

Hyperbranched Polycarbosilanes of Homogeneous Architecture: Regioselective Hydrosilylation of AB₂ Monomers and Consecutive Functionalization

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ABSTRACT: A novel AB_2 monomer, bis(4-(but-3-enyl)phenyl)methylsilane, **1a**, and its analogue AB structure **1b** were synthesized and polymerized with Karstedt's, Speier's, and a Pt-NHC catalyst to obtain hyperbranched and linear polycarbosilanes. Only the Pt-NHC complex afforded a regioselective hydrosilylation reaction. As a consequence, this led to a uniform polymer microstructure and at the same time to significantly increased molecular weights. Functionalization of the remaining double bonds in the obtained polymer was achieved by two exemplary routes. Hydrosilylation with a functional silane yielded chloromethylsilyl capped polymers, hydroboration and subsequent oxidation led to hydroxy-terminated polymers.

Introduction

Hydrosilylation describes the addition of hydrosilanes to multiple bonds. Since the discovery of hexachloroplatinic acid as a very efficient catalyst by Speier in 1957,¹ hydrosilylation has become one of the most important reactions for preparing organosilicon compounds in both industry and academia.

As a quantitative, high yielding reaction hydrosilylation is also used in the synthesis of dendrimers and hyperbranched polymers, one of the fastest growing areas of interest in polymer science in the last few decades.² Although dendrimers with their perfectly branched structure and symmetry are of natural beauty, they have the disadvantage of a very elaborate and purification intensive synthesis. By contrast, hyperbranched polymers offer similar properties with the benefit of a simple one pot polymerization strategy. The utilization of hydrosilylation in the synthesis of hyperbranched polycarbosilanes was first reported by Muzafarov et al. in 1993, who polymerized, among others, methyldiallylsilane and methyldivinylsilane.³ Apart from aliphatic polyalkenylsilanes,⁴ hyperbranched polycarbosilanes with aromatic⁵ and thiophene⁶ moieties are also known.⁷

In the synthesis of hyperbranched polycarbosilanes mostly platinum complexes, especially Speier's or the more active Karstedt's catalyst, are used. Unfortunately, applying these catalysts also leads to numerous side reactions like α -addition yielding the Markovnikov product, dehydrogenative silylation and isomerization.⁸ To overcome these problems, Markó et al. developed several *N*-heterocyclic carbene platinum(0) complexes which showed high efficiency and selectivity in hydrosilylation experiments.^{9–13} We report here on the regioselective synthesis of a novel family of hyperbranched polycarbosilanes with good control of microstructure and polymer architecture via hydrosilylation polymerization using a Pt–NHC complex.

Experimental Section

All reactions were performed under an atmosphere of argon using standard Schlenk techniques. All chemicals were purchased from Sigma-Aldrich or Acros Organics and used as received. Dry solvents were obtained by filtering with a solvent purification system (MB SPS-800, MBraun). Flash chromatography was performed with silica gel 60 (Fluka) with a particle size of 0.040-0.063 mm. ¹H, ¹³C and ²⁹Si NMR spectra were recorded on a Bruker ARX 300 spectrometer at ambient temperature.²⁹Si NMR spectra of the polymers were recorded on a Bruker Avance 500 spectrometer. The spectra were referenced to the residual solvent signals of the deuterated solvents (Deutero); chemical shifts are reported in δ (ppm). GPC was performed with a Polymer Laboratories GPC 50 Plus chromatograph running with HPLC-grade THF at a flow rate of 1 mL/min. Polystyrene standards were used for calibration. GC-MS was measured on a Varian CP-3800 with a quadrupol 1200 L mass spectrometer. Elemental analysis was performed at the microanalytic laboratory, institute of inorganic chemistry, TU Munich.

1-Bromo-4-(but-3-enyl)benzene. The compound was synthesized according to the known literature procedure.¹⁴ The crude product was purified by column chromatography (pentane, $R_f = 0,43$) to yield the product as a colorless liquid (83%).¹H NMR (CDCl₃, 300.13 MHz): $\delta = 7.40$ (d, ${}^{3}J_{\rm HH} = 8.40$ Hz, 2H, Ar–H), 7.06 (d, ${}^{3}J_{\rm HH} = 8.40$ Hz, 2H, Ar–H), 5.82 (ddt, ${}^{3}J_{\rm HH} = 6.57$, 10.20, 16.84 Hz, 1H, H₂C=CH–), 5.02 (m, 2H, H_2 C = CH–), 2.67 (t, ${}^{3}J_{\rm HH} = 8.40$ Hz, 2H, Ar–CH₂–), 2.35 (m, 2H, Ar–CH₂–CH₂–).

