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Polynuclear Cu(II) Complexes with Hyperbranched Polyester Carboxylates

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Abstract—Polydentate carboxylate platforms based on polyester polyol Boltorn H, containing from 8 to 14 carboxy groups in terminal positions were obtained. A method of synthesis of Cu(II) polynuclear complexes with polyester carboxylates Boltorn H with a degree of substitution of 65 and 90% was developed.

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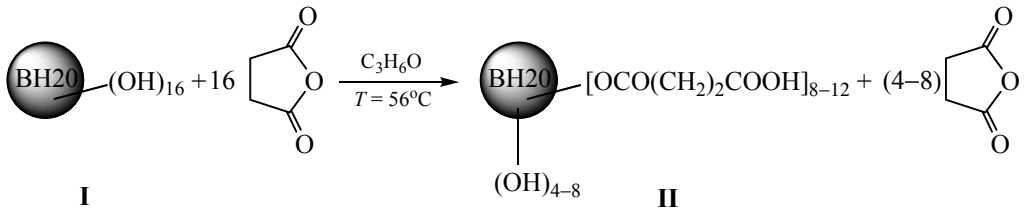
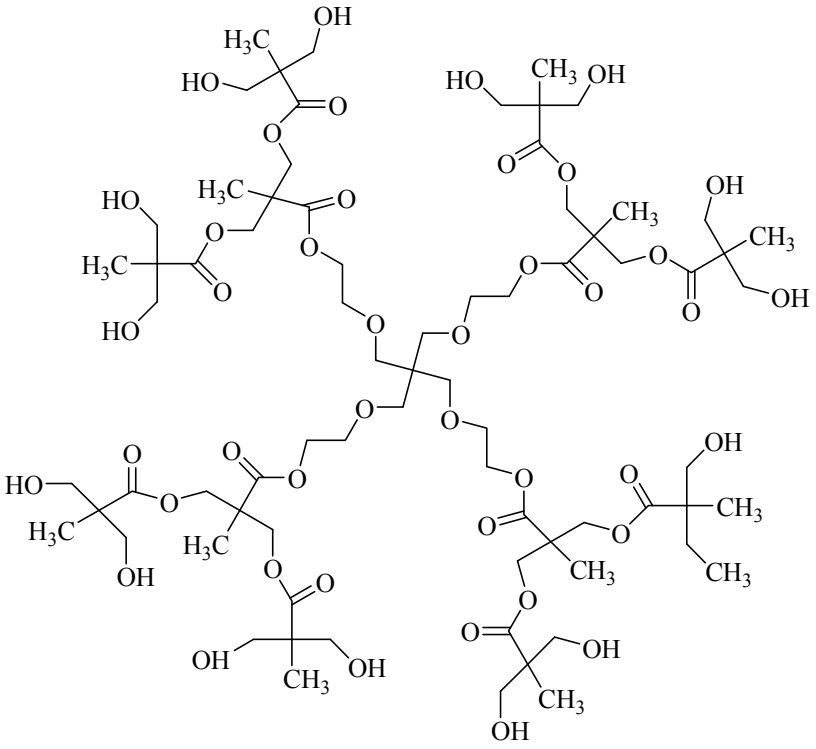
Nano-size and multifunctionality of the molecules of hyperbranched polymers make such reagents attractive for a targeted synthesis of substances with certain coordination properties [1–3]. A high proportion of active local groups leading to the presence of multiple identical ligands in a molecule leads to a marked effect of the activity co-operation of the ligand fragments and the specific properties of structured macromolecule [4]. Coordinating activity of the non-toxic hyperbranched polyester polyols Boltorn H is of fundamental and practical interest. However, we know only a few papers that describe these properties of polydentate nanoplatform Boltorn H [5, 6]. It should be noted that the coordination compounds of the Boltorn macroligand with metal cations are practically unknown. Strengthening of complexing function of the polyol with respect to metal ions is possible at the replacement of OH groups by a more active nucleophilic groups. Earlier in [7] we presented a method for synthesis of polyestercarboxylate based on the Boltorn H20. This work is a continuation of the studies aimed at functionalization of the hyperbranched polyol Boltorn H20 (see the figure) with anhydrides of carboxylic acids with subsequent synthesis of complex compounds with ions of transition metals.

