Poly-1,2,4-triazoles and Poly-1,3,4-oxadiazoles from Precursor Poly-N-acylhydrazines[1]

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ABSTRACT: High molecular weight (η_{inh} = 1.1) soluble poly-N-acylhydrazidine was prepared from low temperature solution polycondensation of 2,6-pyridinediyldihydrazidine with isophthaloyl chloride. Poly-N-acylhydrazidine was converted by heating in strong acids such as trifluoroacetic to the corresponding poly-1,3,4-oxadiazole (η_{inh} = 0.63). Whereas conversion of the precursor poly-N-acylhydrazidine predominantly to poly-1,2,4-triazole (η_{inh} = 0.65) was affected by refluxing in solvents such as *m*-cresol or by solid state advancement at 280° to 350° under an inert atmosphere. The poly-1,2,4-triazole was contaminated with 1.4–4.0% 1,3,4-oxadiazole depending upon the heating rate. Poly-N-acylhydrazidine was of sufficient molecular weight to cast a clear yellow film which exhibited good flexibility. The film, upon thermal treatment to temperatures as high at 300°, became brittle. The poly-1,3,4-oxadiazole and poly-1,2,4-triazole exhibited thermal decompositions by TGA between 450 and 520°. Prior to polymer synthesis, a series of model compounds were prepared as a guide to polymer synthesis and identification.

High molecular weight polyhydrazides obtained from the low temperature solution reaction of hydrazine or arylenedihydrazides with aromatic dicarboxylic acid chlorides are precursors for the formation of thermally stable poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles. Frazer, Wallenberger, and coworkers[2–4] have described their work on the preparation of poly-1,3,4-oxadiazoles by thermal cyclodehydration of the precursor polyhydrazides. Holsten and Lilyquist[5] prepared poly(4-phenyl-1,2,4-triazoles) by reacting the precursor polyhydrazides with aniline in polyphosphoric acid.

Saga and Shono[6] prepared poly-1,3,4-oxadiazoles and poly-1,2,4-triazoles from common precursor polymers, poly-N-acylamidrazones, obtained from the reaction of oxalamidrazone with various dicarboxylic acid chlorides. In addition, Korshak, Kronguaz, and Rusanov[7] recently described their work on the preparation of poly-1,2,4-triazoles by cyclodehydration of precursor polymers obtained from the low-temperature polycondensation of aromatic dihydrazidines (amidrazones) with aromatic dicarboxylic acid chlorides.

Concurrent with the work of Korshak, the versatility of hydrazidines in polymer synthesis was being explored in our laboratories. It was of interest to prepare thermally stable polymers by this route and to determine if quantitative conversion of the precursor polymers, poly-N-acylhydrazidines, to poly-1,2,4-triazoles or poly-1,3,4-oxadiazoles occurred. In this initial effort, polymer work was confined to that obtained from the reaction of 2,6-pyridinediyldihydrazidine and isophthaloyl chloride as shown in eq 1.

Results and Discussion

Model Compounds. Prior to polymer synthesis, a series of model compounds as shown in Table I was prepared to obtain information regarding reaction conditions necessary for polymer formation and to obtain model compounds to aid in polymer identification. Model compounds were prepared from the reaction of 2-pyridylhydrazidine with benzoyl chloride and also with isophthaloyl chloride, and from the reaction of 2,6-pyridinediyldihydrazidine with benzoyl chloride. The latter reaction is shown in eq 2.

The precursor intermediates (N-acylhydrazidines) were prepared in quantitative yields by low temperature solution condensation or by the interfacial method. Quantitative conversion to 1,3,4-oxadiazoles was effected at elevated temperature in solution using strong acids such as dichloroacetic, trifluoroacetic, phosphoric, or sulfuric. Although the N-acylhydrazidines could be readily converted to the corresponding oxadiazole at elevated temperature (100°) in sulfuric acid, degradation occurred as indicated by uv and nmr spectroscopy when the N-acylhydrazidine was allowed to stand at ambient temperature in sulfuric acid.

