Chemistry

Corresponding Member of the Academy of Sciences of the USSR V. V. Korshak, E. S. Krongauz, A. M. Berlin

1963

SovietRxiv

Abstract

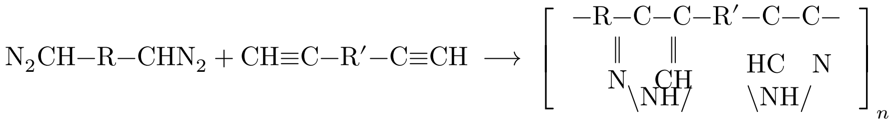
Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR V. V. Korshak, E. S. Krongauz, A. M. Berlin

A New Method for Obtaining Polypyrazoles

In contrast to the method we published earlier for obtaining polypyrazoles by the polycyclization of bis-(β-diketones) with dihydrazides of dicarboxylic acids (^{1}), a new method has been developed for synthesizing polymers containing alternating pyrazole rings in the chain with a free NH group of the pyrazole nucleus. The method consists in the interaction of bis-diazo compounds with *p*-diethynylbenzene or diacetylene according to the following scheme:



$$N_2CH-R-CHN_2 + CH\equiv C-R'-C\equiv CH \longrightarrow \left[\begin{array}{c} -R-C-C-R'-C-C- \\ \| \quad \| \qquad\qquad\qquad \\ N \quad CH \qquad HC \quad N \\ \backslash NH/ \qquad \backslash NH/ \end{array}\right]_n$$

$$\text{where } R = (CH_2)_4;\ C_6H_4; \qquad R' = C_6H_4;\ -.$$

The polymers obtained are yellow powders readily soluble in dimethylformamide and cresol; the reduced viscosity of a 0.5% solution in cresol is 0.2–0.3; the molecular weight is ~ 10000.

The polymer from 1,6-bisdiazohexane and *p*-diethynylbenzene (1) has a melting temperature of 440° (beginning at 416° the polymer darkens); the polymer from bisdiazohexane and diacetylene melts in the interval 350–374°; the polymer based on bisdiazoxylylide and diethynylbenzene does not melt up to 500°.

These polypyrazoles differ from those described by us earlier by their higher melting temperatures, which may be explained by differences in the structure of their polymer chains, which in the case of the polymers under consideration lead to strengthening of interchain interaction and hence to an increase in their thermal stability.

Polypyrazoles synthesized by the polycyclization of bis-(β-diketones) with dihydrazides of dicarboxylic acids may be regarded as heterochain polymers, since the nitrogen of the pyrazole nucleus directly participates in the formation of the polymer chain:

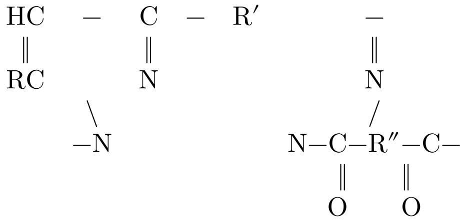
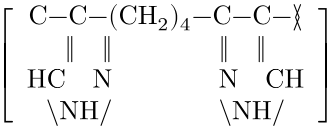


Fig. 1: IR spectrum of the polymers.

Fig. 1



The polymers considered in the present paper may be regarded as carbochain polymers, for the main polymer chain is built only of carbon atoms—

mers; moreover, the pyrazole nitrogen has a hydrogen atom capable of participating in the formation of hydrogen bonds.

In the IR spectrum of the polymers studied there is a broad, diffuse band in the region 3100-3300 cm^{-1}, which corresponds to the NH group and is due to the strong association characteristic of pyrazoles with a free NH group (2) (Fig. 1). It is apparently association through the NH groups that explains the high melting points of these polymers. In the polypyrazoles described by us previously, the hydrogen on nitrogen was substituted; therefore association was absent, as is clearly seen in the spectra of these polymers (absence of absorption in the 3200 cm^{-1} region).

