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LETTERS TO THE EDITOR

Polydentate Nanoplatform Based on Hyperbranched Polyol Boltorn

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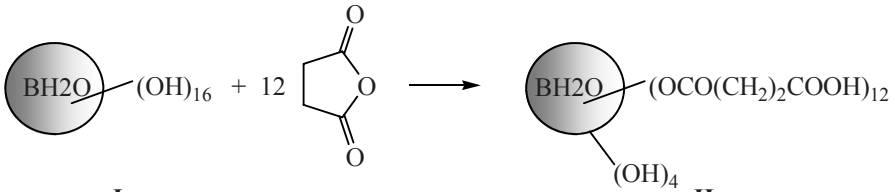
In chemistry and technology now is rapidly developing a direction connected with the synthesis of nano-size hyperbranched polymers (HBP) and related functional derivatives possessing a wide range of practically useful properties [1, 2]. Nontoxic hyperbranched polyols of "Boltorn H" series are promising objects for obtaining the metallocomplex compounds of biomedical application, with the polydentate polyol platform as a ligand [3, 4]. However, the complexes of "Boltorn H" with the *d*-metal ions are very unstable. This may be a consequence of intra- and intermolecular hydrogen bonding of hydroxy groups of the molecule that decreases significantly their steric accessibility and capability of complex formation [5, 6]. A route for overcoming this problem is the modification of HBP by means of substitution of OH groups by the groups more active toward metal ions.

In this work we developed a method for the synthesis of a polydentate coordinationally active nanoplatform based on the BoltornH20 (**I**) HBP functionalized in terminal positions by carboxyl groups. The second generation HBP molecule BoltornH20 (BH20) is formed by polycondensation of 2,2-bis (hydroxymethyl)propanoic acid; the nucleus is tetrahydroxypentaerithritol (see the scheme). Compound **I** contains 16 hydroxy groups.



I **II**

For substitution of all 16 hydroxy groups by carboxyls we carried out esterification of BH20 with succinic anhydride at the molar ratio BH20 : succinic anhydride = 1 : 16. Reaction was carried out with acetone as solvent, at 56° for 12 h. Product **II** was isolated as white flakes. Presence in its IR spectrum of a strong narrow band at 1730 cm^{-1} corresponds to the presence in the molecule of C=O fragment of nondissociated carboxylic group. Broad absorption bands of bound OH groups in the regions of 3200–3400 and 2500–2800 cm^{-1} is consistent with the presence in the substance of inter- and intramolecular hydrogen bonding. Comparison of percentage of carboxylic groups and acid numbers of compounds **I** and **II** according to the procedure in [7] showed that only 75% (12 of 16) of hydroxy groups of BH20 entered into the reaction of substitution with succinic anhydride and hence the reaction proceeds along the scheme.

The product composition remains the same at the increased time of the reaction mixture heating.

Incomplete esterification is connected probably with existence in the molecule **I** not only of terminal, but also of internal hydroxy groups located inside the spherical carcass of the macromolecule and therefore difficultly sterically accessible [5]. The data of comparative analysis of ^{1}H NMR spectra of compounds **I** and **II** dissolved in $(CD_3)_2CO$ and in DMSO together with the data of two-dimensional COSY, HMQS and NOESY spectra and semiempirical quantum-chemical calculations allowed us to reveal degree of branching (DB) that characterizes geometric symmetry of the branched system (as compared with the ideal dendrimer, DB = 1). In the macromolecule **I,** DB = 0.64. After modification with succinic anhydride the DB of the polydentate carboxylated macroligand equals to 0.77 (^{1}H NMR data). In the molecules **I** and **II** are revealed H-bonds of three types, C=O···HO, OH···HO and C=O···HO···HO, that are both of intra- and intermolecular character. In **II** dominates hydrogen bonding of C=O···HO type with involvement of carboxylic and internal OH groups leading to more ordered structure.

The obtained product can be characterized as a polydentate platform of poly-2-carboxypropanoic BoltornH20, which should possess higher coordination activity than parent hyperbranched polyol BoltornH20.

Poly-2-carboxypropanoyl-BoltornH20. To a hot solution of 1.58 g of BH20 (**I**) in 7 ml of anhydrous acetone was added 1.48 g of succinic anhydride to the mole ratio 1:16, then 10 ml of acetone was additionally added. The mixture was stirred at reflux of the solvent (56.5°C) for 12 h. After cooling, the mixture was treated with diethyl ether, and the formed white solid was filtered off and dried in a vacuum. 1.5 g (55.53%) of compound **II** was obtained as white amorphous substance. IR spectrum, ν, cm^{-1}**:** 3430 (OH_{bound}); 2980 ($CH_{3,as}$); 2945, 2886 ($CH_{2,as}$, $CH_{2,s}$); 2594 [OH_{bound} (COOH)]; 1730 [C=O (COOH)]; 1470, 1461 (bending $CH_{3,as,s}$); 1400, 1376 (bending $CH_{2,as,s}$); 1228 (C–O); 1127 (O–C). The ^{1}H NMR spectrum, ppm: CH_3 (T) 1.31, CH_3 (D) 1.20, CH_3 (L) 1.13, [CH_2OH + CH_2 (nucleus) + CH_2(1)] 3.68–3.61, CH_2OR + CH_2(2) 4.26, CH_2–CH_2 2.65–2.55. Found, % C 51.42, H 5.77; Calculated, %: C 50.13, H 5.84.

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