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Novel Aromatic Polyamides from Bis-[*p*/*m*-(Aminobenzoylhydrazino)] Phosphite

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A series of aromatic polyamides from bis-[*p*/*m*-(aminobenzoylhydrazino)]phosphite with N-[*p*/*m*-(carboxyphenyl)]aminoacetyl chloride have been synthesized in N,N-dimethylacetamide at −10°C and characterized by elemental and IR spectral analysis. The inherent viscosity of all polyamides measured at a concentration of 0.5 g dL^{-1} in *m*-cresol at 25 ± 1°C was found to be in the range of 0.09–0.29 dL g^{-1}. Oxidative isothermal weight loss analyses have shown that all the polyamides were stable up to 300°C.

INTRODUCTION

Polyamides containing P—N linkages are of great importance. They are used as coating agents[1], fire retardants[2], plasticizers[3] etc. Among such polyamides, the polymers containing hydrazinophosphite linkage are not reported in literature. We have already reported the synthesis of polymers containing hydrazinophosphite linkage with excellent thermo-oxidative stability.[4] The present investigation is concerned with the synthesis of polyamides from bis-[*p*/*m*-(aminobenzoylhydrazino)]phosphite and to study the inherent viscosity, solubility and thermo-oxidative stability of such polyamides.

EXPERIMENTAL

All the chemicals used were of AR grade. N-[*p*/*m*-(carboxyphenyl)]aminoacetic acid was synthesised by refluxing chloroacetic acid (0.1 mole) and *p*/*m*-aminobenzoic acid (0.1 mole) in water (200 mL) in presence of sodium carbonate (22.0 g) for 3–4 h followed by neutralization of resulting mixture by conc. HCl. The dicarboxylic acid precipitated was crystallized by hot water.

N-[*p*-(carboxyphenyl)]aminoacetic acid: m.p. 218°C; yield 87%. $C_9H_9NO_4$ requires (%): C, 55.38; H, 4.61; N, 7.17; found (%): C, 55.36; H, 4.58; N, 7.15.

N-[*m*-(carboxyphenyl)]aminoacetic acid: m.p. 205°C; yield 70%. $C_9H_9NO_4$, requires (%) C, 55.38; H, 4.61, N, 7.17, found (%): C, 55.32; H; 4.50; N, 7.16.

N-[*p*/*m*-(carboxyphenyl)]aminoacetyl chlorides have been synthesized by the similar procedure as described earlier[5]. *p*/*m*-Sulphinylaminobenzoyl chlorides have been synthesized by refluxing *p*/*m*-aminobenzoic acids (0.1 mole) with thionyl chloride (0.6 mole) for 1–2 h.

p-Sulphinylaminobenzoyl chloride[6]: b.p. 112–116°C/1–2 mm; yield 68%.

m-Sulphinyl aminobenzoyl chloride: b.p. 96–102°C/1–2 mm; yield 42%.

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Diethylhydrogenphosphite[7] was synthesized by refluxing phosphorous trichloride (0.1 mole) with ethanol (160 mL) in carbon tetrachloride (50.0 mL) at 90°C. b.p. 76–78°C/14 mm; yield 95.%

Phosphonicdihydrazide[8] was synthesized by refluxing diethylhydrogenphosphite (0.1 mole) and hydrazine hydrate (90%; 0.2 mole) for 2 h. m.p. 92°C; yield 95%. N_4H_7PO requires (%): H, 6.36; N, 50.90; found (%): H, 6.32; N, 50.09. IR (KBr): 3480 cm^{-1} ν(NH), 1300 cm^{-1} ν(P═O), 1500–1480 cm^{-1} δ(NH) and 960 cm^{-1} δ(H—P═O).

Bis-[*p*/*m*-(aminobenzoylhydrazino)]phosphite: *p*/*m*-Sulphinylaminobenzoylchloride (0.2 mole) was added to the suspension of phosphonichydrazide (0.1 mole) in N,N-dimethylacetamide (25 mL) at −10°C. The mixture was stirred for 2 to 4 h and neutralized by aqueous sodium bicarbonate (10%). The diamine precipitated was crystallized from N,N-dimethylacetamide.

