spectrum showed **19**, approximately 10% of **20**, and traces of starting olefin. After evaporation of the solvent the residue was taken in dichloromethane (10 ml), washed twice with 10 ml of water, dried over magnesium sulfate, filtered, and evaporated. Removal of **20** by crystallization from dichloromethane–ether left **19** in purity as a colorless oil; IR (NaCl neat) 3050 (w, =C—H), 1755 and 1720 ($COOCH_3$), 1655 (C=C); NMR ($CDCl_3$) 2.67 (s, 1, =C—H), 3.58 (t, J = 54 Hz, 1, CF_2H), 6.22 and 6.27 (2s, 12, $COOCH_3$). Anal. Calcd for $C_{12}H_{14}F_2O_8$: C, 44.45; H, 4.35. Found: C, 44.24; H, 4.54.

Tetramethyl 3-Oxa-1,4-pentadiene-1,1,5,5-tetracarboxylate (20). This compound was obtained when **18** was kept in closed vials for a while and is the major constituent of the residue of distillation of the olefin: IR (KBr) 3070 (=C—H), 1725 ($COOCH_3$), and 1615 (C=C); NMR ($CDCl_3$) 2.29 (s, 2, =C—H), 6.18 (s, 6, $COOCH_3$), and 6.22 (s, 6, $COOCH_3$); mass spectrum 302 ($M^{\cdot+}$, 13%), 143 ($(MeOOC)_2C{=}CH^{\cdot+}$) (100%); mp 156–158 °C. Anal. Calcd for $C_{12}H_{14}O_9$: C, 47.69; H, 4.67. Found: C, 47.82, H. 4.73.

Cyanomethylenetriphenylphosphorane (21). Triphenylphosphine (262 g, 1 mol) and chloroacetonitrile (75.5 g, 1 mol, 63 ml) were refluxed overnight in 500 ml of toluene. The crude salt was filtered and dissolved in 1800 ml of water with filtration. Chloroform, 800 ml, was added to the filtrate. To the strongly stirred mixture was added dropwise a solution of 40 g (1 mol) of sodium hydroxide in 270 ml of water. The reaction was followed with pH paper. When the mixture remained neutral, the addition was stopped and the two layers were separated. The water layer was washed with 500 ml of chloroform and the combined organic layers were backwashed with 500 ml of water, dried for several hours over magnesium sulfate, filtered, and evaporated. Crystallization of the residues from benzene gave 221.4 g (overall yield 73%) of cyanomethylenetriphenylphosphorane (**21**), mp 190–192 °C (lit.[12] 186–187 °C).

Dimethyl 2-Cyanoethylene-1,1-dicarboxylate (23). To an ice–water cooled solution of dimethyl oxomalonate (**22**) (14.6 g, 100 mmol) in 200 ml of benzene was added over 1 min cyanomethylenetriphenylphosphorane (**21**) (30.1 g, 100 mmol). After 20 min the benzene was evaporated and ether was added to crystallize as much triphenylphosphine oxide and side product as possible. When no further solid precipitated the remaining liquid was distilled to give, after some fractions containing the olefin and dimethyl oxomalonate, olefin **23** in purity (8.5 g, 50% yield, bp 97–100 °C (1.4 mm)); IR (NaCl neat) 2200 (C≡N), 1725 ($COOCH_3$), 1625 (C=C); NMR ($CDCl_3$) 3.45 (s, 1, C–H), 6.08 and 6.13 (2s, 6, $COOCH_3$). Anal. Calcd for $C_7H_7NO_4$: C, 49.71; H, 4.17; N, 8.28; O, 37.84. Found: C, 49.50; H, 4.16; N, 8.13; O, 38.12.

Copolymerizations. All copolymerizations were done in bulk working with 5 mmol of each monomer and 4 mg of AIBN. At the end of the polymerization the polymers were dissolved in chloroform or dimethyl formamide, precipitated in methanol, washed with methanol, and dried overnight at 54 °C.

