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Synthesis of Some Newer Polyhydrazides Containing Hydrazinophosphite Linkage

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The polyhydrazides having inherent viscosity in the range of 0.18–0.47 dL g^{-1} were prepared by polymerizing a series of diacid chloride with phosphonichydrazide in N,N'-dimethylacetamide. Oxidative thermogravimetric analysis shows that these polymers decomposed in the range of 500–720°C. Their melting points and glass transition temperatures were evaluated from differential thermal analysis.

INTRODUCTION

It has long been observed that incorporation of aromatic rings in the linear polymer backbone yields higher melting, stiffer and corrosion-resistant polymers useful in textile and aerospace technology[1–3]. Most of the organophosphorus polymers of the same class are better flame retardants, less smoky and self-extingushing[1,3]. Among these polymers, polyhydrazide containing hydrazinophosphite linkage have so far not been reported in literature. In the present communication an attempt has been made to synthesize the polyhydrazides containing hydrazinophosphite linkage and their inherent viscosity, solubility and thermal properties have been studied.

EXPERIMENTAL

I. Purification of N,N-dimethylacetamide

Technical grade solvent was dried over barium oxide for 48 hrs, followed by 2 hrs refluxing and distilled under reduced pressure. The fraction boiling at 58–60°C/10 mm was collected.

II. Synthesis of Phosphonichydrazide

Phosphonichydrazide was synthesized by the procedure described earlier[4]. A mixture of diethylhydrogenphosphite (7.0 gm) and hydrazinehydrate (99–100%; 5.0 gm) was refluxed for 1 hr. phosphonichydrazide was separated on cooling, it was filtered and dried. M.pt. 92°C; yield: 4.0 gm (81.6%).

Analysis: N_4H_7PO; Required: H, 6.36%, N, 50.09%; Found: H, 6.32%, N, 50.12%. IR (KBr): 1500–1480 cm^{-1} –NH (bending) 1300 cm^{-1}; H—O=P (stretching), 960 cm^{-1}; P–H (bending).

III. Synthesis of Polyphosphonichydrazides

A suspension of phosphonichydrazide (10%) in dry N,N′-dimethylacetamide was cooled at –10°C and the solution of diacid chloride in dry N,N′-dimethylacetamide was added slowly with constant stirring over 2 hrs. It was then neutralized by lithium hydroxide (90%) to remove the HCl formed during the reaction. The viscous solution was stirred at room temperature for 6 hrs and then poured into 10% methanol solution. A solid polymer was obtained. It was washed with acetone and dried. The polymers prepared by this method are summarized in Table 1.

TABLE 1
POLYPHOSPHONICHYDRAZIDES

Polymer code	Structure and composition[a]	Yield (%)	η^{b}_{inh} (dL g^{-1})
I	–NHNHP(O)HNHNHCORCO– (50/50)	98	0.24
II	–NHNHP(O)HNHNHCOR′CO– (50/50)	96	0.18
III	–NHNHP(O)HNHNHCO$(CH_2)_8$CO– (40/60)	97	0.46
IV	–NHNHP(O)HNHNHCO$(CH_2)_4$CO– (50/50)	96	0.24
V	–NHNHP(O)HNHNHCOCH_2OROCH$_2$CO– (50/50)	98	0.28
VI	–NHNHP(O)HNHNHCOCH_2OR′OCH_2CO– (50/50)	97	0.19
VII	–NHNHP(O)HNHNHCOCH_2NHRCO– (50/50)	96	0.41
VIII	–NHNHP(O)HNHNHCOCH_2NHR′CO– (50/50)	95	0.29
IX	–NHNHP(O)HNHNHCOCH_2NHCORCONHCH$_2$CO– (50/50)	98	0.42
X	–NHNHP(O)HNHNHCOCH_2NHCOR′CONHCH$_2$CO– (50/50)	96	0.26

R = p^-–C_6H_4–; R′ = m^-–C_6H_4–; a = Phosphonichydrazide prereacted with dicarboxylic acid; b = Inherent viscosity, measured at a concentration of 0.6 g dL^{-1} in conc. sulphuric acid at 30 ± 5°C.

