Preliminary communication / Communication

Synthesis of hyperbranched carbosiloxane macromolecule with triallyloxysilane and applications to the dendritic core

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Abstract

A hyperbranched carbosiloxane macromolecule (AB_3-type with Si–O bonds) was prepared by the self-hydrosilation of triallyloxysilane ($H–Si(OCH_2CH=CH_2)_3$) in the presence of a platinum catalyst. The prepared AB_3-type hyperbranched carbosilane was used for the carbosilane dendrimer as the core, which was progressed until the second generation by the use of iterative controlled methods such as hydrosilation and alcoholysis. NMR, MALDI mass and GPC identified the triallyloxysilane-based hyperbranched carbosilanes and dendrimers. *To cite this article: C. Kim, H. Kim, C. R. Chimie 7 (2004)*.
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Résumé

Une macromolécule hyperbranchée d'un carbosiloxane (de type AB_3 avec des liaisons Si–O) a été synthétisée par auto-hydrosilation du triallyloxysilane ($H–Si(OCH_2CH=CH_2)_3$) en présence d'un catalyseur au platine. Le carbosilane hyperbranché préparé, de type AB_3, a été utilisé comme noyau d'un dendrimère mené jusqu'à la seconde génération par l'emploi de méthodes itératives contrôlées telles que l'hydrosilation suivie d'une alcoholyse. Les techniques RMN, MALDI–MS et GPC ont été utilisées pour identifier et caractériser les carbosilanes hyperbranchés et les dendrimères. *Pour citer cet article : C. Kim, H. Kim, C. R. Chimie 7 (2004)*.
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1. Introduction

Dendrimers are synthesized by the use of multistep iterative controlled reaction procedures, whereas hyperbranched polymers are prepared by one pot reaction that results in a less regularly unified structural conformation, accompanied by broad molecular weight distributions [1–5]. Recently, dendrimers have attracted considerable attention due to their new properties caused by their unique structural architecture and useful abilities for new material science [6–9]. However, the preparation of well-characterized and highly

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branched dendritic macromolecules required a time-spending process [10–12]. On the other hand, hyper-branched polymers can be prepared by one-step bulk reaction as a general polymerization process [13]. Hence, the product had an uncontrolled structural conformation containing the average number of unreacted functional groups according to the molecular size everywhere on the molecular surface and inside. The remained functional groups such as double bonds in the hyperbranched polymer could be successfully used as the core of a new type dendrimer [14–15].

The resulting products from the dendritic generation using the hyperbranched core could reveal less regular molecular distribution than the iterative generated general dendrimer, but the prepared dendrimer using hyperbranched core polymer had a molecular group with a different size, which have more functionalities than the core. The hyperbranched polymer with triallylsilane as a general model was prepared without solvents at high temperature and singly identified [16]. However, the hyperbranched polymer with Si–O bonds sourced from triallyloxysilane was not found in published article. In this paper, we wish to report on the synthetic method of a new hyperbranched polymer with triallyloxysilane, and the resulting polymer could be hopefully used as the core of the new type of dendritic molecules.

2. Results and discussion

Triallyloxysilane for the preparation of carbosiloxane hyperbranched polymers was prepared at –78 °C with three equivalents of allylalcohol and one equivalent of trichlorosilane in toluene containing TMEDA at the low temperature. The reaction product revealed very pure and obtained high yield. However, the reaction product was obtained as the mixture of triallyloxysilane and tetraoxyallylsilane at room temperature.