Under an inert atmosphere at elevated temperature (250–300°) in a melt or in refluxing solvents such as N-methylpyrrolidone, *m*-cresol, or hexamethylphosphoramide, the intermediate N-acylhydrazidines were converted predominantly to 1,2,4-triazoles. Analysis of the trapped exit gases revealed small amounts of ammonia which are evolved during the cyclization of the N-acylhydrazidine to oxadiazole. The amount (0.8–3.6%) of ammonia appeared to be dependent upon the heating rate. Introduction of a tube containing the N-acylhydrazidine under nitrogen into a preheated oil bath at 300° resulted in the maximum (3.6%) evolution of ammonia, whereas, when a *m*-cresol solution was heated from ambient temperature to reflux, the minimum (0.8%) evolution of ammonia was observed. The results obtained in this manner compared favorably with those estimated from the nmr spectra of the crude products.

This general route for the synthesis of 1,2,4-triazoles

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[1] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

[2] (a) A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci., Part A*, 2, 1147 (1964); (b) A. H. Frazer and F. T. Wallenberger, *ibid., Part A*, 2, 1171 (1964).

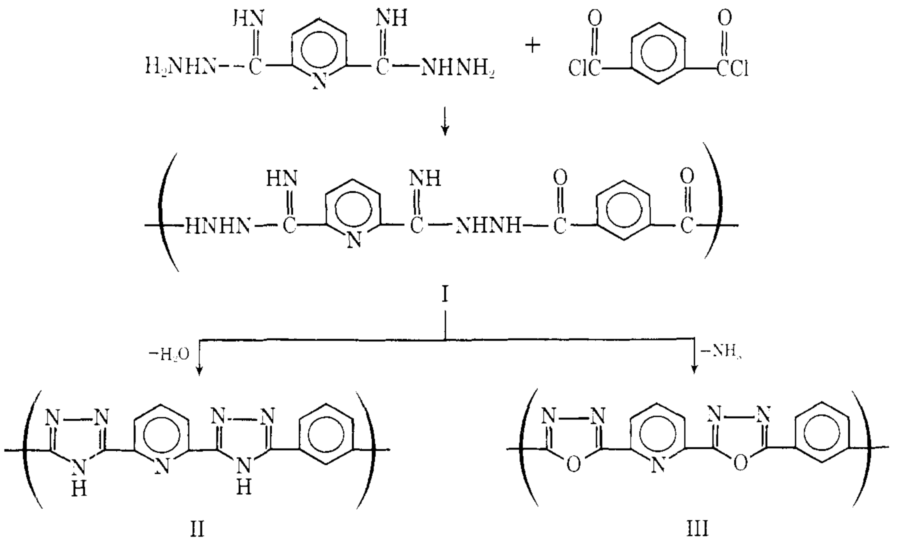
[3] A. H. Frazer, W. Sweeny, and F. T. Wallenberger, *ibid., Part A*, 2, 1157 (1964).

[4] A. H. Frazer and I. M. Sarasohn, *ibid., Part A-1*, 4, 1649 (1966).

[5] J. R. Holsten and M. R. Lilyquist, *ibid., Part A*, 3, 3905 (1965).

[6] M. Saga and T. Shono, *ibid., Part B*, 4, 869 (1966).

[7] V. V. Korshak, Ye S. Krongauz, and A. L. Rusanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 11, 2663 (1968).



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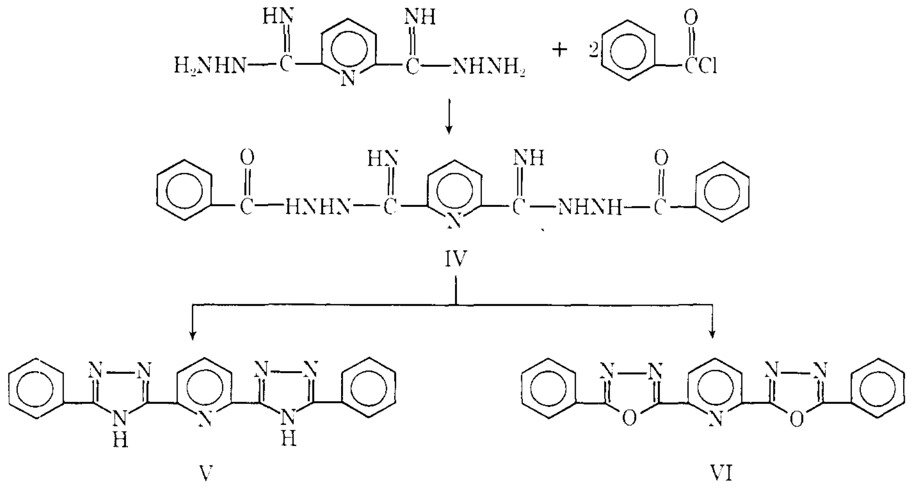
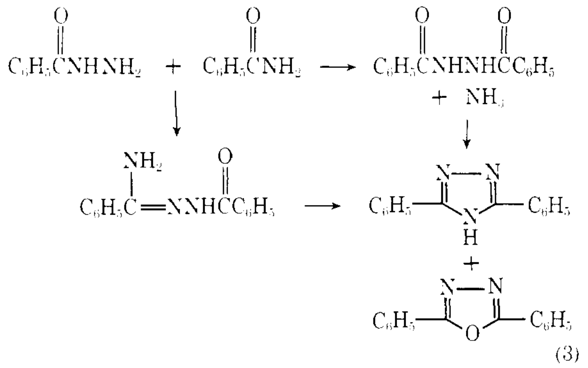


