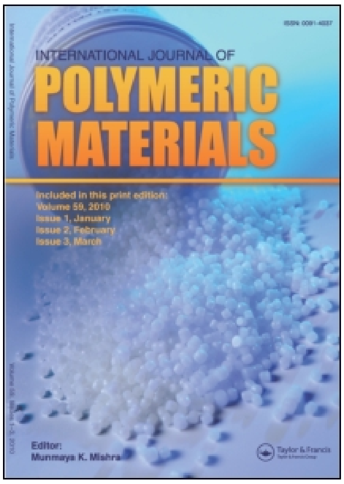

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Studies on Thermally Stable Polyamide Hydrazides Containing 1,3,4-oxadiazole Rings

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To cite this Article Shukla, J. S. and Dwivedi, Harish(1980) 'Studies on Thermally Stable Polyamide Hydrazides Containing 1,3,4-oxadiazole Rings', International Journal of Polymeric Materials, 8: 4, 265 — 273

To link to this Article: DOI: 10.1080/00914038008077954

URL: http://dx.doi.org/10.1080/00914038008077954

Intern. J. Polymeric Mater., 1980, Vol. 8, pp. 265–273
0091–4037/80/0804–0265 $06.50/0

Printed in Great Britain

Studies on Thermally Stable Polyamide Hydrazides Containing 1,3,4-oxadiazole Rings

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(*Received February 19, 1980*)

Polyamide hydrazides were co-polymerized with various amido hydrazides and di-acid chlorides. The study of polyamide hydrazides has been extended to different amido hydrazides which underwent intra molecular cyclization in the presence of polyphosphoric acid. Thermal decomposition of polymers was investigated by using programmed and isothermal thermogravimatric analysis (TGA). Reaction rates and overall activation energies were calculated from isothermal weight loss studies. In all samples, oxidation started above 250°C. Differential thermal analysis data (DTA) was used to determine the melting points of crystalline polymers.

1. INTRODUCTION

In connection with our work on polyhydrazides we report here various other new hydrazides.[1,2] Detailed studies on the polymerization of *N*-substituted dimethacrylamides have shown that the mechanism of cyclopolymerization may be interpreted by thermodynamic considerations and led us to the hypothesis that symmetrical unconjugated dienes having monofunctional counterparts which do not polymerize, were likely to give rise to highly cyclized polymer, if the unconjugated dienes can be polymerized.[3,4]

Certain amides which contain electron-withdrawing groups on their carbon atoms, thermally lose isocyanic acid in a manner which is completely analogous to the decarboxylation of an acid.[5]

The dimerization of styrene has been investigated by using acidic catalysts such as sulphuric acid,[6–10] phosphoric acid[10] and silica gel.[11]

In the continuation of our previous work, which has been reported earlier,[12] we have extended it further. The object of the present investigation was to introduce 1,3,4-oxadiazole rings by intramolecular cyclization by phosphoric acid. Comparative Thermal properties, inherent viscosity and solubility of these polymers were also studied.

2. EXPERIMENTAL

2.1 Starting materials

p-Aminobenzoic acid (BDH) was used without purification, diacids and hydrazine hydrate 99–100% (BDH) were used without purification.

All solvents were used of Sisco Chemical Industries, Bombay, India.

Most of the dihydrazides and di-acid chlorides were prepared several times, but only one experiment is described in this part. All experiments and extraction were carried out in air.

2.2 Synthesis of monomers

(1) *Di-acid chlorides* Di-acid chlorides were prepared by conventional methods.

(2) *Synthesis of octamethylene 8,8′-bis(p-amidobenzoic acid hydrazide)*

2.2.1 Octamethylene 8,8′-bis-(p-amidobenzoic acid ester) In a 500 ml. three necked round bottomed flask equipped with a mechanical stirrer, were placed *p*-amino benzoate (30 g) and dry benzene 150 ml. Di-acid chloride of sebacic acid (21.7 g) in dry benzene (100 ml.) was added drop-wise over a period of two hours. The solution was refluxed gently for two hours. The yellow suspension of octamethylene 8,8′-bis-(*p*-amidobenzoic acid ester) was obtained, it was filtered and unreacted solid was extracted in a soxhlent apparatus with benzene for nearly 3 days (most of the extraction was complete in 8 hours). A pale yellow solid residue was obtained. The desired product crystallized from Dimethyl formamide was filtered and dried. M.P. above 350°C, yield, 42.6 g. (99.4%).

