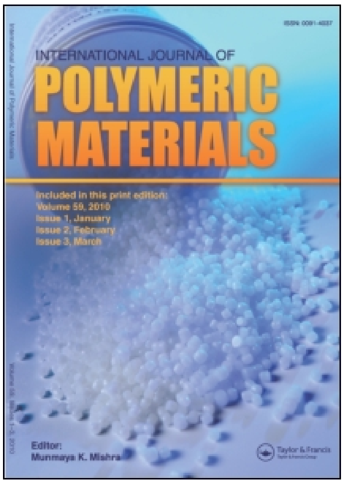

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Studies of Some Newer Polyhydrazides Containing Amide Linkage (Part II)

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Studies of Some Newer Polyhydrazides Containing Amide Linkage (Part II)

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Various *m*-hydrazides were polymerized with aliphatic and aromatic acid chlorides. Inherent viscosities of such newer polymers were measured and found in the range of 1.1 to 2.7. They exhibited high melting points. Thermogravimetric analysis (T.G.A.) and Differential thermal analysis (D.T.A.) were measured. These polymers decomposed between 300° and 350°C.

1. INTRODUCTION

In an earlier communication we have reported the preparation and polymerisation of different *p*-amido benzoic acid hydrazides.[1] Among polyamides reported, wholly aromatic polyamides,[2–4] were most thermally stable due to the stiffness of the polymer chain and hydrogen bonding of amide groups, but had limited solubility in most organic solvents. One approach towards the preparation of aromatic polyamides with good solubility consists in the replacement of the hydrogen of amide bond by an alkyl group. This leads to an increase in the solubility of polymers, accompanied by a decrease in the thermal stability.[5] Another approach is the introduction of cyclic side substituents containing polar groups. It was reported that these substituents did not impair the thermal stability of the modified polymers.[6] On the other hand, Korshak,[7] reported that polybenzimidazoles containing methyl groups in the benzene ring still retained a degree of thermal stability as high as unsubstituted ones and were soluble in organic solvents, while the introduction of a methyl group into the azole ring of polybenzimidazoles led to a more soluble polymer with lower thermal stability.

In the present paper some new polyhydrazides have been prepared. They were shown to have high thermal stability and good solubility in organic solvents.

2. EXPERIMENTAL PART PREPARATION OF MONOMERS

2.1 Synthesis of diacid chlorides

Diacid chlorides were prepared by conventional methods.

2.2 Synthesis of hydrazides: tetramethylene 4,4′-bis(m-amidobenzoic acid hydrazide)

2.2.1 *Tetramethylene 4,4′-bis(m-amidobenzoic acid ester)* In one litre three necked flask equipped with dropping funnel, mechanical stirrer and condenser was placed ethyl *m*-aminobenzoate (50 g) and dry benzene (200 ml). To this solution, di-acid chloride of adipic acid (27.72 g) was added with constant stirring. The mixture was refluxed for 3 hours. A yellowish brown liquid was obtained. It was distilled under reduced pressure. Yield 57.7 g (88%).

The infrared spectrum (KBr) showed a band at 1600–1700 cm^{-1}.

2.2.2 *Tetramethylene 4,4′-bis(m-amidobenzoic acid hydrazide)* In a 250 ml round bottomed flask was placed a mixture of tetramethylene 4,4′-bis(*m*-amidobenzoic acid ester) (20 ml) in dry dioxane and (10 ml) hydrazine hydrate (99–100%). The solution was refluxed gently for 36 hours and then distilled under reduced pressure. Yield 19.61 g (42%).

The infrared spectrum (KBr) showed absorption at 3350–3400 cm^{-1} (NHCO), 1650–1700 cm^{-1} C=O stretching. Analysis:

