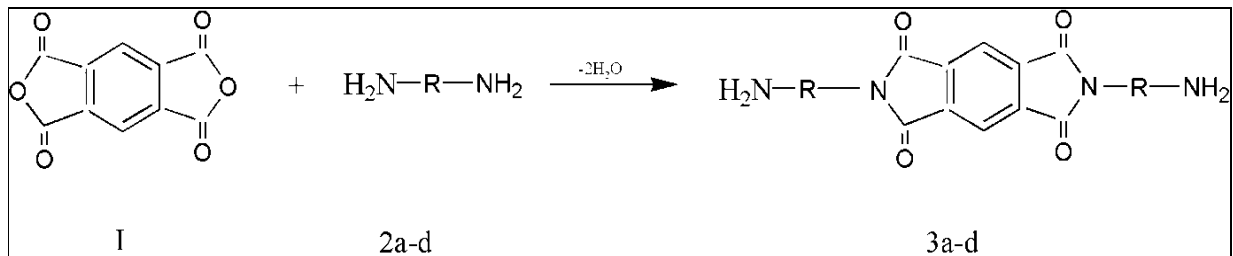
4.1. Measurements

The IR spectra of the polymers were recorded with a Perkin-Elmer spectrophotometer on KBr pellets. ¹H spectra were recorded in DMSO-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. H_2SO_4 at 30°C 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

5.1. Polymer Synthesis



5.2. Polymer Characterization

Characteristic properties of the polymers are shown in Table 1.

Polymer Calcd.	Precipitation medium Found	Colour	Yield	$[\eta]$	dl/g	Nitrogen
P ₁	Methanol	Black	61.9	0.52	10.61	10.1
P ₂	Methanol	Greenish brown	60.3	0.48	8.24	8.0
P ₃	Methanol	Dark brown	69.37	0.43	7.91	7.42
P ₄	Methanol	Light brown	81.31	0.35	6.93	6.1

Table 1: Reaction conditions and physical properties of polymers

5.3. 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 P₄ show better solubility than the other polymers. This is due the fact that incorporation of sulfonyl groups^[3] into the polymer backbones is effective in increasing the solubility of these polymers in H₂SO₄.

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

Table 2

5.4. Spectroscopy

The IR spectra of diimide-diamines and polyamideimides are shown in fig. 1 and fig. 2.

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 ^[4]
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 diimide-diamine 3d and the polymer P ₄

Table 3

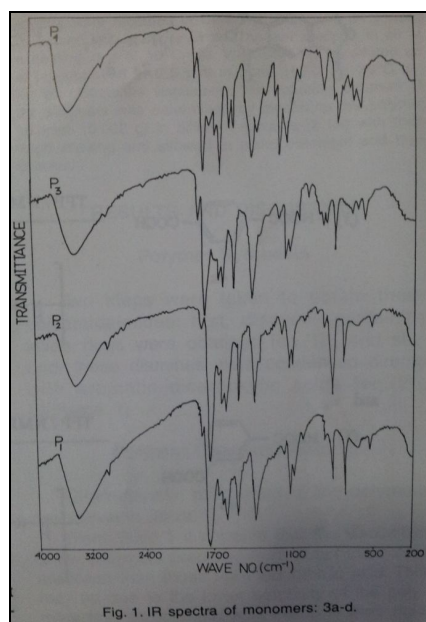


Fig. 1. IR spectra of monomers: 3a-d.

Figure 2

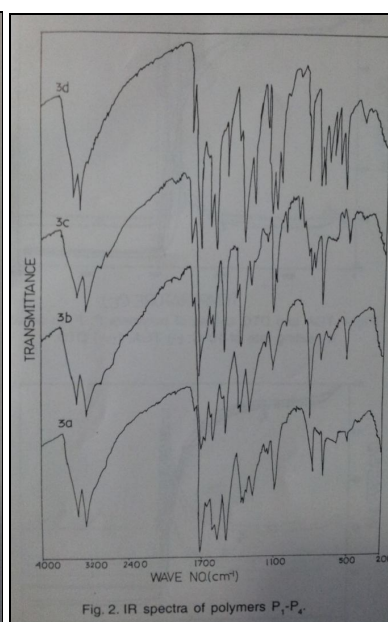


Fig. 2. IR spectra of polymers P₁-P₄.