AB₂ Monomer Bis(4-(but-3-enyl)phenyl)methylsilane (1a). In a three-necked round-bottom flask equipped with dropping funnel, reflux condenser, and argon inlet was dispersed 0.49 g of magnesium (0.02 mol) in 10 mL of dry THF. A solution of 4.30 g of 1-bromo-4-(but-3-enyl)benzene (0.02 mol) in 20 mL of dry THF was slowly added to the stirred magnesium dispersion. After completion of the addition, the grayish solution was heated to reflux for 1 h and afterward cooled to room temperature. Then 1.17 g of dichloromethylsilane (0.01 mol) was added dropwise; meanwhile, a white solid precipitated. The reaction

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Scheme 1. Synthesis and Polymerization of AB and AB₂ Monomer



mixture was again heated to reflux for 2 h. After the mixture was cooled to room temperature, 10 mL of a saturated NH₄Cl solution was carefully added. The white precipitate was dissolved by adding 10 mL of water. The organic phase was separated, washed with water and a saturated NaCl solution, dried over MgSO₄, and concentrated in vacuo. The crude product was purified by column chromatography (pentane, pentane/ethyl acetate 98:2, R_f (pentane) = 0.11) to yield 2.03 g (65%) of the product as a colorless liquid. ¹H NMR (CDCl₃, 300.13 MHz): $\delta = 7.49$ (d, ${}^{3}J_{\text{HH}} = 7.60$ Hz, 4H, Ar–H), 7.21 (d, ${}^{3}J_{\rm HH} = 7.60$ Hz, 4H, Ar–H), 5.87 (ddt, ${}^{3}J_{\rm HH} = 6.54$, 10.18, 16.92 Hz, 2H, H₂C=CH-), 5.02 (m, 4H, H_2 C=CH-), 4.91 (q, ³J_{HH} = 3.78 Hz, 1H, Si-H), 2.72 (t, ³J_{HH} = 8.40 Hz, 4H, Ar- CH_2 -), 2.38 (m, 4H, Ar- CH_2 -C H_2 -), 0.60 (d, ${}^{3}J_{HH}$ = 3.84 Hz, 3H, Si- CH_3). ${}^{13}C$ NMR (75.47 MHz): δ = 143.3, 138.0, 134.9, 132.4, 128.1, 114.9, 35.4, 35.3, -4.9. ${}^{29}Si$ NMR $(59.63 \text{ MHz}): \delta = -17.9$. Anal. Calcd for C₂₁H₂₆Si: C, 82.29; H, 8.55; Si, 9.16. Found: C, 82.40; H, 9.02; Si, 10.02. GC-MS $(M - H^+)$: calcd, 305.17; found, 305.18.

AB Monomer 4-(But-3-enyl)phenyldimethylsilane (1b). The AB monomer was synthesized analogously to the AB₂ monomer by reaction of 0.36 g of magnesium (0.015 mol), 3.15 g of 1-bromo-4-(but-3-enyl)benzene (0.015 mol), and 1.41 g of chlorodimethylsilane (0.015 mol). The crude product was purified by column chromatography (pentane, $R_f = 0.38$) to yield 2.12 g (75%) of the product as a colorless liquid. ¹H NMR (CDCl₃, 300.13 MHz): $\delta = 7.48$ (d, ³J_{HH} = 8.01 Hz, 2H, Ar-H), 7.21 (d, ³J_{HH} = 8.10 Hz, 2H, Ar-H), 5.88 (ddt, ³J_{HH} = 6.54, 10.19, 16.83 Hz, 1H, H₂C=CH-), 5.03 (m, 2H, H_2 C=CH-), 4.43 (m, 1H, Si-H), 2.72 (t, ³J_{HH} = 8.98 Hz, 2H, Ar-CH₂-C), 2.39 (dt, ³J_{HH} = 7.05, 14.16 Hz, 2H, Ar-CH₂-CH₂-), 0.34 (d, ³J_{HH} = 3.60 Hz, 6H, Si-CH₃). ¹³C NMR (75.47 MHz): $\delta = 143.0, 138.0, 134.3, 134.1, 128.0, 114.9, 35.3, -3.7. ²⁹Si NMR: (CDCl₃, 59.63 MHz): <math>\delta$ (ppm) = -17.2. Anal. Calcd for C₁₂H₁₈Si: C, 75.71; H, 9.53; Si, 14.75. Found: C, 75.28; H, 9.35; Si, 13.42. GC-MS (M - H⁺): calcd, 189.11; found, 189.19

