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SYNTHESIS AND STUDY OF POLY (1,3,4-OXADIAZOLES)

A. P. Grekov, S. A. Malyutenko, and K. A. Kornev

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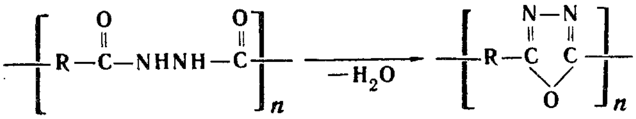
Various conditions for synthesizing poly(1,3,4-oxadiazoles) from carboxylic acids, their hydrazides, and polyhydrazides, are investigated. Methods of cyclodehydration of polyhydrazides using phosphorus oxychloride, sulfuric acid, and certain other reagents are not of general utility for synthesizing poly(1,3,4-oxadiazoles). Vacuum-heating polyhydrazides gives crosslinked polymers. A new method of preparing poly(1,3,4-oxadiazoles) is offered. It is the reaction of hydrazine sulfate or dihydrazides of acids with dicarboxylic acids in oleum solution. Some chemical properties of the compounds synthesized are investigated.

Recently papers have been published [1-4] dealing with the synthesis of poly(1,3,4-oxadiazoles), compounds of high melting point, and high thermal and chemical stability. Films and threads can be obtained from melts and solutions of polymers of this series [3, 4].

For preparing poly(1,3,4-oxadiazoles), use was made of the reaction of 1,4-(tetrazolyl-5) benzene with dicarboxylic acid chlorides [1,2], or cyclodehydration of polyhydrazides at high temperature or under the action of cyclizing reagents [3,4]. Depending on the method of synthesis, the polymers, while they all had the same elementary composition, differed in properties (melting point, solubility, etc). In that connection, the present work investigated various conditions of synthesis of poly(1,3,4-oxadiazoles), starting from carboxylic acids, their hydrazides, and polyhydrazides.

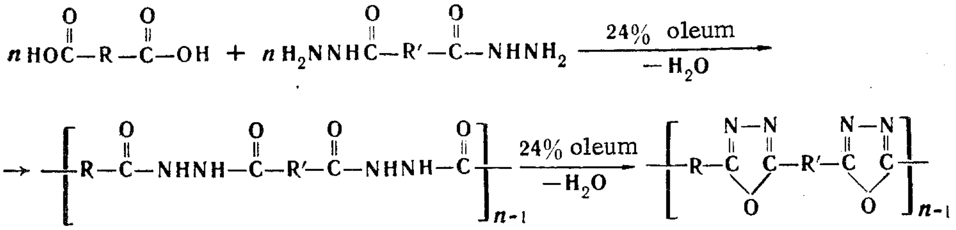
We previously showed [5] that the best results are obtained when the polyhydrazides are prepared by condensing hydrazides with dicarboxylic acids under pressure in an autoclave at 200°-210° C for some hours. The properties of the resultant polyhydrazides corresponded to those disclosed in the references.

The equation for the cyclodehydration of the polyhydrazides is:-



To obtain poly(1,3,4-oxadiazoles) with different alternating carbon bridges, use was made of the appropriate polyhydrazides [5].

The polyhydrazides were cyclized to polyoxidiazoles either under vacuum, in an inert gas, in phosphorus oxychloride solution, or dissolved in sulfuric acid or oleum. Heating polyhydrazides under reduced pressure at 300° C usually gave an elastic crosslinked polymer, which softened at high temperature, and swelled in organic solvents. It was shown that polymer crosslinking was basically due to hydrazine end-groups, since their removal by potassium iodate [6], or by acetylation with acetic anhydride gave soluble linear product melting below 200° C. Further, cyclodehydration of polyhydrazines at high temperature often gives a polyoxadiazole contaminated with starting material, particularly with high-melting polyhydrazides of aromatic acids. In view of what is stated above, it is considered that the authors of paper [3] obtained crosslinked poly(1,3,4-oxadiazoles), melting point over 300° C, which they mistook for linear polymers. The usual methods of cyclodehydration of hydrazides using phosphorus oxychloride, sulfuric acid and other reagents [7] are not generally applicable to preparing poly(1,3,4-oxadiazoles). A synthetic method which we worked out was the most convenient. It was reaction of hydrazine sulfate or dihydrazides of acids with dicarboxylic acids in oleum. The reaction takes 3-4 hrs, and the equations are