figure 3

The IR Spectra of the pyromellitimides and the polyamideimides exhibited peaks at 1770-1780 cm^{-1} and at 1715-1730 cm^{-1} due to symmetrical and unsymmetrical C=O stretching of five membered cyclic imides. The peaks at 720-725 cm^{-1} and 1100-1130 cm^{-1} are due to ring carbonyl deformation of imides. IR peaks at 1630-1680 cm^{-1} and 1550-1590 cm^{-1} are due to C=O stretching of the amido groups of the polyamideimides. A very strong peak at 1100 \pm 10 cm^{-1} which is due to C-N-C stretching vibration and multiple absorption bands in the 900-65 cm^{-1} due to out of plane bending of the aromatic C-H bonds are obtained in the spectra of all the monomers as well as the polymers. absorption at 1407 cm^{-1} and 1143 cm^{-1} are due to the sulfonyl groups in case of diimide-diamine 3d and the polymer P₄. A comparative study of the bands of diimide-diamines and their polyamideimides reveals that absorption due to N-H stretching of amino groups (two bands between 3300-3500 cm^{-1}) are absent in the spectra of the polymer. Instead a band at 3320-3400 cm^{-1} appears due to N-H stretching of the amido groups. Absorption due to N-H stretching of amino groups (two bands between 3300-3500) of diimide-diamine are absent in the spectra of the polymers. Instead a band at 3320-3400 cm^{-1} appears due to N-H stretching of the amido groups.

5.5. ¹H NMR Data for Polyamideimides

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

P1	7.0-7.8 (m, Ar-H, 12H);	8.1 (s, Ar-H, 2H)	11.0 (s, 2H, amide N-H)
P2	7.1-7.6 (m, Ar-H, 20H)	8.0 (s, Ar-H, 2H)	10.9 (s, 2H, amide N-H)
P3	7.3-7.8 (m, Ar-H, 20H);	8.2 (s, Ar-H, 2H)	10.6 (s, 2H, amide N-H); 3.9 (s, methylene, 2H)
P4	7.1 -7.8 (m, Ar-H, 20H)	8.1 (s, Ar-H, 2H)	10.8 (s, 2H, amide N-H)

Table 4

From the values of the ¹H NMR spectra for the polymers it is seen that a peak at 10.5-11.3 appears due to amido proton.

5.6. Thermal Analysis

Polymers	IDT(^o C)	DTmax	Tg (^o C)	IPDT
P1	430	530	109.03	449.4 ^o C
P2	425	527	101.35	447.7 ^o C
P3	420	514	93.14	437 ^o C
P4	423	520	96.89	440 ^o C

Table 5

The TGA and DTG curves of polyamideimides are presented in fig 3. Thermogravimetric analysis shows that about 4-8% initial weight loss occurs upto 80-90^oC due to loss of moisture or entrapped solvent in the polymer. Subsequently, there is only 2-4% weight loss upto 300^oC. The maximum weight loss occurs around 400-600^oC. The initial procedural decomposition temperature (IPDT) values of polymers P₁ and P₂ are almost same having p-phenylene and 4,4'-diphenylene rings respectively in the polymer backbone. The lower values in in case of polymers P₃ and P₄ are due to the presence of -CH₂- and -SO₂- groups in between the phenylene rings. In case of P₄ this value is slightly higher than that of P₃ as expected from the literature^[5].

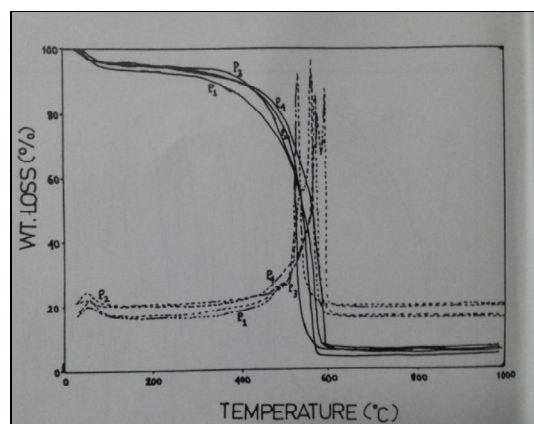


Figure 3: TGA and DTG curves of polymers P₁-P₄ in air at a heating rate of 10^oC; (-) TGA, (---) DTG

6. Conclusion

The successful polycondensation of diamino-pyromellitimides 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. Based on these studies further work may be initiated for preparing other commercially important polyamideimides.

7. Acknowledgement

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8. References

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