The AB$_3$-type hyperbranched carbosiloxane polymer could be prepared from triallyloxysilane (H–Si(OCH$_2$CH=CH$_2$)$_3$ under catalytic mild conditions at room temperature, which was progressed to a colorless polymer with a difficult running liquid type. The ^{1}H NMR spectrum viewed the hyperbranched polymer confirmed by the disappearance of the Si-H signal of triallyloxysilane at 3.71 ppm and saw the new signals
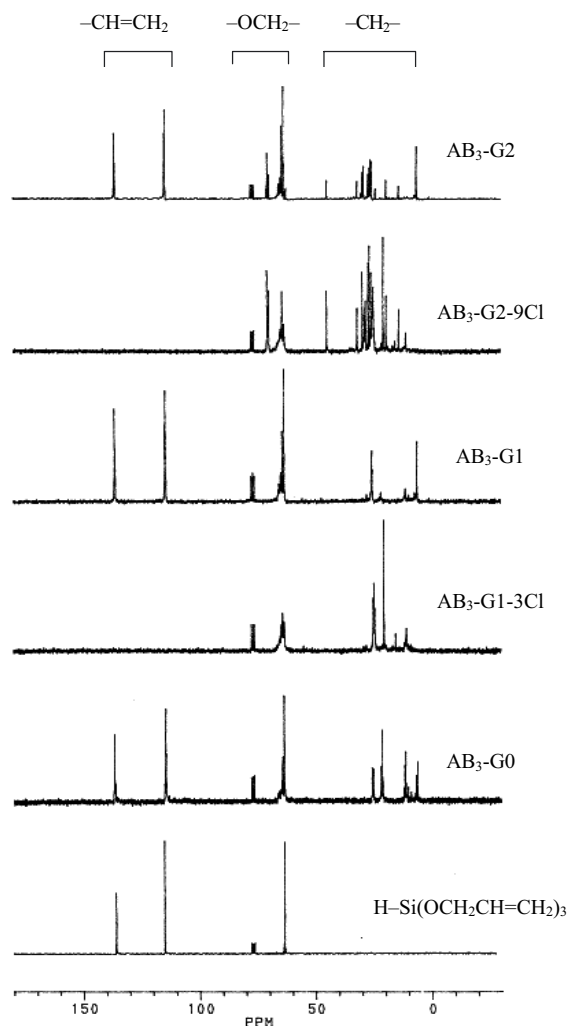

Fig. 1. ^{13}C NMR spectra of H–Si(OCH$_2$CH=CH$_2$)$_3$ and AB$_3$-G0 to AB$_3$-G2.

of the propylene group between 0.51 and 1.81 ppm by the cost of breaking double bonds in monomers. The AB$_3$-G0 type hyperbranched polymer had two times of unreacted allyloxy groups on the polymerized branch. By ^{13}C NMR spectroscopic views, the unreacted allyloxy groups were observed at 113.5–113.7, 133.5–134.7 ppm (Fig. 1). The GPC measurement of hyperbranched polymers (AB$_3$-G0) led to the extremely broad molecular weight distribution of polydispersity index values (PDI; 3.66) at the retention time, which means the hyperbranched carbosilane was constructed by different molecular sizes. The MALDI TOF mass spectrum of AB$_3$-G0 observed a series of molecular

ions with a mass increment of 200 amu as repeating units of triallyloxysilane moieties at m/z = 823, 1023, 1223, etc. So, the mixed hyperbranched polymer increased with the monomer.

The reaction of the AB_3-G0 with trichlorosilane in the presence of H_2PtCl_6 provided broken double bonds and increased $SiCl_3$ groups on the polymer (Fig. 1). The hydrosilation of the hyperbranched polymer could be carried out at the RT. The NMR spectroscopic view of the hyperbranched polymer gave a very simple construction that observed the disappearance of allyl groups at 115 and 136 ppm and the appearance of many signals at sp^3 area (Fig. 1). The hydrosilation of the hyperbranched polymer with trichlorosilane provided the complete disappearance of allyl groups on the polymer backbone. The continual alcoholysis reaction with allylalcohol was progressed to the first generation AB_3-G1, which had three times of functional groups compared with the core polymer (Scheme 1). By GPC, the polydispersity of AB_3-G1 had an almost unchanged value (PDI: 3.86) from the core polymer (PDI: 3.66). This means the conformational distribution of the growing polymer did not contain side reaction such as the copolymerization of cores. Therefore, the hyperbranched polymer could be used as the core for dendrimers. The MALDI TOF spectrum (Fig. 2) of AB_3-G1 observed very complex and regularly observed signals. By the use of the same synthetic procedures such as hydrosilation with trichlorosilane and alcoholysis with allylalcohol, we produced the second generation AB_3-G2 that had nine times of more functionalities than cores. The MALDI TOF spectrum (Fig. 2) of AB_3-G2 observed a series of molecular ions with a mass increment of 200 amu as repeating units of $Si(OCH_2CH=CH_2)_3$ moieties at m/z 679, 879, 1079, 1279, 1480, 1681, etc. which was the same evidence of AB_3-G1 (Fig. 2).

