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Synthesis of Thermally Stable Polyamide Phosphonicdihydrazides

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The low temperature solution polycondensation of bis(3-aminobenzoylhydrazino)phosphite with different aromatic diacid chlorides in N,N-dimethylacetamide at −10°C afforded the fusible and soluble polyamides having inherent viscosity in the range of 0.08–0.17 dL g^{-1}. Isothermal weight loss analysis in air revealed that all the polyamides were stable upto 300°C.

INTRODUCTION

The intrinsic thermo-oxidative stability of aromatic structures has been recognised and a variety of polymers have been made in which benzene rings are linked together in chain. Various aromatic polyamides were precursors to thermally stable polymers due to their intermolecular bonding, chain stiffness and thermal stability[1–3]

The object of the present investigation was to synthesize the monomer, bis(3-aminobenzoylhydrazino)phosphite, to study its copolymerization with different aromatic diacid chlorides and to obtain the IR, thermal properties and solubility.

EXPERIMENTAL

Technical grade N,N-dimethylacetamide was dried over BaO for 48 h followed by 2 h refluxing and distillation under reduced pressure. b.p. 58–60°C/10 mm.

Diethylhydrogenphosphite was synthesised[4] by the esterification of phosphorus trichloride (0.01 mole) and ethanol (0.45 mole) in carbon tetrachloride. b.p. 73–76°C/14 mm (lit.[4] 73–74°C/14 mm); yield 92%; (m.f. $C_4H_{11}O_3P$; % analysis: (Calc.)) C, 33.8, H, 7.8%, (Found) C, 35.0, H, 7.9%.

Phosphonicdihydrazide was synthesized[5] by refluxing diethylhydrogenphosphite (0.01 mole) with hydrazinehydrate (99.0%, 0.30 mole). m.p. 92°C, yield 81.6%. The infrared (IR) spectrum (KBr) showed bands at 1500–1480 cm^{-1}; (—NH-bend.), 1300 cm^{-1} (H- - -O═P stretch.), 960 cm^{-1} (P—H bend.); m.f. N_4H_7PO; % analysis: (Calc.) H, 6.36, N, 50.09%, (Found) H, 6.32, N, 50.12%.

3-Sulfinylaminobenzoylchloride was synthesized by refluxing the mixture of 3-aminobenzoic acid (0.01 mole) and thionylchloride (0.03 mole). b.p. 96–102°C/2 mm; yield 68%. The diacid chlorides were prepared by conventional method.

Bis(3-aminobenzoylhydrazino)phosphite was synthesised by the reaction of phosphonicdihydrazide (0.01 mole) with the solution of 3-amino benzoylchloride (0.03 mole) in N,N-dimethylacetamide at –10°C, followed by the neutralization of the resulting mixture by aqueous sodium bicarbonate solution (0.1 M). m.p. 240°C; yield 60%. The infrared (IR) spectrum (KBr) showed bands at 3600 cm^{-1} (—NH- - -O stretch.), 1600 cm^{-1} (C═O- - -H stretch.), 1440 cm^{-1} (—NH-bend.), 1320 cm^{-1} (P═O- - -H stretch.) and 1000 cm^{-1} (O═P—H bend.).

Synthesis of Polyamides

The solution of diacid chloride in N,N-dimethylacetamide was added dropwise with stirring to a solution of bis(3-aminobenzoylhydrazino)phosphite in N,N-dimethylacetamide over 2 h at –10°C. Lithium hydroxide was added to neutralize the HCl formed during the polycondensation. The polymer was precipitated by aqueous methanol solution (10%); it was washed with acetone and dried (Table 1).