(2)

and 1,3,4-oxadiazoles has been known for many years. In 1889, Bladin[8] condensed carboxylic acid anhydrides and acid chlorides with aryl-substituted amidrazones to obtain aryl-1,2,4-triazoles. A few years later in 1897, Pinner[9] treated N-acylamidrazones with nitrous acid to obtain 1,3,4-oxadiazoles. It is also interesting to note that 1,3,4-oxadiazoles are among the by-products of the Pellizarri reaction which involves heating hydrazides and amides at high temperatures in the absence of a solvent to yield *s*-triazoles. Pellizarri[10] proposed the formation of a diacylhydrazide with the elimination of ammonia to account for 1,3,4-oxadiazole whereas Potts[11] proposed the formation of an intermediate acylhydrazidine which cyclizes to 1,3,4-oxadiazole and 1,2,4-triazole as represented in eq 3.

Other means of converting the N-acylhydrazidines to oxadiazole or triazole such as refluxing in acetic anhydride, thionyl chloride, or in *m*-cresol containing a catalytic amount of *p*-toluenesulfonic acid were given a cursory examination but the crude products obtained were either very impure or not the desired compound.



(3)

For example, when N-benzoyl(2-pyridyl)hydrazidine was refluxed in acetic anhydride, the major component in the product was 3-(2-pyridyl)-5-methyl-1,2,4-triazole.

All the model compounds appeared to be hygroscopic with the relative affinity for hydration decreasing from N-acylhydrazidine to triazole to oxadiazole. In most instances, drying at 100–120° for 4 hr under high vacuum removed the hydrated water except for N,N′-dibenzoyl-2,6-pyridinediyldihydrazidine (IV). Drying to temperatures as high as 200° failed to achieve complete removal of the tightly bound water.

The uv spectra of a series of model compounds from the reaction of 2,6-pyridinediyldihydrazidine and

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(8) J. A. Bladin, *Ber.* **22**, 3114 (1889).
(9) A. Pinner, *Ann.*, **297**, 221 (1897).
(10) G. Pellizarri, *Gazz. Chim. Ital.*, **41**, 20 (1911).
(11) K. T. Potts, *Chem. Rev.*, **61**, 87 (1961).

Table I

Characterization of Model Compounds

Model compound	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % O	Found, % C	Found, % H	Found, % N	Found, % O
N-Benzoyl(2-pyridyl)-hydrazidine	208.5–209.5 dec	64.98	5.04	23.32	6.66	64.72	5.02	23.32	6.86
2-(2-Pyridyl)-5-phenyl-1,2,4-triazole	211.5–212.5[a]	70.25	4.54	25.21		70.16	4.51	25.07	
2-(2-Pyridyl)-5-phenyl-1,3,4-oxadiazole	123.5–124.5	69.94	4.06	18.84	7.17	69.82	4.00	18.88	7.30
N,N′-Dibenzoyl(2,6-pyridinediyl)dihydrazidine dihydrate (IV)	229–230.5 dec	57.65	5.30	22.42		57.48	4.98	22.49	
3,3′-(2,6-Pyridinediyl)-bis(5-phenyl-1,2,4-triazole) (V)	296–297	69.02	4.14	26.84		69.18	4.10	27.00	
2,2′-(2,6-Pyridinediyl)-bis(5-phenyl-1,3,4-oxadiazole) (VI)	267.5–268.5	68.66	3.57	19.02		68.44	3.43	18.96	
N,N′-Isophthaloylbis-[(2-pyridyl)hydrazidine]	278–279 dec	59.69	4.51	27.85		59.47	4.55	27.81	
3,3′-*m*-Phenylenebis[5-(2-pyridyl)-1,2,4-triazole]	326.5–327.5	65.56	3.85	30.59		65.33	3.82	30.74	
2,2′-*m*-Phenylenebis[5-(2-pyridyl)-1,3,4-oxadiazole]	241–242.5	65.21	3.28	22.82		64.95	3.15	22.63	

[a] Lit. mp 212°: K. T. Potts. *J. Chem. Soc.*, 3463 (1954).

