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Studies on Some Newer Polyhydrazides Containing Amide Linkages. Part IV

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ABSTRACT

Various newer polyhydrazides of high thermal stability were prepared by the low temperature solution polymerization of amino hydrazides with dicarboxylic acid chlorides. The inherent viscosity of these polymers varied from 0.20 to 0.34. Results of differential thermal analysis and thermogravimetric analysis indicate that decomposition starts above 180°C and the steep weight loss of the polymer takes place from 300 to 400°C. Melting points of crystalline polymers were determined by differential thermal analysis.

INTRODUCTION

It has long been known that incorporation of aromatic rings in linear polymers yields higher melting, stiffer, and more dimensionally stable polymers than the incorporation of comparable amounts of aliphatic units [1]. The pioneering work on the ordered copolymer approach was carried out mainly by Preston and co-workers of Monsanto [2-5]. Recently, synthesis of some thermally stable polyamides from aromatic diamines, aromatic triacetic anhydrides, aromatic

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bisamines-chloral derivatives, and terephthaloyl chlorides has been reported [6, 7].

In our previous communications we have reported the preparation and polymerization of various substituted bisamidobenzoic acid hydrazides and O,O-bisacetyl hydrazides [8-10].

Further attempts have been made to synthesize some polyhydrazides from different substituted aminobenzamidebenzhydrazides, and a detailed study of their thermal properties, inherent viscosity, and solubility has been carried out.

EXPERIMENTAL

Preparation of Monomers

Synthesis of Diacid Chlorides

Diacid chlorides were prepared by conventional methods.

Synthesis of Aminohydrazides

Ethyl p-(m'-Nitrobenzamido)benzoate. In a three-necked flask equipped with dropping funnel, mechanical stirrer, and condensor, 25 g of benzocaine was dissolved in 100 mL of dry benzene. A solution of m-nitro benzoyl chloride (28.1 g) in dry benzene was added to this solution. It was then refluxed for 3 h. p-(m'-Nitrobenzamido)-benzoic acid ester was obtained and crystallized with ethanol; mp 198°C, yield 45 g (94.5%).

p-(m'-Nitrobenzamido)benzhydrazide. A mixture of p-(m'-nitrobenzamido)benzoic acid ester (50 g), dry dioxane (100 mL), and 10 mL of hydrazine-hydrate (99-100%) was placed in a round-bottom flask. The mixture was refluxed gently for 36 h. A yellowish brown mass was obtained on cooling. It crystallized with dimethylformamide; mp above 350°C, yield 30 g (62.7%).

p-(m'-Aminobenzamido)benzhydrazide. 10 g of p-(m'-nitrobenzamido)benzhydrazide was dissolved in a 10% DMF solution in absolute alcohol. The solution was treated with Raney nickel and hydrazine-hydrate. The compound thus obtained was crystallized from dimethylacetamide; mp 164°C, yield 16 g (88.4%).

Similarly, other aminobenzamidobenzhydrazides were prepared (Table 1). 4,4'-Diaminodiphenyl methane and 4,4'-diaminodiphenyl sulfide were prepared according to the procedures reported in literature [11, 12].

Low Temperature Solution Polymerization

More consistent results were obtained by low temperature solution polymerization. A 10% solution of aminobenzamidobenzhydrazide or

TABLE 1. Characteristic of Monomeric Aminobenzamidobenzhydrazides[a]

Aminobenzamido benzhydrazides	Calc (%)			Found (%)				
	C	H	N	C	H	N	1*	2*
p(p'-Aminobenzamido)-benzhydrazide	62.22	5.18	20.74	61.10	5.74	20.62	3400-3350	1650-1700
p(m'-Aminobenzamido)-benzhydrazide	62.22	5.18	20.74	61.54	5.36	20.64	3480-3360	1650-1700
m-(p'-Aminobenzamido)-benzhydrazide	62.22	5.18	20.74	61.88	5.12	20.58	3380-3400	1650-1700
m-(m'-Aminobenzamido)-benzhydrazide	62.22	5.18	20.74	61.72	5.18	20.56	3400-3400	1650-1700

[a] 1* = IR stretching vibration (N–H cm^{-1}). 2* = IR peak of stretching of C=O.

diamine was cooled to -20°C and a solution of diacid chloride was added in portions with constant stirring for 3 h. It was neutralized by the addition of 95% of the theoretical amount of lithium hydroxide needed to neutralize HCl formed in the polymerization. The viscous solution that formed was stirred at room temperature for 8 h and then poured in a 10% methanol solution. A crystalline polymer was obtained.

