Degradable Hyperbranched Poly(bis(undecenyloxy)methylsilane)s

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Introduction of arborols,[1] dendrimers, or star-burst polymers[2] had a strong impact on the research and development of novel macromolecular architectures, functional polymers, and materials.[3–6] While the actual conception of dendrimers/arborols is focused on the preparation of exactly defined, monodisperse branched molecules, there are also less defined but similarly densely branched molecules, the so-called hyperbranched polymers.[7] The formation of hyperbranched polymers is typically based on the condensation of molecules which contain one functional group A and more than one functional group B, whereby A can react with B and form a link but neither A nor B can react with itself. As a consequence of the particular stoichiometry, gelation or formation of microgels is not possible and polymer chains contain at most one reactive A group.[8] At full monomer conversion, the growth can principally be terminated either by increasing steric screening of the A groups or, depending on the chain flexibility, by ring formation as the A group reacts with a B group of the same polymer.[8,9]

So far, little attention was paid to degradable dendritic polymers besides using controlled degradation as a means to analyze the orginal polymer structure.[10] Because the molecular surface is defined by the topological arrangement of the end groups, a degradable dendritic polymer can be used as a template to create nanometer-sized cavities and, if the end groups remain attached to the matrix, to obtain well-defined cavities with particular chemical groups at the walls. This might be of great interest for enzyme mimicry, catalysis, and molecular separation.

In a first attempt to realize such an approach, we describe here the preparation of degradable hyperbranched organosilicon polymers. Although hyperbranched polymers cannot provide absolutely defined, monodisperse template molecules, they present globular molecules with defined end groups and thus allow one to explore the essential aspects of the concept. The particular advantage is that they can be prepared much more easily, which will be important for potential practical applications.

To achieve degradability, we chose to incorporate silicon–oxygen–carbon bonds. Preparation of hyperbranched poly(siloxysilane)s has been described before by Mathias et al.[11] In this work we describe the synthesis of poly(alkoxysilane)s according to Scheme 1. Alkoxysilane groups are easily hydrolyzed under acidic conditions.

In a first step, methyldichlorosilane was alkoxylated by reaction with 10-undecen-1-ol. Polyaddition to a hyperbranched polymer was performed under various conditions, as listed in Table 1.

Scheme 1

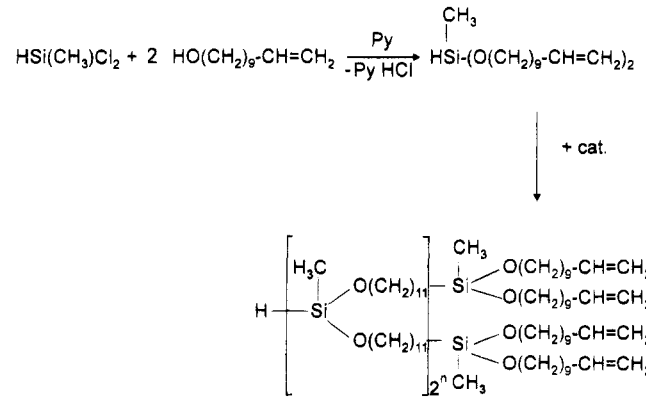
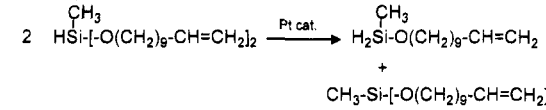


Table 1. Reaction Conditions for Formation of a Hyperbranched Polymer from $H(CH_3)Si[O(CH_2)_9CH=CH_2]_2$ by Hydrosilylation

sample no.	catalyst	reacn mixture	results
1	PC 072[a]	bulk	after 25 min, cross-linked
2	H_2PtCl_6[b]	bulk	after 15 min, cross-linked
3	H_2PtCl_6[b]	30% monomer in hexane	after 90 min, viscous and clear liquid, soluble polymer
4	$Co_2(CO)_8$[c]	bulk	after 25 h viscous, clear liquid, soluble polymer

[a] Platinum–divinyltetramethyldisiloxane complex, 3–3.5 wt % platinum in xylene. [b] In absolute THF, 0.05 g/mL. [c] In absolute hexane, 1×10^{-3} mol of Co/L.

