PREPARATION OF POLYMERS BY POLYCYCLIZATION

VII. Polyphenylenepyrazoles*

E. S. Krongauz, V. V. Korshak, A. M. Berlin, and A. P. Travnikova

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Heating equimolecular amounts of 1,1,2,2,-tetraacetylethane, 1,1,3,3-tetraacetylpropane, 4,4'-bis(acetoacetyl)diphenyloxide, and 1,4-bis(2',2'-diacetoethyl)benzene with 4,4'-dihydrazinodiphenyl gives new thermostable polymers. Some of their characteristics are reported.

We previously developed a method of synthesizing polypyrazoles by reacting bis(β-diketones) with dihydrazides of dicarboxylic acids and dihydrazines [1, 2]. The polymers based on dihydrazides of acids were not, however, highly resistant to heat, while polymers from dihydrazines were low molecular products, and their heat reistances were not investigated. The present work aimed to prepare thermostable polymers of higher degree of polymerization, containing pyrazole rings in the chains. The starting diketones were used 1,1,2,2-tetraacetylethane, 1,1,3,3-tetraacetylpropane, 4,4-bis(acetoacetyl)diphenyloxide, and 1,4-bis(2',2'-diacetoethyl)benzole, and the dihydrazine was 4,4'-dihydrazinodiphenyl.

The polymers were synthesized by heating equimolecular amounts of the starting compounds together without a solvent, first of all at a comparatively low temperature (not over 160°) for 1 hour. The choice of temperature for each ketone was based on the onset of reaction, as judged by the evolution of water. Then after careful grinding to a powder the product was reheated at 1–2 mm/200–300° for some hours. 4,4'-Bis(acetoacetyl)diphenyloxide reacted with 4,4'-dihydrazinodiphenyl in boiling absolute ethanol also gave a polypyrazole.

The conditions of synthesis and some properties of the resultant polypyrazoles are given in Tables 1 and 2.

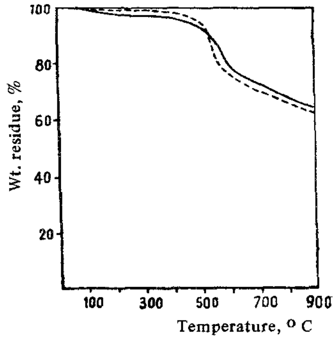

Fig. 1 Thermogravimetric plot of polypyrazole from 1,1,2,2-tetraacetylethane and 4,4'-dihydrazinodiphenyl. Rate of heating 20°/min: 1) in nitrogen; 2) in air.

The results given show that the polymer obtained by reacting 1,1,2,2-tetraacetylethane with 4,4'-dihydrazinodiphenyl was high molecular, η_{ps} 0.70 (in H_2SO_4). It was infusible and was dark brown with a metallic glitter. During heating at 300°, η_{ps} of the polymer increased with simultaneous decrease in solubility. Thermogravimetric analysis of the polymer (Fig. 1) showed it to be very heat resistant both in nitrogen and in air; the polymer did not show appreciable loss in weight on heating at 500°. Thermogravimetric analytical data for the polymer based on 4,4'-bis(acetoacetyl)diphenyloxide showed this polymer to also be stable up to 500°, but to lose much weight on heating to 900° (51%). While decomposition of the polymer from 1,1,3,3-tetraacetylpropane starts at ≈

Table 1

Conditions of Synthesis of Polypyrazole from 1,1,2,2-Tetraacetylethane and 4,4'-Dihydrazinodiphenyl

Run no.	Heating stage I		Heating stage II		Yield, %	η^*_{ps}	
	Temperature, °C	Time, hr,	Temperature, °C (pressure, mm)	Time, hr			
1	140—160	1	200	1	Quantitative	0.26	0.20
2	140—160	1	200—250 (1—2)	3	"	0.32	0.31
3	140—160	1	200—300 (1—2)	6	"	0.54	0.30
4	140—160	1.5—2	200—300 300 (1—2)	6 2.5	"	0.70**	0.33
5	140—160	1.5	200—300 300 (1—2)	6 6.5	"	Insoluble	0.52**

*The viscosities given are for 0.5% solutions of the polypyrazoles in H_2SO_4 (left column) and formic acid (right column).

**Amount undissolved negligible.

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*For Part VII see [2].

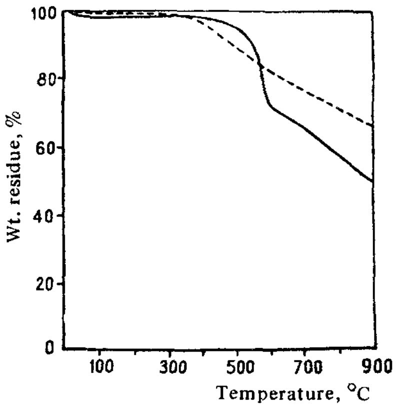


Fig. 2. Thermogravimetric plots for polypyrazoles, from 1,1,3,3-tetraacetylpropane and 4,4'-dihydrazinodiphenyl (1), 4,4'-bis(acetoacetyl)diphenyloxide and 4,4'-dihydrazinodiphenyl (2). Rate of heating in air 20°/min.

