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LETTERS TO THE EDITOR

Synthesis of Hyperbranched Polyesterpolytrimethylsiloxanes

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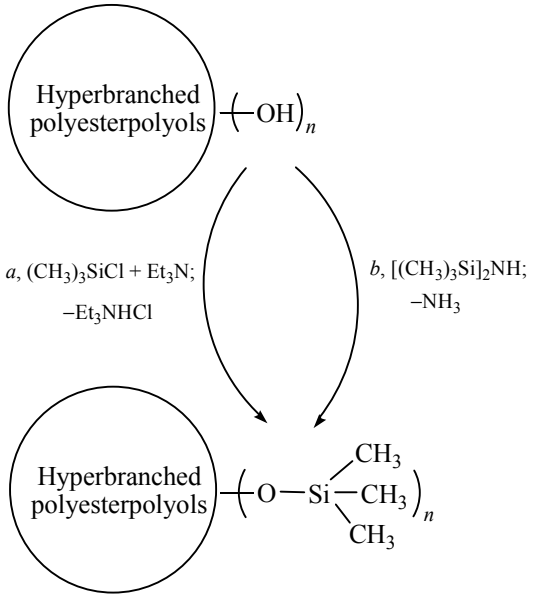
The number of reports on the synthesis of silicon-containing dendrimers with a variety of organic components is steadily increasing. Carboxysilane, siloxane, silane, and so-called "hybrid" dendrimers have been obtained [1], and dendrimers have been also synthesized with inorganic polycyclosiloxane inner sphere and the organic layer on the periphery [2]. At the same time, the silyl derivatives of hyperbranched polyesterpolyols were not described.

We carried out a modification of hyperbranched polyesterpolyols based on 2,2-dihydroxymethylpropanoic acid of second, third, and fourth generation, using two methods. The first is the reaction of hyperbranched polyesterpolyol with trimethylchlorosilane, the second is the reaction with hexamethyldisilazane, as shows the following scheme:



The products are highly viscous fluid resin soluble in organic solvents like acetone, chloroform, diethyl ether. The modification of the initial hyperbranched polyesterpolyols by the introduction of trimethylsilyl fragments led to an increase in fluidity and hydrophobicity of the polymer.

The polyestertrimethylsiloxanes obtained can be used as a composition additive to various polymers to provide them with resistance to frost and heat. They can also be used in electronics, motor-car construction, and metal-working industry for insulating and protective layers and films, in organic synthesis as intermediates, and in the pharmaceutical industry to produce antisclerotic drugs, synthetic antibiotics, and anticancer drugs. To assess the potential of the synthesized compounds, we carried out computer simulation using the PASS program which can predict the biological activity of 114 types from the structural formula of a chemical compound. Testing on an independent set showed that the prediction accuracy exceeds 4.6 times the random probability of "guessing," which allowed us to use the PASS software to search for new pharmacological agents. Analysis showed that the obtained compounds may have biological activity and can be used as anticancer drugs for the treatment of lymphocytic leukemia, lymphoma, brain cancer, melanoma, sarcoma, as well as inhibitors of methyl glutamate dehydrogenase.

***a*. Reaction of polyesterpolyols with trimethylchlorosilane.** To a solution of 5.0 g of polyesterpolyol of the second generation in 15 ml of anhydrous benzene and 15 ml of dry chloroform in a flow of dry argon was added 3.9 g of triethylamine. Then 4.2 g of trimethylchlorosilane was added by portions while stirring. The mixture was stirred for 3 h at 50°C. The

reaction completion was determined by the disappearance in the IR spectrum of the signal of the OH groups at ν 3400 cm^{-1}. After cooling to room temperature the mixture was filtered and the filtrate was evaporated for 1 h in a vacuum of 0.5 mm Hg at 40°C and 1 h in a vacuum of 0.02 mm Hg at 40°C. The residue was a colorless resin, 7.5 g. The product was purified by reprecipitation (chloroform/petroleum ester), the yield was 80%. IR spectrum (film), ν, cm^{-1}: 2955, 2898, 2881 m [$\nu_{as,s}(CH_3, CH_2)$]; 1738 v.s [ν(O–C=O)]; 1474, 1383 m [$\delta_{as,s}(CH_3)$]; 1252 v.s [δ{CH_3(Si)}]; 1178 m [ν(C–O)]; 1090 s [ν(Si–O–C, C–O)] 842, 748 s [δ$(CH_3)_3$Si]. ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 0.08 s [Si$(CH_3)_3$], 1.08, 1.14 two s [OC(O)CCH_3, the outer fragments] 1.21 s [OC(O)CCH_3, internal fragments], 3.61–3.68 m [OCH_2C, CH_2OSi] 4.23–4.26 m [$CH_2OC(O)$]. Found, %: C 50.27; H 9.81; Si 15.20. $C_{121}H_{252}O_{44}Si_{16}$. Calculated, %: C 50.80; H 8.88; Si 15.71.

By a similar method the reactions were performed of trimethylchlorosilane with hyperbranched polyols of the third and the fourth generation.

b. **Reaction of polyesterpolyols with hexamethyldisilazane**. A mixture of 4.7 g of a polyesterpolyol of the second generation and 7.08 g of hexamethyldisilazane was heated with stirring at 100–110°C, until the ammonia ceased to liberate (4 h), the end of the reaction was determined by the disappearance of the OH-group band at ν 3400 cm^{-1} in the IR spectrum. The residue contained 7.2 g (90%) of product as a colorless resin. IR spectrum (film), ν, cm^{-1}: 2957.2899, 2881 m [$\nu_{as,s}(CH_3, CH_2)$]; 1741 v.s [ν(O–C=O)]; 1472, 1372 m [$\delta_{as,s}(CH_3)$]; 1253 v.s [δ CH_3(Si)]; 1178 m [ν(C–O)]; 1083 s [ν(Si–O–C, C–O)] 842, 751 s [δ{CH_3(Si)}]. ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 0.1 s [Si$(CH_3)_3$], 1.1, 1.15 two s [OC(O)CCH_3, outer fragments] 1.21 s [OC(O)CCH_3, internal fragments], 3.62–3.72 m [OCH_2C, CH_2OSi], 4.28–4.3 m [$CH_2OC(O)$]. Found, %: C 51.50; H 8.91; Si 15.30. $C_{121}H_{252}O_{44}Si_{16}$. Calculated, %: C 50.80; H 8.88; Si 15.71.

By a similar procedure the reaction was carried out of hexamethyldisilazane with hyperbranched polyols of the third and the fourth generation.

IR spectra were recorded on a Fourier spectrometer Spectrum 400 (Perkin Elmer) with the NVPO diamond-KRS-5 unit, resolution 1 cm^{-1}, the accumulation of 10 scans during 20 seconds, mesuring range 4000–400 cm^{-1}. ^{1}H NMR spectra were obtained on a spectrometer Avance-600 (600 MHz) in $CDCl_3$.

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