Studies of Some Newer Polyhydrazides Containing Amide Linkages. Part 1

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ABSTRACT

An attempt has been made to prepare some new polyamide hydra-
zides of high thermal stability with different dicarboxylic acid
chlorides by the solution polymerization technique. The polym-
erization was carried out at -20°C. Amide linkage was present
in each polymer unit. Results of thermal degradation and
thermogravimetric analysis indicate that these polymers melt
or decompose above 350°C, and the steep weight loss of the
polymer takes place in the range 360-390°C. Most of the poly-
hydrazides are soluble in organic solvents.

INTRODUCTION

The intrinsic thermal and oxidative stability of aromatic structures
have long been recognized, and a variety of polymers have been pre-
pared in which benzene rings are linked together in chains. In most
cases the connecting groups are less thermally stable than the rings,
and the stability of the polymers is largely determined by the nature
of these groups. Among more stable linking groups which have been
used are the amides and imides [1, 2]. Because of intermolecular
bonding and chain stiffness aromatic polyamides possess high thermal
stability [3-5].

Some polyamidohydrazides have been reported [6]. The physical properties of various polyhydrazides were studied by us [7].

We have further extended the work toward the synthesis of some newer monomers which were copolymerized with different aliphatic and aromatic dicarboxylic acid chlorides. A comparative study of their thermal properties, inherent viscosity, and solubility has been made.

EXPERIMENTAL

Preparation of Monomers

Synthesis of Diacid Chlorides

Diacid chlorides were prepared by conventional methods.

Synthesis of Tetramethylene 4,4'-Bis(p-amido-benzoic Acid Hydrazide)

Tetramethylene 4,4'-Bis(p-amidoethylbenzoate). In a 1-L three-necked flask equipped with dropping funnel, mechanical stirrer, and condenser, benzocaine (50 g) in dry benzene (200 mL) was taken. To this a solution of diacid chloride of adipic acid (27.72 g) in dry benzene was added with constant stirring. The mixture was refluxed for 2 h. A pale yellow mass of tetramethylene 4,4'-bis(p-amidoethyl benzoate) was obtained. It was crystallized from alcohol, mp 350°C, yield 65 g (99%).

The IR spectrum (KBr) showed a band at 1650-1700 cm^{-1}.

Tetramethylene 4,4'-Bis(p-amidobenzoic Acid Hydrazide). In a 500-mL round-bottomed flask was placed a mixture of tetramethylene 4,4'-bis(p-amidoethyl benzoate) (50 g) in dry dioxane and (20 mL) hydrazine hydrate (99-100%). The mixture was refluxed gently for 72 h. On cooling, a solid product was obtained. It was crystallized from dimethylformamide, mp above 350°C, yield 32 g (68.3%).

The IR spectrum (KBr) stretching vibrations were N–H 3300-3400 cm^{-1}, C=O 1670-1700 cm^{-1}.

Analysis: Calculated for $C_{20}H_{24}O_4N_6$: C, 58.25%; H, 5.82%; N, 20.37% Found: C, 57.92%; H, 5.80%; N, 20.28%.

Other hydrazides were prepared similarly.

These hydrazides were found stable toward air, light, moisture, and common organic solvents.

$$Cl\text{--}CO\text{--}(CH_2)_4\text{--}CO\text{--}Cl + 2EtOOC\text{--}\langle\bigcirc\rangle\text{--}NH_2 \longrightarrow$$

$$EtOOC\text{--}\langle\bigcirc\rangle\text{--}NHCO\text{--}(CH_2)_4\text{--}CONH\text{--}\langle\bigcirc\rangle\text{--}COOEt$$

$$EtOOC\text{--}\langle\bigcirc\rangle\text{--}NHCO\text{--}(CH_2)_4\text{--}CONH\text{--}\langle\bigcirc\rangle\text{--}COOEt \xrightarrow[\substack{\text{hydrate} \\ 99\text{-}100\%}]{\text{hydrazine}}$$

