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One- and Two-Dimensional NMR Study on Structural Features of Polyester Derived from Boltorn H20-OH Polyol and Maleic Acid

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Abstract—The structure of hyperbranched Boltorn H20-OH maleate was studied by one- and two-dimensional NMR spectroscopy and AM1 simulation. The polyester was found to have a non-stereoregular structure where two linear branches, as well as terminal and dendritic branches, are brought together in pairs.

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It is known [1, 2] that properties of polyesters derived from hyperbranched polyols can be varied over a fairly wide range via introduction of various functional groups into terminal chains without essential change of the polymer base. It is very important to study the structure of both original polyester and its modified analogs. We previously [3, 4] examined the structure and association of a dendritic polyol, Boltorn H20-OH, and its carboxylated derivative Boltorn H20-COOH in solution. The reaction of Boltorn H20-OH with maleic anhydride leads to polyester containing eight terminal carboxy groups.

The goal of the present work was to study the structure and association of hyperbranched Boltorn H20-OH maleate (**I**) in $(CD_3)_2CO$ solution by one- and two-dimensional NMR spectroscopy.

Comparison of the one- and two-dimensional ^1H and ^{13}C NMR data for compound **I** in $(CD_3)_2CO$ led us to presume that it has a non-stereoregular structure with eight methyl groups, two of which are linear (L), five are dendritic (D), and one is terminal and simultaneously linear (T or TL) (Fig. 1). The polyol branches were denoted as “L,” “D,” and “T” in accordance with the largest number of the corresponding methyl groups in a given branch.

The ^1H and ^{13}C NMR spectra of a solution of **I** in $(CD_3)_2CO$, as well as the spectra of initial Boltorn H20-OH [3, 4], displayed a complicated pattern, and their analysis was difficult owing to the presence of similar groups characterized by approximate chemical shifts. This applies primarily to methylene groups due to their large number in structurally equivalent and different fragments and closeness of their ^1H and ^{13}C chemical shifts, which leads to very strong signal broadening in the ^1H NMR spectrum (Fig. 2). With account taken of their chemical environment, five types of methylene groups were distinguished in molecule **I**: (1) $CH_2OC(O)$ (12 groups); (2) $OCH_2(1)C\mathbf{H}_2(2)OC(O)$ (4 groups); (3) CH_2OH (4 groups); (4) $OC\mathbf{H}_2(1)CH_2$ (4 groups); (5) OCH_2 (core, 4 groups). With respect to ^1H chemical shifts, these five types were grouped in two groups, the first including types (1) and (2), and the second, types (3), (4), and (5).

In the ^1H NMR spectrum of **I** (Fig. 2), the region δ 4.1–4.5 ppm corresponds to $CH_2OC(O)$ and $CH_2(2)$, and the region δ 3.3–3.83 ppm, to CH_2OH, $CH_2(1)$, and CH_2 (core). Likewise, methylene carbon nuclei resonate in the ^{13}C NMR spectrum in two regions, δ_C ~62.0–68.0 and 69.0–72.0 ppm. Unlike strongly broadened methylene proton signals, signals from methyl protons in the ^1H NMR spectrum are well resolved. The expected signal intensity ratio for methyl protons is D : L : T = 5 : 2 : 1. Insofar as the dendritic methyl groups in branches L and D and within the latter are slightly nonequivalent, a set of signals is observed in the resonance region δ 1.13–1.3 ppm (Fig. 2), and their accurate assignment, as well as the assignment of methylene signals, on the basis of only one-dimensional spectra is impossible.

