Chemistry

1964

SovietRxiv

Abstract

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Chemistry

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Synthesis of Polybenzoxazoles

(Presented by Academician S. S. Medvedev, 26 VI 1964)

As is known, compounds of the benzoxazole series are distinguished by considerable thermal stability ([1]). In this connection, in the search for high-temperature-stable polymers we synthesized polybenzoxazoles containing benzoxazole rings in the chain, joined to one another by aromatic residues. Until now, polybenzoxazoles with aliphatic links had been described, obtained by condensation in the melt of aromatic *o*-dioxydiamines with aliphatic dicarboxylic acids or their esters ([2]). The fully aromatic polybenzoxazoles synthesized by us were obtained by the reaction of 3,3′-dioxybenzidine with acid dichlorides of aromatic dicarboxylic acids. The reaction is carried out in two stages: first a polyoxyamide is formed, which on heating undergoes intramolecular cyclization with elimination of water and is converted into a polybenzoxazole:

$$n\,\text{HO–aromatic biphenyl diamine unit–OH} + n\,\text{ClCO–phenylene–COCl} \xrightarrow[0^\circ]{-2n\text{HCl}}$$

$$\longrightarrow \left[\text{HO–biphenyl–OH} - \text{NHCO–phenylene–CO–}\right]_n \xrightarrow[350^\circ]{-2n\text{H}_2\text{O}}$$

$$\longrightarrow \left[\text{benzoxazole-biphenyl-benzoxazole-phenylene unit}\right]_n$$

$$(I) \qquad (II)$$

Thus, for example, to a solution, stirred in an argon atmosphere, of 0.66 g (0.00305 mole) of 3,3′-dioxybenzidine ([3]) in 5 ml of freshly distilled N,N-dimethylacetamide, at 0°, a solution of 0.62 g (0.00305 mole) of isophthaloyl dichloride in 2 ml of absolute benzene is added dropwise over 10 min. Stirring is continued at the same temperature in an argon atmosphere for another 2.5 hr. The poly(3,3′-dioxydiphenylisophthalamide) (I), obtained in the form of a viscous solution, is precipitated with water, extracted with methanol in a Soxhlet apparatus, and dried in vacuum, 0.01 mm, at 70°. Yield 98%; $\eta_{sp} = 0.65$ (0.5% solution in conc. H_2SO_4).

Found, %: C 65.45, 65.69; H 5.23, 5.18; N 6.24, 6.20 $(C_{20}H_{14}N_2O_4)_n$. Calculated, %: C 69.36; H 4.05; N 8.08

Fig. 1. IR spectra of poly-(3,3′-dioxydiphenylisophthalamide) (I) and poly-2,2′-(m-phenylene)-6,6′-dibenzoxazole (II) (IR spectra recorded on a UR-10 double-beam spectrophotometer)

Figure 1: Fig. 1. IR spectra of poly-(3,3′-dioxydiphenylisophthalamide) (I) and poly-2,2′-(m-phenylene)-6,6′-dibenzoxazole (II) (IR spectra recorded on a UR-10 double-beam spectrophotometer)

The polymer is soluble in dimethyl sulfoxide, N-methyl-2-pyrrolidone, and conc. H_2SO_4, and is sparingly soluble in dimethylacetamide. It forms strong flexible films and fibers.

The polyoxyamide is heated at 350° in vacuum, 0.01 mm, for 4.5 hr. The loss in weight in this process is 9.76% (94% of that theoretically possible for cyclodehydration). The resulting poly-2,2′-(*m*-phenylene)-6,6′-dibenzoxazole (II) has $\eta_{sp} = 0.61$ (0.5% solution in conc. H_2SO_4), which is almost no different from η_{sp} of a 0.5% solution of the initial polyoxyamide.

Found, %: C 74.36, 74.29; H 4.01, 4.08; N 8.13, 7.97
$(C_{20}H_{10}N_2O_2)_n$. Calculated, %: C 77.5; H 3.23; N 9.03

The polybenzoxazole obtained dissolves in conc. H_2SO_4 and is insoluble in dimethyl sulfoxide, N-methylpyrrolidone, and dimethylacetamide.

It is interesting to note that solutions of polybenzoxazole in sulfuric acid possess distinct fluorescence, which is not observed for solutions of the starting polyoxyamide.

Figure 1 shows the IR spectra of a polyoxyamide film obtained from a solution in dimethyl sulfoxide, and of the same film after heating at 350°/0.01 mm, i.e., under cyclodehydration conditions. Comparison of the IR spectra shows that the absorption bands in the region 3400–3100 cm^{-1}, attributable

Fig. 1. IR spectra of poly-(3,3′-dioxydiphenylisophthalamide) (I) and poly-2,2′-(*m*-phenylene)-6,6′-dibenzoxazole (II) (IR spectra recorded on a UR-10 double-beam spectrophotometer)

to valence vibrations of OH and NH groups, almost completely disappear after thermal treatment of the film. The band at 1660 cm^{-1}, attributable to deformation vibrations in the amide group, also disappears. The incomplete disappearance of these bands is evidently explained by the presence of a small number of residual amide units in the benzoxazole polymer.

Upon successive heating of a polybenzoxazole sample in vacuum of 0.01 mm at temperatures of 400, 450, and 500°C, with holding for one hour at each temperature, the weight losses were, respectively, 3.67, 0.61, and 2.45%. After such thermal treatment the polymer loses its solubility in sulfuric acid.

Under conditions analogous to those described above, we also obtained poly-(3,3′-dioxydiphenylterephthalamide). To a solution of 0.55 g (0.0025 mole) of

3,3′-dioxibenzidine in 5 ml of dimethylacetamide, 0.52 g (0.0025 mole) of finely ground terephthalic acid dichloride is added with stirring in an argon atmosphere; the mixture is stirred for another 2 hours at 0°, and the thick mass formed is diluted with 15 ml of dimethylformamide and poured into water. The precipitated poly-(3,3′-dioxydiphenylterephthalamide) is washed with water, methyl alcohol, and ether and dried. Yield 93%, $\eta_{ud} = 0.44$ (0.5% solution in conc. H_2SO_4).

Found, %: C 68.26, 68.46; H 4.48, 4.40; N 7.80, 7.77
$(C_{20}H_{14}N_2O_4)_n$. Calculated, %: C 69.36; H 4.05; N 8.08

The spectroscopic data presented were obtained by V. P. Bazov, to whom the authors express their gratitude. The authors also thank A. N. Pravednikov, L. B. Sokolov, V. M. Savinov, and L. V. Turetskii for useful advice and assistance in the work*.

Physical Chemistry Institute
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Received
25 VI 1964

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* Note added in proof. After the present communication had been submitted for publication, it became known that other authors had also reported on the same question (4).

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