



# Synthesis and characterization of silicon-containing hyperbranched polymers via thiol-ene click reaction

Lei Xue, Zhizhou Yang, Dengxu Wang, Yike Wang, Jie Zhang, Shengyu Feng\*

Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Ji'nan 250100, PR China

## ARTICLE INFO

### Article history:

Received 11 October 2012

Received in revised form

19 December 2012

Accepted 29 January 2013

### Keywords:

Hyperbranched polymer

Thiol-ene

Step-grown polymerization

Click reaction

## ABSTRACT

Novel hyperbranched organosilicon polymers were successfully prepared via step-growth thiol-ene click reaction using mercaptopropylmethyldiallylsilane ( $AB_2$ ) and mercaptopropyltriallylsilane ( $AB_3$ ) as hyperbranched monomers. The structures of the prepared polymers were characterized by Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy. The degree of branching (DB) of the polymers was determined using quantitative  $^{29}\text{Si}$  NMR spectroscopy. The DB of the polymers from  $AB_2$  and  $AB_3$  was 0.60 and 0.22, respectively. The results of thermogravimetric analysis showed that the presence of thioether does not affect the thermal stability of the resulting silicon-containing hyperbranched polymers (Si-HBs). The resulting Si-HBs can be used as promising candidate materials for heavy metal adsorption because of the thioether bond.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Highly branched polymers, including hyperbranched polymers and dendrimers, have attracted considerable research interest because of their excellent physical properties and wide potential applications, such as drug delivery, catalytic supports, liquid crystal, and viscosity modification [1–10]. Dendrimers are perfect mono-dispersed macromolecules with regular and highly branched three-dimensional architecture. However, the synthetic process of dendrimers requires multiple high-yield reaction and complex purification steps [11]. Hyperbranched polymers also have many branches, but these branches are distributed randomly throughout the polymers. Compared with the complicated synthetic process of dendrimers, hyperbranched polymers are easy to prepare via a one-pot reaction, making them potential alternatives to dendrimers [12]. Among these hyperbranched polymers, silicon-containing hyperbranched polymers (Si-HBs) are among the most important species [13–15], as they can be used as silicon carbide ceramic precursors, degradable template molecules, and modifiers of composite polymers. Generally, the majority of Si-HBs are prepared through conventional hydrosilylation reaction by using platinum (Pt) catalysts, including Speier's and Karstedt's catalysts [16]. However, the hydrosilylation reaction using Pt catalysts suffers from some deficiencies. For instance, Pt catalyst is expensive, and

the reaction can be affected by moisture and other sensitive functional groups.

Click chemistry has been widely employed in polymer science since Sharpless and co-workers proved the concept of click reaction in 2001 [17–19]. Thiol-ene reaction is under of click chemistry and has the characteristics of click chemistry, such as rapid reaction rates, reduced oxygen inhibition, and high yields [19–23]. Thiol-ene reaction has been used to create many types of dendrimers, including organosilicon dendrimers [11,24,25]. For instance, Son and co-workers utilized thiol-ene reaction to prepare carbosilane-thioether dendrimers [25]. However, to the best of our knowledge, reports on the preparation of Si-HBs via thiol-ene click reaction are scarce. Therefore, the possibility of preparing Si-HBs via thiol-ene reaction must be explored as an alternative approach for hydrosilylation reaction.

In this article, we report a general, simple, efficient and robust method to prepare Si-HBs under ultraviolet (UV) conditions. The structure and degree of branching (DB) of the resulting Si-HBs are determined by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), gel permeation chromatography (GPC) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF). The thermal properties of Si-HBs are characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The resulting polymers had thioether bond internally and excess double-bond externally, which allowed for complexing heavy metal ion and further modification, respectively [26,27].

\* Corresponding author. Tel.: +86 531 88364866; fax: +86 531 88564464.  
E-mail address: [fsy@sdu.edu.cn](mailto:fsy@sdu.edu.cn) (S. Feng).

## 2. Experimental

### 2.1. Materials and general comments

Allyl chloride and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were supplied by Aladdin Co. (China) and used without further purification. 3-Mercaptopropylmethyldimethoxysilane and 3-mercaptopropyltrimethoxysilane were purchased from Diamond Advanced Material of Chemical Inc. (China). Tetrahydrofuran (THF) was purified using routine procedure and distilled over sodium before use. In this work, the synthesis of monomer was carried out in an inert atmosphere, whereas the thiol-ene reaction was carried out under ambient conditions.

