

POLYHYDRAZIDES AND POLY(1,3,4-OXADIAZOLE)S WITH PARABANIC STRUCTURES

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(Received 10 August 1992)

Abstract—Polyhydrazides with parabanic structures were prepared by polycondensation between a new monomer containing a preformed parabanic ring, viz. 1,3 *p*-(bis-chloroformylphenyl) parabanic acid and dihydrazides. By thermal cyclization with polyphosphoric acid, the polyhydrazides were converted to poly(1,3,4-oxadiazole)s with parabanic structures. The films obtained from these polymers exhibit electrical insulating properties and good thermal stability.

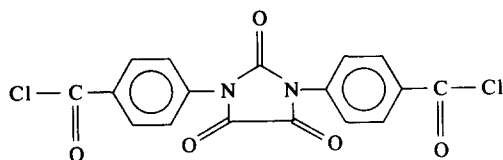
INTRODUCTION

This report continues extensive investigations in the field of polymers and copolymers with parabanic structures [1–7].

It is known that thermally stable polymers with excellent properties (such as aromatic polyamides, polysulphones, polyoxadiazoles etc.) have low solubilities in organic solvents and consequently present processing difficulties. For example, the polyoxadiazoles and polyimides are obtained in the first stage as soluble polyhydrazides or polyamic acids and are then transformed into films. The cyclization occurs by heating only the finished products.

We now describe the syntheses of polyhydrazides with parabanic structures and some attempts to transform them into poly(1,3,4-oxadiazole)s with a view to improving the solubilities of polymers of this type without decreasing the thermal stability.

In the polycondensation, we used a new monomer with preformed parabanic ring (2,4,5 imidazolinetrione), with the American Registry number [120-89-8]. The monomer is 1,3 *p*-(bis-chloroformylphenyl) parabanic acid (CPP) synthesized in our laboratory.



EXPERIMENTAL PROCEDURES

Monomers

p-Aminobenzhydrazide, anhydrous hydrazine, oxalic dihydrazide were prepared as already described [1]. 1,3 *p*-(bis-chloroformylphenyl) parabanic acid was prepared from

p-aminobenzoic acid with phosgene in the first step and oxalyl chloride in the second [5].

Characterization of polymers

Inherent viscosities were measured with an Ubbelohde viscometer in *N*-methyl pyrrolidone (NMP) at 20°. Thermal stabilities of the polymers were evaluated by TGA in a MOM derivatograph.

Synthesis of model compounds

Model compounds **1a**, **1b**, were synthesized as follows. In a flask equipped with mechanical stirrer, N₂ inlet and outlet were placed 0.01 mol. of CPP in 20 ml NMP at 0–5°. At this temperature, 0.02 mol. of freshly purified hydrazide in 10 ml NMP were added. The stirring was continued for 2 hr. Then, 150 ml water were added and the solid was separated by filtration, washed with methanol and dried. The model compounds were purified by recrystallization from DMF–water. The characterizations of model compounds are referred to in Table 1.

Preparation of polymers

A typical example of polycondensation is as follows. In a flask equipped with mechanical stirrer, N₂ inlet and outlet were placed 0.005 mol. CPP; 10 ml NMP were added so that the final concentration of the polymer solution was 12–13%. The solution was allowed to reach room temperature. The viscous solution was poured into water; the polymers were separated by filtration and dried.

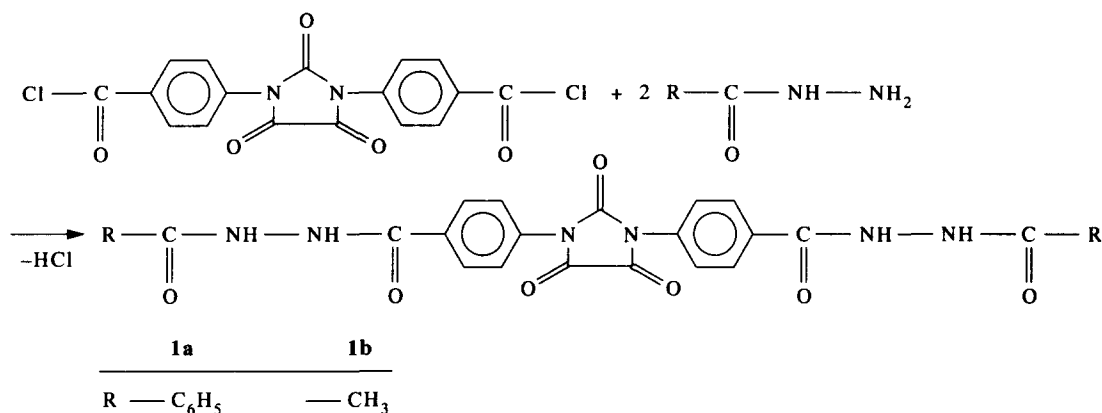
The characteristics of the polymers are shown in the Table 2. To prepare films, viscous polymer solutions were evaporated on glass plates giving flexible or brittle films depending on the polymer structure.†