Thermal Analysis

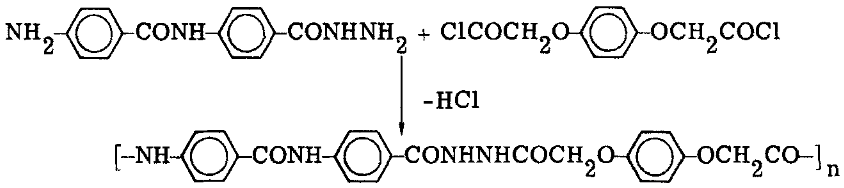
Thermogravimetric and differential thermal analysis were carried out in air. The heating rate was 5°C/min and the sample size was about 100 mg.

Infrared Absorption Spectroscopy

Infrared spectra was obtained on a Jasco Model A-I IR spectrophotometer by use of KBr disk method.

Density

Densities of polyhydrazides were determined by means of a small pycnometer at 30°C with H_2SO_4. The sample size was 500 mg.



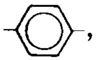
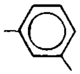
RESULT AND DISCUSSION

Inherent viscosities of polyhydrazides were observed in from 0.20 to 0.34 (Table 2). A comparative study of the inherent viscosity of the polymers revealed that a change from meta to para isomers increased the inherent viscosity remarkably.

IR spectra of polymers showed that the peaks of the para isomer of a polymer were more pronounced than its meta isomer. It may be interpreted as showing that the polymerization of para-substituted monomers is regular and results in more ordered structures, as reported by Preston and co-workers [13].

TABLE 2. Inherent Viscosity of Copolymers[a]

No.	Structure	Inherent viscosity at 30°C
I	$[\text{–NH–R–CONH–R–CONH.NH.COCH}_2\text{O–R–OCH}_2\text{CO–}]_n$	0.34
II	$[\text{–NH–R–CONH–R–CONH.NHCOCH}_2\text{O–R}'\text{–OCH}_2\text{CO–}]_n$	0.28
III	$[\text{–NH–R–CONH–R}'\text{–CONH.NHCOCH}_2\text{O–R–OCH}_2\text{CO–}]_n$	0.30
IV	$[\text{–NH–R–CONH–R}'\text{–CONH.NHCOCH}_2\text{O–R}'\text{–OCH}_2\text{CO–}]_n$	0.25
V	$[\text{–NH–R}'\text{–CONH–R–CONH.NH.COCH}_2\text{O–R–OCH}_2\text{O–}]_n$	0.26
VI	$[\text{–NH–R}'\text{–CONH–R–CONH.NHCOCH}_2\text{O–R}'\text{–OCH}_2\text{CO}]_n$	0.24
VII	$[\text{–NH–R}'\text{–CONH–R}'\text{–CONHNHCOCH}_2\text{O–R–OCH}_2\text{CO–}]_n$	0.22
VIII	$[\text{–NH–R}'\text{–CONH–R}'\text{–CONHNHCOCH}_2\text{O–R}'\text{–OCH}_2\text{CO–}]_n$	0.20
IX	$[\text{–NH–R–CH}_2\text{–R–NHCOCH}_2\text{O–R–OCH}_2\text{CO–}]_n$	0.28
X	$[\text{–NH–R–CH}_2\text{R–NHCOCH}_2\text{O–R}'\text{–OCH}_2\text{CO–}]_n$	0.23
XI	$[\text{–NH–R–S–R–NHCOCH}_2\text{O–R–OCH}_2\text{CO–}]_n$	0.26
XII	$[\text{–NH–R–S–R–NHCOCH}_2\text{O–R}'\text{–OCH}_2\text{CO–}]_n$	0.22

[a] R = , R' = .

THERMAL PROPERTIES OF THE POLYHYDRAZIDES

Thermogravimetric analysis of Polymers II, III, IV, V, and differential thermal analysis of Polymer VI are shown in Figs. 1 and 2, respectively. 100% volatilization of Polymer VI occurred at 460, 480, and 500°C in 3.5, 2.9, and 2.1 h, respectively.

Polyhydrazides showed no effect of temperature up to 180°C. Above that temperature the decomposition of polymers started, and the main region of weight loss was normally between 300 and 480°C. Polymer III showed a higher thermal stability than IV, and Polymer VII melted at a higher temperature than VIII. These variations in thermal stability suggest that a shift from meta to para isomer increases the thermal stability of polyhydrazides remarkably.