General Polymerization Procedure. In a Schlenk flask, 0.25 g of the monomer was dissolved in 3 mL of dry solvent and the catalyst was added. The reaction mixture was stirred at 60 °C for 24 h (48 h when using the Pt–NHC catalyst). After the mixture had cooled to room temperature, the solvent was removed in vacuum. Reactions using Karstedt's catalyst (substrate to catalyst ratio = 10000/1) or the Pt–NHC complex (1000/1) were conducted in dry toluene, reactions with Speier's catalyst (100/1) were performed in dry isopropanol. The polymers were obtained as sticky, colorless to brownish liquids to solids, depending on the degree of polymerization and the catalyst used. For NMR assignment of the polymer signals, see the Supporting Information.

Functionalization of polymers. For the hydrosilylation, 0.10 g (double bond content: 0.33 mmol) of the polymer was dissolved in 5 mL of dry toluene and 0.35 g (3.3 mmol)

of chloromethyldimethylsilane was added to the solution. Karstedt's catalyst was added, and the mixture was stirred at 60 °C for 12 h. After evaporation of the solvent, the residue was dissolved in 1 mL of chloroform and precipitated from cold methanol. The polymer was filtered off and dried in vacuo to yield 90 mg of a brownish solid.

For the hydroboration, 0.50 g (double bond content: 1.6 mmol) of the polymer was dissolved in 15 mL of dry THF, the mixture was cooled to -10 °C, and 6.5 mL of a 9-BBN solution (3.2 mmol, 0.5 M solution in THF) was added slowly. The mixture was stirred at -10 °C for 3 h and at room temperature overnight. For oxidation, the solution was cooled to -10 °C again and 4 mL of a 6 N solution of NaOH followed by 5 mL of a 30% aqueous solution of H₂O₂ was added. After being stirred for 1 h at -10 °C, the mixture was allowed to warm to room temperature and stirred at 50 °C for another hour. The mixture was cooled to room temperature and the organic phase was separated, washed with a saturated solution of NaCl three times, dried over MgSO₄ and the solvent was removed in vacuo. The residue was dissolved in 2 mL of chloroform again and precipitated from cold methanol. The polymer was filtered off and dried in vacuo to give 0.41 g of a colorless sticky solid.

Results and Discussion

One of the possibilities to synthesize hyperbranched polymers is the polyaddition of AB_x monomers ($x \ge 2$). For hyperbranched polycarbosilanes the AB_2 monomers require, for example, one Si-H group and two double bonds. We synthesized bis(4-(but-3-enyl)phenyl)methylsilane (**1a**) as a novel AB_2 monomer and (4-(but-3-enyl)phenyl)dimethylsilane (**1b**) as its AB monomer analogue by two consecutive Grignard reactions each starting from 4-bromobenzyl bromide (see Scheme 1). The monomers were purified by flash chromatography and obtained in good yields. We chose this monomer structure with an aryl spacer between silicon and double bond because simpler spacers like alkyl spacers lead to problems. Medium length alkyl spacers result in cyclization instead of polymerization and longer spacers are not as easily accessible.

For polymerization of the monomers three different catalysts were employed. Apart from the well-known Speier (2) and Karstedt (3) systems, one of the *N*-heterocyclic carbene platinum(0) complexes developed by Markó et al. was also utilized for hydrosilylation (see Figure 1). We decided to use (N,N'-bis(2,4,6-trimethyl-phenyl)imidazol-2-ylidene)platinum(divinyltetramethyldisiloxane) (4) (Pt-NHC) because of its reported high selectivity and reactivity. The complex was synthesized according to the known literature procedure.¹⁰

All polymerization reactions with Karstedt's catalyst and the Pt–NHC complex were conducted in toluene at 60 °C, the reactions using the Speier system were performed in isopropanol at the same temperature. Table 1 summarizes the polymerization



Figure 1. Hydrosilylation catalysts used for polymerization of AB_2 monomers.

