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Communications to the Editor

Enhancing the Degree of Branching of Hyperbranched Polymers by Postsynthetic Modification

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Introduction. Due to their unique properties, and maybe their aesthetic allure, interest in dendrimers[1,2] and hyperbranched polymers[3,4] has been increasing at an amazing rate recently.[5] One of the most intriguing questions in this field is how closely the easily synthesized hyperbranched polymers prepared in a one-pot polymerization of AB_m monomers with or without core molecule B_f can mimic the properties of highly defined but tediously synthesized dendrimers. In this respect, the degree of branching (DB) has been discussed as one of the key parameters for the characterization of hyperbranched polymers.[6] Recently, our group has introduced an improved definition for DB[7,8] as well as a new concept, the *average number of branches (ANB)*, which quantifies the average number of polymer chains emanating from nonterminal branch points in addition to the linear direction, thus providing a measure for directly assessing the "branching density" of a structure and making quantitative comparison of structures prepared from monomers of different functionalities m possible. Equations 1 and 2 show the expressions for

$$\mathrm{DB} = \frac{2\mathrm{D} + \mathrm{sD}}{2\mathrm{D} + {}^{4}/_{3}\mathrm{sD} + {}^{2}/_{3}\mathrm{L}} \tag{1}$$

$$\mathrm{ANB} = \frac{2\mathrm{D} + \mathrm{sD}}{\mathrm{D} + \mathrm{sD} + \mathrm{L}} \tag{2}$$

the calculation of DB and ANB from the relative abundances of linear (L), semidendritic (sD), and dendritic (D) units for an AB_3 system.

In this communication, we would like to report a simple, universal method for enhancing the degree of branching of hyperbranched structures, exemplified for hyperbranched polycarbosilanes.

Experimental Section. General Information. Toluene and diethyl ether were dried over Na. $HSiCl_3$ was distilled before use. Triallylsilane was prepared according to literature procedures.[9] η^2-(1,5-Cycloocta-

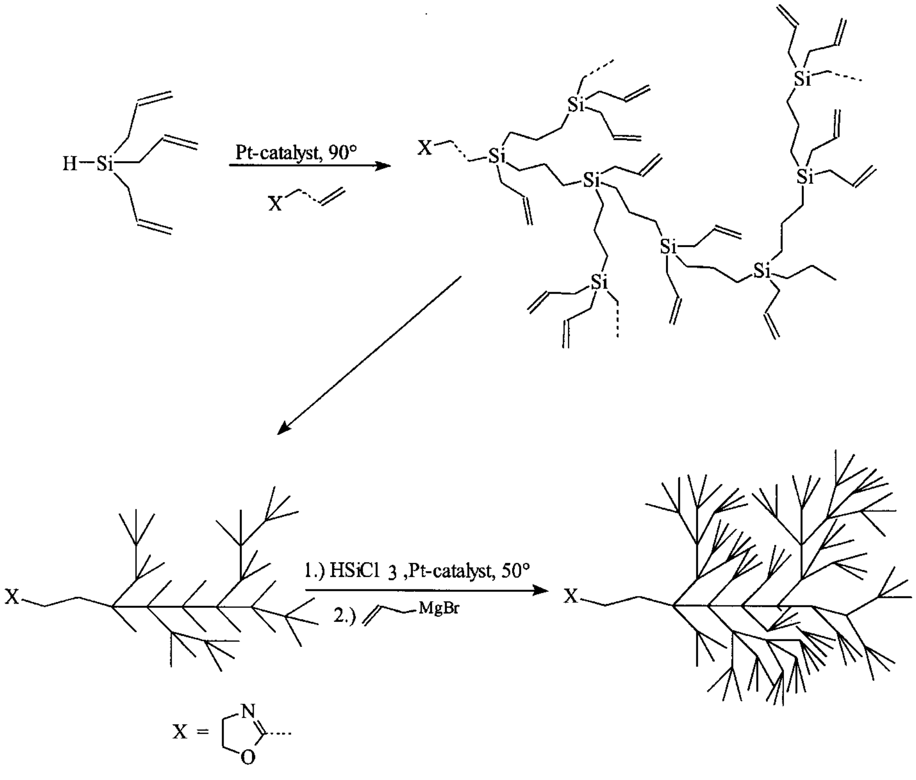

Figure 1. Schematic representation of the reaction sequence used for enhancement of the degree of branching. Hydrosilylation employing $HSiCl_3$ followed by reaction with allylmagnesium bromide transforms all triallylsilane branch points to dendritic units with trichlorosilane groups leading to terminal units.