Poly(1, 3, 4-oxadiazoles)

Compound	Mp, ° C	[η]	Repeating unit formula	N, %		Literature mp, ° C	Yield, %
				Found	Calculated		
Poly [2, 5-(1, 4-phenylene)-1, 3, 4-oxadiazole]	450 (decomp)	0.22	$C_8H_4N_2O$	—	—	465 (decomp)[1]*	87.0
Poly [2, 5-1, 3-phenylene)-1, 3, 4-oxadiazole]	350(decomp)	0.24	$C_8H_4N_2O$	—	—	>400[3]	77.5
Poly [2-tetramethylene-5-(1, 3-phenylene)-1, 3, 4-oxadiazole]	193—195	0.16	$C_{12}H_{12}N_2O$	20.29	20.87	>400[3]	73.1
Poly [2-heptamethylene-5-(1, 3-phenylene)-1, 3, 4-oxadiazole]	216—218	0.12	$C_{15}H_{18}N_2O$	18.16	18.06	—	91.0
Poly [2-octamethylene-5-(1, 3-phenylene)-1, 3, 4-oxadiazole]	166—168	0.23	$C_{16}H_{20}N_2O$	14.35	14.28	95—100[4]; 350[3]	81.2
Poly [2, 5-(octamethylene)-1, 3, 4-oxadiazole]	155—158	0.25	$C_{10}H_{16}N_2O$	15.43	15.50	300[3]	95.2

The order of choice of reactants does not affect yield or quality of the polymer formed. It is also possible to use a polyhydrazide as the starting material, giving a poly(1, 3, 4-oxadiazole) corresponding to the polymer obtained from the hydrazide and dicarboxylic acid. This method was used to prepare poly(1, 3, 4-oxadiazoles) from aromatic acids, as well as polymers with alternating aliphatic and aromatic sections.

The structures of the polymers prepared were proved by retrosynthesis, elementary analysis, and in some cases, by comparing properties with those given in the references [1, 2, 4].

Poly(1, 3, 4-oxadiazoles) are colorless or pale yellow substances, which luminesce in ultraviolet light, are readily soluble in sulfuric, formic, and acetic acids, in dimethylformamide, dimethylsulfoxide, and ethyl cellosolve, but less soluble in dioxane and ethanol. On passing from polyoxadiazoles having aliphatic units, to polymers containing aromatic rings, solubility correspondingly drops, while mp rises. After boiling with dilute mineral acids or alkalies, the polymer is hydrolyzed with opening of the oxadiazole ring, ease of hydrolysis decreasing when the aliphatic sections are replaced by aromatic rings, and this is in good agreement with the results reported in papers [7, 8]. When high melting crosslinked polymers obtained by vacuum-dehydration of polyhydrazides were dissolved in sulfuric acid and reprecipitated by pouring into water, they gave the same products as poly(1, 3, 4-oxadiazoles).

Study of the relative thermostabilities of the polyoxadiazoles prepared showed that all the compounds stand heating to 50°-100° C above their melting points. Polymers containing aromatic rings have a higher thermostability than polymers containing aliphatic groups.

Experimental

Preparation of poly(1, 3, 4-oxadiazoles) by vacuum cyclodehydration of polyhydrazides. 3 g sebacic acid polyhydrazide with blocked terminal hydrazide groups was placed in a heat-resistant glass test tube, connected to a vacuum pump, and the tube contents heated to melting. Heating was continued for 2 hr 30 min to 3 hr, the water evolved being simultaneously pumped off at 1-3 mm. The resultant product was removed from the tube, and twice reprecipitated from EtOH with water. Poly [2, 5-(octamethylene)-1, 3, 4-oxadiazole] was obtained in 95.2% yield as a white powder mp 155°-158° C. Polyhydrazides with free end groups can be treated similarly.

