SYNTHESIS OF POLYPYROMELLITIMIDOAMIDES FROM DIHYDRAZIDES OF AROMATIC AND ALIPHATIC ACIDS AND PYROMELLITIC DIANHYDRIDE

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Polyamido acids have been synthesized from pyromellitic dianhydride and dihydrazides of terephthalic, isophthalic, sebacic, and adipic acids. The polyamido acids obtained have been cyclized at 220° C, and it has been shown by IR spectroscopy that the polymers contain five-membered imide rings.

Investigations of recent years [1–3] have shown that high-molecular-weight compounds containing heterocycles in the main chain possess high heat stability.

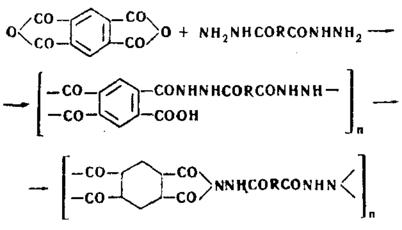
Table 1

Properties of Polymers Obtained from the Dihydrazides, I, II, and III (Ratio of Dianhydride to Dihydrazide = 1 : 1)

Solvent	Isophthalic dihydrazide		Terephthalic dihydrazide	
	Yield, %	η_{sp}^{*}	Yield %	η_{sp}^{**}
Hexamethylphosphoramide	98.0	0.30	72.4	0.23
Dimethylformamide	95.3	0.28	98.3	0.48
Dimethyl sulfoxide	96.4	0.35	79.1	0.26

*0.5% solution in hexamethylphosphoramide.
**0.5% solution in dimethylformamide.

In the present investigation we synthesized polymers from pyromellitic dianhydride (I) and the dihyrazides of terephthalic (II), isophthalic (III), sebacic (IV), and adipic (V) acids in solution at 20° C. We used hexamethylphosphoramide, dimethyl sulfoxide, and dimethylformamide as solvents.



The influence of the solvent on the condensation process was shown by the interaction of I with the dihydrazides II and III. The results of the experiments are given in Table 1.

As can be seen from the table, the replacement of one solvent by another had no effect on the viscosity of polymers obtained from dihydrazides I and II. To obtain a polymer with the maximum molecular weight from the dihydrazide III, the best solvent was dimethylformamide.

In an investigation of the influence of the ratio of the initial reactants on the formation of polyamido acids from the dihydrazide II, it was found that the polymer obtained with a small excess of anhydride in the reaction medium possessed the highest viscosity. On this basis, the synthesis of polymers from the dihydrazides of the other acids was carried out in dimethylformamide solution with an excess (10 mole-%) of dianhydride. Table 2 gives the compositions of the polyamido acids.

As can be seen from Table 2, the highest molecular weight (viscosity of the solution 0.48) was possessed by the polymer obtained from the dihydrazide III. This polyamido acid forms a strong transparent film, on which the following mechanical tests were carried out: tensile strength: 7.2 kg/mm^2; elastic limit: 7.1 kg/mm^2; relative elongation: 160%; modulus of elasticity: 20 kg/mm^2; mean thickness of the film: 60 μ.

Test conditions: dynamometer of the Schopper type, rate of elongation of the film 10 mm/min. Dimensions of the sample: width of the strip 8 mm, clamping length 10 mm.

Table 2

Properties of the Polymers Obtained from Pyromellitic Dianhydride and Dihydrazides (Ratio of Dianhydride to Dihydrazide = 1.1 : 1.0)

Dihydrazide	Yield of polymer, %	η_{sp}^{*}	Formation of film
Isophthalic	95.3	0.28	Transparent, brittle
Terephthalic	97.4	0.48	Transparent, strong, elastic
Sebacic	93.8	0.29	Turbid, brittle
Adipic	96.3	0.35	Turbid, brittle

*0.5% solution in dimethylformamide.

Figure 1 shows the thermogravimetric curve of the polymer. It can be seen from this that the loss in weight of the polymer begins at 200° C, and that at 500° C the polymer is 50% decomposed.

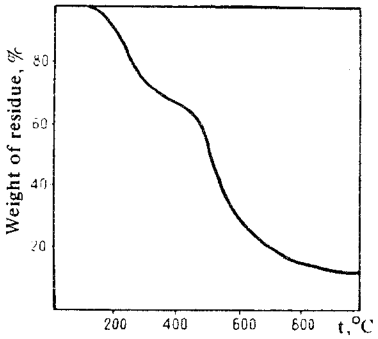


Fig. 1. Thermogravimetric curve of the polymer from pyromellitic dianhydride and terephthalic dihydrazide.

