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Synthesis of Hyperbranched Polyester Polymaleic Acids Third Generation

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Abstract—The third generation hyperbranched polyesterpolyol has been modified with maleic anhydride at various ratios of the polyol to the modifying agent, from 1 : 6 to 1 : 18. The prepared modified polyols are capable of the complex formation with copper(II), cobalt(II), and nickel(II) ions.

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Most of the biopolymers found in living organisms are polyanions. The biological activity of polyanions is fairly diverse, like that of glycoproteins and nucleic acids. Polyanions possess some antiviral activity, likely due to the modulation of the absorbing cells action; therefore, polyanions may be applied as components of antiviral vaccines, antitumor and immunomodulating agents [1]. In view of this, the non-toxic hyperbranched polymers containing carboxylic acid fragments are of interest; moreover, they are known to possess the complexing ability towards the biologically active metal ions. Such polymers can be prepared via chemical modification of hyperbranched polyesterpolyols. The increase of the starting hyperbranched polymer generation enhances the possibility to alter the amount of functional groups in the modified polymer and thus to manage the amount of metal ions in the formed complexes. Furthermore, the macromolecular nature of the ligand increases the complex stability due to additional polarization of the metal ion in the inhomogeneous electrostatic ligand field and protecting the metal coordination sphere from the incurporation of interfering reagents [2]. Previously polycarboxylic acids were synthesized on the poyester polyol second generation Boltorn H20 [core is ethoxylated pentaerythritol, monomer is 2,2-bis (hydroxymethyl) propionic acid] [3, 4]. In this work, we present the modification of commercially available third generation hyperbranched polyol Boltorn H30 (**I**) (Perstorp Specialty Chemicals AB) with maleic anhydride (see Scheme 1).

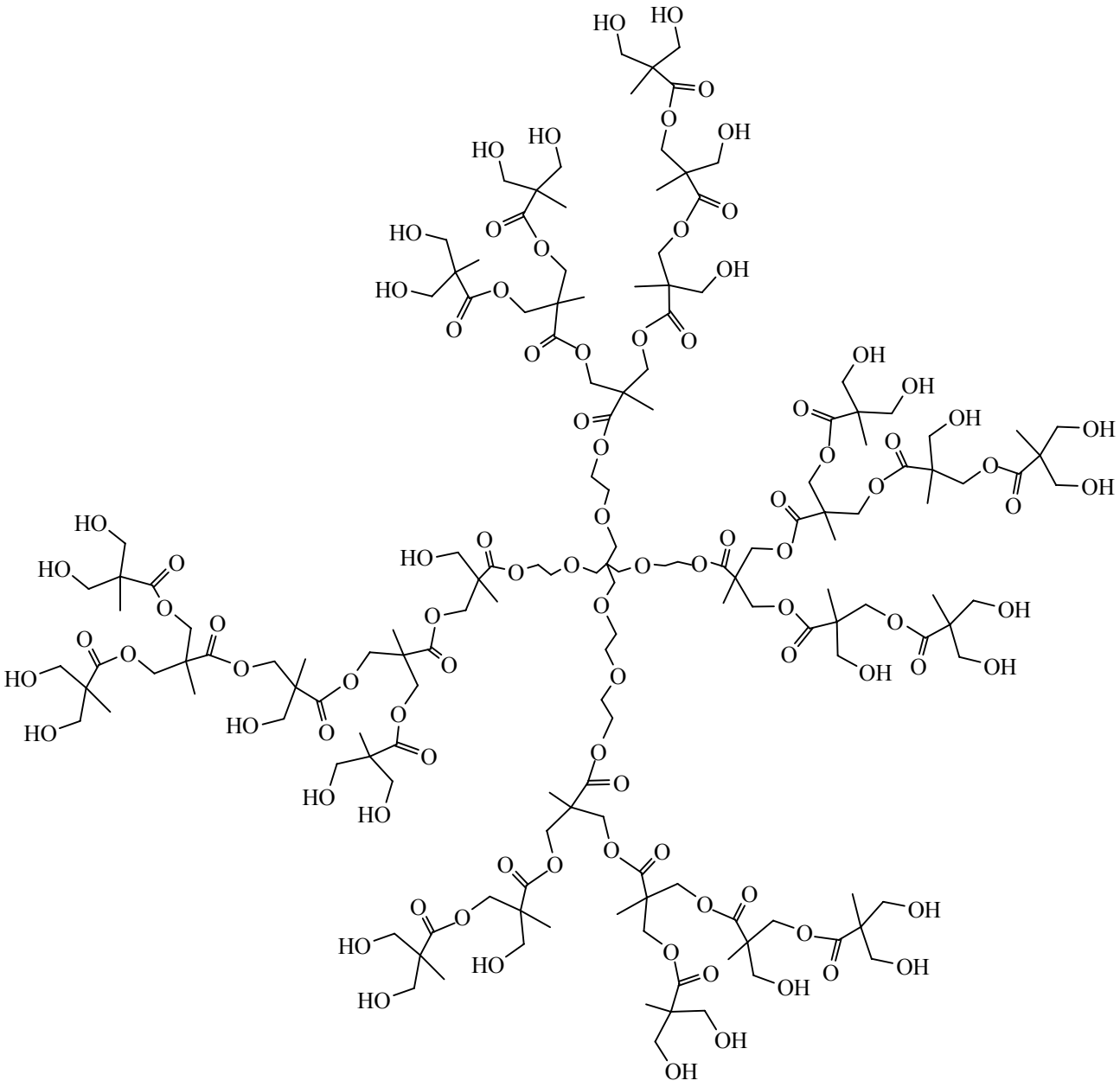
The modification of hydroxy groups of **I** with maleic anhydride was performed at various ratio of the reagents, 1 : 6 to 1 : 18.