In conclusion, we have shown that the preparation of hyperbranched polymers with triallyloxysilane at room temperature can be achieved via one simple-step platinum-catalyzed protocol. The prepared polymer can be used as the core of a carbosilane dendrimer.

3. Experimental

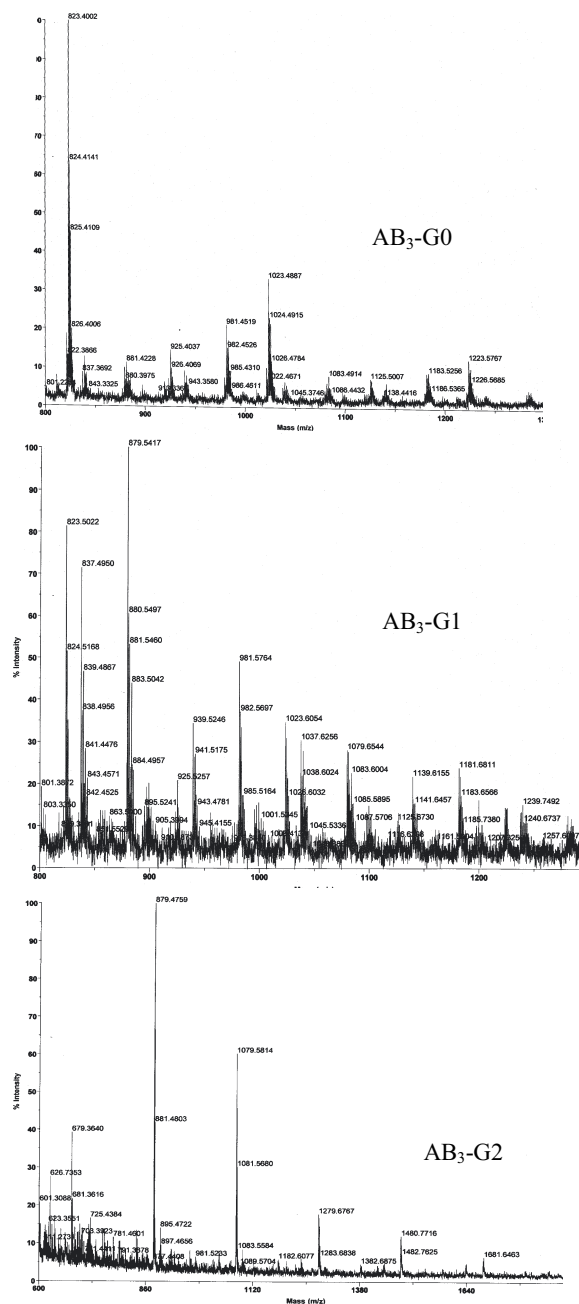All reactions were carried out under a dried N_2 atmosphere and THF was dried by sodium-

Fig. 2. MALDI mass spectrum of AB_3-G0 (top), AB_3-G1 (center) and AB_3-G2 (bottom).