To create coordinationally active macromolecules we developed two methods of functionalization of the parent compound BH20 (**I**) with succinic anhydride. Interaction of compounds BH20 with succinic anhydride in acetone leads to incomplete functionalization of the original platform **I** [7]. The percentage of carboxy groups and acid number in the compound **II** indicate that the functionalization of BH20 with succinic anhydride in this case reaches 50–75%. Thus, 8 to 12 OH groups of BH20 react with succinic anhydride.



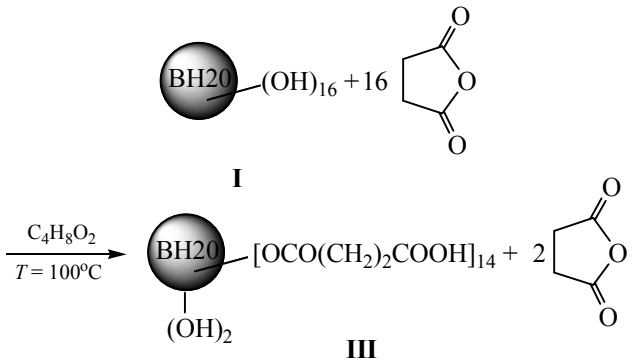
I **II**

The inactivating packaging of hydrogen bonds in the molecule of BH20 is destroyed at heating above 130°C [8, 9] leading to the appearance in the IR spectra of two individual bands with frequencies 3456 and 1260 cm^{-1} that correspond to the presence of unbound OH groups in the polyol. Basing on this



Molecule of compound BH20 (**I**).

observation, we advanced a second method for functionalization of BH20 with succinic anhydride using 1,4-dioxane as a solvent, which led to 90% functionalization: 14 of 16 groups reacted with succinic anhydride in this case.



I

III

The IR spectrum of compound **III** contains a strong band of C=O groups at 1736 cm^{-1}. This band is shifted to longer wavelengths relative to the corresponding bands of compound **II** that may indicate a decrease in the degree of hydrogen bonding in the obtained compound **III**. Moreover, the intensity of this band is 9.8 times higher than the intensity of the C=O vibrations of derivative **II**. We estimated the coordinating activity of compounds **II** and **III** with different degree of functionalization. For the complexation we selected polycarboxy-BH20 samples with a degree of functionalization 65% (10 COOH groups) and 90% (14 COOH groups). As the complexing ion the cation Cu(II) was chosen. From the sodium salts of polycarboxy-BH20 we obtained two complex compound: dark green (**IV**) and light green (**V**), from the low- and high-substituted BH20, respectively. In the electron absorption spectra of the complex compound **IV** two bands appeaed, at λ 271 and 327 nm; in the spectrum of **V**, one band at λ 322 nm. In the IR spectrum of the sodium salts appeared characteristic strong broad bands related to the dissociated COO^- group at 1440 and 1548 cm^{-1}. The formation of complexes **IV** and **V** leads to a high-frequency shift of the bands of COO^- antisymmetric and symmetric stretching vibrations. In addition, in the spectra of the complex compounds a new strong broad band appears at 1622 cm^{-1} in **IV** and at 1623 cm^{-1} in **V**, characteristic of carboxy groups involved in the formation of chelate structures. Thus, we obtained macromolecular polynuclear Cu(II) carboxylates with the coordination of the central atom through the oxygen atoms of the dissociated peripheral carboxy groups of the hyperbranched macroligand.

EXPERIMENTAL

We used second generation hyperbranched polyester carboxylate Boltorn of the series H (BH20), and salts $NaHCO_3$ and $Cu(NO_3)_2 \cdot 3H_2O$ of analytically pure grade. The IR spectra were recorded on a Varian-22 instrument from the suspensions in mineral oil in the wavenumber range 200–4000 cm^{-1}. Electron absorption spectra were recorded on a Lambda 35 spectrophotometer (Perkin Elmer, UK) in the wavelength range 190–900 nm at $T = 25 \pm 0.01$°C.