The purity of the prepared products was confirmed by the absence in the IR spectra of the bands characteristic of the stretching vibrations of maleic anhydride carbonyls at 1848 and 1790 cm^{-1}. The modified polyols were characterized by acid number (AN) and the amount of carboxy groups (*m*), both determined by potentiometric titration [5]. The products prepared at different reagents ratios showed the following characteristics: AN = 52 and *m* = 6 (**II**); AN = 101 and *m* = 12 (**III**); AN = 137 and *m* = 18 (**IV**). The complex formation ability was probed by spectrophotometry, using Co(II), Ni(II), and Cu(II) salt solutions as examples. In particular, the solutions of **II–IV** in DMSO possessed negligible absorption in the UV and visible light spectral ranges. The addition of salts [$Cu(NO_3)_2$, $Co(NO_3)_2$, or $Ni(NO_3)_2$] to the solutions of **II–IV** led to the appearance of new absorption bands, absent in the spectra of pure salts solutions. The absorption bands maxima of the formed complexes were as follows: Co(II), 536 nm; Ni(II), 766 nm; and Cu(II), 812 nm (see Scheme 2).

EXPERIMENTAL

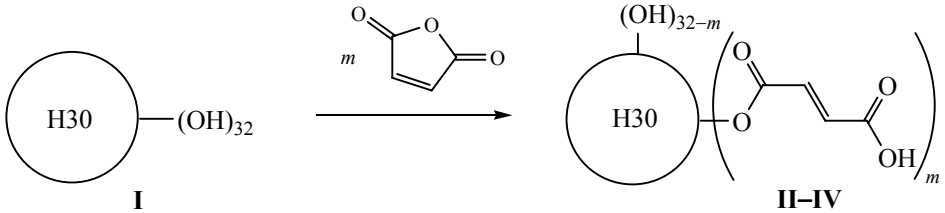
Potentiometric titration was performed using AT-210 (Kioto Electronics, Japan) modular titration station. IR absorption spectra of the solid samples were Registered on a Spectrum 400 (Perkin Elmer) Fourier spectrometer equipped with Almaz KRS-5 ATR attachment:

Scheme 1.