benzophenone ketyl, while toluene was distilled from sodium metal. The NMR spectra were recorded on a Bruker AC-200 Spectrometer. With THF as a solvent for GPC, all GPC data were referred to polystyrene standards, and a combination of columns 10^5, 10^4, and
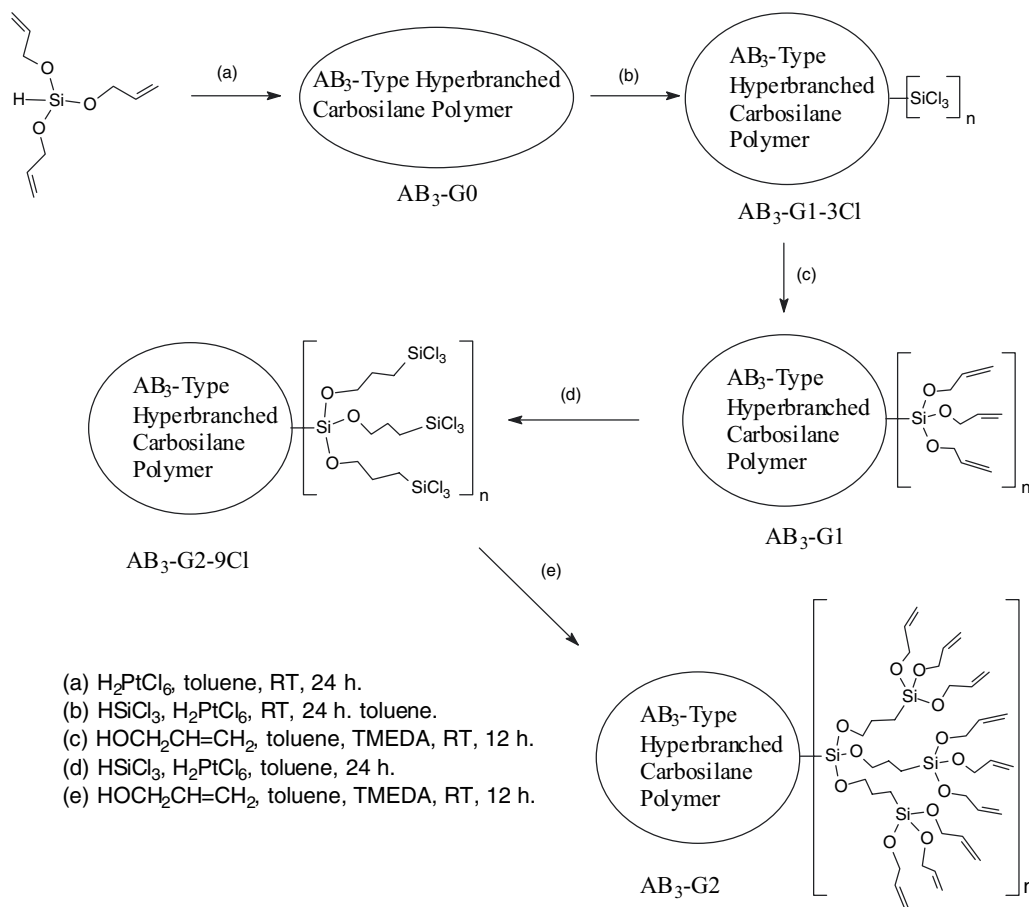
Scheme 1. Schematic view of the dendronizing process of a hyperbranched polymer.

10^3 was employed. The Busan and Daejeon Branches of the Korean Basic Science Institute (KBSI) performed MALDI mass and elemental analysis.

3.1. Preparation of triallyloxysilane (H–Si(OCH₂CH=CH₂)₃)

8.0 g (59.06 mmol; 5.96 ml) of fresh distilled trichlorosilane were dissolved in 200 ml of pentane and cooled to –78 °C and slowly added to 10.43 g (179.68 mmol) of allylalcohol. The reaction mixture was stirred 10 min at this temperature and continually slowly added to 6.80 g (58.51 mmol) of TMEDA and stirred for 1 h at this temperature. The product was isolated from the white salt by filtration and distilled the fine product at room temperature by vacuum. Yield: 7.41 g (37.00 mmol, 62%) of a colorless liquid. ^{1}H NMR (ppm, CDCl₃): δ = 4.17 (s, Si–H), 4.33 (s, OCH₂), 5.02–5.40 (m, CH₂=), 5.82–6.00 (m, CH=). ^{13}C NMR (ppm, CDCl₃): δ = 63.48 (OCH₂), 114.98 (CH₂=), 135.91 (CH=). MS: 199 (M-H)$^+$, 158 (M–CH₂CHCH₂)$^+$, 142 (M–OCH₂CHCH₂)$^+$, 101 (SiO₂CH₂CH=CH₂)$^+$.