Table 1. Summary of Polymerization Results with Different Catalysts

entry	monomer	catalyst ^a	% isomerization ^{b}	$M_{\rm n}^{\ c}$ (g/mol)	PDI^{c}
P1	AB_2	2	10	1400	1.30
P2	AB_2	3	29	3900	6.38
P3	AB_2	4	d	18 600	2.41
P4	AB	3	6	4800	2.08
P5	AB	4	d	9500	1.77

^{*a*} Reactions with Speier's and Karstedt's catalyst were stirred at 60 °C for 24 h, reactions with Pt–NHC catalyst for 48 h. ^{*b*} Determined by ¹H NMR spectroscopy. ^{*c*} Determined by GPC in THF versus polystyrene standards. ^{*d*} Only trace amounts of isomerized double bonds were detectable.



Figure 2. ¹H NMR spectra of (a) AB_2 monomer **1a**, (b) partially isomerized polymer **P2** (Karstedt's catalyst) and (c) polymer **P3** without isomerization (Pt–NHC) (300 MHz, CDCl₃, 300 K, solvent and H₂O signals are marked with an asterisk).

results and trends obtained for the different catalysts with selected examples P1 - P5.

When using Speier's or Karstedt's catalyst, polymers with moderate molecular weights and high PDI were obtained. However, considerable amounts of internal double bonds occurred from a side reaction during polymerization. Figure 2a shows the ¹H NMR spectrum of AB₂ monomer **1a** with the signals for the terminal double bond at 5.9 and 5.0 ppm and the signal for the Si–H group at 4.9 ppm. The spectrum of the hyperbranched polymer **P2** obtained with Karstedt's catalyst (Figure 2b) clearly shows two new signals at 5.6 and 3.3 ppm which can be assigned to the double bond protons and the adjacent methylene group of an isomerized internal double bond. This isomerization is a well-known side reaction in hydrosilylation.¹⁵ As the internal double



Figure 3. ²⁹Si NMR of (a) partially isomerized polymer **P2** (Karstedt's catalyst) and (b) polymer **P3** without isomerization (Pt–NHC) (500 MHz, CDCl₃, 300 K).

bond is unreactive in hydrosilylation under the given conditions this reaction limits the number of reactive double bonds available for polymer growth.⁷

The Pt–NHC complexes developed by Markó et al. are known to be less active but more selective than Karstedt's catalyst with hardly any isomerization observed. Therefore, **4** was also tested in the hydrosilylation of the AB₂ monomer **1a**. The resulting polymer **P3** showed only trace amounts of isomerized double bonds in the ¹H NMR spectrum (Figure 2c) and the molecular weight was significantly higher (see Table 1). At the same time a narrow molecular weight distribution was found, which also corresponds to the homogeneous polymer architecture. The uniformity of polymer **P3** is also clarified by its ²⁹Si NMR spectrum (Figure 3b), which mainly shows one signal at -7.8 ppm. Figure 3a displays the spectrum of the partially isomerized polymer **P2** with additional signals at -0.7, -2.6, and -11.7 ppm, most likely deriving from the inhomogenous polymer microstructure.

The trends observed for the hyperbranched polymers were also detected for the linear polymers which result from hydrosilylation of the AB monomer 1b. Compared to Karstedt's catalyst the molecular weight of the polymer is significantly increased and again no internal double bonds could be detected when using the Pt-NHC complex. The lower degree of isomerization observed for the linear polymer in comparison to the hyperbranched polymer clearly results from the higher reaction rate of the hydrosilylation compared to isomerization. During the polymerization of the AB₂ monomer only 50% of the double bonds can be consumed, the others remain unreacted in the polymer. By comparison, in the polymerization of the AB monomer, all double bonds will eventually be consumed during the reaction. All remaining double bonds can be isomerized by the catalyst during the whole polymerization process which should lead to higher degrees of isomerization for the hyperbranched polymer because of the higher double bond content.