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker 300 or 400 spectrometer at 25 °C using  $\text{CDCl}_3$  as solvent and without the interior label (chemical shifts are referenced to signals of the solvents used). Quantitative  $^{29}\text{Si}$  NMR spectroscopy was performed using an inverse gated  $^1\text{H}$ -decoupling sequence. Samples were prepared in  $\text{Cr}(\text{acac})_3/\text{CDCl}_3$  solution (0.1 M  $\text{Cr}(\text{acac})_3$ ). Fourier transform infrared spectra (FT-IR) were recorded on a Bruker TENSOR27 infrared spectrophotometer with KBr pellet technique within the 4000–400  $\text{cm}^{-1}$  region. Mass spectrometry was performed on Agilent Technologies 6510 Q-TOF MS. Elemental analysis was measured on a Vario El III elemental analyzer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed with an AXIMA-CFRplus mass spectrometer (Shimadzu Corporation, Japan). Dithranol was used as a matrix, and silver trifluoroacetate was used as a cationization agent. Thermogravimetric analysis (TGA) was performed using a TA SDTQ600 with a heating rate of 10 °C/min from room temperature to 600 °C under  $\text{N}_2$ . Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 Phoenix and measurements were done under nitrogen atmosphere at a heating rate of 10 °C/min from –160 °C to room temperature. Size exclusion chromatography measurements were carried out in THF (1 mL  $\text{min}^{-1}$ ) at 40 °C with a Waters 515 liquid chromatograph (Milford, MA) equipped with three Styragel columns (HR-3, HR-4 and HR-6) and a refractive-index detector 2414. Ultraviolet (UV) light irradiation of the samples was carried out with high voltage mercury lamp (Spectroline SB-100P, emphasis of intensive at  $\lambda_{\text{max}} = 365 \text{ nm}$ ).

### 2.2. Preparation of allylmagnesium chloride

Allylmagnesium chloride was prepared in anhydrous THF by reacting the magnesium metal coil with allyl chloride at room temperature according to previous literature [28].

### 2.3. Preparation of mercaptopropylmethyldiallylsilane (**M1**)

A 250 mL three-necked round-bottomed flask with an addition funnel, reflux condenser, and a stir bar was charged with allylmagnesium chloride (100.0 mmol) in 100 mL of anhydrous THF. Mercaptopropylmethyldimethoxysilane (3.00 g, 16.67 mmol) in 30 mL THF was then slowly dropped into the allylmagnesium chloride solution via the addition funnel for over 30 min, and the mixture was stirred at room temperature overnight. When the reaction was completed, the reaction was quenched with methanol and then filtered. The organic phase was dried over anhydrous magnesium sulfate. After the solvent was evaporated under vacuum, the residue was further purified by using column chromatography on silica gel with ether/hexane as eluent to yield **M1** as colorless liquid (2.35 g, yield: 78.3%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 0.02$  (s,  $-\text{SiCH}_3$ , 3H), 0.65–0.70 (m,  $-\text{SiCH}_2-$ , 2H), 1.34–1.37 (t,  $-\text{SH}$ ,  $J = 7.9 \text{ Hz}$ , 1H), 1.57–1.63 (m,  $-\text{SiCH}_2\text{CH}=\text{CH}_2$ ,

4H), 1.64–1.68 (m,  $-\text{CH}_2\text{CH}_2\text{SH}$ , 2H), 2.51–2.57 (m,  $-\text{CH}_2\text{SH}$ , 2H), 4.85–4.92 (m,  $-\text{CH}_2\text{CH}=\text{CH}_2$ , 4H), 5.74–5.84 (m,  $-\text{CH}_2\text{CH}=\text{CH}_2$ , 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = -5.90$ , 12.20, 21.16, 25.52, 28.52, 113.30, 134.31;  $^{29}\text{Si}$  NMR (59.60 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 0.80$ ; MS: 199.08 [ $\text{M}^+ - \text{H}$ ]. FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3076$ , 2959, 2917, 2881, 2558, 1629, 1419, 1253, 1157, 992. Anal. Calc. for  $\text{C}_{10}\text{H}_{20}\text{SSi}$ , C, 59.93; H, 10.06; S, 16.00%. Found: C, 59.89; H, 9.96; S, 15.75%.