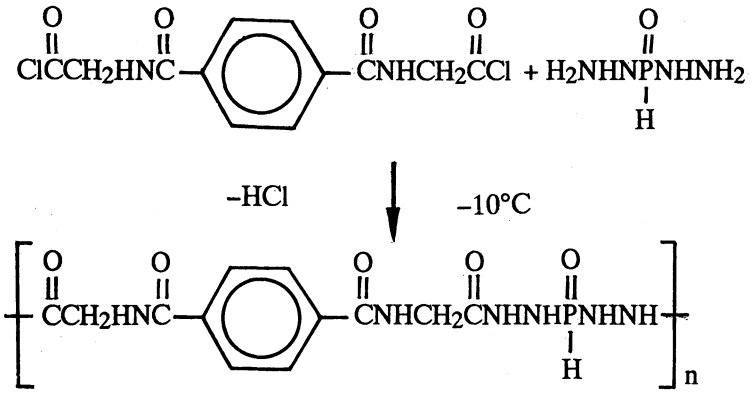

Fig. 1

RESULTS AND DISCUSSION

Inherent viscosities (η_{inh}) of all the polyhydrazides were in the range of 0.18–0.47 dL g^{-1}. Polyhydrazides having octamethylene unit have shown the maximum η_{inh}. A change from *meta*- to *para*-substitution in monomers also showed a regular increase in the inherent viscosity (Table 1).

Structure of repeating unit (Fig. 1) shows that polyhydrazides have a number of free hydrogen bonding sites due to the presence of P=O, C=O and N–H groups. These hydrogen bonding sites produce intermolecular as well as intramolecular bonding and thus provide rigidity and coiled structure to polyhydrazides.

The IR spectra of polymers showed characteristic absorption bands in 3500–3000 cm^{-1} (N–H stretching), 1680–1610 cm^{-1} (νC=O), 1280–1210 cm^{-1} (P=O . . . H stretching) and 870–815 cm^{-1} (H–P=O bending). The peaks of the *para* isomers were more pronounced than *meta* isomers. It may be inferred that *para* substituted monomers polymerized in a more regular and ordered way as compared to *meta* isomers. These observations have also been reported by Preston and coworkers[2,6].

The structure of polymers from different combinations of monomers showed some differences in solubility. All the polymers were insoluble in a wide range of organic solvents such as dioxane, acetone, ethanol etc. but were freely soluble in conc. sulphuric acid.

The T.G.A. profiles of polyhydrazides I, III, IX and X are shown in Fig. 2. The highly crystalline polyhydrazide (I) exhibited a monotonic curve of DTA having an endotherm at 490°C (Table 4). The 50% weight loss of the polymers (I and IX) took place at 380°C and 370°C respectively (Table 3).

The polyhydrazides (I and IX) with terephthaloyl linkage melted at higher temperatures than those having octamethylene and isophthaloyl linkage (III and IX). The lowest melting point was recorded in case of III (415°C). These results suggested that thermal stability of polyhydrazides was greatly influenced by

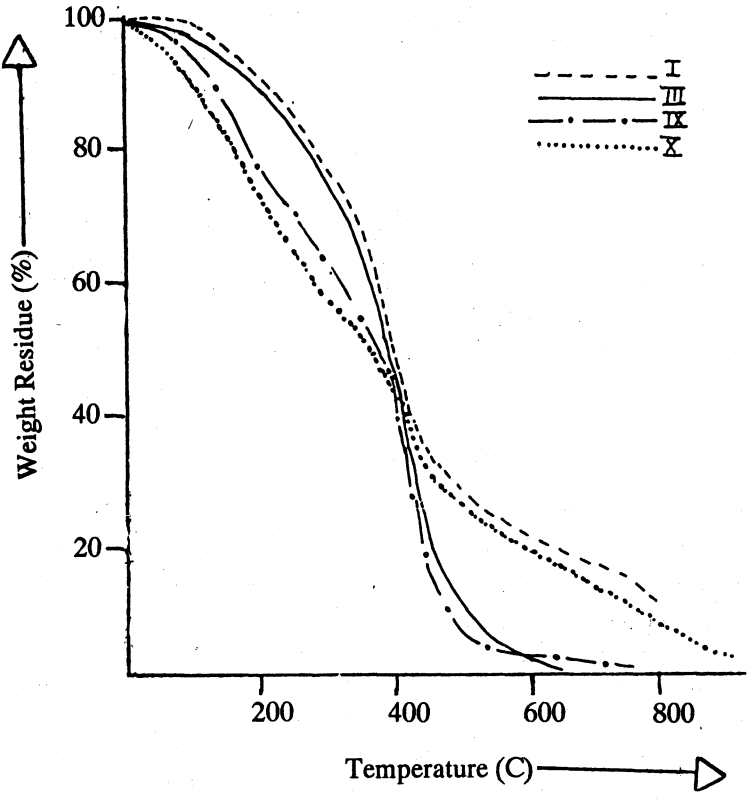

Fig. 2 T.G.A. profiles of poliphosphonichydrazides in air

TABLE 2
SOLUBILITY OF POLYHYDRAZIDES AT (30 ± 5°C)