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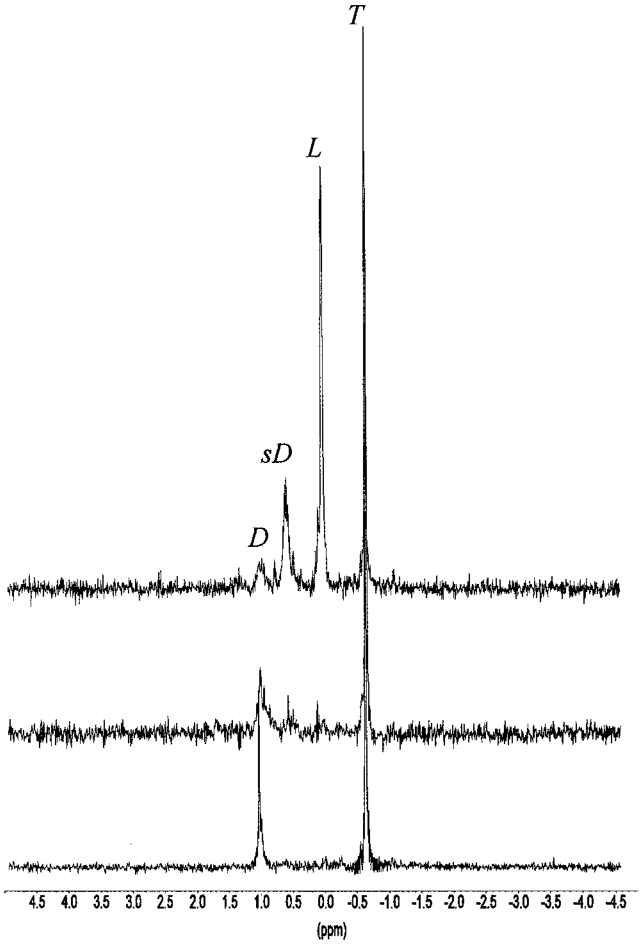

Figure 2. Comparison of ^{29}Si NMR spectra for (from top to bottom) hyperbranched polymer, hyperbranched polymer after modification, and dendrimer. Signals correspond to (from left to right) D, sD, L, and T units with 0, 1, 2, and 3 allyl substituents, respectively.

dienyl)platinum(II) dichloride was a gift from Wacker Chemie GmbH, platinum divinyltetramethyldisiloxane is a product of ABCR. NMR spectra were recorded on a Bruker ARX-300 spectrometer.

Synthesis.[9] In a dry two-necked flask, 1 mL of triallylsilane and 0.2 mL of 2-(10-decen-1-yl)-1,3-oxazoline were dissolved in 4 mL of toluene. After addition of a few crystals of η^2-(1,5-cyclooctadienyl)platinum(II) dichloride, the reaction mixture was heated to 90 °C for 2 h and allowed to cool to room temperature. Then 4 mL of trichlorosilane and 50 μL of platinum divinyltetramethyldisiloxane (ABCR PC0-72) were added and the reaction mixture was heated to 80 °C for another 30 h. From that mixture, toluene and excess trichlorosilane were removed in vacuo, and the residue was dissolved in 5 mL of diethyl ether. That mixture was transferred to a 500 mL three-necked flask, and a solution in 160 mL of diethyl ether of allylmagnesium bromide prepared from 16 mL of allyl bromide was added slowly. After the mixture was heated to reflux for 98 h, the reaction mixture was hydrolyzed by carefully adding 200 mL of 2% H_2SO_4. The aqueous phase was separated and extracted with 80 mL of diethyl ether thrice. The combined organic phases were dried using $MgSO_4$ and filtered, and the solvent was removed in vacuo. The resulting polymer was obtained as a clear, viscous liquid, which was used for all characterizations.

Results and Discussion. In recent theoretical work, we have discussed several methods for achieving degrees of branching significantly higher than those expected in a random one-pot polymerization of AB_m monomers.[8] Additionally, we present here a reaction sequence that allows us to enhance DB postsynthetically. To this end, we combine a reaction sequence well-known from carbosilane dendrimer synthesis, namely the hydrosilylation of terminal double bonds employing trichlorosilane and the subsequent nucleophilic displacement of the chloride groups by allylmagnesium bromide, with the previously reported synthesis of hyperbranched poly(triallylsilanes).[9,10] Hyperbranched polycarbosilanes can also be prepared by following a different pathway.[11] Since all residual double bonds should be consumed by trichlorosilane, all triallylsilane molecules will be transformed to dendritic units in the final polymer. Addition of allylmagnesium bromide will then transform the pendant trichlorosilane groups to terminal units, thus, according to eq 1, resulting in a completely branched structure with DB = 1 in the case of complete reaction.