### 2.4. Preparation of mercaptopropyltriallylsilane (**M2**)

Mercaptopropyltriallylsilane **M2** was prepared using the same process as the **M1**. Data for **M2**: colorless liquid (yield: 76.2%);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 0.66$ –0.72 (m,  $-\text{SiCH}_2\text{CH}_2$ , 2H), 1.31–1.36 (t,  $-\text{SH}$ ,  $J = 8.1 \text{ Hz}$ , 1H), 1.58–1.62 (m,  $-\text{SiCH}_2\text{CH}=\text{CH}_2$ , 6H), 1.64–1.71 (m,  $-\text{CH}_2\text{CH}_2\text{SH}$ , 2H), 2.43–2.55 (m,  $-\text{CH}_2\text{SH}$ , 2H), 4.85–4.93 (m,  $-\text{CH}_2\text{CH}=\text{CH}_2$ , 6H), 5.71–5.85 (m,  $-\text{CH}_2\text{CH}=\text{CH}_2$ , 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 11.19$ , 19.55, 23.99, 24.20, 113.73, 134.15;  $^{29}\text{Si}$  NMR (59.60 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = -0.59$ ; MS: 225.09 [ $\text{M}^+ - \text{H}$ ]. FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3078$ , 2970, 2914, 2882, 2551, 1629, 1419, 1158, 991. Anal. Calc. for  $\text{C}_{12}\text{H}_{22}\text{SSi}$ , C, 63.65; H, 9.79; S, 14.16. Found: C, 63.76; H, 9.94; S, 14.05.

### 2.5. Preparation of **P1**

The mixture of **M1** (1.00 g), DMPA (0.02 g) and THF (1 mL) was placed under a UV lamp for 20 min. After the solvent was removed through evaporation, the **P1** was purified three times by precipitation into methanol at low temperature. Data for **P1**: colorless viscous liquid (yield: 70.5%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 0.01$ –0.03 ( $-\text{SiCH}_3$ ), 0.59–0.73 ( $-\text{SiCH}_2-$ ), 1.53–1.73 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ,  $-\text{CH}_2\text{CH}_2\text{S}-$ ), 2.47–2.52 ( $-\text{CH}_2\text{S}-$ ), 4.82–4.89 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.69–5.84 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = -6.15$ , 12.49, 20.63, 23.63, 35.19, 112.67, 133.87;  $^{29}\text{Si}$  NMR (59.60 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 0.77$ , 2.01, 3.19; FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3077$ , 2945, 2907, 2842, 2794, 1629, 1445, 1254.

### 2.6. Preparation of **P2**

The **P2** samples were prepared from **M2** by using a similar procedure as that for **P1**. Data for **P2**: colorless viscous liquid (yield: 72.5%);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 0.50$ –0.76 ( $-\text{SiCH}_2-$ ), 1.56–1.67 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ,  $-\text{CH}_2\text{CH}_2\text{S}-$ ), 2.47–2.53 ( $-\text{CH}_2\text{S}-$ ), 4.87–4.94 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.75–5.85 ( $-\text{CH}_2\text{CH}=\text{CH}_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 11.54$ , 19.54, 24.07, 35.82, 113.75, 134.15;  $^{29}\text{Si}$  NMR (59.60 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = -0.61$ , 0.77, 2.22; FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3078$ , 2970, 2916, 2876, 2845, 2796, 1629, 1417.

### 2.7. Preparation of **P1Tn** (Polymer modification)

#### 2.7.1. Synthesis of **P1T1**

The mixture of **P1** (0.50 g), 3-mercaptopropyltrimethoxysilane (0.60 g, 3 mmol, 1.2 equiv to allyl groups), DMPA (0.02 g) and THF (5 mL) was placed under a UV lamp for 20 min. After the solvent was removed through evaporation, the **P1T1** was purified by precipitation into methanol three times at low temperature. The **P1T1** was obtained as a colorless viscous liquid (0.95 g, 95%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 0.01$ –0.03 ( $-\text{SiCH}_3$ ), 0.55–0.78 ( $-\text{SiCH}_2-$ ), 1.51–1.75 ( $-\text{SiCH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$ ), 2.48–2.55 ( $-\text{CH}_2\text{SCH}_2-$ ), 3.57 ( $-\text{Si}(\text{OCH}_3)_3$ ).

#### 2.7.2. Synthesis of **P1T2**

The mixture of **P1** (0.50 g), 2-mercaptoethanol (0.24 g, 3 mmol, 1.2 equiv of allyl groups), DMPA (0.02 g) and THF (5 mL) was placed under a UV lamp for 20 min. After the solvent was removed

Download English Version:

<https://daneshyari.com/en/article/1324507>

Download Persian Version:

<https://daneshyari.com/article/1324507>

[Daneshyari.com](https://daneshyari.com)