Bis-[*p*-(aminobenzoylhydrazino)]phosphite: m.p. 290°C; yield 54%. $C_{14}H_{17}N_6O_3P$ requires (%): C, 48.27; H, 4.88; N, 24.14; found (%): C, 48.20; H, 4.80; N, 24.08. IR (KBr): 3300 cm^{-1} ν(NH), 1680–1620 cm^{-1} ν(C═O), 1340–1320 cm^{-1} ν(P═O), 1480 cm^{-1} δ(NH) and 1040 cm^{-1} δ(H—P═O).

Bis-[*m*-(aminobenzoylhydrazino)]phosphite: m.p. 240°C; yield 60%. $C_{14}H_{17}N_6O_3P$: found (%): C, 48.22; H, 4.85; N, 24.00. IR (KBr): 3600 cm^{-1} ν(NH), 1600 cm^{-1} ν(C═O), 1320 cm^{-1} ν(P═O), 1440 cm^{-1} δ(NH) and 1000 cm^{-1} δ(H—P═O).

Synthesis of polyamides

All the polyamides have been synthesized by stirring the solution of diamine (0.2 mole) in N,N-dimethylacetamide with appropriate diacid chloride (0.1 mole) up to 4 h at −10°C. The inherent viscosity-time dependence relationships for all the polyamides during the course of polymerization have also been studied (Fig. 1). Thereafter lithium hydroxide was added in required quantity to remove the HCl formed during the reaction. All such polyamides were precipitated by aqueous methanol (10%), washed with water and acetone and dried below 50°C. Their physico-chemical and analytical data are summarized in Table-1, and the method of synthesis is outlined in Fig. 2.

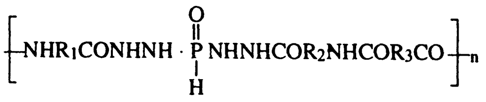
RESULTS AND DISCUSSION

The inherent viscosity of all polyamides was measured at a concentration of 0.5 g dL^{-1} in *m*-cresol solution at 25 ± 1°C and was found in the range of 0.09–0.29 dL g^{-1}. In fact the molecular mass of polymers is a linear function of their inherent viscosity. Therefore, from Table-1, the molecular masses of all the polyamides containing *p*-phenylene rings were found to be greater than corresponding *m*-isomers. From these observations one can conclude that all the monomers containing *p*-phenylene rings were polymerized more regularly and orderly than the corresponding *m*-isomers.[9]

All the polyamides were insoluble in benzene, acetone, dioxane, dichloromethane etc., but were soluble in protogenic solvents such as *m*-cresol, conc. sulphuric acid and chlorosulphonic acid. In general, the solubility of polyamides was related to their crystallinity. From these solubility results one can infer that

TABLE-1

PHYSICO-CHEMICAL AND ANALYTICAL DATA OF POLYAMIDES



$$\left[\text{NHR}_1\text{CONHNH}\cdot\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}\text{NHNHCOR}_2\text{NHCOR}_3\text{CO} \right]_n$$

Polymer Code No.	R_1	R_2	R_3	Yield %	η^a_{inh}	SP^b	Elemental Analysis^c (Found)			IR (KBr) (cm^{-1})			
							C	H	N	ν(HN)	ν(C=O)	ν(P—H) (def.)	δ(H—P=O)
I	*p*-C_6H_4—	*p*-C_6H_4—	*p*-C_6H_4—	95	0.29	(± ±)	55.32	3.96	17.76	3300	1660	1110	860
II	*p*-C_6H_4—	*p*-C_6H_4—	*m*-C_6H_4—	94	0.18	(± ±)	55.28	3.90	17.69	3200	1640	1020	840
III	*m*-C_6H_4—	*m*-C_6H_4—	*p*-C_6H_4—	98	0.16	(+)	55.30	3.92	17.79	3600	1660	1140	1080
IV	*m*-C_6H_4—	*m*-C_6H_4—	*m*-C_6H_4—	97	0.09	(+)	55.29	3.93	17.78	3400	1620	1100	1040

a: Inherent viscosity measured at a concentration of 0.5 g dL^{-1} in *m*-cresol at 25 ± 1°C

b: Solubility in polymeric medium: (± ±) Precipitated, (+) soluble,

c: Found values of elemental analysis against the calculated value for $(C_{22}H_{19}O_5N_6P)_n$: C, 55.34;H,3.98; N,. 17.81%