Table II

Ultraviolet Spectral Data for Model Compounds

Model compd	λ_{max}, mμ	$\epsilon \times 10^{-3}$
I	267	22.6
II	264	14.6
	295	18.0
III	241	5.5
	271	12.3
	314	26.1
IV	262	31.5
V	248	25.9
	289	44.2
VI	234	14.9
	264	21.5
	302	51.8
VII	270	33.4
VIII	265	34.6
	338	22.3
IX	278	28.5
	349	30.7

Table III

Effect of Reaction Time on the Molecular Weight of Poly(N-acylhydrazidine)

Time, hr	η_{inh}
0.5	0.51
1.0	0.55
2.0	0.63
5.0	0.71
16.0	0.80

benzoyl chloride are shown in Figure 1 while additional uv data for all the model compounds is given in Table II.

Polymer. Polymer synthesis was confined to the reaction of 2,6-pyridinediyldihydrazidine with isophthaloyl chloride. High molecular weight (η_{inh} = 0.4–0.8, 0.5% H_2SO_4 solution at 25°) precursor polymer (poly-N-acylhydrazidine, I) was prepared by low-temperature (0–7°) polycondensation in N,N-dimethylacetamide or hexamethylphosphoramide containing 5% lithium chloride. Poly-N-acylhydrazidine (η_{inh} = 0.4–0.5) was obtained using the solvent as the acid acceptor while higher molecular weight polymer (η_{inh} = 0.8) was obtained when anhydrous sodium acetate was employed as the base. Other bases such as sodium carbonate and triethylamine were also given a cursory examination but polymer with $\eta_{inh} > 0.7$ was not obtained. The increase in molecular weight as a function of reaction time in hexamethylphosphoramide is summarized in Table III. Interfacial condensation under various reaction parameters gave polymer with $\eta_{inh} < 0.21$.

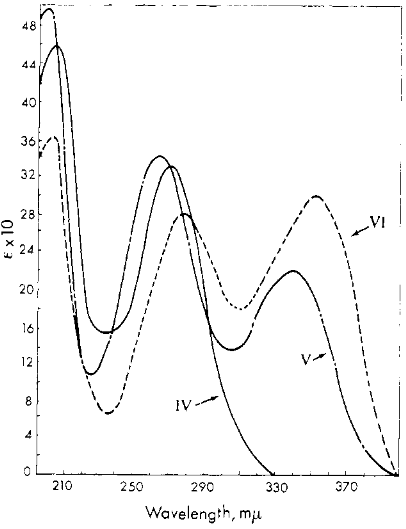
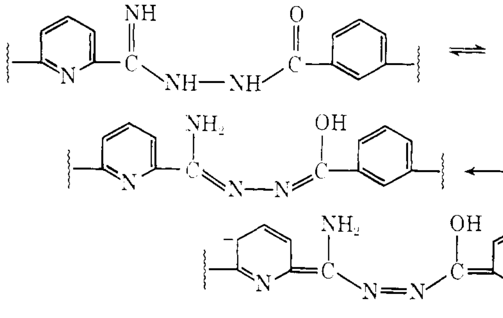


Figure 1. Ultraviolet spectra (H_2SO_4) of model compounds.

The poly-N-acylhydrazidine is soluble in strongly polar solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, and hexamethylphosphoramide immediately after its synthesis. After drying at 100°, the polymer exhibits only partial solubility in the aforementioned solvents. Perhaps this thermal treatment induces some degree of ordering of the polymer chains. Frazer and Wallenberger[2a] have shown that a copolyhydrazide from isophthalic dihydrazide and terephthaloyl chloride underwent crystallization by heating in N,N-dimethylacetamide at 120–130°. The poly-N-acylhydrazidine also precipitated from a N,N-dimethylacetamide solution after heating at 120°. Although no X-ray diffraction pattern has yet been taken, this phenomenon is tentatively attributed to induced crystallinity.