RESULTS AND DISCUSSION

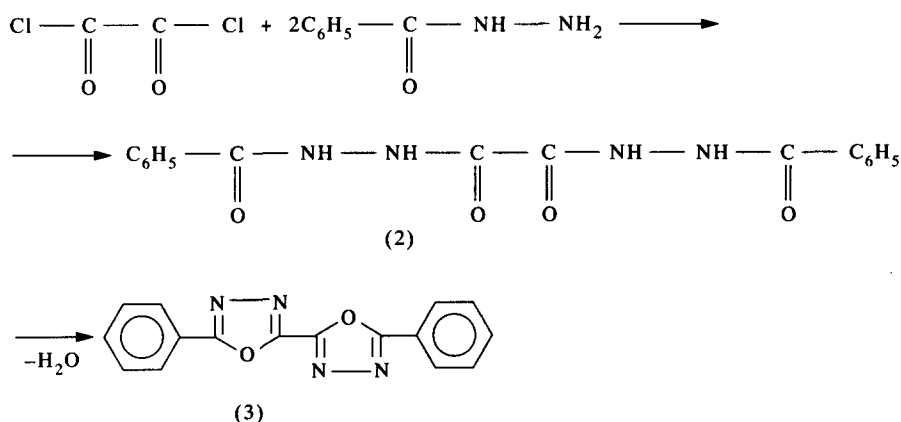
Model compounds were synthesized to assist in determining the structures of polymers, to study the thermal behaviour and also the reaction conditions. Two model compounds were prepared by reaction between CPP and benzoyl and acetyl hydrazide in molar ratio 1:2.

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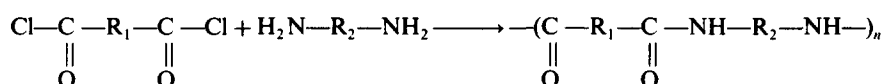
†Full information about the characterization of the polymers can be supplied by the authors.



Another model compound was prepared by the reaction between oxalyl chloride and benzoylhydrazide in molar ratio 1:2 in order to investigate the thermal cyclization of two vicinal dihydrazide groups into oxadiazole rings.



Polyhydrazides containing parabanic rings (Table 2) were obtained from the polycondensation between CPP and dihydrazide.



These syntheses lead to polymers and copolymers containing various groups (A-J) (Table 3).

We can arrange the polymers by a scheme which shows the sequences. This scheme is the representation of a statistical average; it does not represent the exact structures of polymers because the reaction takes place in steps without the isolation of intermediate products.

Polymers and copolymers with enhanced inherent viscosity were obtained (≈ 0.96 dl/g) because the overall balance of the reacting functional groups is maintained strictly equimolar.

Film-forming capability, electrical properties as well as the possibility to transform these polymers into polyoxadiazoles have been investigated.

All the polymers gave flexible films by evaporation on glass plates except those in which the dibenzyl structure was present. The dibenzyl system introduces sequences able to orientate around ethylenic groups and to pack easily into crystalline form.

