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## SYNTHESIS AND THERMAL CONVERSIONS OF POLYCYANHYDBAZIDES\*

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Polycyanhydrazides have been synthesized by low temperature polycondensation of 2,5-dicyanterephthaloyl chloride and isophthalic acid dihydrazide. The polymers are readily isomerizable to polyamidoiminoimides. It was found that heat treatment of the latter at  $300-400^{\circ}$  results, along with degradative processes, in the formation of polycyan-1,3,4-oxadiazoles. A study was made of the structure and thermal conversions of the respective model compounds.

In an earlier report [1] it was shown that polycyanamides may be converted by way of isomerizing cyclization to a novel group of compounds, namely polyiminoimides [1], which possess interesting electrophysical properties. Polyiminoimides having as the *ortho* substituents different functional groups are capable of further thermal cycloconversions with formation of polyheteroarylenes of semi-ladder or ladder structure [2].

In this connection it was of interest to investigate the isomerizing cyclization reaction, taking polycyanhydrazides (PCH) as examples. In the latter case the formation of a polyiminoimide structure may occur as well, through interaction between the CH group and the hydrazide group of the polymer chain.

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It is also known that polyhydrazides that contain no nitrile groups split off water on heating and form poly-1,3,4-oxadiazoles [3]. One would expect the respective polycyan-1,3,4-oxadiazoles (POD) to be similarly formed through the dehydration of PCH, and that the dehydration of polyamidoiminoimides (PAII), will result in polybenzoylenetriazoles



To investigate the feasibility of these reactions we took as an example a PCH prepared from 2,5-dicyanterephthaloyl chloride (2,5-DCTPC) and isophthalic acid dihydrazide. The structure of the polymers and their transformations were verified by the synthesis and analysis of appropriate model compounds.

Starting compounds. Dihydrazide of isophthalic acid, m.p. 219-220° (from aqueous methanol) [4]; 2,5-DCTPC, m.p. 195-196° (from abs. benzene) [1]; o-cyanbenzoyl chloride, m.p. 71-72° (abs. hexane) [1]; benzahydrazide, m.p. 112° (from water [5]).

Model compounds. N-(o-cyanbenzoyl)-benzhydrazide (I) was prepared from o-cyanbenzoyl chloride and benzhydrazide in N,N-dimethylacetamide (DMAA) solution, yield 70%; the substance isolated from DMAA with aqueous alcohol gives one spot on the chromatographic plate,  $R_{10}$  (ethyl acctate). TLC was carried out under the following conditions: carrier—sulphol, mobile phase—ethyl acetate or an ethyl acetate-benzene mixture in various ratios, development-by water vapour or by UV light. Found, %: C 67.44; H 4.64; N 15.80. C<sub>18</sub>H<sub>10</sub>N<sub>3</sub>O. Calculated, %: C 68.00; 4.15; N 15.80. The IR spectrum of I (KBr disc) has absorption bands as follows: 3440, 3210 cm<sup>-1</sup> (HN group), 2230 cm<sup>-1</sup> (CN group), 1665, 1610, 1580, 1280 cm<sup>-1</sup> (amide bands). The melting point in this case does not characterize the individuality of the compound in view of the isomerization of I, on heating, to 2-benzamido-3-iminoisoindolinone (II). The latter was prepared by thermal isomerization of I in a sealed evacuated ampoule at 150-160°, or in DMAA solution at 165° for 1 hr. Yield 80%, m.p. 224-225° (from abs. benzene), R, 0.3 (ethyl acetate). Found, %: C 67.83; H 3.98; N 15.43. C15H10N2O. Calculated, %: C 68 00; H 4 15; N 15 80. The IR spectrum of II has absorption bands at 3280, 1675 cm<sup>-1</sup> (C=NH), 1750 cm<sup>-1</sup> (C=O) and the band of the CN group (2230 cm<sup>-1</sup>) disappears.