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N,N'-Biisomaleimide. 2. Polyhydrazides[1]

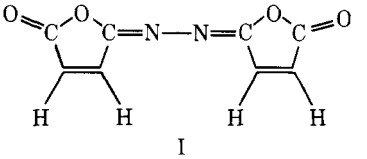
Y. L. Fan

Union Carbide Corporation, Chemicals and Plastics, Research and Development Department, Bound Brook, New Jersey 08805. *Received October 4, 1976*

ABSTRACT: *N,N'*-Biisomaleimide undergoes a rapid ring-opening polymerization with a variety of dihydrazides in polar media to yield the corresponding polyhydrazides. These polyhydrazides are largely amorphous and exhibit many nylon-like properties. Upon heating at elevated temperatures, the hydrazide linkages in these polymers are converted to the corresponding 1,3,4-oxadiazole ring structure.

The synthesis of low molecular weight polyhydrazides was first reported in 1942 in a French patent[2] from the condensation of hydrazine with dicarboxylic acids in alcohol. A high-temperature solution polymerization technique developed by McFarlane and Miller[3] produced usually either insoluble polymeric products or low molecular weight materials. The low-temperature solution polymerization route using a dihydrazide and a diacylchloride, developed by Frazer and Wallenberger,[4] was shown to yield soluble polyhydrazides of much higher molecular weight. The polyhydrazides and their post-cyclization derivatives have been studied quite extensively both in this country[5] and abroad.[6,7]

The polymerization of *N,N'*-biisomaleimide with various dihydrazides, characterizations of the resulting polyhydrazides, and their post-cyclization reactions were studied in the present work.



I

Experimental Section

***N,N'*-Biisomaleimide (I)** was prepared from hydrazine and maleic anhydride and purified according to the procedures given in the literature.[8] The product used for polymerization had an mp of 260 °C (lit.[3] 260 °C). Anal. Calcd for $C_8H_4N_2O_4$: C, 50.00; H, 2.04; N, 14.58. Found: C, 50.15; H, 2.19; N, 14.68.

Dihydrazides were prepared from the reaction of dimethyl (or diethyl) ester of a dibasic acid and excess hydrazine hydrate in methanol. The crude product was purified by recrystalization from aqueous ethanol solution. Dihydrazides so prepared include: oxalyl dihydrazide

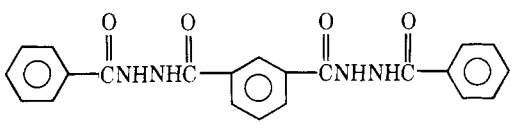
Table I
Solution Polymerization of *N,N'*-Biisomaleimide with Aliphatic Dihydrazides

$(CH_2)_n$-$(C(O)NHNH_2)_2$ where n =	Polym conditions: Solvent	T, °C	t, h	Reduced viscosity,[a] dL/g	T_g, °C	T_t,[b] °C	T_d,[c] °C	Characteristics of polymer
0	DMSO	45	50	0.13	71	146	215	Greenish yellow solid
1	DMSO	RT	17	0.29	65	173	219	Greenish yellow solid[d]
1	DMSO	15	21	0.28				Greenish yellow solid
1	DMSO	67	17	0.22				Greenish yellow solid
1	DMSO	80	22	0.15				Greenish yellow solid
2	DMSO	RT	22	0.27	76	137	200	Greenish yellow solid
4	DMSO	RT	22	0.23	78	183	225	Greenish yellow solid
8	DMSO	RT	18	0.58				Greenish yellow solid[e]
8	HMPA	RT	18	0.36	77	144	210	Yellow solid

[a] Measured in DMSO at 25 °C. [b] $\alpha\beta$ transition temperature. [c] Decomposition temperature. [d] Calcd for $C_{11}H_{12}N_6O_6$: C, 40.74; H, 3.70; N, 25.93. Found: C, 40.39; H, 3.68; N, 25.74. [e] Calcd for $C_{18}H_{26}N_6O_6$: C, 51.18; H, 6.16; N, 19.91. Found: C, 51.63; H, 6.21; N, 20.01.

mp 241 °C (lit.[9] 241 °C), malonyl dihydrazide mp 155–157 °C (lit.[9] 154 °C), succinyl dihydrazide mp 168–169 °C (lit.[9] 168 °C), adipoyl dihydrazide mp 176 °C (lit.[9] 178 °C), sebacyl dihydrazide 179 °C (lit.[9] 184–185 °C), terephthaloyl dihydrazide mp > 300 °C (lit.[10] 325 °C dec), isophthaloyl dihydrazide mp 224–225 °C (lit.[10] 224–225.6 °C), phthaloyl dihydrazide mp > 300 °C, fumaryl dihydrazide mp 126–127 °C, and acetylene dicarboxyloyl dihydrazide mp > 300 °C.