Poly-N-acylhydrazidine ($\eta_{\text{inh}} = 0.7$) was of sufficient molecular weight to cast a clear yellow film which exhibited good flexibility (fingernail creasable). However, upon thermal treatment (cyclization) to temperatures as high as 300°, the resulting film became brittle (failed fingernail crease).

Since the end groups of the poly-N-acylhydrazidine are heterocyclic or aromatic, the N-acylhydrazidine similar to polyhydrazides is able to partake in extended conjugation due to tautomerism to the enol form as indicated in the following representative form.



In strong bases such as 1 *N* sodium hydroxide, the poly-N-acylhydrazidine turns bright yellow but reverts to its original pale yellow color upon neutralization.

Conversion of the poly-N-acylhydrazidine predominantly to poly-1,2,4-triazole (II) was effected as with the model compounds in solvents boiling >200° or by solid-state advancement at 280–350° under an inert atmosphere. During the latter thermal treatment, the poly-N-acylhydrazidine sintered slightly but failed to melt under 350°. Exit gases were trapped and analyzed to confirm the findings of the model compound work. Ammonia (1.4–4.0%) was evolved which indicated a corresponding amount of oxadiazole formation within the polymer chain. This was also confirmed by nmr.

Similar to the model compounds, poly-N-acylhydrazidine was quantitatively converted to poly-1,3,4-oxadiazole (III) by heating in strong acids. Viscous solutions (5% solids) of poly-1,3,4-oxadiazole were obtained by refluxing the poly-N-acylhydrazidine in trifluoroacetic acid or by stirring in polyphosphoric acid at 200°. In sulfuric acid at 100°, only relatively low molecular weight ($\eta_{\text{inh}} < 0.4$) poly-1,3,4-oxadiazole was obtained. Apparently, the poly-N-acylhydrazidine undergoes cyclization to oxadiazole accompanied by partial cleavage of the chain. This was further evidenced when the η_{inh} (0.71) of a sulfuric acid solution (0.5% solids) of poly-N-acylhydrazidine decreased to 0.34 after standing at ambient temperature for 18 hr. The same sample exhibited an η_{inh} of 1.1 in hexamethylphosphormaide (0.5% solution at 25°) and remained unchanged for 3 days.

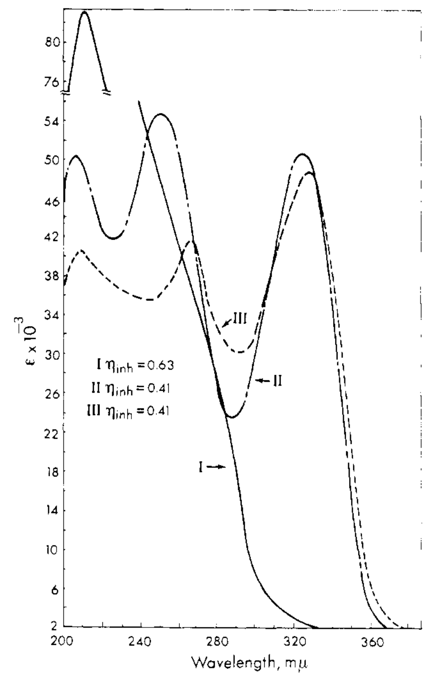


Figure 2. Ultraviolet spectra (H_2SO_4) of polymers.

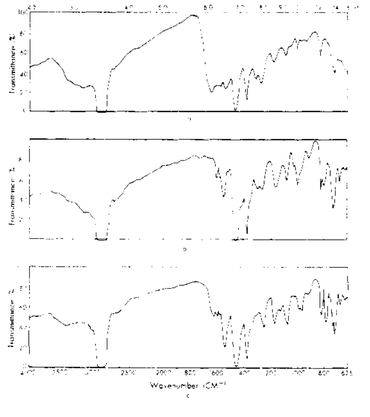


Figure 3. Infrared spectra (Nujol mulls) of polymers: (a) poly-N-acylhydrazidine, (b) poly-1,2,4-triazole, (c) poly-1,3,4-oxadiazole.