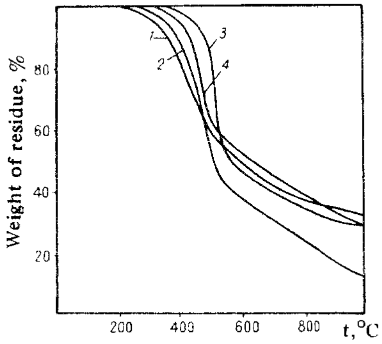


Fig. 2. Thermogravimetric curves of cyclic polymers: 1) polypyromellitimidoisophthalamide; 2) polypyromellitimidoterephthalamide; 3) polypyromellitimidoadipamide; 4) 4) polypyromellitimidosebacamide.

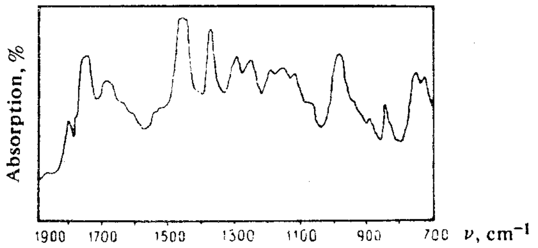


Fig. 3. IR spectrum (in paraffin oil) of polypyromellitimidoterephthalamide (UR-10 spectrometer with NaCl prism).

All the amido acids that we obtained were soluble in hexamethylphosphoramide, dimethylformamide, dimethyl sulfoxide, aqueous alkalis, and sulfuric acid.

Table 3

Characteristics of the Dihydrazides

Dihydrazides	Solvent	Mp, °C (literature data)
Isophthalic	Toluene	224 (220 [4])
Terephthalic	Toluene	310 (decomp) (300 [4])
Sebacic	Ethanol	184.5 (184–185 [5])
Adipic	Ethanol	171 (171 [6])

The second stage of the reaction, cyclization, was carried out at elevated temperatures. To investigate the influence of the reaction temperature on the cyclization of the polyamido acids from the dihydrazide (II), a series of experiments was carried out at 200, 220, 250, 280, and 300° C, with the other parameters constant. It was found that the performance of the cyclization reaction at 250° C and above led to the decomposition of the polymer (the carbon content in the final product was 1–3% higher than the calculated figure).

The optimum temperature at which cyclization took place at an adequate rate without a change in the composition of the cyclic polymer was 200°–220° C.

A study of the influence of the reaction time on the cyclization process showed that a time of 12 hr was sufficient for the conversion of the linear polymer into the cyclic polymer. Under these conditions, cyclic polymers were obtained from the dihydrazides II–V. Their thermogravimetric curves were recorded (Fig. 2). All the polymers were fairly stable to heating. Thus, appreciable loss in weight of the polymers began at 300° C for the polymers from the dihydrazides of aromatic acids and at 400° C for the polymers from the dihydrazides of the aliphatic acids.

The structure of the cyclic polymers was shown by IR spectroscopy. Figure 3 gives the IR spectrum of polypyromellitimidoterephthalamide, and from this it can be seen that the polymers produced contained five-membered imide rings with an absorption band at 1790 cm^{-1}.

EXPERIMENTAL

The dihydrazides were obtained from the methyl or ethyl esters of the corresponding acids in toluene or ethanol solution at the boiling point of a mixture with hydrazine hydrate, which was taken in 1.5–2-fold excess. The dihydrazides were recrystallized from ethanol to constant melting point. The characteristics of the dihydrazides are given in Table 3.

The hexamethylphosphoramide [7] was synthesized from dimethylamine and phosphorus oxychloride at −60° C. Bp 76°–78° C (1–2 mm); n_D^{20} 1.4569.

Synthesis of a polymer. With vigorous stirring, over 2–2 1/2 hr, pyromellitic anhydride was added in several portions with vigorous stirring to a solution of the dihydrazide at 20° C, and the mixture was stirred for a further 1–1 1/2 hr. The resulting solution was precipitated with dry ether and the product was dried at 30°–40° C in vacuum.

The cyclization of the polyamido acids was carried out at 220° C in a current of nitrogen for 12 hr.

REFERENCES

1. J. Amborski, Ind. Eng. Chem. Prod. Res. Develop., **2**, 3, 189, 1963; Khim. i tekh. polim., **8**, 7, 74, 1964.
2. G. Bower and L. Frost, J. Pol. Sci., **A1**, 3135, 1963.
3. T. Unishi, J. Pol. Sci., P-B, **3**, 689, 1965.
4. I. Davidis, J. pr. Chem., 1896, **54**, 66, 1896.
5. W. Steller, J. pr. Chem., **62**, 212, 1900.
6. T. Curtius, J. pr. Chem., **91**, 1, 1915.
7. M. Pianka and B. Owen, J. Appl. Chem., **5**, 525, 1955.

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