The infrared spectrum (KBr Disk) showed absorption at 2850 cm^{-1} (sym. stretching of CH_2), 3937 cm^{-1} (asym. stretching of CH_2, 3250 cm^{-1} (NHCO) stretching, 1650 cm^{-1}, C=O stretching and 1525 cm^{-1} NH bending.

Analysis:

$C_{28}H_{36}O_6N_2$ Requires: C, 67.74%; H, 7.25%; N, 5.65%.

Found: C, 67.62%; H, 7.10%; N, 5.48%.

2.2.2 Octamethylene 8,8′-bis-(p-amidobenzoic acid hydrazide) In a 500 ml round bottomed flask was placed a mixture of octamethylene 8,8′-bis-(*p*-

TABLE I

Characteristics of monomeric hydrazides

P-amidobenzoic acid 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-(*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	6.86	17.82	3250–3350	,,
3. Phenyl-4,4′-bis-(*p*-amidobenzoic 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	,,

amidoethyl benzoate) (50 g) in dry dioxane and (20 ml) hydrazine hydrate (99–100 %). The mixture was refluxed gently for 72 hours. On cooling a solid product was obtained. It was crystallized from dimethyl formamide M.P. above 350°C, yield, 32 g. (67.9 %).

The infrared spectrum showed absorption at 1520 cm^{-1} (NH bending). Analysis:

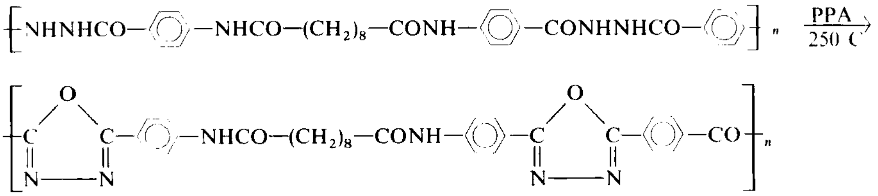
$C_{24}H_{32}O_4N_6$ Requires: C, 61.53 %; H, 6.83 %; N, 17.98 %.
Found: C, 61.44 %; H, 6.84 %; N, 17.82 %.

Similarly other hydrazides were prepared (Table I), octamethylene 8,8′-bis-(*p*-amido benzoic acid hydrazide) of high purity were obtained by thin layer chromatography (TLC). It is also important to note that these hydrazides were found to be stable towards air, light, moisture and common organic solvents.

2.2.3 Preparation of polyamide hydrazides We found that better results were obtained by low temperature solution polymerization.

A 10 % solution of hydrazide was cooled below −20°C and the solution of di-acid chloride was added to it by portionwise with constant stirring over 2 hours. It was then neutralized by the addition of 95 % of the theoretical amount of Lithium hydroxide needed for HCl formed during the reaction. The highly viscous solution of polymer was stirred at room temperature for 8 hours and then poured into 10 % methanol solution. A crystalline polymer was obtained.

2.2.4 Intramolecular cyclization In a three necked flask equipped with dropping funnel, mechanical stirrer and condenser polyamide hydrazide (20 g) was dissolved in 50 ml. dry DMAc. To this cold polyphosphoric acid acid was added with constant stirring. The mixture was heated slowly up to 250°C. The acid was neutralized by sodium carbonate solution. A crystalline polymer was obtained.



2.2.5 Thermal analysis Thermogravimetric and differential thermal analysis (TG-DTA) were carried out in air. 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. Heating rate was 10°C/min. The activation energy (EA) of thermal decomposition was obtained from analysis data of DSC at four different heating rates i.e. 5, 10, 15 and 25°C/min. according to the following equation.