Characterization of the polymers is given in Table IV. The ultraviolet, infrared, and nuclear magnetic resonance spectra of the polymers are shown in Figures 2, 3, and 4, respectively. The thermal stability (Figures 5, 6, and 7) of the polymers was determined by thermogravimetric analysis (TGA) and by differential thermal analysis (DTA). The TGA and DTA curves for the precursor polymer (Figure 5) indicated that adsorbed water is lost at ~100° followed by thermal cyclization with the elimination of volatiles at ~250°. The endotherm occurring at ~400° may be due to transitions in the polymer chain of primary or secondary nature (*e.g.*, melting or glass transition). The thermogams for the poly-1,2,4-triazole (Figure 6) and the poly-

TABLE IV

POLYMER CHARACTERIZATION

Polymer	η_{inh},[a] dl/g	Formula	Calcd, % C	H	N	O	Found, % C	H	N	O
Poly-N-acylhydrazidine (I)	0.71	$(C_{15}H_{13}N_7O_2\cdot H_2O)_n$	52.78	4.43	29.73	14.06	52.26	4.38	28.27	13.34
Poly-1,2,4-triazole (II)	0.65	$(C_{15}H_9N_7\cdot H_2O)_n$	59.01	3.63	32.12	5.24	58.97	3.34	30.28	5.61
Poly-1,3,4-oxadiazole (III)	0.63	$(C_{15}H_7N_5O_2)_n$	62.28	2.44	24.21	11.06	61.98	2.32	23.95	11.31

[a] 0.5% H_2SO_4 at 25°.

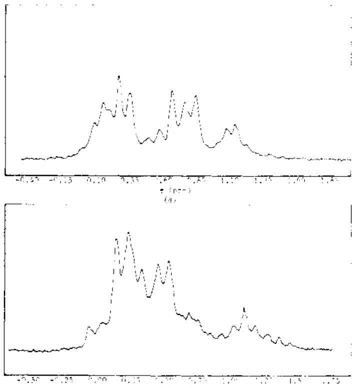


Figure 4. Nuclear magnetic resonance spectra (D_2SO_4) of polymers at 100 Mcps relative to TMS, 10.0 ppm: (a) poly-1,2,4-triazole (η_{inh} = 0.41), (b) poly-1,3,4-oxadiazole (η_{inh} = 0.41).

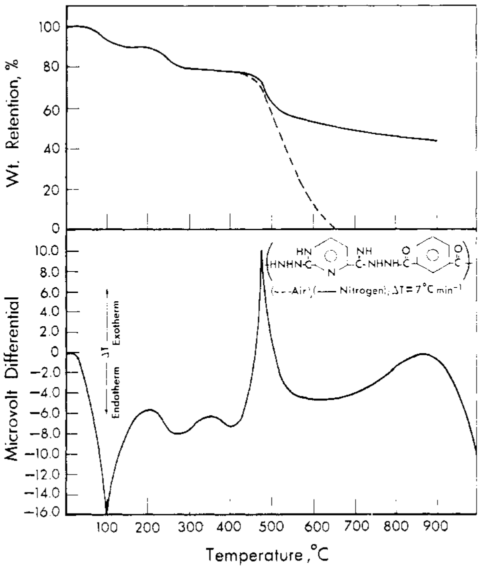


Figure 5. TGA and DTA of poly-N-acylhydrazidine.

1,3,4-oxadiazole (Figure 7) are similar and show the elimination of adsorbed water commencing ~80° and the decomposition temperature commencing ~420°. An endotherm at ~380° in the DTA curve for the poly-1,3,4-oxadiazole may be due to melting or a second-order transition. A similar transition was not observed in the DTA curve for the poly-1,2,4-triazole.

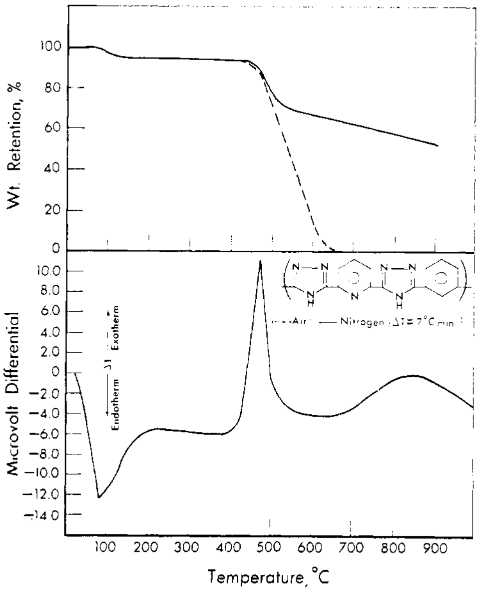


Figure 6. TGA and DTA of poly-1,2,4-triazole.

