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Abstract

Full Text

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PREPARATION OF POLYMERS WITH DIBENZBORIMIDAZOLINE UNITS IN THE MAIN CHAIN

Earlier we (ˆ1) synthesized polymers containing dibenzimidazoline units in the main chain. Continuing studies on the synthesis of heat-resistant polymers containing rigid heterocyclic units in the main chain, we synthesized polymers containing dibenzborimidazoline units linked to one another both by *p*-phenylene units and by oxygen atoms, in order to study the influence of the structure of the polymer chain on its thermal stability.

Polymers containing dibenzborimidazoline units alternating with *p*-phenylene rings were described by Marvel (ˆ2), whereas polymers in which the boron atoms are linked to one another through oxygen have been obtained by us for the first time.

The synthesis of polymers with dibenzborimidazoline units in the main chain was carried out by the polycondensation reaction of 3,3′-diaminobenzidine with tetrafunctional diboron-containing compounds. Thus, a polymer containing alternating dibenzborimidazoline and *p*-phenylene units in the main chain was obtained by the interaction of 3,3′-diaminobenzidine with the tetrabutyl ester of *p*-phenylenediboronic acid according to the equation:

$$\mathrm{H_2N{-}}\text{biphenyl ring system}\mathrm{{-}NH_2} \;+\; (\mathrm{C_4H_9O})_2\mathrm{B{-}C_6H_4{-}B(OC_4H_9)_2} \longrightarrow$$

$$\longrightarrow \left[-\mathrm{B}\begin{matrix}\mathrm{NH}\\ \mathrm{NH}\end{matrix}\text{–biphenyl ring system–}\begin{matrix}\mathrm{NH}\\ \mathrm{NH}\end{matrix}\mathrm{B{-}C_6H_4{-}}\right]_{\mathrm{n}}$$

Another polymer, in which the dibenzborimidazoline units are linked by oxygen atoms, was obtained by the polycondensation reaction of 3,3′-diaminobenzidine with tetraacetyldiborate according to the equation:

$$\mathrm{H_2N{-}}\text{biphenyl ring system}\mathrm{{-}NH_2} \;+\; (\mathrm{CH_3CO})_2\mathrm{B{-}O{-}B(COCH_3)_2} \longrightarrow$$

$$\longrightarrow \left[-\mathrm{B}\begin{matrix}\mathrm{NH}\\ \mathrm{NH}\end{matrix}-\text{biphenyl ring system}-\begin{matrix}\mathrm{NH}\\ \mathrm{NH}\end{matrix}\mathrm{B}-\mathrm{O}-\right]_{\mathrm{n}}$$

Infrared spectra were recorded for the polymers obtained (Fig. 1); they contain absorption bands in the region of 3360 cm^{-1}, corresponding to stretching vibrations of the NH group. The absorption band in the region of 800 cm^{-1} is attributed to the system of fused rings characteristic of polymers of this type.

The polymers obtained are infusible dark-brown powders soluble in sulfuric acid. The properties of the polymers obtained are presented in Table 1.

Table 1

Properties of the polymers

Formula of the polymer chain unit	$[\eta]$	Weight loss, % at 300°	Weight loss, % at 400°	Weight loss, % at 500°
–B–NH– C_6H_3– C_6H_3–NH –B–C_6H_4 – |	0.22	4.82	24.31	46.53
| NH B–NH– C_6H_3– C_6H_3–NH –B–O– | | NH NH	0.26	4.0	6.6	30.7

As can be seen from the data in Table 1, the polymers obtained are of low molecular weight and possess thermal stability at temperatures from 300 to 400° when heated in air; moreover, the polymer in which the boron atoms are bonded directly to the oxygen of the chain has the greater thermal stability.

The polymer containing oxygen atoms in the main chain hydrolyzes in moist air.

Fig. 1. IR absorption spectra of dibenzborimidazolines obtained by polycondensation of 3,3-diaminobenzidine: **1** –with the tetrabutyl ester of *p*-phenylenediboronic acid; **2** –with tetraethyldiborate.

Experimental Part

Tributyl borate ([3]) was obtained by the reaction of boric anhydride with *n*-butyl alcohol. The tributyl borate had a boiling point of 88-90°/3 mm (lit. ([3]):

Fig. 1. IR absorption spectra of dibenzborimidazolines obtained by polycondensation of 3,3-diaminobenzidine: 1 —with the tetrabutyl ester of *p*-phenylenediboronic acid, 2 —with tetraethyldiborate

Figure 1: Fig. 1. IR absorption spectra of dibenzborimidazolines obtained by polycondensation of 3,3-diaminobenzidine: 1 —with the tetrabutyl ester of *p*-phenylenediboronic acid, 2 —with tetraethyldiborate

b.p. 103–105°/8 mm). Yield 85%.

***p*-Phenylenediboronic acid** ([4]) was obtained by the reaction of *p*-dilithiobenzene ([5]) with tributyl borate in an argon atmosphere at −70°. After recrystallization from water, *p*-phenylenediboronic acid was obtained in the form of white crystals, not melting up to 420° (lit.: m.p. above 420°).

Tetrabutyl ester of *p*-phenylenediboronic acid ([4]) was obtained by the esterification reaction of *p*-phenylenediboronic acid with *n*-butyl alcohol, with simultaneous distillation of the azeotropic water–

butanol. The tetrabutyl ester of *p*-phenylenediboronic acid was purified by distillation in vacuum and had a boiling point of 142–144°/$7 \cdot 10^{-2}$ mm (lit. (4): b.p. 160–176°/0.4 mm).

Tetraacetyldiborate ([6]) was obtained by heating orthoboric acid with acetic anhydride at 50–70° in an argon atmosphere. Tetraacetyldiborate was purified by precipitation with ether from a solution in acetic acid and had a melting point of 146–147° (lit.: m.p. 147–148°).

Polycondensation of 3,3-diaminobenzidine with tetrafunctional diboron-containing compounds was carried out by heating an equimolecular mixture of the reactants in a stream of argon at 250–260° for 1.5 hours, followed by heating in vacuum ($3 \cdot 10^{-2}$ mm Hg) at 260° for one hour.

The thermal stability of the polymers was determined from the weight loss of the polymers upon heating in air for one hour successively at temperatures of 300, 400, and 500°.

The intrinsic viscosities of the polymers were determined in 0.5% sulfuric acid solution. To determine the resistance to hydrolysis, a sample of polymer containing B–O–B bonds ($[\eta] = 0.26$) was kept in a desiccator with water for one week. Under these conditions, considerable hydrolysis of the polymer was observed, and the intrinsic viscosity of the polymer decreased to $[\eta] = 0.097$.

Polymer samples for study of their IR spectra were prepared by pressing with potassium bromide. The authors express their gratitude to E. I. Pokrovskii for recording the infrared spectra.

By the polycondensation reaction of 3,3-diaminobenzidine with tetraacetyldiborate, a new polymer was obtained containing dibenzborimidazoline units

and oxygen atoms in the main chain, more thermally stable than poly-*p*-phenylenedibenzborimidazoline.

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