Scheme 2



Unwanted gelation, which was observed when the rather active Pt catalysts were used in bulk condensation, indicates rearrangement of the monomer structure during the polyaddition reaction. Gelation was not observed when $H(CH_3)Si(CH_2CH=CH_2)_2$ was reacted under the same conditions.[9] Gelation can be tentatively explained by the rearrangement described in Scheme 2, yielding monomers of types B_3 and A_2B.[12]

Dilution of the reaction components with hexane suppressed the rearrangement and yielded a soluble polymer. Gelation could also be avoided when $Co_2(CO)_8$, a more selective hydrosilylation catalyst, was used. The latter approach appears superior because the stability of the reaction product is not hampered by the remaining traces of catalyst.

Figure 1 gives the GPC diagram for a $Co_2(CO)_8$-catalyzed polymerization. The diagram shows a broad distribution, as is typical for hyperbranched polymers.

Three different procedures were employed for degradation of the hyperbranched polymer (sample 4): (i) 1 g of polymer was dissolved in 40 mL of absolute THF, and the solution was mixed with 40 mL of methanol; (ii) the polymer was treated with methanol together with a small amount of aqueous HCl; (iii) the polymer was treated with methanol and HCl but the amount of water was increased.

Degradation with dry methanol was complete after 40 h of stirring under reflux. Only mono(dialkoxymethylalkylsilane)s were identified. The ^{29}Si-NMR spectrum shown in Figure 2a shows peaks between 0

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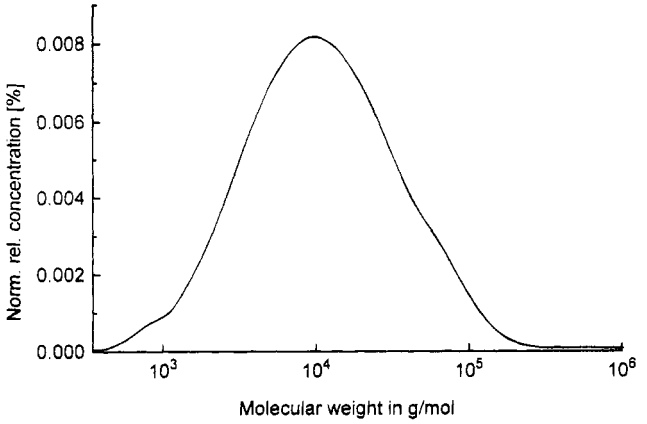

Figure 1. GPC trace of sample #4 after 25 h of reaction.

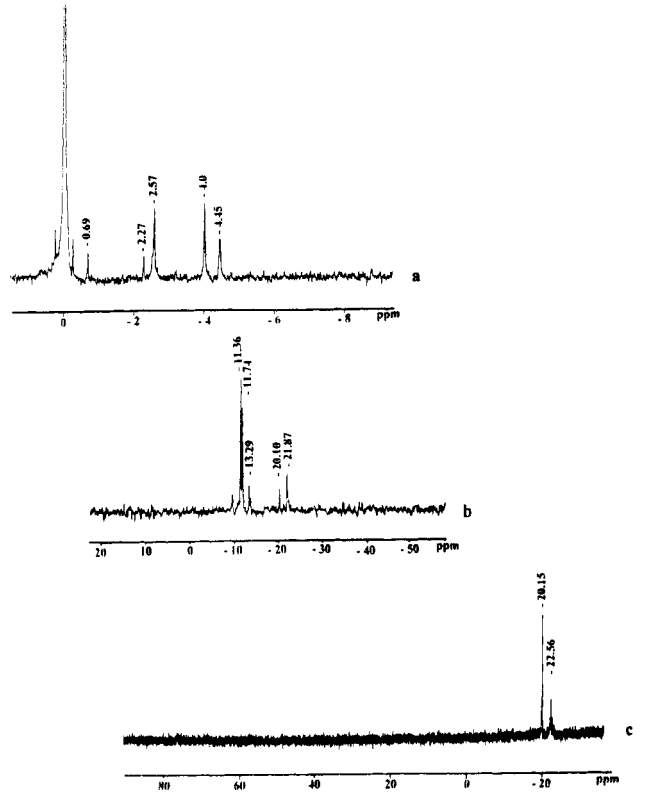

Figure 2. (a) ^{29}Si-NMR spectra of degradation product in dry methanol. Peaks between 0 and −5 ppm indicate monomeric dialkoxysiloxanes. Oligomeric products are absent. (b) ^{29}Si-NMR spectra of degradation product obtained with a small amount of aqueous hydrochloric acid showing formation of oligo(alkoxysiloxane)s and oligosiloxanes. (c) ^{29}Si-NMR spectra of oligosiloxanes formed when a large amount of water was added for the degradation.

and −5 ppm, which can be assigned to mono(dialkoxymethylalkylsilane)s with different alkoxy substitutents, i.e., methoxy, undecenyloxy, silaundecenyloxy.