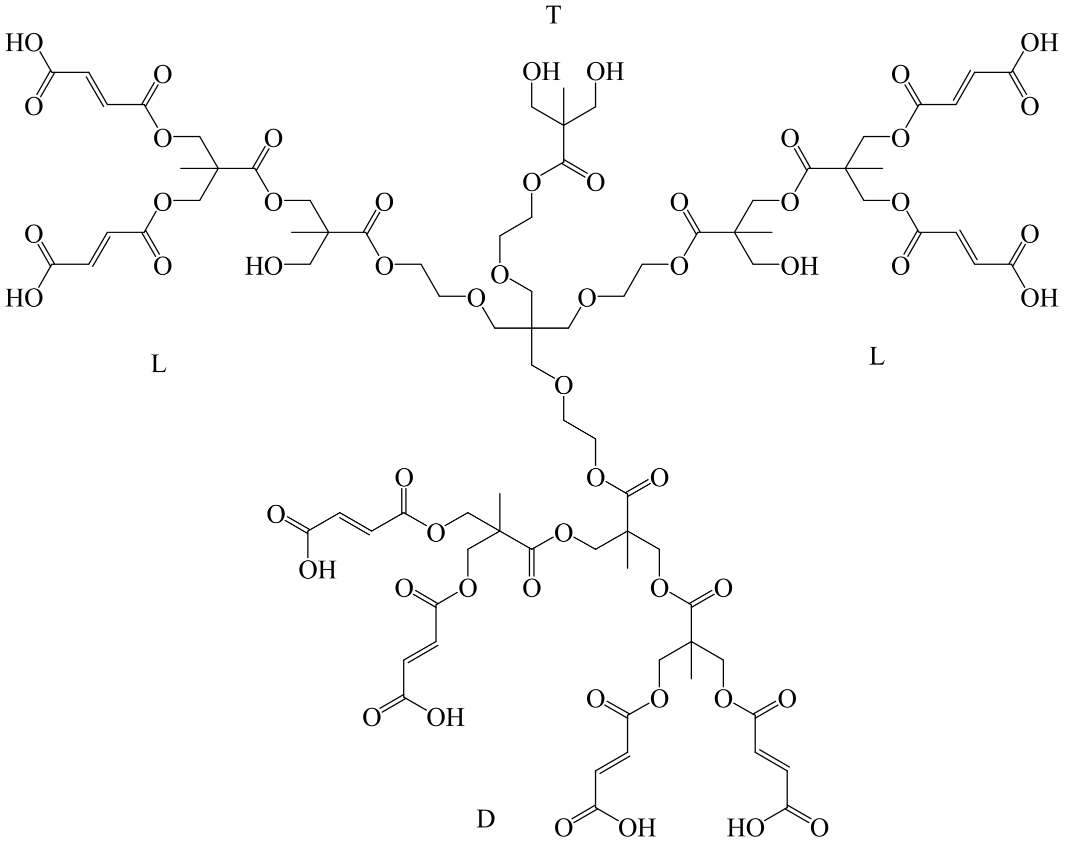

Fig. 1. Structure of hyperbranched polyester **I** formed by Boltorn H20-OH polyol and maleic acid.

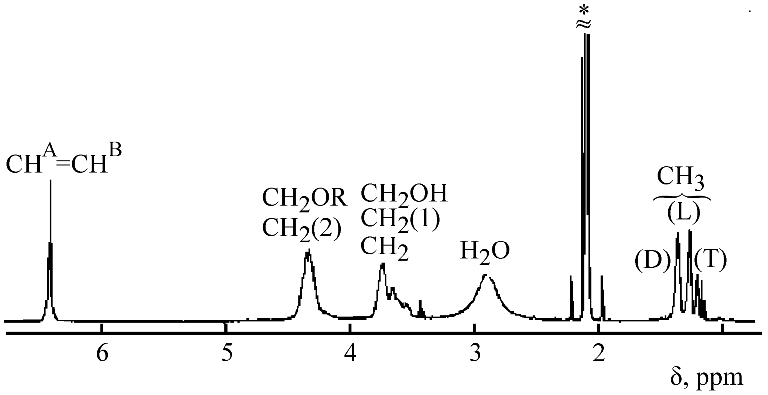

Fig. 2. ^{1}H NMR spectrum of polyester **I** in $(CD_3)_2CO$ at 318 K.

Protons in the CH_A=CH_B fragment resonate at δ 6.38 and 6.35 ppm as an *AA'* two-spin system and are oriented *cis* with respect to each other (according to calculations).