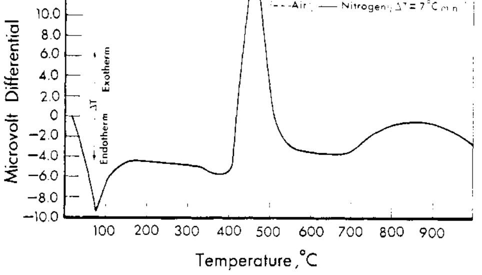


Figure 7. TGA and DTA of poly-1,3,4-oxadiazole.

Experimental Section

Reactants. Isophthalolyl chloride and all solvents were purified in the conventional manner by distillation in an inert atmosphere over a drying agent where appropriate and maintained under dry conditions prior to use.

2,6-Pyridinediyldihydrazidine. This reactant was prepared as previously reported[12] as pale yellow needles, mp 231–232° dec.

Anal. Calcd for $C_7H_{11}N_7$: C, 43.51; H, 5.74; N, 50.76. Found: C, 43.76; H, 5.75; N, 50.70.

Model Compounds. Since the experimental procedures for the preparation of the model compounds are similar, the synthesis of a representative series from the reaction of 2,6-pyridinediyldihydrazidine and benzoyl chloride is presented.

N,N′-Dibenzoyl(2,6-pyridinediyl)dihydrazidine Dihydrate (IV). To a slurry of 2,6-pyridinediyldihydrazidine (1.93 g, 0.01 mol) and anhydrous sodium carbonate (2.22 g, 0.02 mol) in N,N-dimethylacetamide (30 ml) at 0°, a solution of benzoyl chloride (2.80 g, 0.02 mol) in N,N-dimethylacetamide (15 ml) was added dropwise during 0.5 hr. The pale yellow reaction mixture was stirred at ambient temperature for 3 hr followed by pouring into ice water to precipitate a very pale yellow solid. The isolated solid was washed with water followed by drying *in vacuo* over phosphorus pentoxide at 80° for 4 hr to yield 4.1 g (94% yield) of N,N′-dibenzoyl-(2,6-pyridinediyl)dihydrazidine dihydrate (VII), mp 229–230.5° dec (Table I).

3,3′-(2,6-Pyridinediyl)bis(5-phenyl-1,2,4-triazole) (V). N,-N′-Dibenzoyl(2,6-pyridinediyl)dihydrazidine dihydrate (1.0 g) was dissolved in *m*-cresol (25 ml) and refluxed for 0.5 hr under nitrogen. The resulting clear yellow solution was concentrated by simple distillation to about 7 ml and diluted with methanol. Further dilution with water gave a white precipitate which was isolated and dried in air at 60°. The resulting white solid (0.82 g, 93% yield) melted at 216.5–218° dec for the monohydrate of 3,3′-(2,6-pyridinediyl)bis(5-phenyl-1,2,4-triazole).

Anal. Calcd for $C_{21}H_{17}N_7O$: C, 65.78; H, 4.47; N, 25.57. Found: C, 66.76; H, 4.32; N, 25.78.

Further drying at 120° *in vacuo* for 4 hr provided the anhydrous material, mp 293–296°, which was recrystallized from a mixture of methanol and water to yield an amorphous white solid, mp 296–297° (Table I) after drying.

2,2′-(2,6-Pyridinediyl)bis(5-phenyl-1,3,4-oxadiazole) (VI). N,N′-Dibenzoyl(2,6-pyridinediyl)dihydrazidine dihydrate (1.0 g) was dissolved in trifluoroacetic acid (20 ml) and refluxed for 4 hr under nitrogen. The resulting clear orange solution was poured into ice water to precipitate a white solid which was successively washed with aqueous sodium carbonate and water followed by drying at 100° *in vacuo* for 4 hr. The resulting white solid (0.80 g, 95% yield), mp 260–263°, was recrystallized from methanol to give white crystals of 3,3′-(2,6-pyridinediyl)bis(5-phenyl-1,3,4-oxadiazole) (IX), mp 267.5–268.5° (Table I).