Table 1. Model compounds

Model	m.p. (°C)	Formula (molecular weight)	Elemental analyses		Weight loss on cyclization
			C%	H%	
1a	311-314 (dec)	$\text{C}_{31}\text{H}_{22}\text{N}_6\text{O}_7$ (590)	Calc. 63.05	3.72	Calc. 6.09
			Found 63.11	4.01	Found 7
1b	258-260 (dec)	$\text{C}_{21}\text{H}_{18}\text{N}_6\text{O}_7$ (470)	Calc. 54.07	3.86	Calc. 7.7
			Found 54.09	3.52	Found 8
2	290-293 (dec)	$\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_4$ (326)	Calc. 53.03	4.97	Calc. 11.04
			Found 53.82	4.59	Found —

Table 2. The structures of polyhydrazides containing parabanic rings

Polymer	R ₁	R ₂
1H	—Ph—P*—Ph—	†
2H	—Ph—P*—Ph—	—NH—CO—CO—NH—
3H	—Ph—P*—Ph—	—NH—CO—(CH ₂) ₈ —CO—NH—
4H	—Ph—P—Ph—	—Ph—CO—NH—
5H	O $\begin{cases} \text{Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—NH—CO—Ph—P—Ph—} \end{cases}$	†
6H	O $\begin{cases} \text{Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—NH—CO—Ph—P—Ph—} \end{cases}$	—NH—CO—CO—NH—
7H	O $\begin{cases} \text{Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—NH—CO—Ph—P—Ph—} \end{cases}$	—NH—CO—(CH ₂) ₈ —CO—NH—
8H	O $\begin{cases} \text{Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—NH—CO—Ph—P—Ph—} \end{cases}$	—Ph—CO—NH—
9H	SO ₂ $\begin{cases} \text{Ph—O—Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—O—Ph—NH—CO—Ph—P—Ph—} \end{cases}$	†
10H	SO ₂ $\begin{cases} \text{Ph—O—Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—O—Ph—NH—CO—Ph—P—Ph—} \end{cases}$	—NH—CO—CO—NH—
11H	SO ₂ $\begin{cases} \text{Ph—O—Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—O—Ph—NH—CO—Ph—P—Ph—} \end{cases}$	—NH—CO—(CH ₂) ₈ —CO—NH—
12H	SO ₂ $\begin{cases} \text{Ph—O—Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—O—Ph—NH—CO—Ph—P—Ph—} \end{cases}$	—Ph—CO—NH—
13H	CH ₂ $\begin{cases} \text{Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—NH—CO—Ph—P—Ph—} \end{cases}$	†
14H	CH ₂ $\begin{cases} \text{Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—NH—CO—Ph—P—Ph—} \end{cases}$	—NH—CO—CO—NH—
15H	CH ₂ $\begin{cases} \text{Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—NH—CO—Ph—P—Ph—} \end{cases}$	—Ph—CO—NH—
16H	(CH ₂) ₂ $\begin{cases} \text{Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—NH—CO—Ph—P—Ph—} \end{cases}$	†
17H	(CH ₂) ₂ $\begin{cases} \text{Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—NH—CO—Ph—P—Ph—} \end{cases}$	—NH—CO—CO—NH—
18H	(CH ₂) ₂ $\begin{cases} \text{Ph—NH—CO—Ph—P—Ph—} \\ \text{Ph—NH—CO—Ph—P—Ph—} \end{cases}$	—Ph—CO—NH—

*Parabanic ring.

†Hydrazine.

The cyclization of polyhydrazides

The possibility to transform the polyhydrazides into polyoxadiazoles by thermal cyclization was studied for the model compounds. The model compounds **1a**, **1b**, examined by thermogravimetry, showed a thermal weight loss in good agreement with the values calculated for cyclization and oxadiazole ring formation.

When the cyclization is carried out by heating of a larger quantity of model compound at the temperatures indicated by TGA, we observe different behaviour: in the case of model **1a** when the temperature is below the melting point, the cyclization does not occur, as shown in i.r. spectra (Fig. 1).

In the case of model **1b** heated above the melting point, we observed destruction of the parabanic ring and the disappearance of the corresponding i.r. frequency at 1730 cm⁻¹ probably because of hydrolysis by water.

The same destruction of the parabanic ring was observed in the attempt at thermal cyclization of polyhydrazides. The process is more pronounced as the quantity of water is greater.