Polymer code	Solubility in polymeric medium	Solvents				
		Conc. H_2SO_4	DMF[a]	DMA[b]	DMSO[c]	Dioxane
I	±±	+	+	–	–	–
II	+	+	+	+	+	–
III	±±	+	–	–	±	–
IV	±±	+	+	–	–	–
V	±±	+	+	+	+	–
VI	+	+	+	+	±	–
VII	+	+	+	+	±	–
VIII	+	+	+	+	±	–
IX	±±	+	±	–	–	–
X	+	+	±	+	–	–

±± Precipitated; + Soluble; ± partially soluble; – insoluble.
a = N,N-dimethylformamide; b = N,N-dimethylacetamide; c = Dimethylsulphoxide.

variation in the isomeric form of dicarboxylic component and to a relatively small degree of methylene groups in the polymer chain.

TABLE 3
THERMAL DECOMPOSITION OF POLYHYDRAZIDES IN AIR HEATING RATE: 5°C/MIN.

Polymer Code	Sample size (mg)	T_{max} (°C)	DT at different weight residue (°C)				
			10%	30%	50%	70%	90%
I	4.25	600	500	435	380	320	190
III	4.00	–	–	480	400	360	200
IX	8.06	850	480	430	370	250	130
X	8.00	920	760	460	360	210	100

T_{max} = Temperature at 100% weight loss.

The glass transition temperature (T_g) of all the polyhydrazides was evaluated by the empirical relation,

$$Tg = \frac{2}{3} Tm$$

The T_g of these polymers was found to be in the range of 280.0–333.3°C. The flow temperature (T_f) and other thermal properties of the polyhydrazides are summarized in Table 4, which show their excellent thermoxidative stability above their melting points, better than those polymers having P–N bonds already reported in literature[1,3].

TABLE 4
THERMAL PROPERTIES OF POLYHYDRAZIDES

Polymer Code	To[a]	SWR[b]	D^c_{max}	Tm[d]	Tg[e]	Tf[f]
I	320°C	430–460°C	500°C	490°C	326.6°C	500°C
III	330°C	360–400°C	530°C	415°C	280.0°C	460°C
IX	350°C	410–450°C	630°C	500°C	300.0°C	465°C
X	300°C	440–450°C	720°C	450°C	333.3°C	470°C

a = Initial decomposition temperature; b = Steep weight loss region; c = Maximum decomposition temperature; d = Polymer melt temprature; e = Calculated glass transition temperature; f = Flow temperature.

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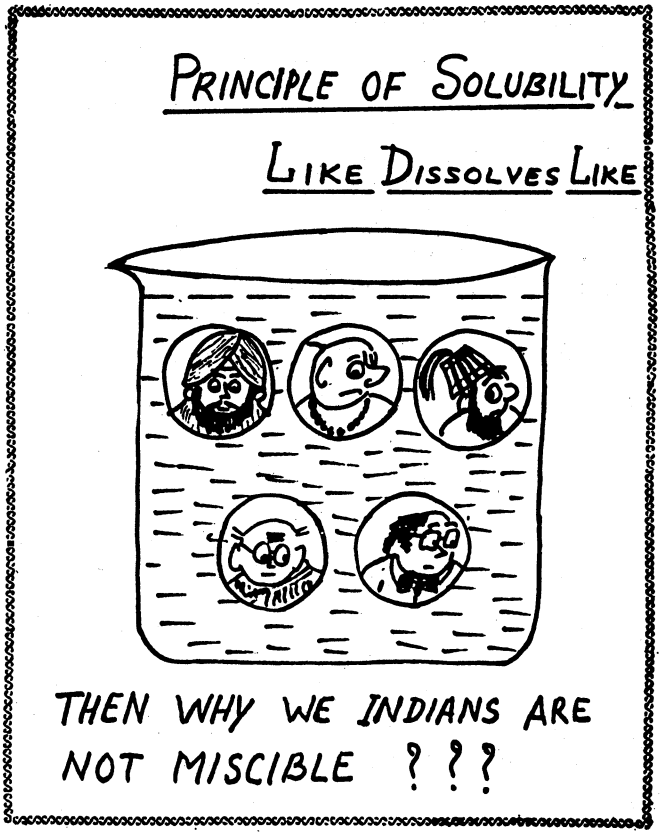

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