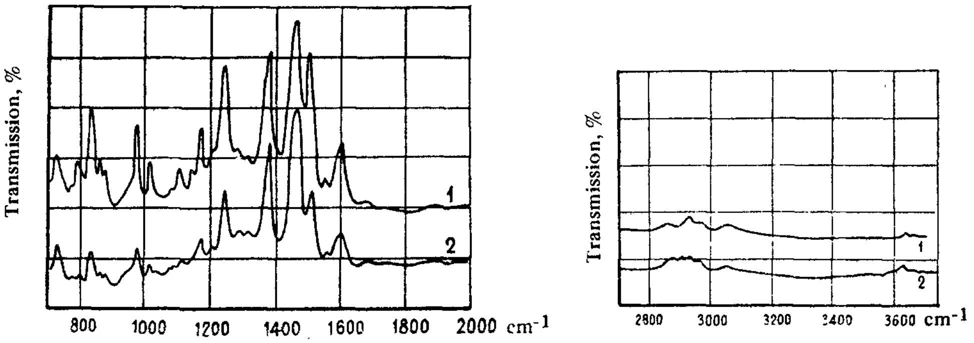
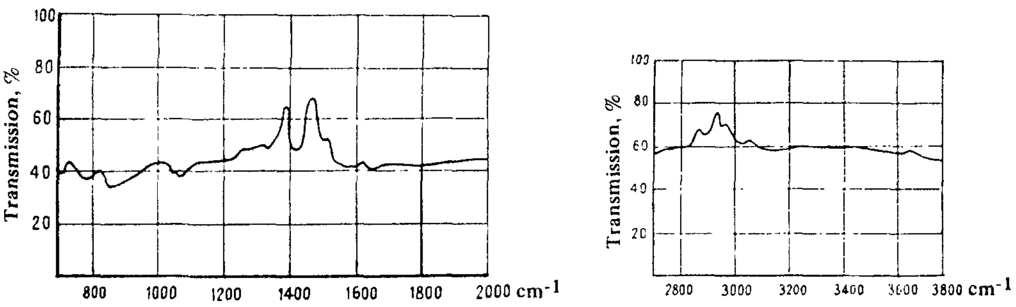


Fig. 3 & 4. IR spectra of polypyrazole from 4,4'-bis(acetoacetyl)diphenyloxide and 4',4'-dihydra- - zinodiphenyl: 1) polymer prepared in solution; 2)polymer prepared from melt.



Figs. 5 & 6. IR spectra of polypyrazole from 1,1, 2,2-tetraacetylethane and 4,4'-dihydrazinodiphenyl.

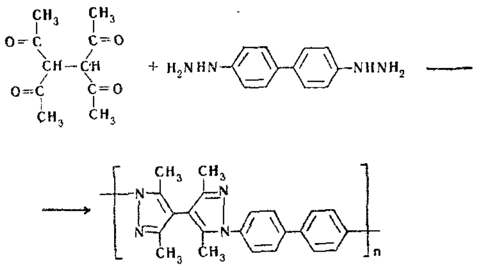
Table 2
Properties of the Polypyrazoles

Run no.	Starting materials		Temperature, °C (pressure mm), solvent	Time, hr	Yield, %	Softening temperature, °C	η^*_{ps}
	Bis(β-diketones)	Dihydrazine					
1	1,1,3,3-tetra-acetylpropane	4,4'-Dihydrazinodiphenyl	140—160 160—200 (2 mm) 200—300 (2 mm)	2 1.5 5	84	Does not melt	0.1** 0.21** insol.
2	4,4'-Bis(acetoacetyl)diphenyloxide	„	135—145 145—200 (2 mm)	2 6	88	210—220	0.18
3		„	Absolute EtOH, 79°	9	Quantitative	210—230	0.18
4	1,4-Bis(2',2'-diacetoacetyl)benzene	„	115—150 150—280 (2 mm)	2 6	94	180—190	0.19

*0.5% solution in cresol.
**0.5% H_2SO_4 solution.

≈350° (Fig. 2). The IR spectrum of the polymer lacks absorption bands in the regions 1600–1720 and 3200–3400 cm^{-1}, due to carbonyl and NH group valence vibrations, indicating full completion of the polycyclization process (Figs. 5 and6). The 3200–3400 cm^{-1} band is also lacking from the spectrum based on 4,4'-bis(acetoacetyl)diphenyloxide (Table 2, nos. 2,3), but there is a weak band at 1600–1615 cm^{-1}, obviously due to end groups of the starting ketone (Figs. 3,4).