Particular behaviour was noted for the hydrazides derived from oxalic acid (model **2**). In this case, the thermal cyclization into the corresponding vicinal oxadiazoles does not occur even during the thermogravimetric analyses. To avoid the hydrolysis of the parabanic ring by reaction with water, we performed thermal cyclization by addition

Table 3. Structures of polymers

A—NH—NH— B—NH—Ph—P—Ph—CO— C—CO—CO— D—CO—(CH ₂) ₈ —CO— E—NH—Ph—CO— F—NH—Ph—O—Ph—NH— G—CS—NH— H—NH—Ph—O—Ph—SO ₂ —Ph—O—Ph—NH— I—NH—Ph—CH ₂ —Ph—NH— J—NH—Ph—(CH ₂) ₂ —Ph—NH—							
Sequence	AB	ACA	ADA	EAB	BFB	ABHB	
Number of polymer	1-8	2,6,10,14,17	3,11	4,7,12,18	5,6,7,8	9,10,11,12	
Sequence	BIB		BJB	AGB	GBF	HB	IBI
Number of polymer	13,14,15		16,17,18	8	7	12	15

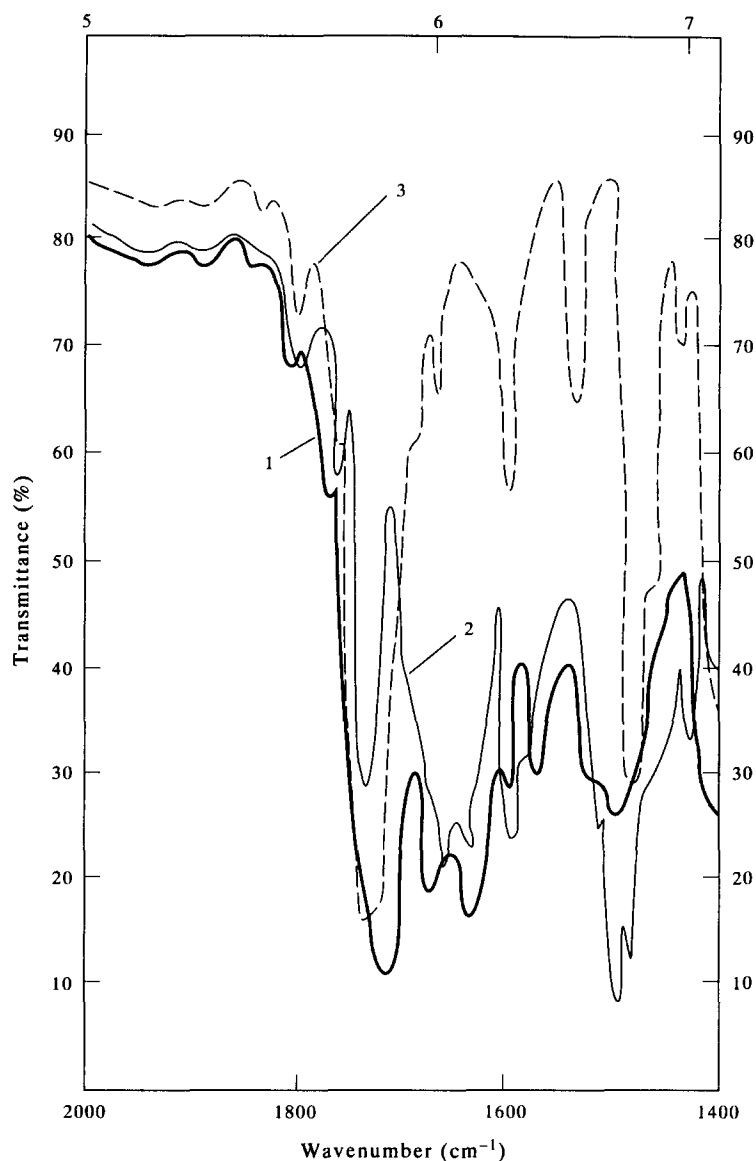


Fig. 1. Infrared spectra of model **1a** and model **1a** after cyclization: 1, model **1a**; 2, thermal cyclization model **1a**; 3, thermal cyclization of model **1a** with addition of water-acceptor.

of polyphosphoric acid (PPA) as a water-acceptor. In this manner, all the model compounds **1a**, **1b** and **2** were converted into the corresponding 1,3,4-oxadiazole derivatives.

Similarly the thermal cyclization of all polyhydrazide-parabanates gave poly(1,3,4-oxadiazole parabanate)s by heating in the presence of PPA at 160–170°. The presence of PPA decreased the temperature required for cyclization.