On heating either I or II in a sealed ampoule at  $200-220^{\circ}$ C it was found that a complex mixture of substances results; chromatographic analysis of the latter was carried out in a column containing SiO<sub>2</sub> and the following individual substances were separated with benzene and characterized by means of IR, mass spectrometric and elemental analyses: phthalimide, m.p. 234°, 3-iminoizoindolinone (V) with m.p. 203° [6], N-benzamidophthalimide

(III) with m.p.  $216^{\circ}$  [7]; 2-phenyl-5-(o-cyanphenyl)-1,3,4-oxadiazole (IV) with m.p. 143-145°, the IR spectrum of which had absorption bands characteristic of the oxadiazole ring: 1630-1610, 1555, 1070 cm<sup>-1</sup> and a band at 2230 cm<sup>-1</sup> (CN group) etc.; moreover, sublimed in the top part of the ampoule were substances from which benzamide (m.p. 130°), benzoic acid (m.p. 122°) and phthalimide (m.p. 234°) were separated and identified by melting points, IR analysis and GLC.

Bis-(o-cyanbenzoyl) dihydrazide of isophthalic acid was prepared, like compound I, from isophthalic acid dihydrazide and o-cyanbenzoyl chloride in solution in N-methylpyrrolidone (N-MP). The product was precipitated with water, yield 95%, m.p. 257-258°. Found, %: C 63.70; H 3.75; N 18.50.  $C_{34}H_{15}N_{6}O_{4}$ . Calculated, %: C 63.71; H 3.54; N 18.58.

N,N'-Bis-(3-iminoisoindolinone) diamide of isophthalic acid (VII) was prepared by thermal isomerization of VI in a stream of argon under atmospheric pressure at 260° for 15 min, or in N-MP solution at 150-160° (30 min). Yield of VII 50%, m.p. 263-265° (benz-ene-hexane). The structures of VI and VII were verified by infrared.

Thermal isomerization of either VI or VII at 260–280° for 1 hr led to the isolation and characterization of degradation products of VI and VII similar to those described above (see also the tabulated results of mass spectrometric analysis); N,N'-bis-(phthalimide)diamide of isophthalic acid, m.p. 258–259° (aqueous alcohol), resulting from hydrolysis of the imino-group of VII. In addition to the above compounds we obtained from the melt a substance which could not be purified to an individual compound in view of its poor solubility. The IR spectrum has bands at 2230 (C=N), 1570 (>C=N-), 1080 (C-O-C) and 970 cm<sup>-1</sup> (oxadiazole ring), and bands relating to the hydrazide group disappear. In the light of all these findings it appears that 1,3-bis-[5,5' (o-cyanphenyl)-1,3,4-oxadiazoly] benzene is formed.

Compound	<i>T</i> , °C	Composition of volatiles, mole %				
		N <sub>2</sub>	CO	CO	NH,	HCN
PAII	250	17.35	71.30	11.05		0.30
	300	29.70	53.90	15.60	0.60	0.20
	<b>35</b> 0	24.50	69.60	5.00	0.75	0.15
	<b>40</b> 0	24.60	70.30	4.75	0.03	0.02
	<b>45</b> 0	31.70	62·90	4.90		0.4
II	215	84.70	5.60	9.7	_	.—
VIII	350	79.10	20.60		0.3	-

Composition of gaseous products of thermal degradation of PAII and model compounds II and VII\*

• Mass spectrometer of type MI-1305.

The polycondensation. 0.0388 g of isophthalic acid dihydrazide was dissolved, whilst heating gently, in 5 ml of dry N-MP containing 0.085 g of LiCl. The solution was cooled, and 0.506 g of 2,5-DCTCP was added gradually in a current of argon, while stirring rapidly, at a temperature of 0°. The reaction solution was stirred for 3 hr, the polymer was precipitated with water and dried *in vacuo* after extraction of LiCl. Translucent yellow films were cast from the reaction solution. Yield 95%,  $\eta_{log}$  for the obtained PCH 0.30 (0.5% solution in N-MP, 25°). The polycondensation was also carried out in the normal manner at a 10– 15% concentration of the reagents and temperature in the range 0 to 20° in hexamethylphosphortriamide (HMPA) solutions or in an HMPA-N-MP mixture (2 : 1); the respective values of  $\eta_{log}$  are 0.25 and 0.23. After drying the polymer dissolved in amide type solvents. Cyclization of the resulting PCH was carried out at  $10^{-3}$  torr under constant evacuation, whilst heating by stages in the interval 150-450°. The cyclized polymers were in the form of films and powders.