Some inconsistency between the signal intensity ratio of methyl and methylene protons and the overall number of the corresponding groups in structure **I** is likely to be related to the presence in the same regions of signals from low-molecular impurities (water and ethanol) and strongly broadened (almost to baseline) signals from hydroxy protons. An indirect support of the latter assumption is that no separate OH signals were observed in the spectrum. In addition, this fact indicates formation of strong hydrogen bonds, both intra-, and intermolecular [3, 4]. Signals from compounds with different molecular weights were identified using DOSY experiments (diffusion-ordered spectroscopy) [5]. We thus succeeded in unambiguously distinguishing signals belonging to the

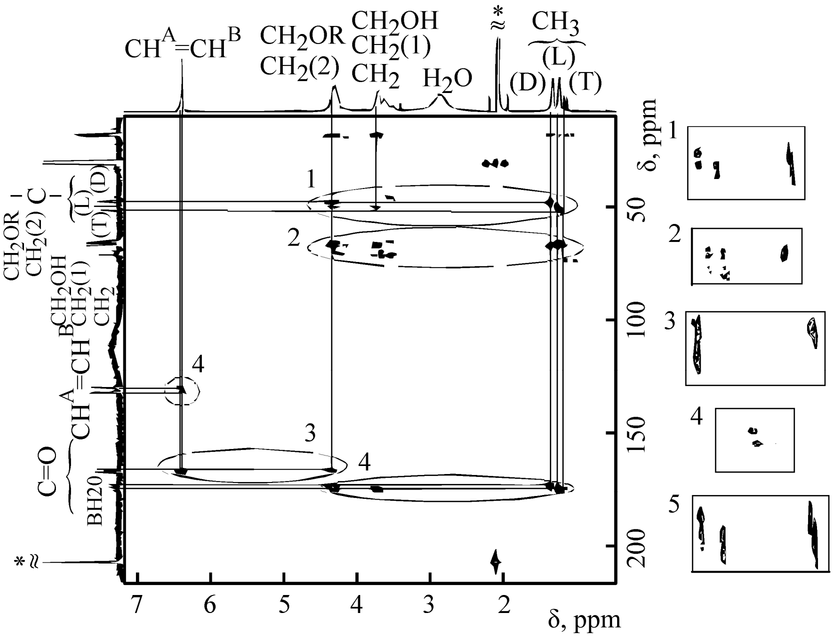

Fig. 3. HMBC spectrum of compound **I** in $(CD_3)_2CO$. Magnified cross peaks are shown at the right.

polyester itself from those of low-molecular compounds (water, solvent, and ethanol or diethyl ether). An important consequence was the improved signal intensity ratio of the CH_2 and CH_3 groups toward better agreement with structure **I**.

With the aid of two-dimensional ^1H–^1H COSY technique we identified signals from methylene protons in the $OCH_2(1)CH_2(2)OC(O)$ fragment neighboring to the polyester core. The COSY spectrum contained two pairs of cross peaks corresponding to spin–spin coupling between protons in the above fragments. Due to similarity of chemical shifts of the olefinic protons in the $(O)CCH_A{=}CH_BC(O)OH$ fragments, the respective cross peaks almost coincided with their diagonal signals (δ ~6.42 ppm). Heteronuclear correlation experiment (HSQC) [5] allowed us to identify signals from carbon atoms and protons directly attached thereto ($^1J_{CH}$).