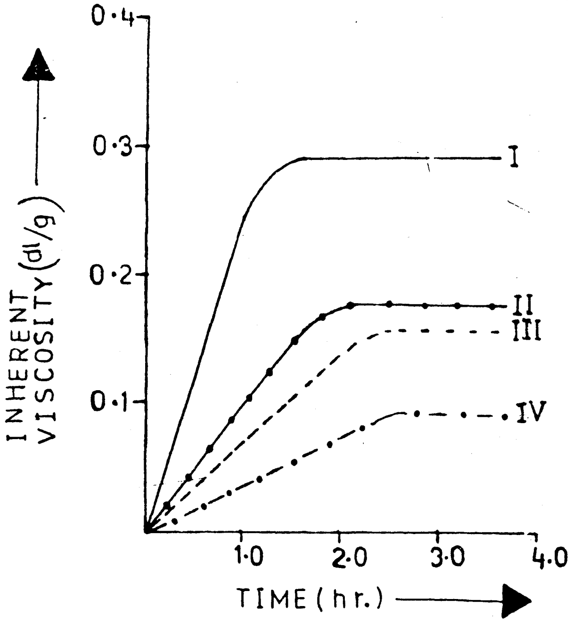


Fig. 1. Inherent viscosity-time dependence of polyamides during polymerization

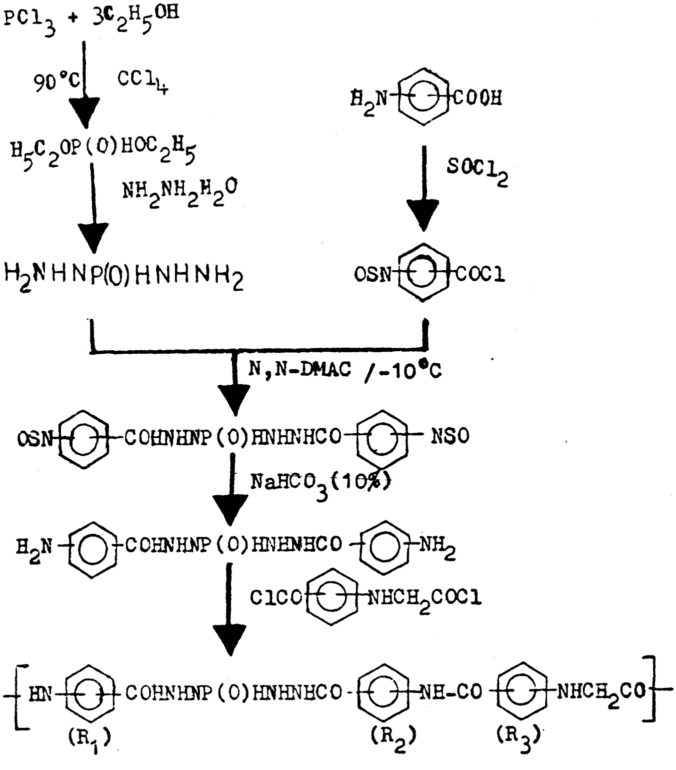


Fig. 2. Synthesis of polyamides

by the appropriate structural combinations of monomers, one can synthesize the polyamides of appreciable solubility, so that it may be used in membrane, transportation, fabrics and other technologies.[1-3]

All the polyamides have been characterized by IR spectra and elemental analysis. The IR spectral peaks of *p*-phenylene substituted polyamides were found to be more intense and pronounced than the corresponding *m*-isomers. A considerable reduction in vibration frequency of IR bands revealed that these polyamides exist as coiled structure due to hydrogen bonding, which will provide extra mechanical strength and rigidity to the segments of these polyamides.