In the light of the data presented in the experimental section it can be seen that thermal isomerization of the model cyanhydrazides leads mainly to the formation of amidoiminoimide structures (compounds II and VII). Several processes take place simultaneously if the temperature is raised above 200°, including displacement of the equilibrium of the isomerizing cyclization reaction towards formation of the initial cyanhydrazide (I, VI), detachment of water and formation of the cyan-containing 1,3,4-oxadiazole (IV), degradation of II with N—N bond fracture and hydrolysis of compound II and of some degradation products by the water evolved



Similar processes take place in the polymer as well. The results of the IR analysis show that polymers with the PCH structure appear solely in the reaction solutions. This is indicated by the intense band of the reaction solution (2230 cm<sup>-1</sup>, CN group) which becomes less intense as heating proceeds. On heating the reaction solution to  $100-110^{\circ}$  for 1 hr it was found that the polymer separates out, which is attributable to formation of the stiffer PAII structure under these conditions. Formation of the latter structure (see Figure, spectrum 1) is borne out by IR analyses of powders of the polymers prepared by precipitation from the reaction solutions, and similarly by analysis of the polymer films, the results of which show the absence of the 2230 cm<sup>-1</sup> band relating to the PCH CN group, and the presence of bands at 1750, 1680 and 730 cm<sup>-1</sup>. This means that isomerizing conversion of PCH to PAII (see scheme) takes place already in the reaction solution, and then later on during drying of the polymer films and powders.

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On heating the polymers in a vacuum for 1 hr at each temperature (180, 250°) no change in the IR spectra of the polymers is detectable (see Figure, spectra 2 and 3). A change appears in the spectra after the PAII powder has been heated in a vacuum at 300, 350 and 400° (see Figure, spectra 4-5). As the heating of PAII



IR spectra of polymers based on 2,5-DCTPC and dihydrazide of isophthalic acid (KBr disc, UR-10 spectrophotometer): 1—PAII, separated from the reaction solution, 2-6—PAII after heat treatment *in vacuo* for 1 hr at temperatures: 2—180, 3—250, 4—300, 5—350, 6—400°.

proceeds a band appearing at 2230 cm<sup>-1</sup> (CN group) becomes more intense, and bands appear at 1630 and 1650–1670 cm<sup>-1</sup>, which may point to a possible displacement of the equilibrium at high temperatures towards formation of the initial PCH, which, after dehydration, forms poly-1,3,4-oxadiazole (Figure, spectra 5, 6). Evidence of this is seen in the increased intensity of the 1170 cm<sup>-1</sup> band assigned to the C-O-C bond of the oxadiazole ring, and further evidence is seen in the results of analyses of thermal conversions of the model compounds. Similar thermal cycloconversions were observed by us in the case of polymer films cast from the reaction solutions.

Further heating of the polymer films and powders *in vacuo* at temperatures above 350° was accompanied by the onset of processes of degradation of uncyclized parts of the polymer chain, and similarly of polyheteroarylenes (see Table) formed in the cyclization process.

The data obtained in regard to the composition of degradation products of the polymers and model compounds point to preferential decomposition of the weakest hydrazide units (evolution of N) and to predominance of hydrolytic processes of degradation (evolution of considerable quantities of  $CO_2$ ), as was also pointed out in [8].

According to the results of thermogravimetric analysis, the onset of PAII decomposition in air appears at 330° (10% weight loss). The value of  $T_g$ , based on the thermomechanical measurements, is 300°.

Translated by R. J. A. HENDRY

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# THE EFFECT OF *p*-RADIATION ON THE PROPERTIES OF A CARDIC POLYAMIDE OF ANILINEFLUORENE AND TEREPHTHALIC ACID\*

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The behaviour of one of the most promising cardic aromatic polyamides has been investigated under the action of y-radiation in air and in a vacuum. The irradiation in air leads mainly to degradation of the polymer chains complicated by branching processes, whereas well defined crosslinking is observed in a vacuum. The amide bond is the most vulnerable point in the polyamide macromolecules, although its radiation resistance exceeds that of the ester bond of a polyarylate of similar structure. Probability parameters for branching, crosslinking and degradation of the polymer chains have been calculated. In the light of the experimental data along with an analysis of the radiolysis products a conceptual scheme is proposed for radiation-chemical conversions of macrochains of the polyamide under the action of y-radiation.

**DESPITE** much study that has been devoted to analysis of the properties of cardic aromatic polyamides, scarcely any information has been published in regard to their behaviour under the action of ionizing radiations. Our aim in this investigation was to examine radiation-chemical changes occurring in polyamide PA-9,

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