Complete analysis of the most complicated region of the ^{13}C NMR spectrum, i.e., that containing methylene carbon signals, was performed using ^1H–^{13}C heteronuclear correlation spectroscopy (HMBC, Fig. 3). Cross peaks in an HMBC spectrum characterize spin–spin coupling of protons with carbon nuclei through 2–4 bonds [5]. The HMBC spectrum of **I** displayed correlations between carbon atoms in the $\mathbf{C}H_2OR$ $[OCH_2C(O)]$ and protons in the CH_2OR (through 3 bonds) and $CH_3(D)$ groups (through 3 bonds) in the two linear (L) and dendritic (D) branches; between $\mathbf{C}H_2OH$ and protons in the CH_2OH, $CH_3(L)$, and $CH_3(T)$ groups in the two linear and terminal branches; between $\mathbf{C}H_2$(core) and $CH_2(1)$ and $CH_2(2)$ protons; between $\mathbf{C}H_2(1)$ and CH_2(core) and $CH_2(2)$ protons; and between $\mathbf{C}H_2(2)$ and $C\mathbf{H}_2(1)$. In addition, weak cross peaks between $\mathbf{C}H_2(2)$ and protons in the dendritic CH_2OR group and CH_2OH protons in the two linear branches (all through five bonds) were observed. Furthermore, on the basis of the HMBC data we assigned signals from quaternary carbon atoms in branches D [cross peaks with CH_2OR and $CH_3(D)$], L [CH_2OR, CH_2OH, and $CH_3(L)$], and T [CH_2OH and $CH_3(T)$] and from the carbonyl carbon atoms in the maleic acid fragments $CCH_2O\mathbf{C}(O)CH{=}CH\mathbf{C}OOH$. One of the latter ($\delta_C$ 166.84 ppm) displayed a cross peak with the CH_2OR protons, so that we were able to assign signals from the other carbon atoms in the $CCH_2OC(O)\mathbf{C}H_A{=}\mathbf{C}H_BCOOH$ fragment. The C=O carbon atoms in branch D of Boltorn H20 ester showed cross peaks with CH_2OR and $CH_3(D)$ protons, in branches L, with CH_2OR, CH_2OH, and $CH_3(L)$, and in branch T, with CH_2OH and $CH_3(T)$.

Molecule **I** contains 24 carbonyl groups which may be arbitrarily divided into seven types with account taken of their (dis)similar positions in branches L, T, and D (Fig. 1). Broadened signals in the region δ_C 173.4–177.0 ppm with an intensity ratio I of about

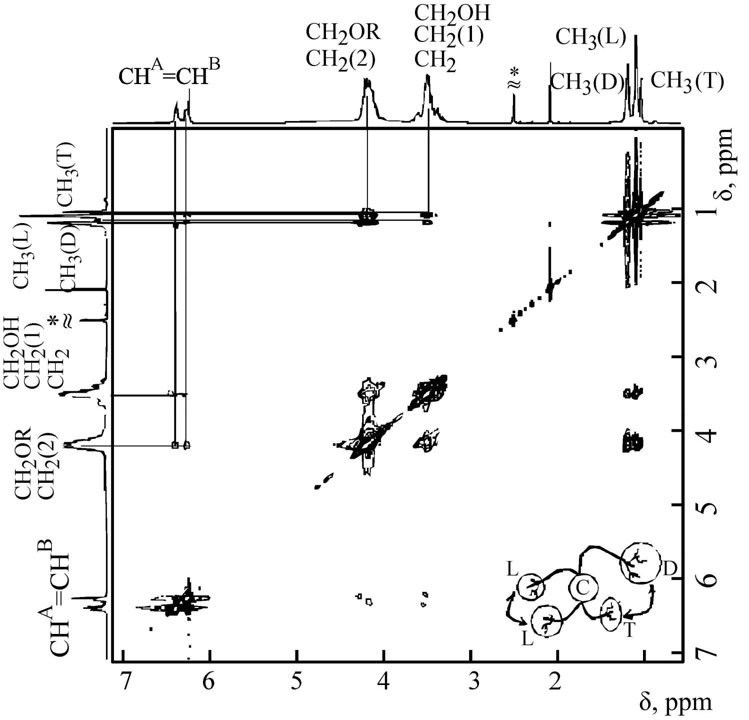

Fig. 4. ^1H NOESY spectrum of compound **I** in $(CD_3)_2CO$ (τ_{mix} 0.6 s). A sketch of molecule **I** is shown at the right bottom corner.