Poly-2-carboxypropiono-Boltorn H20 (II). To a heated solution of 1.58 g of compound BH20 (**I**) in 7 ml of anhydrous acetone was added 1.48 g of succinic anhydride in a molar ratio of 1:16, then was added another 10 ml portion of acetone. The mixture was stirred at the boiling point of the solvent (56.5°C) for 12 h. After cooling, the mixture was treated with diethyl ether, and the formed white product was separated and dried in a vacuum. 1.5 g (55.53%) of compound **II** was obtained as a white amorphous substance. IR spectrum, ν, cm^{-1}: 3430 (OH_{bound}), 2980 (CH_{3as}), 2945, 2886 (CH_{2as}, CH_{2s}), 2594 [OH_{bound} (COOH)], 1730 (C=O), 1470, 1461 (deformation $CH_{3as,s}$), 1400, 1376 (deformation $CH_{2as,s}$), 1228 (C–O), 1127 (O–C). The data of elemental analysis of $C_{113}H_{164}O_{64}$ (65% substitution). Found, %: C 51.42, H 6.38, O 42.2. $C_{113}H_{164}O_{64}$. Calculated, %: C 52.3, H 6.45, O 40.25.

Poly-2-carboxypropiono-Boltorn H20 (III). A sample of 5.0 g of compound BH20 (**I**) was heated to 140°C, cooled to 50°C and then dissolved in 15 ml of 1,4-dioxane. To the hot solution of compound BH20 was added 4.58 g of succinic anhydride in a molar ratio of 1:16, and $SnCl_2$ in a catalytic amount. The mixture was stirred at 100°C for 36 h. After cooling, white amorphous product **III** formed, from which solvent was removed in a vacuum. 5.27 g of compound **III** was obtained (yield 55.0%). IR spectrum, ν, cm^{-1}: 3451 (OH_{bound}), 2963 (CH_{3as}), 2888 (CH_{3s}), 2922, 2857 (CH_{2as}, CH_{2s}), 2594 [OH_{bound} (COOH)], 1736 (C=O), 1470, 1461 (deformation $CH_{3as,s}$), 1400, 1376 (deformation $CH_{2as,s}$), 1228 (C–O), 1127 (O–C). $C_{125}H_{180}O_{72}$ (90% substitution). Found, %: C 50.42, H 6.22 , O 40.2. $C_{125}H_{180}O_{72}$. Calculated, %: C 51.30; H 6.11; O 39.41%.

Copper(II) poly-2-carboxypropionate-Boltorn H20 (IV, V). For the preparation of Cu(II) complexes, the carboxylic acid derivatives of compound BH20 were transformed to the sodium salt by the reaction with sodium hydrogen carbonate $NaHCO_3$. A sample of 3.92 g of compound **II** (or **III**) was dissolved in 15 ml of acetone and 1.57 g of $NaHCO_3$ was added. The mixture was heated to 56.5°C and stirred for 16 h. Unreacted $NaHCO_3$ was filtered off, to the solution was added 4.53 g of $Cu(NO_3)_3$ in the molar ratio polymer : inorganic salt = 1 : 16, and the mixture was stirred at 56.5°C for 10 h. After cooling, the mixture was treated with diethyl ether, the formed product was separated and dried in a vacuum. We obtained two complex compounds, $Cu_nBH20(COO)^-$ **IV** and **V,** as green powders. Compound **IV:** yield 55.53%. IR spectrum, ν, cm^{-1}: 3394 (OH_{bound}), 2923 (CH_{3s}), 2854, 2941 (CH_{2s}, CH_{2as}), 1724 v.w (C=O), 1622 (COO^-_{bound}), 1463 (CH_{3as}), 1377 (deformation $CH_{2as,s}$), 1130 (O–C), 1047 (C–O), 502 (Cu^{2+}). Compound **V**: yield 55.01%. IR spectrum, ν, cm^{-1}: 3416 (OH_{bound}), 2923 (CH3s), 2949, 2853 (CH2as, CH_{2s}), 1734 (C=O), 1623 (COO^-_{bound}), 1564 (COO^-), 1461 (deformation $CH_{3as,s}$), 1377 (deformation $CH_{2as,s}$), 1243, 1299 (C–O), 1119 (O–C), 1046 (C–O), 502 (Cu^{2+}).

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