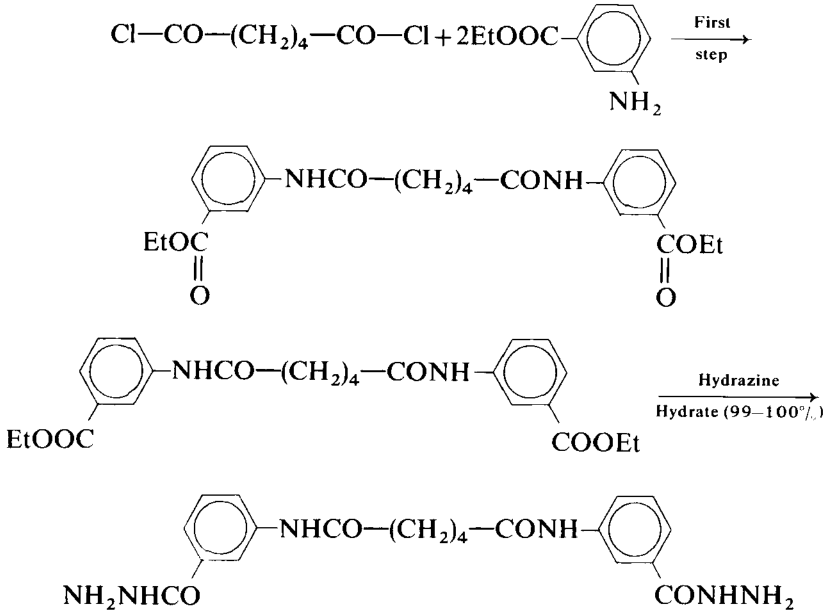
$C_{20}H_{24}O_4N_6$ Requires, C, 58.25%, H, 5.82%, N, 20.37%

Found, C, 58.20%, H, 5.72%, N, 20.31%.

In the same way the other hydrazide were prepared (Table I). These hydrazides were found stable towards air, light and moisture.

2.3 Low temperature solution polymerization

In a polymer container equipped with dropping funnel mechanical stirrer and condenser. bis(*m*-amido-hydrazide) in dimethyl acetamide was placed. The solution was cooled below −20°C by liquid air. To this, a solution of diacid chloride in DMAc was added portionwise with constant stirring for two hours. It was then neutralized by adding 95% of theoretical amount of lithium-hydroxide to neutralize HCl formed during reaction. The solution was stirred



for 8 h and poured into 10% methanol solution and the crystalline polymers were obtained.

By this method different polymers were prepared. They are given in Table II.

2.4 Thermal analysis

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

2.5 Activation energy

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

$$\log(\phi/T^2) = Ea/2.3\,RT + \text{constant}$$

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

TABLE I

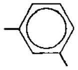
Characteristics of monomeric hydrazides

Hydrazides	Calculated % C	H	N	Found% C	H	N	I.R. Stretching vibration N—H	I.R. Peak of stretching of C═O
1. Tetramethylene 4,4′-bis(*m*-amidobenzoic acid hydrazide)	58.25	5.82	20.37	58.20	5.72	20.31	3300–3400	1650–1700
2. Octamethylene-8,8′-bis (*m*-amidobenzoic acid hydrazide)	61.53	6.83	17.98	61.92	6.72	17.42	3250–3300	1650–1700
3. Phenyl-4,4′-bis(*m*-amidobenzoic acid hydrazide)	61.11	4.62	19.44	61.34	4.55	19.43	3350–3400	1650–1700
4. Phenyl-3,3′-bis(*m*-amidobenzoid acid hydrazide)	61.11	4.62	19.44	60.94	4.60	19.28	3350–3400	1650–1700

TABLE II

Polyhydrazides

No.	Structure	Composition[a]	Yield	Inherent viscosity at 30°C
I	—NHNHCO—R′—NHCO—$(CH_2)_8$—CONH—R′—CONHNHCO—R—CO—	(50/50)	100	2.1
II	—NHNHCO—R′—NHCO—$(CH_2)_8$—CONH—R′—CONHNHCO—R′—CO—	(50/50)	99	1.5
III	—NHNHCO—R′—NHCO—$(CH_2)_8$—CONH—R′—CONHNHCO—$(CH_2)_8$—CO—	(50/50)	99	1.4
IV	—NHNHCO—R′—NHCO—$(CH_2)_8$—CONH—R′—CONHNHCO—$(CH_2)_4$—CO—	(40/60)	98	1.2
V	—NHNHCO—R′—NHCO—$(CH_2)_4$—CONH—R′—CONHNHCO—R—CO—	(50/50)	100	1.9
VI	—NHNHCO—R′—NHCO—$(CH_2)_4$—CONH—R′—CONHNHCO—R′—CO—	(50/50)	99	1.6
VII	—NHNHCO—R′—NHCO—$(CH_2)_4$—CONH—R′—CONHNHCO—$(CH_2)_8$—CO—	(50/50)	99	1.4
VIII	—NHNHCO—R′—NHCO—$(CH_2)_4$—CONH—R′—CONHNHCO—$(CH_2)_4$—CO—	(40/60)	98	1.1
IX	—NHNHCO—R′—NHCO—R—CONH—R′—CONHNHCO—R—CO—	(50/50)	99	2.7
X	—NHNHCO—R′—NHCO—R—CONH—R′—CONHNHCO—R′—CO—	(50/50)	98	2.3
XI	—NHNHCO—R′—NHCO—R—CONH—R′—CONHNHCO—$(CH_2)_8$—CO	(50/50)	98	2.4
XII	—NHNHCO—R′—NHCO—R—CONH—R′—CONHNHCO—$(CH_2)_4$—CO—	(40/60)	97	2.1
XIII	—NHNHCO—R′—NHCO—R′—CONH—R′—CONHNHCO—R—CO—	(50/50)	98	2.1
XIV	—NHNHCO—R′—NHCO—R′—CONH—R′—CONHNHCO—R′—CO—	(50/50)	99	1.8
XV	—NHNHCO—R′—NHCO—R′—CONH—R′—CONHNHCO—$(CH_2)_8$—CO—	(50/50)	98	1.5
XVI	—NHNHCO—R′—NHCO—R′—CONH—R′—CONHNHCO—$(CH_2)_4$—CO—	(50/50)	98	1.3