$$NH_2NHCO\text{--}\langle\bigcirc\rangle\text{--}CONH\text{--}(CH_2)_4\text{--}CONH\text{--}\langle\bigcirc\rangle\text{--}CONHNH_2$$
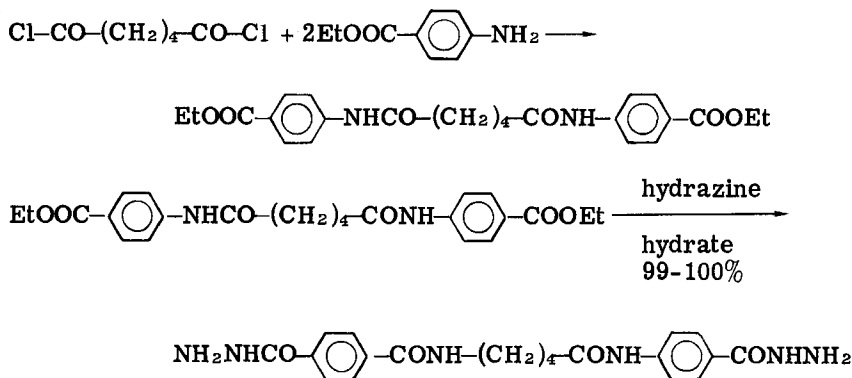
Low Temperature Solution Polymerization

We found that better results were obtained by low temperature solution polymerization than by any other type of polymerization.

A 10% solution of hydrazide was cooled to below -20°C and the solution of diacid chloride was added to it slowly with constant stirring over 2 h. Lithium hydroxide was added to neutralize the HCl formed during the reaction. The highly viscous solution of the polymer was stirred at room temperature for 8 h and then poured into a 10% methanol solution. A crystalline polymer was obtained.

Thermal Analysis

Thermogravimetric and differential thermal analysis (TG-DTA) were carried out in air. The heating rate was 10°C/min and the sample size was about 10 mg.

Differential scanning calorimetry (DSC) was performed. The sample size was about 12 mg and the heating rate was 10°C/min. The activation energy E_a of this thermal decomposition was obtained from an analysis of data from DSC at four different heating rates (5, 10, 15, and 20°C/min) according to

$$\log (\phi/T^2) = -E_a/2.4RT + \text{constant}$$

where ϕ is the heating rate, R is the gas constant, and T is the decomposition temperature. In this study the T is that of the vertex of the exothermic peak in the DSC curve.

Infrared Absorption Spectroscopy

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

TABLE 1. Characteristics of Monomeric Hydrazides

| p-Amidobenzoic acid hydrazides	Calculated, %			Found, %			Infrared stretching vibration N–H	Infrared peak of stretching of C=O
	C	H	N	C	H	N		
1. Tetramethylene-4,4'-bis(p-amidobenzoic acid hydrazide)	58.25	5.82	20.37	57.92	5.80	20.28	3300-3400	1670-1700
2. Octamethylene-8,8'-bis-(p-amidobenzoic acid hydrazide)	61.53	6.83	17.98	61.44	6.84	17.82	3250-3350	"
3. Phenyl,4,4'-bis-(p-amidobenzoid acid hydrazide)	61.11	4.62	19.44	61.22	4.62	19.43	3350-3450	"
4. Phenyl-3,3'-bis(p-amidobenzoic acid hydrazide)	61.11	4.62	19.44	61.02	4.60	19.04	3300-3400	"
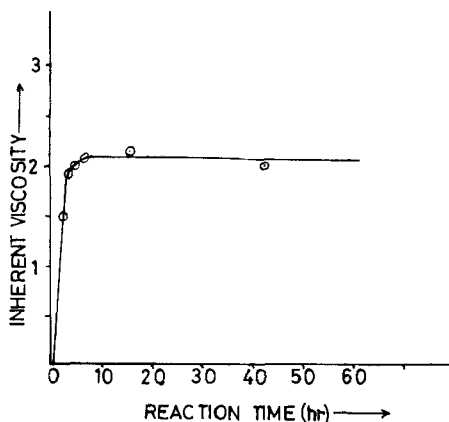
FIG. 1. Polymerization of octamethylene 8,8'-bis-(p-aminobenzoic acid hydrazide) with adipic acid chloride at room temperature.

Density

Densities of model compounds and polyhydrazides were determined by means of a small pycnometer at $30°C$ with H_2SO_4. The sample size was 100 mg.

RESULTS AND DISCUSSION

The model reaction between octamethylene 8,8'-bis-(p-amido-benzoic acid hydrazide) and adipic acid chloride was attempted. Infrared data showed that the products obtained from their reaction in dimethyl acetamide from $-20°C$ to room temperature for 4 h included a large amount of starting material. But when the reaction mixture was stirred at room temperature for 8 h, the expected results were obtained.