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

(where $\emptyset$ = Heating rate, R = gas constant, T = decomposition temp.)

2.2.6 Infrared absorption spectroscopy Infrared spectra were obtained on a JASCO Model A-1 infrared spectrophotometer by use of the KBr Disk method.

2.2.7 Density Density of model compounds and polyoxadiazoles were determined by means of a small pyknometer at 30°C with H_2SO_4. The sample size was 100 mg.

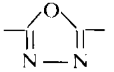
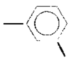
3. RESULTS AND DISCUSSION

The rate of cyclization of amidohydrazide in terms of inherent viscosity are given in Figure 1. The cyclization took place rapidly and reaction was complete in 4.5 hours at 250°C. This phenomenon corresponds well with the results of model compounds studied. It is also important to note that at room temperature, the polymer IX (Table II) showed a very slow change in

TABLE II

Poly 1,3,4-oxadiazoles

No.	Structure	Temp[a] (°C)	Yield %	PMT[b]	Inherent viscosity of 30°C	Solubility
I.	—R—R′—NHCO—$(CH_2)_8$—CONH—R′—R—R′—CO—	200	92	300	3.0	+ +
II.	—R—R′—NHCO—$(CH_2)_8$—CONH—R′—R—R″—CO—	200	90	300	2.8	+ +
III.	—R—R′—NHCO—$(CH_2)_8$—CONH—R′—R—$(CH_2)_8$—CO—	200	88	300	2.8	+ +
IV.	—R—R′—NHCO—$(CH_2)_8$—CONH—R′—R—$(CH_2)_4$—CO—	200	85	250	2.5	± ±
V.	—R—R′—NHCO—$(CH_2)_4$—CONH—R′—R—R′—CO—	150	86	250	2.9	± ±
VI.	—R—R′—NHCO—$(CH_2)_4$—CONH—R′—R—R″—CO—	150	85	250	2.6	+ +
VII.	—R—R′—NHCO—$(CH_2)_4$—CONH—R′—R—$(CH_2)_8$—CO—	150	85	250	2.7	+ +
VIII.	—R—R′—NHCO—$(CH_2)_4$—CONH—R′—R—$(CH_2)_4$—CO—	150	86	250	2.4	±
IX.	—R—R′—NHCO—R′—CONH—R′—R—R′—CO—	250	90	325	3.4	±
X.	—R—R′—NHCO—R′—CONH—R′—R—R″—CO—	250	92	325	3.2	±
XI.	—R—R′—NHCO—R′—CONH—R′—R—$(CH_2)_8$—CO—	250	90	325	3.1	± ±
XII.	—R—R′—NHCO—R′—CONH—R′—R—$(CH_2)_4$—CO—	250	90	300	3.0	± ±
XIII.	—R—R′—NHCO—R″—CONH—R′—R—R′—CO—	250	91	350	2.9	±
XIV.	—R—R′—NHCO—R″—CONH—R′—R—R″—CO—	250	88	350	2.8	±
XV.	—R—R′—NHCO—R″—CONH—R′—R—$(CH_2)_8$—CO—	250	85	300	2.6	± ±
XVI.	—R—R′—NHCO—R″—CONH—R′—R—$(CH_2)_4$—CO—	250	85	250	2.5	± ±

where R =  ; R′ =  ; R″ = 

[a] Temperature of cyclization.
[b] Polymer melt temperature.
[c] Solubility in cyclization medium.
Elemental analysis of C, H, and N was in the range of ±0.5%.