where R =  R′ = 

[a] bis Amido benzoic acid hydrazide, prereacted with dicarboxylic acid chloride.

3. RESULTS AND DISCUSSION

The polymers were synthesized and they are summarized in Table II. They were characterized by their elemental analysis and infrared spectra.

The model reaction between octamethylene 8,8′-bis-(*m*-amidobenzoic acid hydrazide) and adipic acid chloride was attempted.

Infrared data showed that the reaction was very slow. Because products obtained from their reaction in DMAc from −20°C to room temperature for 4 h included a large amount of starting material. When the reaction mixture was stirred at room temperature for 8 h, the expected results were obtained.

Figure 1 showed the rate of the polymerization of octamethylene, 8,8′-bis-(*m*-amido benzoic acid hydrazide) with adipic acid chloride at room temperature in terms of inherent viscosity of the resulting polymer. The polymerization of both monomers progressed with a reasonable reaction rate and went essentially to completion within 8 h. The polymerization of the same hydrazide with aromatic acid chlorides took place much more slowly.

It can be seen from Table II that the polyhydrazides were shown to have inherent viscosity in the range of 1.1 to 2.7. Increase in carbon chain of diacid chloride of aliphatic acid affected the viscosity remarkably. In the same way para-isomers also showed regular increase in inherent viscosity from meta-isomers.

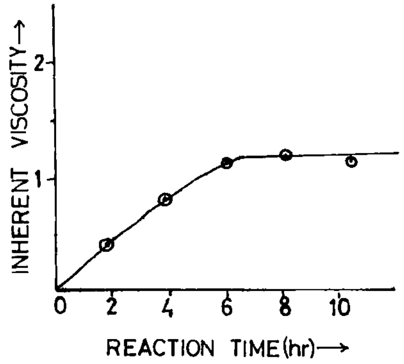


FIGURE 1 Polymerization of octamethylene 8,8′-bis(*m*-amidobenzoic acid hydrazide) with adipic acid.

3.1 Thermal properties of the polyhydrazides

The DTA and TGA profiles of polyhydrazides VI, IX, X, XI and XII (Table II) are shown in Figures 2 and 3. The crystalline polyhydrazides VI (Table II) exhibited monotonous curves of DTA having an endotherm above 350°C. On the other hand, polyhydrazides containing a metal linkage showed the peak corresponding to the glass transition temperature in the low temperature range about 250°C.

The thermal properties of polyamide hydrazides are summarized in Table III. The melting points of the polymer (PMT) was determined by the DTA endotherm that appears before the point maximal rate of weight loss of TGA. Polymer I, melted at higher temperature than II and polymer III melted a bit higher than IV. The polyhydrazide containing an isophthalyl linkage melted in the temperature range of about 240 to 280°C, while the polymer containing terephthaloyl linkage melted in the temperature range of about 280–300°C. Therefore both of the structural changes, that is change in isomeric form and change in length of carbon portion in aliphatic acid chloride, lowered the PMT by 30–40°C. These results suggest that thermal stability of polyhydrazides is greatly influenced by the variation in the isomeric form of the dicarboxylate acids component and to a relatively small degree by the introduction of methylene groups in the polymeric chain.