The method for obtaining polypyrazoles with a free NH group is as follows: to a freshly prepared solution of a diazo compound in ether or alcohol are added equimolecular amounts of a diethynyl derivative, either neat or as an ethereal solution. The resulting reaction mixture is left at room temperature or in a refrigerator; the reaction usually begins after 15-20 min, but is completed on standing for several days. The polymers formed are isolated as powders.

Experimental Part

1. To an ethereal solution of 1,6-bisdiazohexane, obtained from 2.69 g of N,N -dinitroso-N,N -diacetylhexamethylenediamine (3), a solution of 1.16 g of diethynylbenzene in 10 ml of ether was added. After 15 min the appearance of a precipitate was observed. The reaction mixture was left for several days, until precipitation ceased and the solution changed from bright orange to pale yellow. The yield was quantitative. The substance

is almost completely reprecipitated by ether from DMF, m.p. 440° with darkening; reduced viscosity 0.3.

$C_{16}H_{16}N_4$. Found % : C 72.47; 72.48; H 6.47; 6.69
Calculated % : C 72.69; H 6.10

2. To an ethereal solution of 1.3 g of 1,6-bisdiazohexane was added diacetylene (0.5 g), cooled to −15—20°. After the reaction mixture had stood for five days, 0.7 g of polymer was obtained; reduced viscosity 0.2, m.p. 350-374°.

$C_{10}H_{12}N_4$. Found % : C 62.33; 62.22; H 7.00; 6.92
Calculated % : C 63.80; H 6.42

After evaporation of the ether, a further 0.71 g of polymer of lower molecular weight was obtained; reduced viscosity 0.06, m.p. 250°.

$C_{10}H_{12}N_4$. Found % : C 65.88; 65.79; H 6.85; 6.84
Calculated % : C 63.80; H 6.42

3. **Preparation of a polymer based on bisdiazoxylylene and *p*-diethynylbenzene.**

a. Nitrosation of N,N -diacetylxylylenediamine (4) was carried out in an acetic acid—acetic anhydride mixture while passing N_2O_3 into the cooled solution until a dark-green color appeared. On the following day the reaction mixture was diluted with an equal volume of ice water. The resulting yellow crystals were filtered off, washed with ice water, and crystallized from ethyl alcohol; m.p. 103-104°, yield 80-90% of theoretical.

$C_{12}H_{14}N_4O_4$. Found % : C 51.60; 51.76; H 5.14; 5.09; N 20.60; 20.61
Calculated % : C 51.79; H 5.07; N 20.14

b. To a solution of 0.5 g of N,N -dinitroso-N,N -diacetylxylylenediamine in 20 ml of absolute ether, placed in a three-necked flask equipped with a stirrer, drop—

with a dropping funnel and a condenser with a calcium chloride tube, while cooling, 0.5 ml of a solution of sodium methylate in absolute methanol was added. The solution acquired a reddish-orange color; it was filtered to remove turbidity, and 0.2 g of *p*-diethynylbenzene was added to it. The reaction mixture was kept at room temperature for 8 days. 0.2 g of polymer was obtained in the form of a light-yellow powder; reduced viscosity 0.24; it does not melt up to 500°.

Found, %: C 72.60; 72.49; H 5.11; 5.23
$C_9H_6N_2$. Calculated, %: C 76.03; H 4.25

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
13 VII 1963

REFERENCES

1. V. V. Korshak, E. S. Krongauz et al., DAN, **149**, No. 3 (1963).
2. W. Hü kel, J. Datow, E. Simmersbach, *Zs. phys. Chem.*, **186A**, 129 (1940).
3. H. Reimlinger, *Ber.*, **92**, 970 (1959).
4. I. P. Losev, O. Ya. Fedotova, M. L. Kerber, ZhOKh, **26**, 548 (1956).

Note: Figure translations are in progress. See original paper for figures.