Dibenzoylisophthaloyl Dihydrazide (II). A solution of 0.21 mol of benzoyl chloride in 50 ml of hexamethylphosphoramide (HMPA) was added slowly into a slurry containing 0.1 mol of isophthaloyl dihydrazide and 100 ml of HMPA. The reaction was carried out under a nitrogen blanket and was kept below 10 °C with an external ice bath. A clear solution was obtained after overnight stirring. A white solid was recovered by pouring the solution in water. The product was washed with water repeatedly, filtered, and dried at 70 °C under vacuum. The yield was 99%, and the product had a mp of 232 °C. Anal. Calcd for $C_{22}H_{18}N_4O_4$: C, 65.67; H, 4.48; N, 13.93. Found: C, 65.38; H, 4.53; N, 13.77



II

Solution Polymerization of I and Dihydrazides. To a solution of 0.01 mol of dihydrazide in 50 ml of dry dimethyl sulfoxide (DMSO) was added at room temperature 0.01 mol of I. A mild exothermic reaction occurred immediately and the reaction mixture was stirred under nitrogen overnight. Polymer was recovered by coagulating in either water or an acetone–ether mixture and followed by vacuum drying at 70 °C.

Low-Temperature Solution Polymerization. A slurry of 0.005 mol of I and 0.01 mol of dihydrazide in 20 ml of *N,N'*-dimethylacetamide (DMAA) was stirred and warmed gently, if necessary, under a nitrogen atmosphere, to give a homogeneous solution. The latter was cooled with an external brine bath to a temperature between −10 and −20 °C, and 0.01 mol of a finely divided lithium chloride powder was added under vigorous stirring. Thereafter, a solution of 0.005 mol of a diacid chloride in 5 ml of DMAA, which had been precooled to −5 °C, was rapidly introduced into the reaction vessel with a hypodermic syringe. An exothermic reaction occurred immediately and the reaction medium became viscous rapidly. Polymer was recovered by the same procedures described earlier.

Post Cyclization in Argon Atmosphere. Finely divided polyhydrazide powder was carefully dried under vacuum at 100 °C. A sample was weighed and placed in a ceramic disk. The latter was transferred immediately into a Hoskins Furnace equipped with a quartz tube which had been preheated to the desired temperature. The system was under an argon atmosphere throughout the experiment. At the end of the heating cycle the sample was removed from the furnace and allowed to cool down to room temperature under argon atmosphere. The sample was then weighed and characterized.

Post Cyclization in Polyphosphoric Acid Solution. Twenty milliliters of polyphosphoric acid was preheated under a nitrogen atmosphere to 200 °C. While under vigorous stirring, 0.0025 residual weight of a polyhydrazide as finely divided particles was added all at once. The mixture was stirred at 200 °C for the desired period of time. After cooling to room temperature, the product was recovered by pouring the reaction mixture into a large excess of ice–water which was filtered, washed repeatedly with water, and dried under vacuum at 100 °C.

Instrumentation. IR spectra were obtained from potassium bromide pellets using a Beckman IR-5 instrument. DSC traces were measured with a Du Pont 990 thermal analyzer in nitrogen at a heating rate of 10 °C/min. Melting points were taken with a Thomas-Hoover capillary apparatus. Unless otherwise specified, all reduced viscosities were measured in DMSO at 25 °C with a capillary viscometer. Mechanical properties were determined in accordance with the ASTM procedures using solution-cast films.

Results and Discussion

Solution Polymerization of *N,N'*-Biisomaleimide with Dihydrazides. *N,N'*-Biisomaleimide reacts readily with the aliphatic dihydrazides in a polar medium such as DMSO or HMPA. Because a dihydrazide is usually a poorer nucleophile than its corresponding diamine, a longer reaction time is usually required to complete the reaction. The polymerization conditions and some characterizations of the resulting polyhydrazides are listed in Table I.

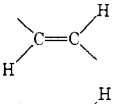
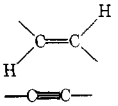
In the aliphatic polyhydrazide series, reasonably high reduced viscosity polymers were obtained only from the higher homologues of the dihydrazides. Polymerizations carried out at temperatures greater than room temperature tend to yield products of significantly lower molecular weights.

