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Phosphorus-containing Hyperbranched Structures. Phosphorylation of Hyperbranched Polyols with 2-(Diethylamino)-1,2,3-dioxaphosphinane

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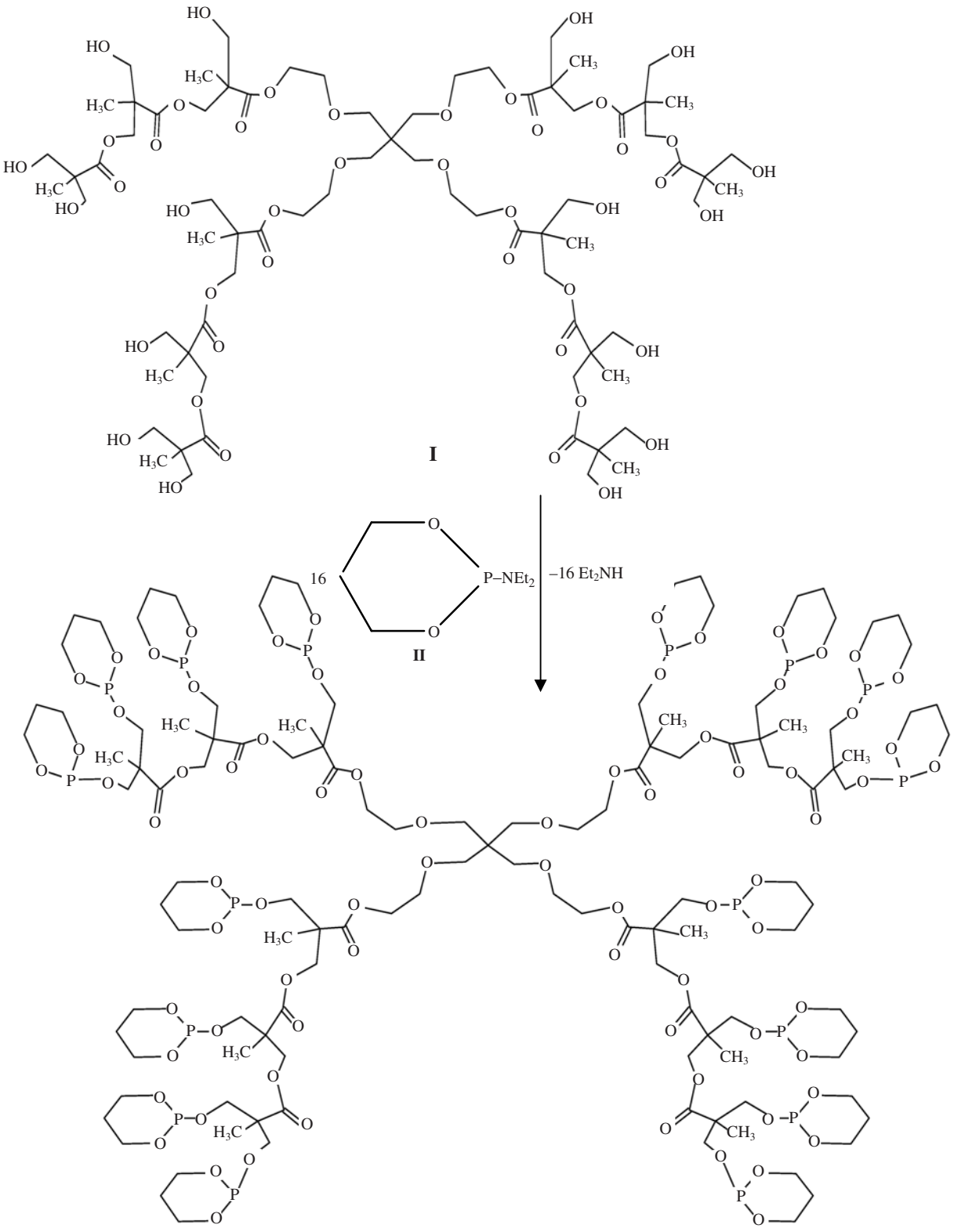
Modification of Boltorn H20, H30 and H40 hyperbranched polymers by partial or full esterification of their hydroxyl end-chain groups with saturated and unsaturated carboxylic acids, related acid chlorides, epichlorohydrin, and other oxygen-containing compounds results in a decrease in viscosity and glass transition point, appearance of the crystal phase, weakening of hydrogen bonding, etc. [1, 2]. Phosphorylation of the OH groups with phosphorus-containing compounds, too, can be expected to change the rheological properties of hyperbranched polymers and endow these compounds with new properties. Convenient phosphorylating agents are phosphoramidites with labile P–N bonds. We found that Boltorn H20 (**I**) reacts by all its 16 OH groups with 2-(diethylamino)-1,3,2-dioxaphosphinane (**II**) under heating at 180°C with liberation of diethylamine and formation of [*O*-(1,3,2-dioxaphosphinane-2-yl)]$_{16}$Boltorn H20 (**III**). ^{31}P NMR spectra of compound **III** contain a singlet at δ_P 130.2 ppm, i.e. in the region characteristic of phosphites [3], whereas the signal of starting phosphoramidite **II** is observed at δ_P 145 ppm [3]. Three-coordinate phosphorus derivative **III** takes up sulfur in a *p*-xylene medium at 120°C to form the corresponding thionophosphate with δ_P 62.0 ppm.