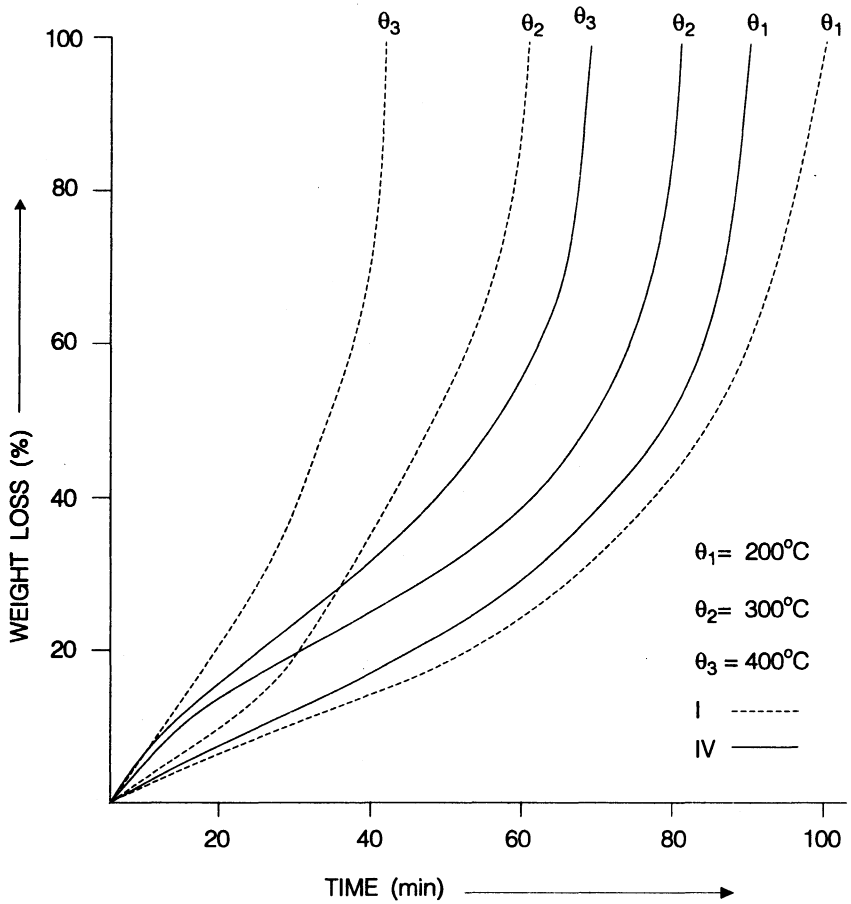


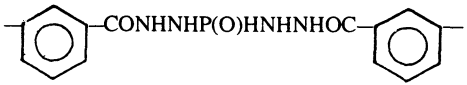
Fig. 1

TABLE I
POLYAMIDES

Polymer Code No.	Structure	Monomer[a] composition	Yield (%)	η_{inh}^{b} (dLg^{-1})^{b} (30 ± 5°C)	Solubility (30 ± 5°C)				
					Sp[c]	DMAc[d]	DMF[e]	Chlorosulfonic acid	Dioxane
I	$[NHR''NHCOCH_2OROCH_2CO]_n$	(50/50)	97.2	0.17	±	±	+	+	–
II	$[NHR''NHCOCH_2OROCH_2CO]_n$	(40/60)	95.6	0.12	±	+	+	+	–
III	$[NHR''NHCOCH_2NHRCO]_n$	(50/50)	96.8	0.16	+	±	+	+	–
IV	$[NHR''NHCOCH_2NHRCO]_n$	(40/60)	96.6	0.08	+	+	+	+	–

a = Diamine prereacted with dicarboxylic acid
b = Inherent viscosity: measured at a concentration of 0.5 g/dL^{-1} in conc. sulphuric acid solution
c = Solubility in polymeric medium
d = N, N-dimethylacetamide
e = N,N-dimethylformamide
+ = Soluble, ± = partially soluble

R″ =



RESULTS AND DISCUSSION

The structures and their related properties of various *p*- and *m*-phenylene ring-substituted polyamides are summarised in Table 1.

All the copolymers were soluble in polar solvents but were insoluble in non-polar solvents, solubilities of these polyamides were increased with polarity of solvents. The polyamides I and II containing ether linkage were swollen in polymeric medium.

IR spectra of polyamides showed a characteristic absorption band in the range of 3600–3500 cm^{-1} (—NH- stretching), 1340–1320 cm^{-1} (P═O---H stretching) and 1140–1100 cm^{-1} (H—P═O bending). The peaks of *p*-isomers were more pronounced than corresponding *m*-isomers. It may be concluded that *p*-substituted monomers polymerized more regularly and orderly in comparison to *m*-isomers[3].

Inherent viscosities of polymers were in the range of 0.08–0.17 dL g^{-1}. A considerable fall in the η_{inh} was observed in case of *m*-isomers. The least η_{inh} was observed in case of IV.

The scan for isothermal weight loss of polyamide (IV) is shown in Fig. 1. The 100% volatilization of polymer was recorded in 90, 80 and 70 mts at 200, 300 and 400°C under thermoxidative conditions. It has been concluded that the thermal stability of polymers was affected mostly by variation in the dicarboxylic acid components.

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