Polymerization of *N,N'*-biisomaleimide with the aromatic dihydrazides leads, in most instances, to low molecular weight polymers. DMSO is again the preferred polymerization medium. Polyhydrazides based on fumaric or acetylene dicarboxylic dihydrazides exhibit only limited solubility in DMSO and would precipitate from the medium at low degrees of polymerization. They are soluble, however, in concentrated sulfuric acid.

Low-Temperature Solution Polymerization. Because of the limited success in the preparation of aromatic polyhydrazides via the solution polymerization method described above, a low-temperature solution polymerization technique[4] was investigated. By this method, 1 mol of I is reacted with 2 mol of a dihydrazide to form the hypothetic adduct III. The latter is subsequently polymerized with 1 mol of a diacyl chloride at low temperatures in the presence of an acid acceptor. The sequence of reactions is represented schematically in Scheme I, where X and Y are divalent arylene radicals; aromatic polyhydrazides having reduced viscosities up to 0.57 have been prepared by this method. Experimental results are compiled in Table III.

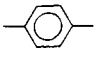
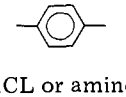
DMAA containing lithium chloride was used as the polymerization medium in most of the preparations. It functions not only as a solvent for the polymer but also an acid acceptor to facilitate the condensation reaction. The use of more basic

Table II
Solution Polymerization of *N,N'*-Biisomaleimide with Aromatic and Olefinic Dihydrazides

$R(C(O)NHNH_2)_2$ Where R =	Polym conditions: Solvent	T, °C	t, h	Reduced viscosity, dL/g[a]	T_t, °C	T_d, °C	Characteristics of polymer
	DMSO	RT	23	0.10	169	245	Greenish yellow solid
	HMPA	0–5	4	0.15	172	226	Greenish yellow solid
	DMAA	RT	14	0.14			Greenish yellow solid
	DMSO	RT	19	0.30			Greenish yellow solid
	DMSO	RT	65	0.05	152	218	Yellow solid
	DMSO	RT	0.5	Insoluble	142	214	Greenish yellow solid
	DMSO/ pyridine	10	4	0.15[b]			Yellow solid[e]
	DMSO	RT	1.5	Insoluble	[f]	280[c]	Pale yellow solid

[a] Measured in DMSO at 25 °C. [b] Measured in H_2SO_4 at 25 °C. [c] Measured by melting point technique. [d] Calcd for $C_{16}H_{14}O_6N_6$: C, 49.74; H, 3.63; N, 21.76. Found: C, 49.37; H, 3.59; N, 21.71. [e] Calcd for $C_{12}H_{12}O_6N_6$: C, 42.85; H, 3.57; N, 25.00. Found: C, 42.61; H, 3.51; N, 25.32. [f] Not detected in DSC traces.

Table III
Low-Temperature Solution Polymerization of I–Dihydrazide Adducts with Diacyl Chloride

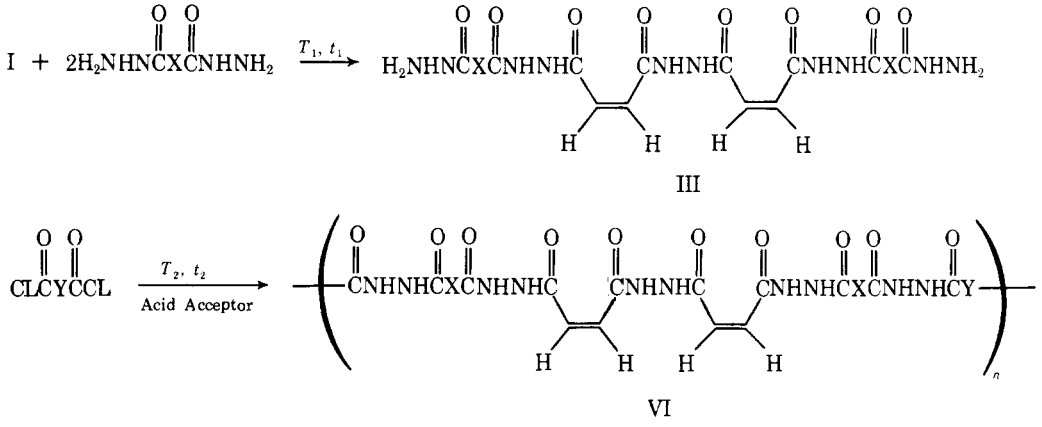
$H_2NHNC(O)$-$XC(O)NHNH_2$ where X =	ClC(O)-YC(O)Cl where Y =	Polym conditions: Solvent[a]	T_1, °C	t_1, h	T_2, °C	t_2, min	Reduced viscosity,[b] dL/g	T_t, °C	T_d, °C	Characteristics of polymers
Hydrazine		DMAA LiCL	−20	0.5	−20	180	0.12	168	230	Yellow solid
		DMAA LiCL	RT	4	−20	150	0.57	[c]	230	Greenish yellow solid[e]
		DMAA Triisopropyl-amine	RT	16	−20	80	0.22		225[d]	Greenish yellow solid
		DMAA Triethylene-diamine	RT	16	−20	80	0.19		225[d]	Greenish yellow solid
		DMAA pyridine	RT	16	−20	80	0.17		225[d]	Greenish yellow solid
		DMAA LiCL	RT	2	−5	180	0.39	186	257	Greenish yellow solid[f]
		DMAA LiCL	RT	2	−12	180	0.36	186	257	Greenish yellow solid