Table 1. Relative Abundances (%) of Terminal (T), Linear (L), Semidendritic (sD), and Dendritic (D) Groups as Well as DB and ANB Calculated According to Eqs 1 and 2, in Comparison to a Random AB_3 Polycondensation and a Dendrimer[a]

	T	L	sD	D	DB	ANB
random AB_3 polycondensation (theoretical values[7])	30	44	22	4	0.45	0.43
hyperbranched polymer	31	42	22	5	0.48	0.46
modified hyperbranched polymer	62	4	8	26	0.92	1.58
dendrimer						
Gen1	80			20	1	2
Gen2	71			29	1	2
Gen3	68			32	1	2

[a] Experimental percentages contain an absolute error of ± 3%.

^{29}Si NMR spectroscopy allowed us to quantify terminal (T), linear (L), semidendritic (sD), and dendritic (D) branch points, which can be identified as separate signals due to the fact that they each carry a different number of allyl substituents. Figure 2 shows the ^{29}Si NMR spectra of a generation 1 carbosilane dendrimer, a modified (i.e., "enhanced") hyperbranched polymer, and the random hyperbranched polymer, respectively. The four signals that can be discerned in the random hyperbranched molecule (top) correspond to (from left to right) dendritic, semidendritic, linear, and terminal units, each type of branch unit bearing one more allyl substituent than the one before. As can be easily seen, there is a significant decrease in the integral of the linear and semidendritic groups in the spectrum of the enhanced polymer while the dendrimer shows exclusively the signals for dendritic and terminal groups.

Table 1 gives the relative abundances from integration of the ^{29}Si spectra of T, L, sD, and D units for the regular and enhanced hyperbranched polymers, as well as their respective DB's and ANB's.

Interestingly, the reaction of the terminal double bonds did not go to completion even after prolonged reaction times, contrary to our experience from carbosilane dendrimer synthesis. We feel that incomplete conversion of the double bonds may be due to the inaccessibility of functionalities near the center of the hyperbranched fragments, which should be rather dense structures at the later stages of the reaction. This assumption is supported by the fact that the ensuing substitution reaction with allylmagnesium bromide also

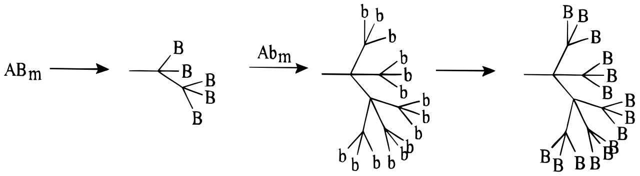

Figure 3. General concept for enhancement of the degree of branching by postsynthetic modification: (a) hyperbranched polymer reacted with an excess of B-protected Ab_m monomer; (b) deprotection of the b functionalities yielding the modified polymer with DB $\approx$ 1.

requires longer reaction times to go to completion than for the highest generation dendrimers prepared in our group so far, which at 25 000 g/mol are much larger molecules than our hyperbranched polymer, which showed a PS-equivalent M_w of 1800. On the other hand, this once more illustrates the well-known fact that in dendrimers the terminal groups are highly accessible.

Physical properties of the hyperbranched polymers with enhanced DB including the effect of degree of polymerization on the modification reaction, effect of DB on viscosity, and thermal properties are currently under investigation.

Conclusion. Using the example of hyperbranched poly(triallylsilane)s, a concept has been introduced that should be universally applicable for the enhancement of the degree of branching of hyperbranched polymers. After formation of the hyperbranched structure, a B-protected molecule Ab_m is added to the reaction mixture, which leads to complete or nearly complete consumption of B groups. Subsequent deprotection of the terminal b groups (b → B) leads to the modified hyperbranched polymer with DB close to 1. Figure 3 shows a general scheme for this reaction.

While we are aware of the fact that the structures obtained by this method are not identical to those obtained by a “real” completely branching polymerization, i.e., one that inherently yields only dendritic and terminal units[8], we feel that they nevertheless will enrich our understanding of the differences and similarities of dendrimers and hyperbranched polymers.

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