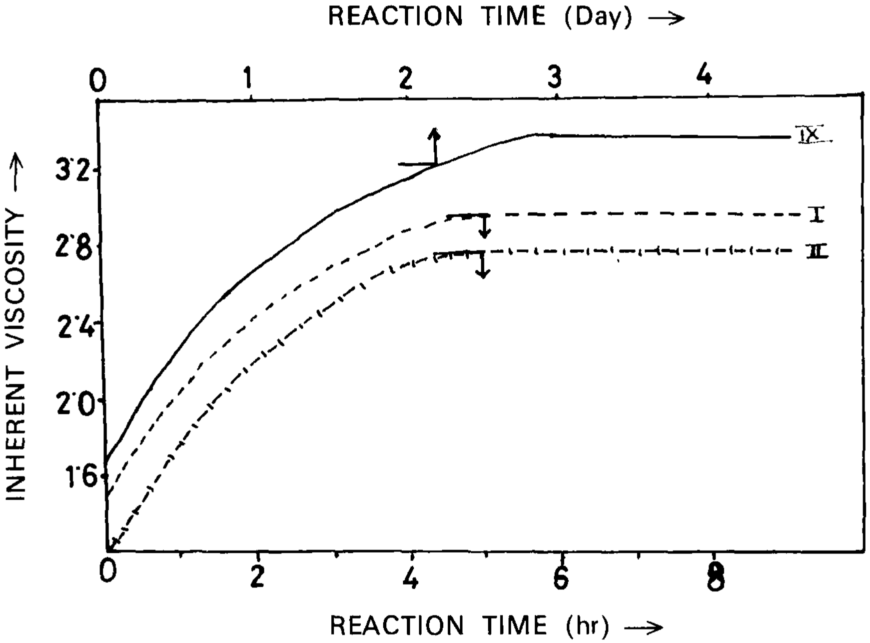


FIGURE 1

inherent viscosity. In about 3 days the maximum viscosity reached 3.4. But polymers I and II showed a very fast change in inherent viscosity and in about 5 hours they gained maximum inherent viscosity i.e. 3 and 2.8 respectively.

In general, reasonably high molecular weight polyamide-oxadiazole (ηinh = 2.4) could be made quite readily from the aromatic polyamide hydrazides in polar aprotic solvents, in which the polymer remained dissolved and thus had the opportunity to reach maximum molecular weight. On the other hand, with some exceptions, the poly amidohydrazide of aliphatic di-hydrazide in the cyclization media produced polymer precipitation which yielded limited molecular weight polyamides (ηinh = 2.4).

Polymers thus obtained were identified by means of infrared spectroscopy and elemental analysis. The infrared spectra of the polymer showed a characteristic carbonyl absorption at 1650–1700 cm^{-1} and N—H stretching band in the range of 3250–3400 cm^{-1}. These spectra closely resembled those of the model compounds.

3.1 Properties of polymers

The structure of the polymers from different combinations of monomers gave some differences in solubility but not in thermal stability. The solubility of polymers is given in Table III, they were not soluble in a wide range of solvents. Although all polymers were soluble in concentrated H_2SO_4 and partially soluble or swallen in other polar aprotic solvents.

The thermal stability of a pure organic material is regularly determined by the so-called "decomposition temperature", which depends critically on experimental conditions. This dependence on operational procedure is particularly severe with T.G. Techniques for polymer characterization.

Thermal stability properly adopted in the present investigation, is known as Integral Procedural Decomposition Temperature (IPDT). The data analysis technique was developed primarily for estimating relative thermal stability from dynamic T.G. analysis data.

The thermal behaviour of the poly(amide oxadiazoles) was calculated by means of differential thermal analysis (DTA) and thermo gravimetric analysis (TGA). Figures 2 and 3 show the DTA and TGA curves of polymer V, I, II, and III (Table II) and some of the polyamide oxadiazoles having aliphatic chains had melting a temperature of around 350°C as determined by DTA, while the aromatic poly(amide hydrazide) showed no observable transitions below 400°C. In air these polyamide hydrazides began to decompose at about 400°C and weight losses were gradual until temperatures of 400–450°C were reached, when decomposition occurred rapidly. Thus there

TABLE III

Solubility of Polyoxadiazoles

			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 swallen; (−) insoluble.