3.2. Preparation of AB₃-G0

4.60 g (23.00 mmol) of triallyloxysilane and 0.06 g of H₂PtCl₆ were dissolved in 25 ml of toluene and stirred 24 h at the RT. Yield: 4.10 g (89%) of a light yellow liquid. ^{1}H NMR (ppm, CDCl₃): δ = 0.51–1.81 (m, CH₂), 3.6–4.2 (m, OCH₂), 4.30 (m, OCH₂), 5.0–5.4 (m, CH₂=), 5.91 (m, CH=). ^{13}C NMR (ppm, CDCl₃): δ = 6.19–25.65 (CH₂), 63.48–66.21 (OCH₂), 114.23–114.89 (CH₂=), 136.12–136.67 (CH=).

3.3. Preparation of AB₃-G1-3Cl

10.74 g (79.27mmol) of $HSiCl_3$, added to 4.0 g of G0, were dissolved in 15 ml of toluene and continually added to 0.04 g of H_2PtCl_6 and stirred at the RT for 1 day. Yield: 9.16 g of a light yellow gel. The increasing rate of G0 was 5.16 g, which means 38.09 mmol of trichlorosilane was added to the core molecule. ^{1}H NMR (ppm, $CDCl_3$) δ = 0.80–2.20 (m, CH_2), 3.85 (s, OCH_2), 5.50~6.02 (m, $CH=CH_2$). ^{13}C NMR (ppm, $CDCl_3$): δ = 10.90–25.18 (CH_2), 63.52–65.24 (OCH_2), 76.36–77.62.

3.4. Preparation of the first generation (AB₃-G1)

9.16 g of G1P (increasing rate: 5.16 g; 38.09 mmol of trichlorosilane) were dissolved in 200 ml of toluene and added slowly to 8.2 g (141.26 mmol) of allylalcohol and cooled the reaction mixture. Continually added 6.64 g (57.09 mmol) of TMEDA to the cooled reaction mixture. The reaction mixture was warmed at the RT and stirred the reaction mixture for 1 day. The reaction product was purified by chromatography on a silica gel with THF as an eluent. Yield: 10.07 g (84%) of light yellow AB₃-G1. ^{1}H NMR (ppm, $CDCl_3$) δ =0.51–0.80 (m, CH_2), 1.43–1.92 (m, CH_2), 3.60–4.01 (m, OCH_2), 4.29 (s, OCH_2), 4.91–5.41 (m, $=CH_2$), 5.72–6.12 (m, $=CH$).

3.5. Preparation of AB₃-9Cl

The same procedure as that for the preparation of AB₃-G1-3Cl was used in the reaction of 4.00 g (69.47 mmol) of AB₃-G1, 10.66 g (69.47 mmol) of $HSiCl_3$ and 0.10 g (1.30 mmol) of Pt/C. ^{1}H NMR (ppm, $CDCl_3$) δ = 0.80–1.09 (m, CH_2), 1.32–1.62 (m, CH_2), 1.62–2.10 (m, CH), 3.34–3.63 (m, OCH_2), 3.63–4.12 (m, OCH_2). ^{13}C NMR (ppm, $CDCl_3$) δ = 10.96–29.52, 44.91 (CH_2), 63.34–66.51, 69.89–70.64 (OCH_2).

3.6. Preparation of the second generation (AB₃-G2)

The same procedure as that for the preparation of **AB₃-G1** was used in the reaction of 0.73 g (3.65 mmol)

of AB3-G2-9Cl, 2.50 g (43.06 mmol) of allylalcohol and 2.00 g (17.47 mmol) of TMEDA. The product was purified by chromatography on a silica gel with chloroform with a mixed eluent ($CHCl_3$: THF = 9:1). Yield: 1.12 g of a colorless gel. ^{1}H NMR (ppm, $CDCl_3$): δ = ^{1}H NMR (ppm, $CDCl_3$) δ = 0.50–1.12 (m, CH_2), 1.20–1.40 (m, CH_2), 1.64 (s, CH_2), 3.12–4.00 (m, OCH_2), 4.29 (s, OCH_2), 4.98–5.20 (m, $=CH_2$), 5.80–6.12 (m, $=CH$). ^{13}C NMR (ppm, $CDCl_3$) δ = 6.11–29.43, 44.72–44.80 (CH_2), 62.50–65.68, 69.73–70.79 (OCH_2), 114.52–114.75 ($=CH_2$), 136.03–136.36 ($=CH$).

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