Polymers. Poly[N,N′-(2,6-pyridinediimodyl)-N″,N‴-isophthaloyldihydrazine] (I). The following preparation was performed under conditions to exclude moisture using solvent and reactants of high purity. A cold solution of isophthaloyl chloride (4.060 g, 0.020 mol) in hexamethylphosphoramide (24 ml) was added during 0.5 hr under nitrogen to a vigorously stirred slurry of 2,6-pyridinediyldihydrazidine (3.862 g, 0.020 mol), anhydrous sodium acetate (3.280 g, 0.040 mol), and anhydrous lithium chloride (2.50 g) in hexamethylphosphoramide (47 ml) at 5–7°. After complete addition, the viscous yellow reaction mixture was stirred at 5° for 3 hr followed by stirring at ambient temperature for 18 hr. The resulting, very viscous, yellow reaction mixture was poured into water in a Waring Blendor to precipitate a fibrous yellow solid which was thoroughly washed with water and methanol to yield poly-N-acylhydrazidine as a yellow solid (6.5 g, 95.5% yield based upon the monohydrate), η_{inh} = 0.71 (Table III). The precursor polymer was also prepared in the following manner by interfacial polycondensation. A solution of isophthaloyl chloride (2.030 g, 0.010 mol) in methylene chloride (150 ml) was added during 10 min to a vigorously stirred solution of 2,6-pyridinediyldihydrazidine (1.932 g, 0.010 mol) in water (500 ml) at 20°. A yellow precipitate appeared upon the initial addition of the diacid chloride. After complete addition, the reaction mixture was stirred at ambient temperature for 1 hr followed by filtration. The isolated yellow solid was thoroughly washed with water and methanol to afford a quantitative yield of poly-N-acylhydrazidine (η_{inh} = 0.21).

Poly[3,3′-(2,6-pyridinediyl)-5,5′-(*m*-phenylene)di(1,2,4-triazole)] (II). Poly-N-acylhydrazidine (1.0 g) in *m*-cresol (20 ml) under nitrogen was heated to the reflux temperature during 1.5 hr and maintained at the reflux temperature for 18 hr. The resulting cooled yellow suspension was diluted with methanol and filtered to afford a quantitative yield of poly-1,2,4-triazole, η_{inh} = 0.65 (Table III). The polymer readily adsorbed water to form a hydrate where one molecule of water is attached per mer unit.

An alternate means of converting the poly-N-acylhydrazidine to poly-1,2,4-triazole was accomplished by solid-state advancement. A test tube with a side arm containing poly-N-acylhydrazidine (1.0 g) under nitrogen was introduced into a preheated oil bath at 280°. The temperature was increased to 350° during 1 hr and maintained at 350° for 1 hr. During this thermal treatment, the original pale yellow solid sintered slightly and turned a slight beige color but exhibited no evidence of melting. A weight loss of 15.6% (15.9% theroetical weight loss for hydrated poly-N-acylhydrazidine) was recorded. The polymer exhibited an η_{inh} = 0.61.

Poly[2,2′-(2,6-pyridinediyl)-5,5′-(*m*-phenylene)di(1,3,4-oxadiazole)] (III). A yellow solution of poly-N-acylhydrazidine (1.0 g) in trifluoroacetic acid (20 ml) under nitrogen was refluxed for 18 hr. The resulting orange solution was poured into water to precipitate a white solid which was isolated by filtration and washed successively with aqueous sodium carbonate, water, and methanol. Poly-1,3,4-oxadiazole was obtained in quantitative yield as a white solid which exhibited an η_{inh} of 0.63 (Table III). The poly-1,3,4-oxadiazole did not exhibit as strong a tendency to adsorb water as the poly-1,2,4-triazole.

Physical and Structural Characterization. Ultraviolet spectra were obtained in sulfuric acid using a Cary Model 14 recording spectrophotometer. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer Model 257 grating infrared spectrophotometer. The nuclear magnetic resonance spectra were obtained in deuterated sulfuric acid at 100° due to the viscosities of the polymer solutions on a Varian HA-100D spectrometer. Thermogravimetric analyses (TGA) were determined using a Du Pont 950 thermal gravimetric analyzer while the differential thermal analyses were obtained on a Stone DS-2 instrument. The inherent viscosity (η_{inh}) measurements were determined on hexamethylphosphoramide or sulfuric acid solutions as indicated at a concentration of 0.50 g/100 ml of solvent at 25°.

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