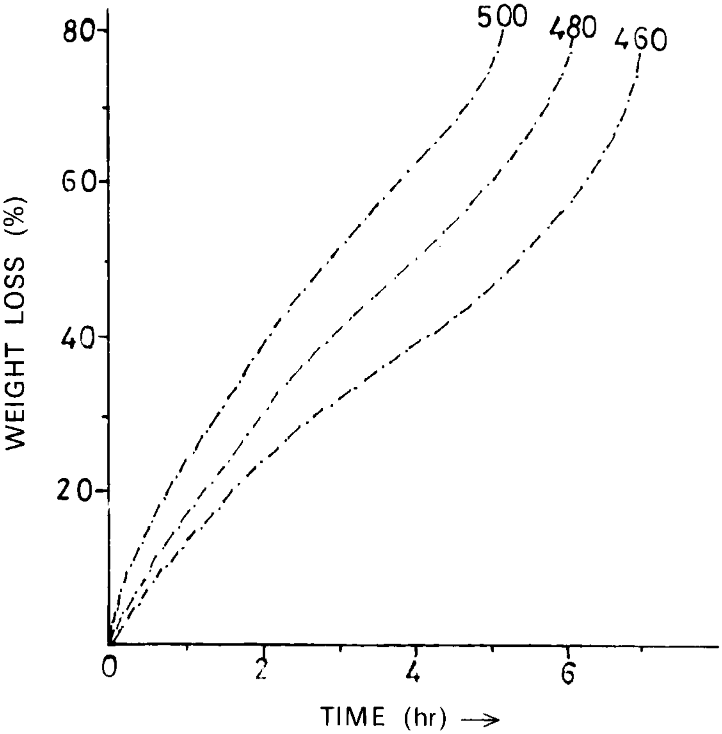


FIGURE 2

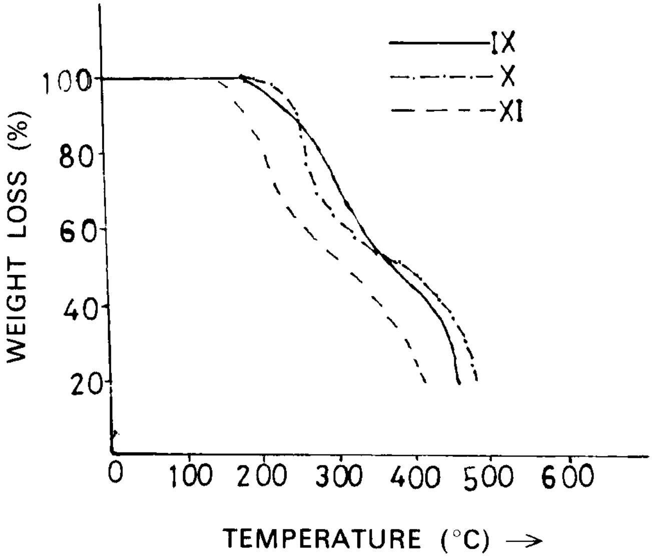


FIGURE 3

TABLE IV

Thermodynamic parameters of the pyrolysis of polyhydrazides at 400°C. Determined from DSC data

	Decomposition temp. at various heating rate °C				
Code	5°C/min	10°C/min	15°C/min	20°C/min	E KCal/mol
I	399	407	420	424	57.50
II	395	404	408	418	58.48
III	393	402	407	415	66.21
IV	391	400	405	415	62.43

is remarkable stability by the introduction of oxidiazole ring on to the polymer backbone, and thermal stability of all the poly(amido oxadiazole) appeared to be higher than polyamidehydrazides.

Table IV gives thermogravimetric parameters for the pyrolysis in the vicinity of 400°C determined from differential scanning calorimetry (DSC). Polymer III and IV (Table II) have the abnormally large value of activation energy Ea for thermal decomposition. In general it is expected that the thermal decomposition of polymer occurs in the amorphous region. Marshall and Tida, in their study of the thermal degradation of poly(ethylene terephthalate) reported that the value for Ea of viscous flow was about 40 KCal/mol. Therefore, if the production of the amorphous region participates in the rate determining step, the apparent value for Ea of thermal decomposition should be about 40 KCal/mol. From the results of activation energy it is also clear that these poly(amide oxadiazoles) are quite stable.

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