[a] Containing LiCL or amine equivalent to twice the molar amount of acyl chloride used. [b] Measured in DMSO at 25 °C. [c] Not detected in DSC traces. [d] Measured by melting-point technique. [e] Calcd for $C_{32}H_{26}N_{10}O_{10}$: C, 54.08; H, 3.66; N, 19.72. Found: C, 53.61; H, 3.39; N, 20.01. [f] Calcd for $C_{32}H_{26}N_{10}O_{10}$: C, 54.08; H, 3.66; N, 19.72. Found: C, 53.59; H, 3.40; N, 19.65.

agents, such as tertiary amines, as acid acceptors resulted in lower molecular weight products. We suspect that it may be the consequent of a chain-terminating reaction between an acyl chloride group at a growing chain end and a tertiary amine molecule to give a monomide group and an alkyl halide.[11]

Attempts to prepare aliphatic polyhydrazides by this method led only to insoluble products. The occurrence of isomerization at the maleic double bonds[1] also could be responsible in addition to the known limited solubility of aliphatic polyhydrazides in these solvents.[4]

Scheme I



Polymer Structure. On the basis of model reactions studied earlier,[12] polymers prepared by the solution polymerization and low-temperature solution polymerization techniques may be represented by structures V and IV, respectively.

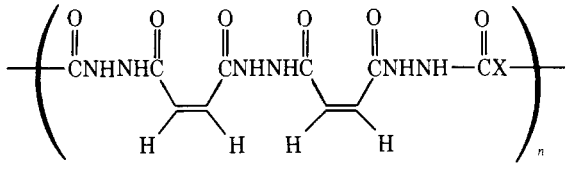
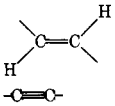
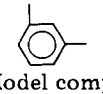


Table IV lists the characteristic frequencies in the infrared region of these polymers together with those of a model compound, II. The presence of hydrazide linkages in these polymers is consistent with the observed spectra. The latter are also in good agreement to assignments reported by Mashima[13] on some similar hydrazide compounds.

The occurrence of maleic double bonds in these polymers can be readily detected by the use of NMR spectroscopy. Isomerization induced either thermally or catalytically will lead eventually to insoluble materials.[1]

Physical Properties. Polyhydrazides derived from I are solids with a characteristic greenish yellow or yellow color.

Table IV
Infrared Frequencies[a] of Polyhydrazides Derived From *N,N'*-Biisomaleimide

Polymer X =	NH stretching, cm^{-1}	Amide I, cm^{-1}	Amide II, cm^{-1}	Amide III, cm^{-1}
$-CH_2-$	3230	1665	1535	1240
$-(CH_2)_4-$	3240	1670	1500	*b*
$-(CH_2)_8$	3250	1690	1525	1290
	3220	1665	1540	*b*
$-C\equiv C-$	3200	1720	1550	1270
	3260	1670	1530	1260
	3250	1660	1530	1260
X = Y = 	3250	1650	1500	1246
Model compd II	3240	1690 1640	1535	1300 1270

[a] Measured from KBr pellets. [b] Not detected.

Their solubility behavior is similar to that of the (amide–hydrazide) copolymers reported earlier.[1] Film or fiber may be fabricated from their solutions.

X-ray diffraction patterns measured at room temperature revealed little crystallinity in these polyhydrazides. Some physical and mechanical properties of two representing members are shown in Table V.