Preparation of poly(1, 3, 4-oxadiazoles) by cyclodehydrating polyhydrazides in concentrated sulfuric acid. 1 g sebacic acid polyhydrazide with its end hydrazide groups acetylated was dissolved in 10 ml H_2SO_4 (d 1.84) heated to 90°-100° C, and kept at that temperature for 3-4 hr. Then, with vigorous stirring, the reaction products were poured on ice, the precipitated product filtered off, washed with water until neutral, and dried. Two reprecipitations from MeOH, using water, gave poly-[2, 5-(octamethylene)-1, 3, 4-oxadiazole] mp 75°-95° C, yield 50-60%.

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*Superscript numbers refer to the references at the end of the article.

Preparation of poly (1, 3, 4-oxadiazoles) by condensation in oleum. 7.5 g hydrazine sulfate and 40 ml 24% oleum were placed in a three-necked flask, fitted with a mechanical stirrer and thermometer. To the resultant solution was added 10 g isophthalic acid at such a rate that the temperature did not rise above 20° C. Then the contents of the flask were slowly heated to 55°–60° C and held there for 4 hr, the reaction products poured on to ice, the colorless product which separated filtered off, washed, on the filter, with 5% Na_2CO_3 solution until neutral, then washed with water, and dried. The resultant poly [2, 5-(1, 3-phenylene)-1, 3, 4-oxadiazole] was reprecipitated from dimethylformamide with water, and then formed a colorless material mp 350° C (decomp), yield 77.5%.

Preparation of poly (1, 3, 4-oxadiazoles) containing aliphatic and aromatic units, by condensation in oleum. 55.3 g isophthalic acid and 500 ml 24% oleum were placed in a three-necked flask fitted with a mechanical stirrer and thermometer. 76.7 g sebacic acid dihydrazide was added to the solution formed, the contents of the flask heated to 55°–60° C and held there for 3–4 hr, after which the reaction products were poured on to ice, the reaction product precipitated filtered off, washed until neutral and dried. After repeated precipitation from dimethylformamide by means of water, an 81.2% yield of colorless poly [2-(octamethylene)-5-(1, 3-phenylene)-1, 3, 4-oxadiazole], mp 166°–168° C, was obtained.

The table shows all the polyoxadiazoles prepared by the above methods.

The intrinsic viscosities of the poly (1, 3, 4-oxadiazoles) were determined in concentrated sulfuric acid (d 1.84), with an Ostwald viscometer, temperature 25 ± 0.05° C. The thermal stabilities of these compounds were determined thermogravimetrically, using a specimen heating rate of 2°–3° C/min. Weight losses were checked periodically by weighing on a torsion balance.

REFERENCE

1. J. Sauer, R. Huisgen, and H. Sturm, Tetrahedron, 11, 241, 1960.
2. C. Abshire and C. Marvel, Makrom. Chem., 44–46, 388, 1961.
3. A. Frazer and F. Wellenberger, J. Pol. Sci., 2, 1157, 1171, 1964.
4. M. Hasegawa and T. Unishi, J. Pol. Sci., 2, 237, 1964.
5. V. A. Yanchevskii, A. P. Grekov, and K. A. Kornev, collection: Synthesis and Physical Chemistry of Polymers [in Russian], Naukova dumka, Kiev., p. 34, 1964.
6. A. P. Grekov, S. A. Sukhorukova, and K. A. Kornev, Plast. massy, no. 8, 50, 1964.
7. E. P. Nesynov and A. P. Grekov, Usp. khim., 33, 1184, 1964.
8. A. P. Grekov and R. S. Azen, ZhOKh, 31, 407, 1961.

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Chemistry of High-Molecular Compounds Institute,
AS UkrSSR, Kiev