The temperature of 100% weight loss of starting polymer was used as another measure of thermal stability of polyhydrazides. Among the polyhydrazides II, IV, VII and VIII exhibited less thermal stability. The cause of this result has already been explained.

Table IV gives the thermodynamid parameters of the pyrolysis in the vicinity determined from differential scanning calorimetry (DSC). The value of *Ea* also explains the thermal stability. On taking a large value for thermal decomposition, this idea appears to be of importance to the system in this work. Therefore, it is probable that the production of an amorphous region in the closely packed structure participates essentially in the thermal de-

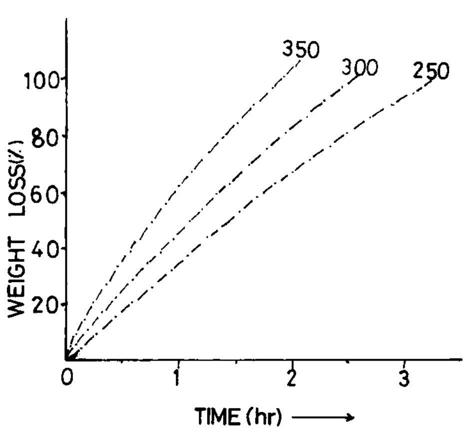


FIGURE 2 Thermal degradation of polymer VI.

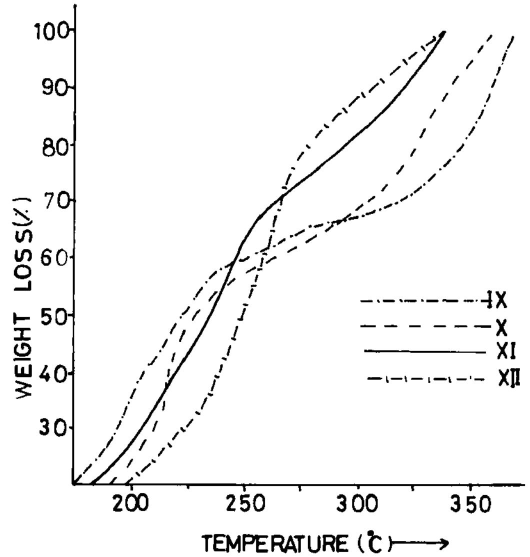


FIGURE 3 T.G.A. curves of polymer IX, X, XI and XII in air.

TABLE III

Thermal properties of polyhydrazides

Polymer code	TDT[a] °C	DT at different weight losses 20%	40%	60%	80%	100%	D Max[b]
I	165	175	225	250	262	375	360
II	154	183	213	265	302	362	350
III	144	180	223	247	300	345	325
IV	141	148	232	255	280	332	300

[a] Initial decomposition temperature.

[b] Decomposition maximum.

TABLE IV

Thermodynamic parameter of the pyrolysis of polyhydrazides at 400°C (determined from DSC data)

Polymer code	Decomposition temp. at various heating rate °C 5°C/min	10°C/min	15°C/min	20°C/min	*Ea* kcal/mole
I	352	360	365	368	54
II	346	350	355	360	60
III	318	325	328	330	62
IV	292	300	305	311	48

TABLE V

	Solubility[a]				
Solvents	Polymer I	Polymer II	Polymer III	Polymer IV	Polymer V
1. H_2SO_4 (concentrated)	++	++	++	++	++
2. CF_3COOH	++	++	++	++	++
3. Pyridine	±	±	+	+	++
4. DMF	+	++	++	++	++
5. DMAc	++	++	++	++	++
6. DMSO	+	++	++	++	++
7. Dioxane	±	±	+	+	+
8. Ethanol	−	−	±	±	−
9. Acetone	±	±	+	+	−
10. Benzene	−	−	−	−	−

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

composition of high-melting polymer and consequently requires large value of *Ea*.

3.2 Solubility of polyhydrazides

The solubility of polyhydrazides is given in Table V. All the polyhydrazides were soluble in strong acids such as concentrated sulphuric acid and trifloro acetic acid. In these solutions, there would be appreciable acid base interaction between solvent and solute molecules. By adding 5% lithium chloride the solubility of polymers increases.

In general the solubility of polymers is inversely related to its crystallinity. In this series the polyhydrazides of aromatic acid chlorides have less solubility than aliphatic. These results suggest that a particular type of properties may be developed by the appropriate combination of the monomers.

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