I

Scheme 2.



I **II–IV**

m = 6 (**II**), 12 (**III**), 18 (**IV**).

resolution of 4 cm^{-1}, 14 scans at 4000–400 cm^{-1}. NMR spectra of $(CD_3)_2CO$ solutions were recorded on an Avance 400 (Bruker) spectrometer at 400 MHz (^1H) and at 125.77 MHz (^{13}C).

Modification of **I** with maleic anhydride was performed as described in [3]. The products **II–IV** were white or yellow amorphous substances.

Compound II. Yield 67.5%. IR spectrum, ν, cm^{-1}: 3394 br.m (OH_{bound}), 2978–2883 m (CH_3, CH_2), 1721 v.s (–C=O), 1643 m (C=C), 1466 m [$\delta_{as}(CH_3)$], 1404, 1375 w [$\delta(CH_2)$], 1214, 1119, 1037 m (C–O–C). ^1H NMR spectrum, δ, ppm: 1.14 s, 1.21 s, 1.32 s [OC(O)·CCH_3], 3.63–3.72 m (OCH_2CH_2), 4.11 s, 4.13 s [$C(CH_2OC)_4$], 4.28–4.30 m [$CH_2OC(O)$], 6.40 s (CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 18.1, 19.4, 20.7 (CH_3), 43.7 [$C(CH_2OC)_4$], 50.5 [$H_3C–C(CH_2)_2$], 64.9–68.9 m (CH_2), 132.1 (CH=CH), 175.1 (C=O).

Compound III. Yield 72.6%. IR spectrum, ν, cm^{-1}: 3423 br.m (OH_{bound}), 2978–2883 m (CH_3, CH_2), 1725 v.s (C=O), 1643 m (C=C), 1466 m [$\delta_{as}(CH_3)$], 1400, 1370 w [$\delta(CH_2)$], 1218, 1119, 1041 m (C–O–C). ^1H NMR spectrum, δ, ppm: 1.14 s, 1.21 s, 1.32 s [OC(O)·$C\underline{CH_3}$], 3.63–3.72 m ($O\underline{CH_2}CH_2$), 4.11 s, 4.14 s [$C(\underline{CH_2}OC)_4$], 4.28–4.30 m [$\underline{CH_2}OC(O)$], 6.40 s (CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 17.1, 18.4, 19.7 (CH_3), 42.7 [$\underline{C}(CH_2OC)_4$], 49.5 [$H_3C\underline{C}(CH_2)_2$], 64.0–67.6 m ($CH_2$), 133.2 (CH=CH), 174.2 (C=O).

Compound IV. Yield 69.15%. IR spectrum, ν, cm^{-1}: 3452 br.m (OH_{bound}), 2978–2891 m (CH_3, CH_2), 1721 v.s. (C=O), 1639 m (C=C), 1466 m [$\delta_{as}(CH_3)$], 1404, 1375 w [$\delta(CH_2)$], 1222, 1119, 1041 m (C–O–C). ^1H NMR spectrum, δ, ppm: 1.13 s, 1.21 s, 1.32 s [OC(O)$C\underline{CH_3}$], 3.64–3.71 m ($O\underline{CH_2}CH_2$), 4.11 s, 4.14 s [$C(\underline{CH_2}OC)_4$], 4.28–4.33 m [$\underline{CH_2}OC(O)$], 6.41 s (CH=CH). ^{13}C NMR spectrum, δ_C, ppm: 18.1, 19.4, 20.7 (CH_3), 43.8 [$\underline{C}(CH_2OC)_4$], 50.5 [$H_3C–\underline{C}(CH_2)_2$], 64.9–67.8 ($CH_2$), 133.6 (CH=CH), 175.2 (C=O).

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