This transformation was indicated by i.r. spectra by the disappearance of the absorption at 1670 cm⁻¹, characteristic of the urea groups, simultaneously with the appearance of intense absorptions at 1070, 765 and 500 cm⁻¹.

Figure 2 shows the thermogravimetric curves of polyhydrazides with and without adding chemical dehydration reagent. From TGA, we observe that the polymers have good thermal stability. They

exhibit a weight loss <5% at temperatures between 300 and 350°. The lowest stability was recorded for the polyoxadiazole (**2**). In this structure, two hydrazide vicinal groups are present, creating a special situation. Although the i.r. spectra show that the reaction takes place, it is possible that there are some sequences of uncyclized hydrazide, or the appearance of some secondary reaction, difficult to detect by i.r. because this polymer is insoluble except in H₂SO₄. The polymers were characterized by elemental analyses.

Electrical properties

The films of polyhydrazides were tested for electrical properties. The resistivity, dielectric loss and dielectric constant were measured for films (Table 4). Polymer 10H exhibits remarkable

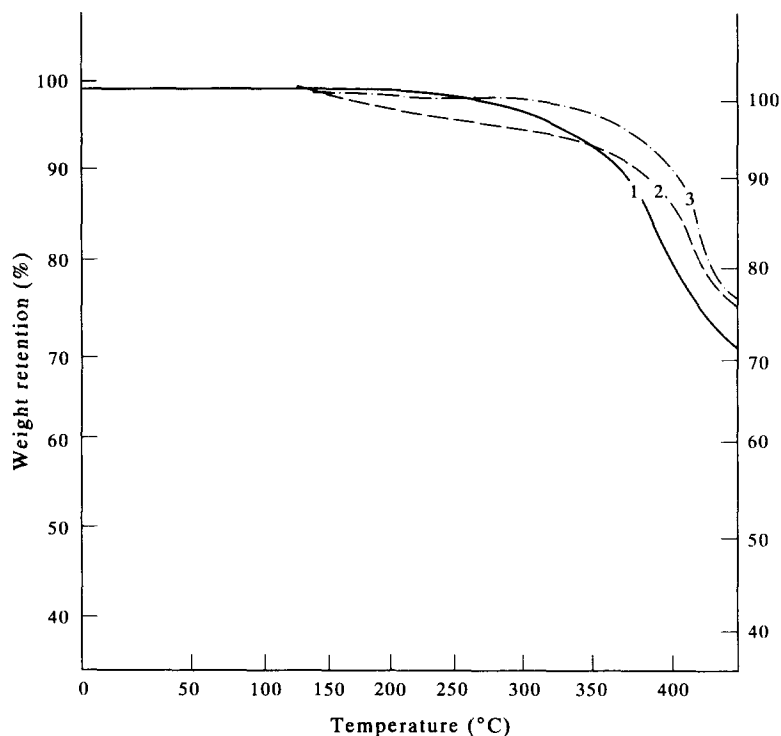


Fig. 2. Thermal behaviour of polyhydrazide (1H) and poly-1,3,4-oxadiazole (10); 1, poly-1,3,4-oxadiazole obtained by thermal dehydration without water-acceptor; 2, polyhydrazide 1H; 3, poly-1,3,4-oxadiazole obtained with addition of water-acceptor.

Table 4. Electrical properties of polyhydrazides

Polymer	Resistivity ($\Omega^{-1}\text{cm}^{-1}$)	Dielectric constant	Dissipation factor
1H	1.4×10^9	2.05	2.2×10^{-2}
9H	1.8×10^{11}	3.60	4.8×10^{-2}
10H	1.6×10^{10}	1.62	1.9×10^{-3}
12H	7.8×10^9	3.08	5.6×10^{-2}
14H	1.5×10^9	2.15	3.6×10^{-2}

insulating properties having high resistivity and low dielectric constant, while polymer 9H can be used in a condenser because it exhibits increased resistivity and relative dielectric constant as well as an increased loss dissipation factor.

CONCLUSIONS

A wide range of polyhydrazides and polyhydrazide-amides containing parabanic units have been obtained, showing characteristic properties. The polymers show medium or good thermal

stability and most of them have good solubility in polar aprotic solvents. These polymers can be converted into poly(1,3,4-oxadiazole)s with parabanic units, by addition of a dehydration reagent. The polyoxadiazoles are soluble only in H_2SO_4 .

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