The formation of the polymer from 1,1,2,2-tetraacetylethane can be represented by the following equation:



A special study of the structure of the polymer was not made. However, Mosby again showed conclusively that the reaction of 1,1,2,2-tetraacetylethane with hydrazine gives a compound of the type put forward. This view is also confirmed by the recent work of Bertram and Schaefer [4].

Since the marcromolecule of this polypyrazole consists only of aromatic rings, one would expect semiconducting properties, due to the system of conjugated double bonds. It gives a narrow EPR signal, the concentration of unpaired electrons being 2 × × 10^{16}/g. Its other properties are being investigated.

EXPERIMENTAL

4,4'-Dihydrazinodiphenyl hydrochloride. Korshak and Pozhil'stova's modified method of synthesis was used [5]. 18.6 g benzidine was dissolved in 123 ml HCl (23 ml conc. HCl in 100 ml distilled water) at 90°, the solution cooled to 35°, and a further 123 ml of the HCl, at 90°, added. The solution was cooled to −8–10°, and 70 ml cold 20% $NaNO_2$ solution added. The reactants were held at −5–10° for a few minutes, then portions added in small rapidly to a solution of 120 g $SnCl_2$ in 200 ml conc HCl at −10°, contained in a 3-necked flask fitted with a stirrer, reflux condenser, and tube for introducing argon. After adding the diazotized product the temperature was raised to 90°, and heating continued for 3 hr, after which the almost white frothy mass was dissolved in boiling distilled water (solution of the entire mass required ≈15 ml water) and the solution filtered hot. On cooling the filtrate gave a precipitate pure of 4,4'-dihydrazinodiphenyl hydrochloride, as a powder. After recrystallizing from distilled water the product was washed with MeOH and vacuum dried. Yield 22.1 g (77%) calculated on the benzidine reacted. Found: C 50.14; 50.05; H 5.63; 5.63; N 19.53; 19.73%, calculated for $C_{12}H_{16}N_4Cl_2$: C 50.18; H 5.62; N 19.51%.

All the operations were run in a current of argon; if this was not done, the reaction mixture resinified.

4,4'-Dihydrazinodiphenyl. A boiling solution of 1.14 g AcONa in 20 ml distilled water was added to a stirred boiling solution of 2 g of the hydrochloride in distilled water (≈150 ml). A precipitate of light yellow glistening needles formed. After cooling the precipitate was filtered off, washed with water, then with cold MeOH, and dried in a vacuum desiccator. Everything was done in a current of argon. The water for dissolving and washing the products was boiled and cooled in a current of that gas. Yield of 4,4'-dihydrazinodiphenyl 1.17 g (78%), mp 194–198° (sealed capillary). Found: C 67.77; 67.98; H 6.60; 6.61; N 25.71; 25.59%, calculated for $C_{12}H_{14}N_4$: C 67.27; H 6.59; N 26.15%.

Polyprazoles from bis(8-diketones) and 4,4'-dihydrazinodiphenyl.

a) From 1,1,2,2-tetraacetylethane. Carefully mixed equimolecular amounts of the starting materials were heated together for 1 hr in a condensing test tube, filled with argon, at 140–160°. The product was repowdered and again heated in a current of argon, under vacuum at 200–300°, for 6 hr. The resultant polymer did not melt. Quantitative yield. Found: C 77.51; 77.38; H 5.93; 5.97; N 15.54; 15.32%, calculated for $C_{22}H_{20}N_4$: C 77.62; H 5.92; N 16.46%.

b) From 4,4-bis(acetoacetyl)diphenyloxide. The method used was similar to that described above. The mixed reactants were heated at 135–145°, then the temperature raised to 200°. The resultant polymer was dark yellow and brittle, soluble in cresol, H_2SO_4, and formic acid. Found: C 78.66; 78.71; H 5.26; 5.12; N 11.16; 10.92%, calculated for $C_{32}H_{24}N_4O$: C 79.98; H 5.03; N 11.66%.

c) From 1,4-bis(2',2'-diacetoethyl)benzene. The polymer was obtained as a pale brown brittle substance, by first heating the reactants together at 115–150°, then to 280°. It is soluble in DMFA, and ether precipitated it well from a solution in that solvent. It was also soluble in H_2SO_4 and formic acid. Found C 78.97; 79.03; H 6.35; 6.41; N 12.63; 12.80%, calculated for $C_{30}H_{28}N_4$: C 81.04; H 6.35; N 12.60%.

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Institute of Hetero-Organic Compounds,
AS USSR, Moscow