[*O*-(1,3,2-Dioxaphosphorinan-2-yl)]$_{16}$Boltorn H20 (III). **A** mixture of 5.0 g of polyester **I** and 8.3 g of phosphoramidite **II**, preparated under dry argon, was heated smoothly for 1 h in a distillation flask from 70 to 180°C with distilling off volatile components. Diethylamine, 2.9 g (85%), was separated, bp 55–56°C, n_D^{20} 1.3865(published data [4]: bp 55.5°C, n_D^{18} 1.3873). The residue was kept for 1 h under a vacuum of 0.5 mm Hg at 40°C and for 1 h under a vacuum of 0.02 mm Hg at 40°C to obtain 11.3 g (85%) of compound **III** as a colorless viscous oil. IR spectrum, ν, cm^{-1}: 2966 vs, 2891 vs, [$\nu_{as,s}(CH_3)$, $\nu_{as,s}(CH_2)$]; 1738 s [ν(O=C–O)]; 1471 s [$\delta_{as}(CH_3)$]; 1374 m [$\delta_s(CH_3)$]; 1060 vs [ν(P)O–C]; 935 vs [ν(OC–C)]; 783 m, 725 vs [$\nu_{as,s}(PO_2)$]. ^{1}H NMR spectrum, δ, ppm: 1.23 br.s [24H, internal O*C*(O)CC*H*$_3$ fragments]; 1.51 s and 1.52 s [12H, terminal O*C*(O)CC*H* fragments]; 1.80–1.36 m [ring POC*H*$_2$CH$_2$CH$_2$O, $^3J_{HH}$ 5.9]; 2.91 t and 3.01 t [8H, CCH$_2$OC*H*$_2$CH$_2$OC, $^3J_{HH}$ 7.2]; 3.58 t [8H, COCH$_2$C*H*$_2$OC(O)O, $^3J_{HH}$ 7.2]; 3.72 s [8H, C(C*H*$_2$OC)$_4$]; 3.91 d.t [64H, ring POC*H*$_2$CH$_2$C*H*$_2$O, $^3J_{HH}$ 5.9, $^3J_{PH}$ 8.6]; 4.23 d [32H, POC*H*$_2$CC(O)O, $^3J_{HH}$ 8.1]; 4.34 br. s [16H, CH$_3$CC*H*$_2$OC(O)]. ^{13}C NMR spectrum (parenthesized are shapes of the ^{13}C–{^{1}H} signals), δ_C, ppm: 17.7 s(q) [*C*H$_3$*C*, $^1J_{HC}$ 126.8]; 28.5 s (t) [POCH$_2$·*C*H$_2$CH$_2$O cycl., $^1J_{HC}$ 127.4]; 41.9 s (s) [*C*C$_4$]; 46.6 s (s) (CH$_3$*C*(CH$_2$OP)]; 48.1 s (s) [CH$_3$*C*(CH$_2$OC)CH$_2$OP, middle fragments]; 49.3 s (s) [internal CH$_3$*C*(CH$_2$OC)CH$_2$OP fragments]; 53.9 d (t.d) [internal CH$_3$C(*C*H$_2$OP)$_2$ fragments, $^2J_{PC}$ 18.3, $^1J_{HC}$ 147.2]; 59.6 d (d.t) [ring POCH$_2$CH$_2$*C*H$_2$O, $^2J_{PC}$ 10.7, $^1J_{HC}$ 146.0]; 64.0 d (d.t) [OC(O)C(CH$_3$)*C*H$_2$OPOCH$_2$C, $^2J_{PC}$ 19.3,


I
16
P–NEt2
–16 Et2NH
II
III

$^1J_{HC}$ 135.2]; 64.7 m (m) (CH_2O); 65.2 m (m) (CH_2O); 67.10 s (t) and 67.14 s (t) [C(CH_2O)$_4$, $^1J_{HC}$ 150.2]; 172.2 s (s) [internal O*C*=O fragments]; 174.0 s (s) [terminal OC=O fragments]. Found, %: *C* 43.44; H 6.33; P 14.32; $C_{121}H_{204}O_{76}P_{16}$. Calculated, %: *C* 43.09; H 6.11; P 14.71.

The IR spectra were recorded on a Bruker Vector 22 FT–IR spectrometer (film, KBr). The ^1H and the ^{13}C NMR spectra were obtained on an Avance-600 spectrometer (600 and 100.6 MHz, respectively) in $CDCl_3$. The ^{31}P spectra were measured on a Bruker CXP-100 instrument (36.5 MHz) in CH_2Cl_2 against external 85% H_3PO_4.

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