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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 ^{1}H 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 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 $CaCl_2$ 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.

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

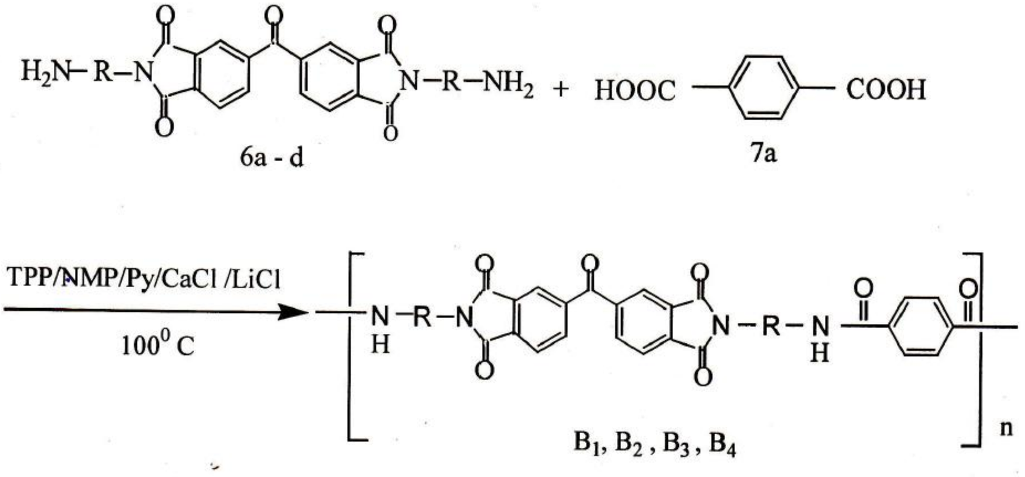
A mixture of diimide-diamine(6a-d) (1.25 mmol), terephthalic acid(7a) (1.25 mmol), 0.3 g of $CaCl_2$, 0.6 g LiCl, 0.8 ml of TPP, 1.6 ml of pyridine and 7 ml of NMP was heated with stirring at 100°C for 8 h under nitrogen.The obtained polymer solution was trickled on 500 ml of methanol, collected by filtration and dried.

Measurements

The IR spectra of the polymers were recorded with a Perkin-Elmer spectrophotometer on KBr pellets.^{1}H 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°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 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



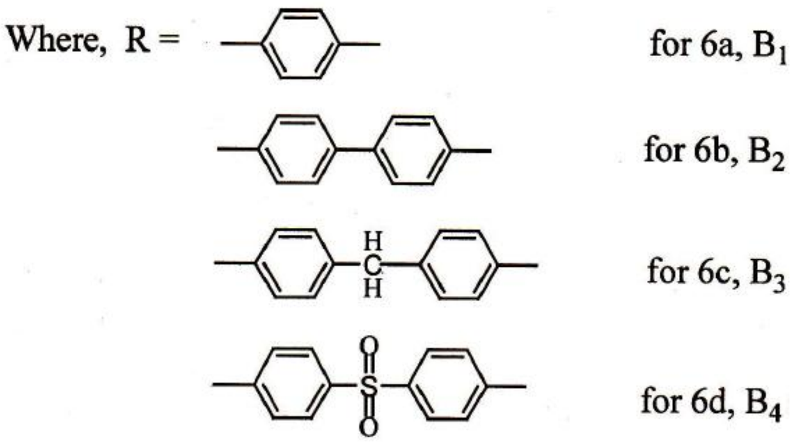


Table 1: Characterization Of Diamino-Benzophenone-3,3′,4,4′-Tetracarboxylic Diimide (Diimide-Diamine):

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 (%)	[ŋ] dl/g	Nitrogen Cald.	Found
B_1	Methanol	Blackish brown	70.2	0.322	11.16	11.0
B_2	Methanol	Greenish yellow	69.46	0.30	8.56	8.52
B_3	Methanol	Brown	72.3	0.276	8.21	7.98
B_4	Methanol	Light yellow	77.5	0.25	7.16	7.02

Polymer B_4 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 B_4 show better solubility than the other polymers. The incorporation of sulfonyl groups[5] in the polymer B_4 into the polymer backbones is effective in increasing the solubility of these polymers in H_2SO_4.

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_2SO_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.

^{1}H NMR DATA FOR POLYAMIDEIMIDES

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

B_1	∂ 6.0-6.6 (m, Ar-H, 8H);	∂ 7.1-7.5 (m, Ar-H, 4H),∂7.8-8.2 (m,Ar-H ,6H)	∂ 11.4 (s, amide N-H, 2H)
B_2	∂ 6.8-7.4 (m, Ar-H, 16H)	∂ 7.5-7.8 m, Ar-H, 4H), ∂ 8.0-8.3(m, Ar-H, 6H)	∂ 10.7 (s, amide N-H, , 2H)
B_3	∂ 3.8 (s, methylene,4H), ∂ 7.2-7.5 (m, Ar-H, 16H); ∂ 7.6-8.0 (m, , Ar-H,4H)	∂ 8.1-8.4 (s, Ar-H, 6H)	∂ 11.2 (s, amide N-H, 2H);
B_4	∂ 6.1—6.8 (m, Ar-H, 16H), ∂ 7.1-7.6 (m, Ar-H,4H)	∂ 7.8-8.3 (m, Ar-H, 6H)	∂ 11.0 (s, amide N-H, 2H)

A careful examination of the ^{1}H NMR spectra for the monomers and the polymers reveal that the peak at about ∂ 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(^{0}C)	DT$_{max}$ (^{0}C)	Tg (^{0}C)	IPDT(^{0}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 B$_1$ is presented in fig 1.

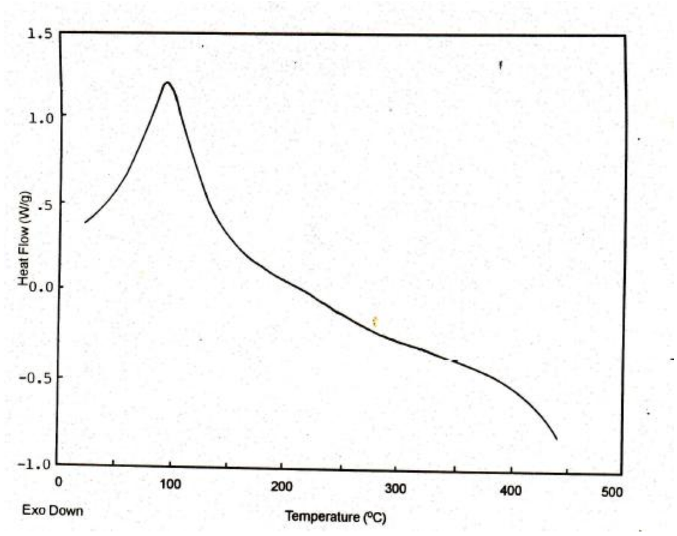


Fig: 1 DSC curve of B$_1$

Thermogravimetric analysis shows that an initial weight loss of about 3- 6% occurs upto 75 – 85^{0}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^{0}C. The maximum weight loss occurs around 390-650 ^{0}C .The IPDT values of the polymers B$_1$ and B$_2$ are almost same having p-phenylene and $4,4^{'}$- diphenylene rings respectively in the polymer backbone. In case of B$_4$ this value is slightly higher than that of B$_3$ 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.

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