1:1:3:3 belong to the Boltorn H20-OH fragment (eight C=O groups), and 16 carbonyl groups in the maleic acid residues resonate as two signals with equal intensities at δ_C 166.84 and 167.88 ppm. Structural units of Boltorn H20-OH and Boltorn H20-COOH were described in detail in [3, 4]. Analogous analysis was performed to identify signals from quaternary carbon atoms (total of 9 carbon atoms, one of which being the central one). The $CH_A=CH_B$ olefinic carbon atoms in the maleic acid fragments were assigned signals at δ_C 130.84 and 132.76 ppm.

Analysis of a large number of cross peaks observed in the 2D NOESY ^1H NMR spectrum (Fig. 4) revealed spatially close structural fragments in molecule **I**, which allowed us to determine its conformation. It was found that the terminal (T) and dendritic (D) branches, as well as the two linear branches (L), are brought together (Fig. 5). The key proof for spatially close orientation of branches T and D was the presence of cross peaks between the terminal CH_3 group (T) and vinylic protons in the maleic acid fragment in branch D. Approach of the linear branches to each other is favored by C=O···HO hydrogen bonding. These findings are consistent with the results of calculations performed for polyester **I**; unlike Boltorn H20-OH [2], the ester carbonyl group and OH group in **I** appear close to each other. The contribution of C=O···HO type hydrogen bonds (Fig. 5) dominates.

To conclude, one- and two-dimensional ^1H and ^{13}C NMR study on the maleic acid polyester derived from the second-generation hyperbranched polyol Boltorn H20-OH showed that this compound has a non-stereoregular structure which, unlike previously studied Boltorn H20-OH polyester with succinic acid,

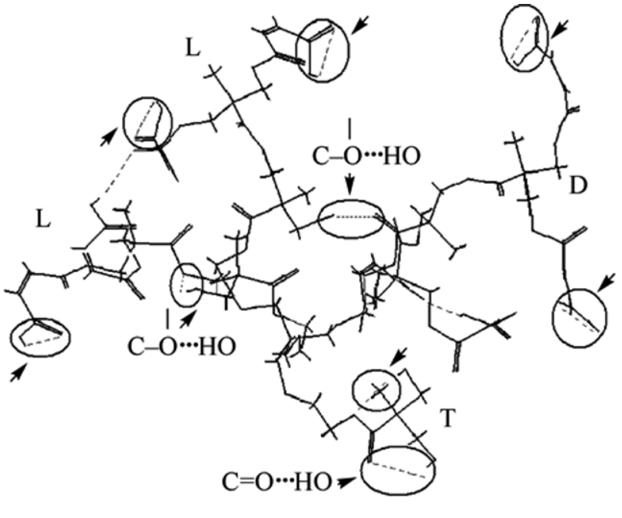

Fig. 5. Steric structure of molecule **I** with account taken of different modes of hydrogen bonding.

is characterized by spatially close orientation of the linear branches and of the terminal and dendritic branches. The results are in agreement with the calculated structure of polyester **I** where (unlike Boltorn H20-OH succinate) the C–O ester fragment and OH group approach each other and hydrogen bonding of C=O···HO type predominates.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker Avance II spectrometer with Fourier transform at 500.13 MHz for ^{1}H and 125.77 MHz for ^{13}C. The one-dimensional spectra were obtained using 30° pulses with a scan delay of 2 s. The spectral width was up to 15 ppm, and the scan number was up to 64 (depending on the solubility). The ^{13}C NMR spectra were acquired using 30°–45° pulses and broad-band decoupling from protons (pulse delay 0.2 s, width 200 ppm, scan number 300 to 4000. Magnetic field was stabilized by the deuterium signals of the solvent.

The two-dimensional NMR spectra were recorded following standard procedures. Phase cycling was applied to enhance pulse calibration accuracy. The number of scans n_t in the COESY spectra was no less than 4. The number of iterations n_i over the time interval t_2 for the second frequency axis was selected from the condition $n_i = (sw \times 1/2)$, where sw is the spectral window.

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