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SYNTHESIS OF POLYBENZOXAZOLES

One of the promising routes to the preparation of heat-resistant polymers, which are acquiring ever greater importance, is the synthesis of polymers containing various carbo- and heterocycles in the chain ([1]-[3]). The synthesis of such cyclochain polymers is carried out by various methods, among which the reaction of "polycyclization," leading to the formation of cyclochain polymers by ring closure, is of particular interest ([4]). At present, the preparation by this route of polybenzimidazoles ([5], [6]), polythiazoles ([7]), polypyrazoles ([4]), polypyromellitimides ([8]), polyaminotriazoles ([9]), and other heterocyclochain polymers ([3]) has been described.

Recently, reports have appeared on the preparation of polybenzoxazoles by means of a polycyclization reaction proceeding through the interaction of 3,3′-dihydroxybenzidine with aliphatic dicarboxylic acids ([10]) or with isophthaloyl chloride ([11]). The products obtained possess high thermal stability, especially those having a completely aromatic structure. However, a major drawback of the polymers described is their poor solubility. This drawback, evidently, can be eliminated, and this was the aim of the present investigation.

For the preparation of polybenzoxazoles we used dioxydiamines of the general structure

HO-benzene ring-R-benzene ring-OH, with H_2N and NH_2 ortho to the hydroxyl groups,

where $R = -C(CH_3)_2-$ and a cyclic ketal fragment containing $-C-$ and CO

in the hope that the polymers formed in this case would be more readily soluble because of the more flexible chain and the presence of an internal plasticization effect caused by side substituents ([11]). The condensation of dioxydiamines with diphenyl esters of such dicarboxylic acids as sebacic, isophthalic, and terephthalic acids was carried out in a nitrogen atmosphere, followed by heating in vacuum at a higher temperature.

The formation of polybenzoxazoles proceeds through the intermediate stage of polyoxyamides according to the equation:

$$
\begin{aligned}
&x\,\mathrm{H_2N{-}Ar(OH){-}R{-}Ar(OH){-}NH_2} + x\,\mathrm{C_6H_5OOC{-}R'{-}COOC_6H_5} \longrightarrow\\
&[\mathrm{-R{-}Ar(OH){-}NH{-}COOC_6H_5{-}R'{-}COOC_6H_5{-}NH{-}Ar(OH){-}}]_x \longrightarrow\\
&[\mathrm{-R{-}Ar(OH){-}NH{-}CO{-}R'{-}CO{-}NH{-}Ar(OH){-}}]_x \quad \text{polyoxyamide} \longrightarrow\\
&[\mathrm{-R{-}Ar(OH){-}N{=}C(OH){-}R'{-}C(OH){=}N{-}Ar(OH){-}}]_x \longrightarrow\\
&[\mathrm{-R{-}benzoxazole{-}R'{-}benzoxazole{-}}]_x \quad \text{polybenzoxazole.}
\end{aligned}
$$

The temperature at which the first stage of condensation occurs—the formation of the polyoxyamide—depends on the melting temperature of the mixture of starting reagents and lies within the range 160–200°; the temperature of the second stage of condensation, leading to the production of polybenzoxazoles, is above 220°; the exception is condensation with diphenyl terephthalate. In this case cyclization occurs only at a temperature above 290°.

Table 1

No.	Elementary unit of the polymer	T_d, °C	Reduced viscosity	Solvent	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N
1.	Structural formula shown: polybenzoxazole unit with isopropylidene bridge and aliphatic chain $-(CH_2)_8-$	425	0.21 pyridine; 0.38 chloroform	Chloroform, tricresol, tetrahydrofuran, pyridine, sulfuric acid, formic acid	77.47; 77.28	7.47; 7.62	6.96; 6.99	77.29	7.26	7.21

No.	Elementary unit of the polymer	T_d, °C	Reduced viscosity	Solvent	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N
2.	Structural formula shown: polybenzoxazole unit with isopropylidene bridge and phenylene fragment	500	0.15 chloroform	Chloroform, tricresol, tetrahydrofuran, pyridine, benzyl alcohol, tetrachloroethane, sulfuric acid, formic acid	79.14; 78.41; 77.51	4.74; 5.27; 4.79	7.36; 7.33	78.39	4.58	7.95

No.	Elementary unit of the polymer	T_d, °C	Reduced viscosity	Solvent	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N
3.	Structural formula shown: polybenzoxazole unit with isopropylidene bridge and phenylene fragment	510	0.16 chloroform	Chloroform, tricresol, sulfuric acid, formic acid	78.97; 77.16	4.77; 4.80; 4.77	7.34; 7.32	78.39	4.58	7.95
4.	Structural formula shown: polyoxyamide unit based on phthalide structure and aliphatic chain $-(CH_2)_8-$	335	0.17 sulfuric acid	Sulfuric acid	69.27; 69.02; 69.49	5.72; 5.69; 5.88	5.35; 5.48	70.02	5.88	5.44

Fig. 1. Thermograms of polymers

Figure 1: Fig. 1. Thermograms of polymers

As can be seen from the data in Table 1, polymers based on 2,2-bis-(3-amino-4-hydroxyphenyl)-propane possess good solubility in a broad range of organic solvents. In contrast, the product of the interaction of 3,3-bis-(3-amino-4-hydroxyphenyl)-phthalide even with sebacic acid ester dissolves only in concentrated sulfuric acid. It is interesting to note that heating this product at a temperature of 275° and above leads to the formation of a polymer completely insoluble in sulfuric acid, which, evidently, can be explained by the formation of a polymer of three-dimensional structure according to the following scheme:

$$\cdots - (CH_2)_8 - CO - NH - [\text{hydroxyphenyl-phthalide-aminophenyl unit}] \xrightarrow{-H_2O}$$

crosslinked polymer structure containing phthalide, amide, hydroxyl, and benzoxazole fragments, as shown

As a result of the formation of a three-dimensional structure, in this case no closure of benzoxazole rings takes place, and the polyoxyamide structure of the polymer is retained (see Table 1).

The possibility of such a reaction mechanism is supported by the fact that *o*-aminophenol reacts with phthalic anhydride with the formation of 2-phenylbenzoxazole (^{12}).

Fig. 1. Thermograms of polymers: **1** —poly-2,2′-(octamethylene)-5,5′-dibenzoxazole-2,2-propane; **2** —poly-2,2′-(*m*-phenylene)-5,5′-dibenzoxazole-2,2-propane; **3** —poly-2,2′-(*p*-phenylene)-5,5′-dibenzoxazole-2,2-propane; **4** —poly-2,2′-dioxydiphenyloctamethyleneamide-3,3′-phthalide.

Determination of the molecular weight of poly-2,2′-(octamethylene)-5,5′-dibenzoxazole-2,2-propane in pyridine solution by the sedimentation method in an ultracentrifuge showed that this polymer, despite the relatively low value of its reduced viscosity (0.21), has a sufficiently high molecular weight (~30000).

The results of thermogravimetric analysis indicate the high thermal stability of the synthesized polymers. Figure 1 gives thermograms of the polymers at a specimen heating rate of 10 deg/min in air. Curve 1, representing the weight loss of poly-2,2′-(octamethylene)-5,5′-dibenzoxazole-2,2-propane, shows that the polymer begins to decompose only at 420–430°. Polymers obtained from aromatic acids are distinguished by still higher thermal stability—the loss in weight begins at a temperature of 500°. It is interesting to note that in fully aromatic polybenzoxazoles a decrease in weight is also observed at a temperature of 500° (^{11}).

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