The rates of polymerization for all polyamides have been studied and it was observed that these were in the following increasing order:

IV < III < II < I

In general, replacement of *p*-phenylene unit by *m*-isomer reduced the rate of polymerization (Fig. 2).

Isothermal weight loss analyses of all the polyamides in air have been studied and the changes in weight as a function of time at the three different temperatures viz., 200, 300 and 400°C have been recorded for all polyamides. The polymer (I) having *p*-phenylene units has shown maximum thermo-oxidative stability than (II) (Fig. 3) while the polyamide (III) was more stable than (IV) (Fig. 4). The thermo-oxidative stability of all such polyamides was in the following decreasing order:

I > II > III > IV

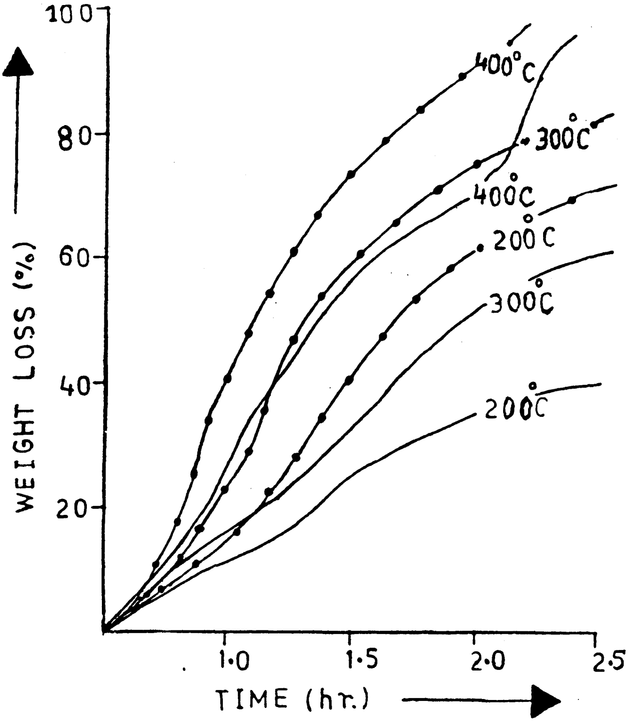


Fig. 3. Isothermal weight loss of polyamides from bis-*p*-(aminobenzoylhydrazino)phosphite.

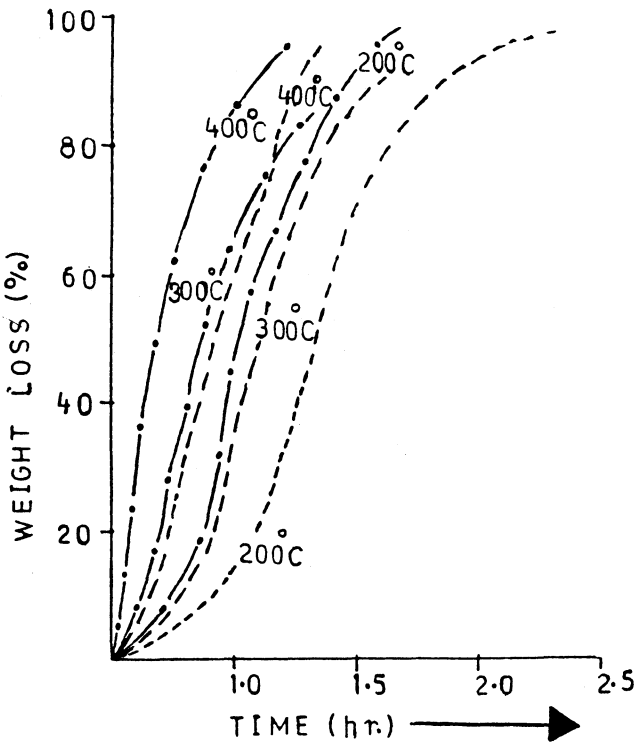


Fig. 4. Isothermal weight loss of polyamides from bis-*m*-(aminobenzoylhydrazino)phosphite.

From the above results it can be inferred that these polyamides have shown excellent solubility, inherent viscosity and thermooxidative stability than the polyamides containing P—N bonds[1-4] already reported in literature.

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