Figure 1 shows the rate of polymerization of octamethylene 8,8'-bis-(p-amidobenzoic acid hydrazide) with adipic acid chloride in dimethyl acetamide at room temperature in terms of the inherent viscosity of the resulting polymer. The polymerization of both monomers progressed at a reasonable reaction rate and went essentially to completion within 10 h at room temperature. The polymerization of octamethylene 8.8'-bis(p-amidobenzoic acid hydrazide) and aromatic acid chloride took place much more slowly.

It can be seen from Table 2 that because the polyhydrazides have inherent viscosities in the range of 3.2 to 2.1, the reaction variables had no or little effect on the attained molecular weight of the polyhydrazides. In the case of the reaction of phenyl-4,4'-bis-p-amido-benzoic acid hydrazide) with different aromatic *acid chlorides, the*

TABLE 2. Polyhydrazides[a]

No.	Structure	Inherent viscosity at 30°C
I	$-NHNHCO-R-NHCO-(CH_2)_8-CONH-R-CONHNHCO-R-CO-$	2.7
II	$-NHNHCO-R-NHCO-(CH_2)_8-CONH-R-CONHNHCO-R'-CO-$	2.5
III	$-NHNHCO-R-NHCO-(CH_2)_8-CONH-R-CONHNHCO-(CH_2)_8-CO-$	2.2
IV	$-NHNHCO-R-NHCO-(CH_2)_8-CONH-R-CONHNHCO-(CH_2)_4-CO-$	2.1
V	$-NHNHCO-R-NHCO-(CH_2)_4-CONH-R-CONHNHCO-R-CO-$	2.6
VI	$-NHNHCO-R-NHCO-(CH_2)_4-CONH-R-CONHNHCO-R'-CO-$	2.4
VII	$-NHNHCO-R-NHCO-(CH_2)_4-CONH-R-CONHNHCO-(CH_2)_8-CO-$	2.4
VIII	$-NHNHCO-R-NHCO-(CH_2)_4-CONH-R-CONHNHCO-(CH_2)_4-CO-$	2.0
IX	$-NHNHCO-R-NHCO-R-CONH-R-CONHNHCO-R-CO-$	3.2
X	$-NHNHCO-R-NHCO-R-CONH-R-CONHNHCO-R'-CO-$	2.9
XI	$-NHNHCO-R-NHCO-R-CONH-R-CONHNHCO-(CH_2)_8-CO-$	2.5
XII	$-NHNHCO-R-NHCO-R-CONH-R-CONHNHCO-(CH_2)_4-CO-$	2.2
XIII	$-NHNHCO-R-NHCO-R'-CONH-R-CONHNHCO-R-CO-$	2.3
XIV	$-NHNHCO-R-NHCO-R'-CONH-R-CONHNHCO-R'-CO-$	2.1
XV	$-NHNHCO-R-NHCO-R'-CONH-R-CONHNHCO-(CH_2)_8-CO-$	2.2
XVI	$-NHNHCO-R-NHCO-R'-CONH-R-CONHNHCO-(CH_2)_4-CO-$	2.1

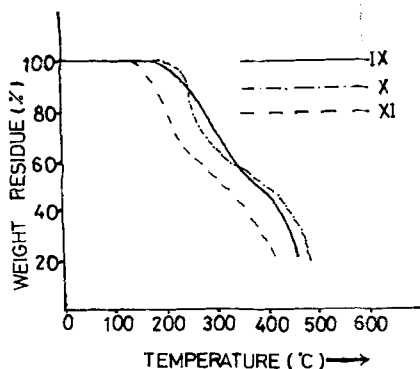[a] Where R = -⟨C₆H₄ (para)⟩- ; R' = -⟨C₆H₄ (meta)⟩-

FIG. 2. TGA curves of Polymers IX, X, and XI in air.

polymer formed an apparent gel or precipitated out of the reaction mixture during polymerization. This may be due to the limited solubility of the resulting polyhydrazides.

The polymers were identified as polyhydrazides by means of IR spectroscopy and elemental analysis. The IR spectra of the polymer showed a characteristic carbonyl absorption at 1650 to 1700 cm^{-1} and a N–H stretching band in the region of 3300 to 3400 cm^{-1}.

THERMAL PROPERTIES OF THE POLYHYDRAZIDES

Figures 2 and 3 show the results of thermogravimetric analysis (TGA) and differential thermal analysis (DTA), respectively, of the
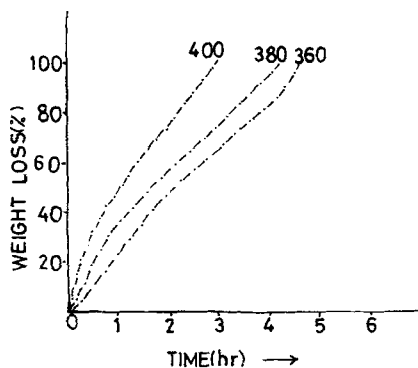

FIG. 3. Thermal degradation of Polymer VI in air.