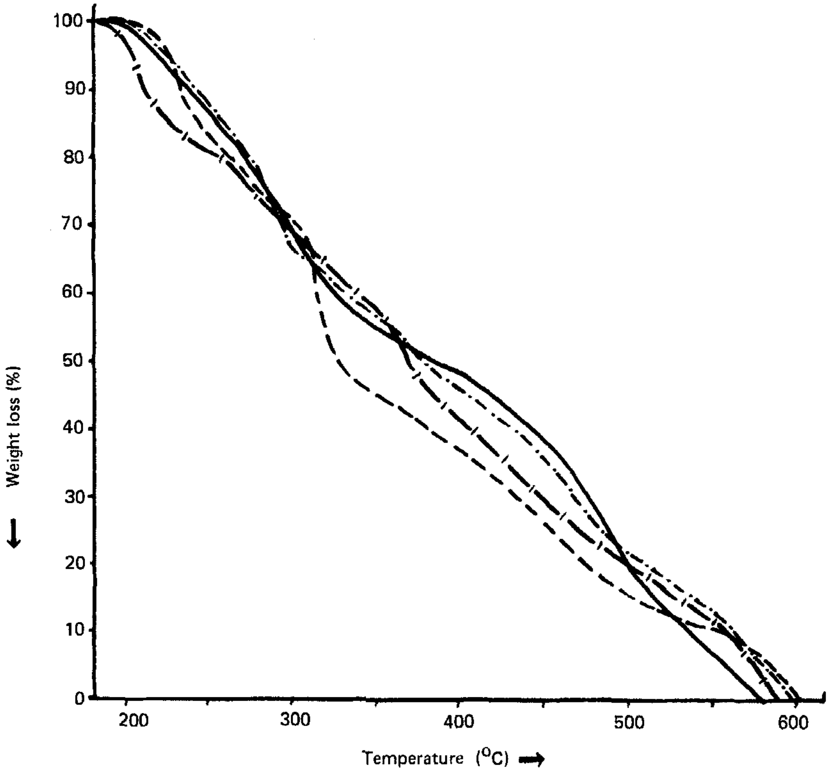


FIG. 1. TGA curves of Polymers II (--), III (-·-), IV (—), and V (-|-) in air.

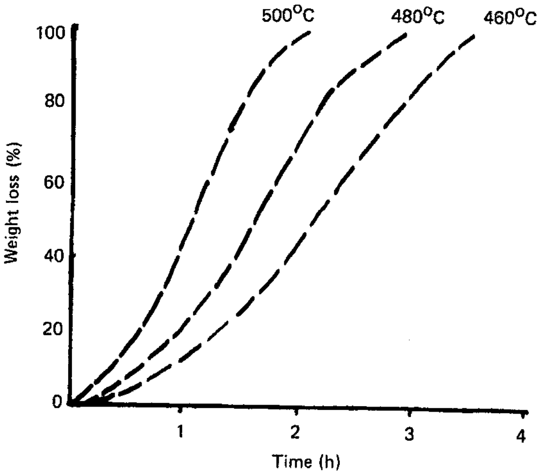


FIG. 2. Thermal degradation of Polymer VI.

SOLUBILITY OF POLYHYDRAZIDES

The solubilities of polyhydrazides are summarized in Table 3. All the polyhydrazides were soluble in strong acids, e.g., concentrated sulfuric acid and trifluoroacetic acid, as well as in such polar solvents as dimethylformamide and dimethylacetamide. The solubility of the polymers increased with the polarity of the solvents.

TABLE 3. Solubility of Polyhydrazides

	Solubility[a]			
Solvents	I	II	III	IV
H_2SO_4	++	++	++	++
CF_3COOH	++	++	++	++
DMF	++	++	++	++
DMAC	++	+	++	++
DMSO	+	++	+	++
Ethanol	-	-	-	±
Acetone	-	-	±	±

[a] ++ = Soluble at room temperature. + = Soluble on heating. ± = Partially soluble. - = Insoluble.

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REFERENCES

[1] R. Hill and E. E. Walker, J. Polym. Sci., 3, 609 (1948).
[2] J. Preston, Am. Chem. Soc., Polym. Prepr., 9, 1068 (1968).
[3] F. Dobinson and J. Preston, Ibid., 4, 2093 (1966).
[4] J. Preston and W. B. Black, J. Polym. Sci., Part C, 19, 7 (1967).
[5] J. Preston, H. S. Morgan, and W. B. Black, J. Macromol. Sci.–Chem., A7(1), 325 (1973).
[6] Sumitomo Chemical Co., Japanese Kokai Tokkyo Koho 80 120,628 (1980).
[7] Z. K. Brzozowski, A. Grakowska-Roslek, and Z. Przybzsz, J. Macromol. Sci.–Chem., A16(7), 1193 (1981).
[8] J. S. Shukla and H. Dwivedi, Ibid., A16(3), 681 (1981).
[9] J. S. Shukla and H. Dwivedi, Int. J. Polym. Mater., 9, 63 (1981).
[10] J. S. Shukla and P. K. Misra, "Studies on Some Newer Polyhydrazides Containing Amide Linkages. Part III," J. Polym. Sci., Polym. Chem. Ed., Communicated.
[11] Rivier and Farine, Helv. Chim. Acta, 12, 866 (1929).
[12] J. Preston, Sci. Technol., 2, 297 (1967).
[13] J. Preston, W. B. Black, and W. L. Hotterbert, Jr., J. Macromol. Sci.–Chem., 7(1), 67 (1973).

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