When small amounts of aqueous HCl had been added, siloxane bonds were formed and identified by ^{29}Si-NMR.[13,14] A mixture of oligo(alkoxysiloxane)s and oligosiloxanes resulted with peaks at −11 to −13 ppm and at −20 to −22 ppm (Figure 2b). When the water content during degradation was increased further, mostly oligocyclosiloxanes were formed (Figure 2c).

In summary, it can be stated that (i) hydrosilylation of bis(alkenyloxy)methylsilanes can be employed to obtain hyperbranched silicon polymers in an easy one step reaction; (ii) the polymers obtained can be degraded easily to well-defined methyldialkoxysilyl alcohols; (iii) the hyperbranched poly(alkyloxysilane)s contain an "outer" shell of vinyl groups which is susceptible to further chemical modification by a second reaction step. It is proposed to use such polymers as template molecules to create functional cavities in a suitable matrix polymer, e.g., by copolymerization or embedding in a resin.

Experimental Section. Materials. Dichloromethylsilane, $HSi(CH_3)Cl_2$ (Petrarch), 10-undecenol (Aldrich, 98 mol %), and PC072 (platinum−divinyltetramethyldisiloxane, 3−3.5 wt % platinum in xylene, Hüls) were used as received. $Co_2(CO)_8$ (Alfa, 98 mol %) was dissolved in hexane (1×10^{-3} mol of Co/L); $H_2PtCl_6 \cdot 6H_2O$ (Merck) was dissolved under argon in absolute THF (1×10^{-4} mol of Pt/L); *n*-hexane was dried and distilled over potassium, and pyridine was dried over BaO and CaH_2 and stored under argon. Ether p.a. (Merck) was dried over CaH_2.

Methylbis(10-undecenyloxy)silane. A solution of 34.27 g (298 mmol) of methyldichlorosilane in 100 mL of dry hexane was added dropwise at room temperature to 101.5 g (596 mmol) of 10-undecenol in 600 mL of a 1:1 mixture by volume of dry hexane and dry diethyl ether containing 47.1 g (596 mmol) of pyridine. The reaction mixture was stirred under reflux for another 2 h, and precipitated pyridinium hydrochloride was removed by filtration under nitrogen. After evaporation of the solvent, pure methylbis(undecenyloxy)silane was isolated by distillation under reduced pressure: Yield: 107.2 g (94%). Bp = 145−147 °C (1 mmHg). Purity > 97% (GC). ^{1}H-NMR (ppm): 0.19 (s), CH_3Si; 1.3 (s, broad), $(CH_2)_n$; 1.56 (t), $=CH-CH_2-$; 2.03 (q), OCH_2CH_2-; 3.72 (t), OCH_2; 4.57 (s), SiH; 4.98 (d), $CH_2=$; 5.8 (tt), $=CH-$

Polyaddition reaction. The catalyst was added under inert gas to 3.82 g (0.01 mol) of freshly distilled methylbis(undecenyloxy)silane either in bulk or with the amount of solvent indicated in Table 1. Either 1 μL of a 0.1% solution of the Pt catalysts in THF was employed or 50 μL of a solution of dicobalt octacarbonyl in hexane. In this case, a viscous, bluish transparent solution was obtained from which 3.2 g (84%) of polymer was isolated by precipitation in ethanol and immediately dried under vacuum.

Characterization. Analytical GLC was performed on a Perkin-Elmer Autosystem instrument with a PE-2 capillary column (25 m × 0.32 mm × 0.51 μm) in combination with a flame ionization detector and a split/splitless injector. Conditions: injector temperature, 280 °C; column, 50 °C to 315 °C at 20 °C/min (8 min); detector, 280 °C; gas flow, 1 mL/min N_2. GPC experiments were performed with toluene on Waters μ-Styragel columns (pore sizes: 10^5, 10^4, 10^3, and 10^6 Å) using a Waters 410 differential refractometer and a Viscotek H502B detector. Molecular weights were calculated on the basis of narrow molecular weight distribution (MWD) polystyrene standards using PSS (Mainz) software. ^{1}H-NMR spectra and ^{29}Si-NMR spectra were recorded on a Bruker AC 200 spectrometer at 200 MHz and a Bruker AMX 500 spectrometer at 99.4 MHz, respectively. In the case of ^{29}Si measurements, inverse gated decoupling was used in order to eliminate the negative NOE. $CDCl_3$ was used as a solvent. Chemical shifts are relative to TMS.

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