TABLE 3. Thermodynamic Parameters of the Pyrolysis of Poly-
hydrazides at 400°C Determined from DSC Data

| | Decomposition temperature at various heating rates, °C | | | | |
No.	5°C/min	10°C/min	15°C/min	20°C/min	kcal/mol
I	395	404	409	412	56.50
II	392	402	407	411	60.49
III	393	400	406	410	65.22
IV	372	383	390	401	26.69

Polyhydrazides IX, X, XI, and VI (Table 2) in air. The TGA data
indicate that the thermal decomposition of the polyhydrazides proceeds
in three stages. The slope of the curve is a maximum at 300 to 360°C,
which shows the decomposition temperature.

From the results of thermal degradation of Polymer VI, it appears
that 100% volatilization occurred at 360°C in 4.5 h.

It is speculated that the latter moiety decomposed to a volatile
species by subsequent scission, resulting in a weight loss primarily
in the range 300 to 360, which indicated sublimation of the former
moiety.

Table 3 gives the thermodynamic parameters of pyrolysis in the
vicinity of 400°C as determined from differential scanning calorimetry
(DSC). Polyhydrazides I, II, and III (Table 2) have abnormally large
values of activation energy $[E_a]$ for thermal decomposition. In gen-
eral, it is accepted that thermal decomposition of polymer occurred
in the amorphous region. Marshall and Todd [8], in their study of
thermal degradation of poly(ethylene terephthalate), reported that the
value for E_a of viscous flow is about 40 kcal/mol. Therefore, if pro-
duction in the amorphous region participates in the rate-determining
step, the apparent value for E_a of thermal decomposition should be
about 40 kcal/mol. On the other hand, Patterson and Sheldon [9]
observed large values (77 and 88 kcal/mol) for dyeing with disperse
dyes. It seems that this idea is of importance to the system of
thermal decomposition in the present work.

SOLUBILITY OF POLYHYDRAZIDES

The solubility of the polyhydrazides is summarized in Table 4.
All were easily soluble in strong acids. The solubility of polyhydra-
zides increased in the following order: I < II < III < IV < V.

TABLE 4. Solubility of Polyhydrazides

Solvents	Solubility[a]				
	Polymer I	Polymer II	Polymer III	Polymer IV	Polymer V
H_2SO_4 (concentrated)	++	++	++	++	++
CF_3COOH	++	++	++	++	++
Pyridine	-	+	+	+	++
DMF	+	++	++	++	++
DMAc	++	++	++	++	++
DMSO	-	±	±	+	++
Dioxane	-	-	±	+	+
Ethanol	-	-	-	-	-
Acetone	-	-	-	-	±
Benzene	-	-	-	-	-

[a]Solubility: (++) soluble at room temperature, (+) soluble on heating, (±) partially soluble or swollen, (-) insoluble.

Polyhydrazides formed by aromatic acid chlorides were found less soluble than aliphatic acid chlorides. Introduction of a benzene ring instead of an aliphatic chain prevented solubility.

The solubility of polyhydrazides decreased with an increase in their crystallinity, which is in the reverse order of thermal stability. Therefore, by selecting the proper structural combination, it is possible to obtain polyhydrazides soluble in aprotic polar solvents and with high thermal stability.

REFERENCES

[1] H. Lee, D. Stoffey, and K. Nerille, New Linear Polymers, McGraw-Hill, New York, 1967.
[2] A. H. Frazer, High Temperature Resistant Polymers, Wiley-Interscience, New York, 1968.
[3] J. Preston, J. Polym. Sci., Part A-1, 4, 529 (1966).
[4] F. Dobinson and J. Preston, Ibid., 4, 2093 (1966).
[5] J. Preston and W. B. Black, J. Polym. Sci., Part C, 19, 7 (1967).

[6] J. Preston, H. S. Morgan, and W. B. Black, J. Macromol. Sci.–
     Chem., A7(1), 325 (1973).
[7] J. S. Shukla and H. Dwivedi, J. Polym. Sci., In Press.
[8] J. Marshall and A. Todd, Trans. Faraday Soc., 49, 67 (1953).
[9] D. Patterson and R. P. Sheldon, Trans. Faraday Soc., 55, 1254
     (1959).