Aliphatic polyhydrazides were found by DSC measurement to have a T_g between 65 and 80 °C. The DSC values were about 10 to 15 °C lower than those determined by the temperature-modulus measurements. Because of the likelihood of moisture absorption during the sample preparation and/or measurement, these values may be substantially below the true value. Aromatic polyhydrazides failed to exhibit a well-defined T_g in their DSC traces. Temperature-modulus measurements revealed, however, that some could have a T_g as high as 170 °C.

A small exotherm was observed in the DSC traces of most of the polyhydrazides within the temperature range from 140 to 190 °C. This phenomenon was also observed on other polyhydrazides[14] and has been suggested to arise from a $\alpha\beta$ transition between the intra- and intermolecularly hydrogen-bonded structures.[16] This transition temperature is designated as T_t in Tables I–III.

Post Cyclization. When these polyhydrazides are heated in an inert atmosphere to temperatures around or greater than 200 °C, an apparent chemical reaction takes place as evidenced by a rapid darkening in color and gas evolution. This decomposition temperature (T_d) is accompanied by a strong exotherm in the DSC traces. Such a reaction has been shown

Table V
Some Physical and Mechanical Properties of Polyhydrazides Derived from *N,N'*-Biisomaleimide

Polymer	V X = $-(CH_2)_8-$	IV X =  Y = 
Reduced viscosity, dL/g[a]	0.58	0.34
Tensile strength,[b] psi	4600	6000
Tensile modulus,[b] psi	340 000	340 000
Elongation,[b] %	5	1–7
Tensile impact strength,[c] (ft. lb.)/in.[3]	30	Low
Oxygen permeability,[d] (mL (STP) mil)/(100 in.^{2} 24 h atm)	4.4	2.5
Water absorption,[e] % by wt	17	21

[a] Measured in DMSO at 25 °C. [b] ASTM D638. [c] ASTM D1822. [d] ASTM D1434-66 method M. [e] ASTM D-570-63.

Table VI
Cyclodehydration of Polyhydrazides

Polyhydrazide		Conditions			Poly(1,3,4-oxadiazole)			
Type	RV,[a] dL/g	Medium	T, °C	t, min	Characteristics	RV,[b] dL/g	Mp, °C	Conversion, %
V, X = $-(CH_2)_8-$	0.42	Argon	300	1/2	Dark brown, brittle solid	0.085	180–210	71
	0.42	Argon	180	120	Dark brown, brittle solid	0.09	183–210	57
	0.42	Polyphosphoric acid	200	180	Dark brown, solid	0.12	186–310	Low[d]
IV, X = Y = 	0.57	Polyphosphoric acid	200	120	Dark brown, solid	0.09	>310	100[d]

[a]Measured in DMSO at 25 °C. [b]Measured in H_2SO_4 at 25 °C. [c]Calculated from weight loss. [d]Calculated from oxygen analysis.

by previous workers to arise from an intramolecular cyclization of the hydrazide linkage to the corresponding 1,3,4-oxadiazole ring.[4]

As shown in Table VI, cyclodehydration of the aliphatic polyhydrazides resulted in partially converted products as determined by either weight-loss or oxygen-analysis methods.

Progress of the cyclodehydration was also followed by the disappearance of the NH stretching and amide I frequencies which are characteristic of the hydrazide group and the appearance of new absorption frequencies (1720–1430 cm^{-1}) due to the formation of 1,3,4-oxadiazole ring in the infrared.[5,13,16] The presence of residual NH stretching frequencies in the resulting polymers is consistent to the observation that only partially converted poly(1,3,4-oxadiazoles) were obtained.

Transformation to the poly(1,3,4-oxadiazole) appeared to occur more readily with the aromatic polyhydrazides. As shown in Table VI, an aromatic polyhydrazide was converted quantitatively to the corresponding poly(1,3,4-oxadiazole) through dehydration in a hot polyphosphoric acid solution.

Poly(1,3,4-oxadiazoles) prepared by these methods are brittle, dark-brown solids of apparently low molecular weight nature. They exhibit very little solubility in organic solvents but are soluble in concentrated sulfuric acid. Other poly(1,3,4-oxadiazoles) were reported to have similar solubility behavior.[5]

Acknowledgment. The author is indebted to Dr. D. F. Pollart of the Union Carbide Corporation for helpful discussions throughout the course of this investigation.

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