The improvement of molecular weight and PDI with the Pt–NHC catalyst can also clearly be seen from Figure 4 which shows the GPC traces of polymer P3 (solid line) and P2 (dashed line). Not only does P3 have the higher molecular weight but also it has a much narrower weight distribution, resulting in a more uniform polymer. In our opinion, this improvement of molecular



Figure 4. GPC traces of partially isomerized polymer P2 (Karstedt's catalyst, dashed line) and polymer P3 without isomerization (Pt-NHC, solid line).



Figure 5. ¹H NMR spectra of functionalized hyperbranched polymers. (a) after hydrosilylation and (b) after hydroboration and oxidation (300 MHz, CDCl₃, 300 K).

weight arises principally for the following two reasons. The insertion of the olefin into the Pt–H bond at the active center of **4** occurs regioselectively, which leads to no isomerization. As all internal double bonds are unavailable for further polymer growth, isomerization can be regarded as a termination reaction of the hydrosilylation polymerization. A selective catalyst suppressing isomerization should therefore lead to higher molecular weights. Second the lower activity of the Pt–NHC complex compared to Karstedt's catalyst results in a slower but more uniform growth of the polymer and therefore in smaller PDIs.

In an additional step the obtained polymer was functionalized in two different ways. Because of its homogeneous microstructure the polymer obtained with the Pt-NHC catalyst is suited particularly well for functionalization because all remaining double bonds are equally reactive. The polymer gained, e.g., with Karstedt's catalyst on the other hand partly consists of isomerized internal double bonds that are less reactive and thus harder to functionalize. As a first method for introducing functional groups to the polymer we performed an additional hydrosilylation step. A functional silane, chloromethyldimethylsilane, was hydrosilylated to the remaining double bonds of the polymer. The success of this functionalization can be seen from the ¹H NMR spectrum of the polymer (Figure 5a). The signals of the double bond at 5.9 and 5.0 ppm have completely disappeared and new signals originating from the functionalization emerged (signals a-f in Figure 5a).

Another possibility of functionalization, already applied to carbosilane dendrimers,¹⁶ is a hydroboration of the double bonds with 9-BBN and subsequent oxidation with H_2O_2 leading to a hydroxyl-group-containing hyperbranched polymer. Figure 5b shows that all double bonds have successfully been converted to hydroxy groups. The addition of the borane proceeds in an anti-Markovnikov fashion and the functionalized polymer could easily be separated from impurities like 1,5-cyclooctanediol by precipitation from methanol.

The simple application of the two presented derivatization methods and the homogeneity of the resulting polymers show that these hyperbranched polymers could be used as an alternative to dendrimers which are much more tedious to prepare. In particular, the hydrosilylation approach for functionalization is very promising as any functional silane with one Si-H group can be utilized. Apart from chloromethyldimethylsilane used in the presented work, a lot of other silanes such as, e.g., ethoxydimethylsilane are imaginable. Functionalization and polymerization rely on the same reaction, the hydrosilvlation, so the same catalyst can be used in both. The derivatization could be a follow up-reaction to the polymerization without the need of a work-up in between. First experiments in our group show that a one pot functionalization without preceding isolation of the polymer is possible. This is a straightforward approach toward diversely functionalized dendritic polymers.

Conclusion

Our novel AB and AB₂ monomers were polymerized with Karstedt's, Speier's, and a Pt-NHC catalyst to obtain linear and hyperbranched polycarbosilanes. 2 and 3 only yielded polymers with moderate molecular weights and high PDI due to the double bond isomerization. Additionally such polymers are of nonuniform polymer microstructure. However, application of the Pt-NHC complex 4 gave polymers with higher molecular weights and narrower weight distributions. We believe this improvement to be caused by the regioselectivity of 4, noticeable in the absence of any isomerized, unreactive double bonds, always observed with Karstedt's and Speier's catalyst. The regioselectivity greatly increases the uniformity of the hyperbranched polymers synthesized with the Pt-NHC catalyst. The polymers were quantitatively functionalized in an additional hydrosilylation step or by hydroboration of the remaining double bonds. This complete derivatization is a consequence of the uniformity of the polymer, as only the terminal double bonds can easily be addressed for functionalization. The Pt-NHC catalyst thus not only yields polymers with higher molecular weights but also gives the opportunity for quantitative functionalization. The homogeneity of the polymers and the straightforward introduction of functional groups make these hyperbranched polycarbosilanes an easily accessible mimic of dendrimers which would require a tedious multistep synthesis.

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Supporting Information Available: Figures showing NMR spectra of monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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