## Supporting Information for

# Fabrication of transparent UV cured coatings with allyl terminated hyperbranched polycarbosilanes and thiol silicone resins

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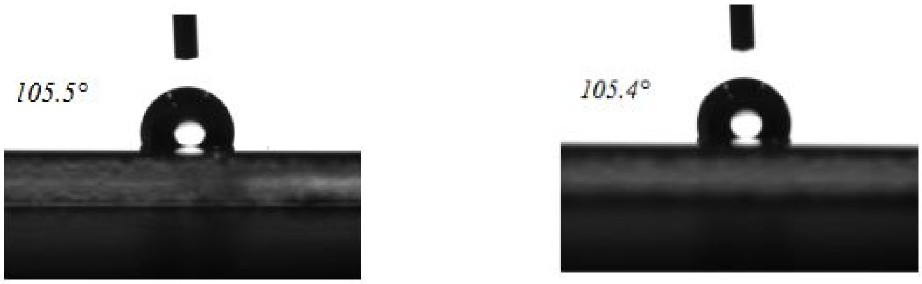
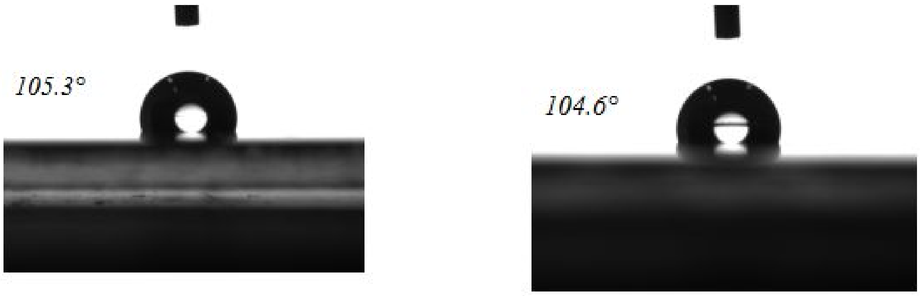
**Number of Figures: 6; Number of Tables: 1; Number of scheme: 1.**

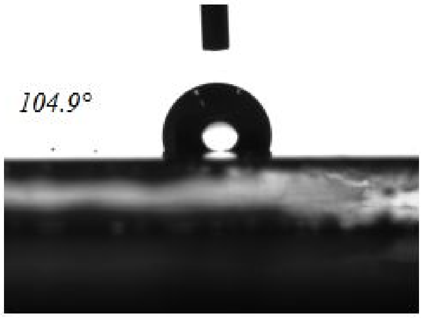
## *1 Contact angle for the coatings with various of content of thiol*



Thiol content is 0.002 mol·g$^{-1}$ Thiol content is 0.003 mol·g$^{-1}$



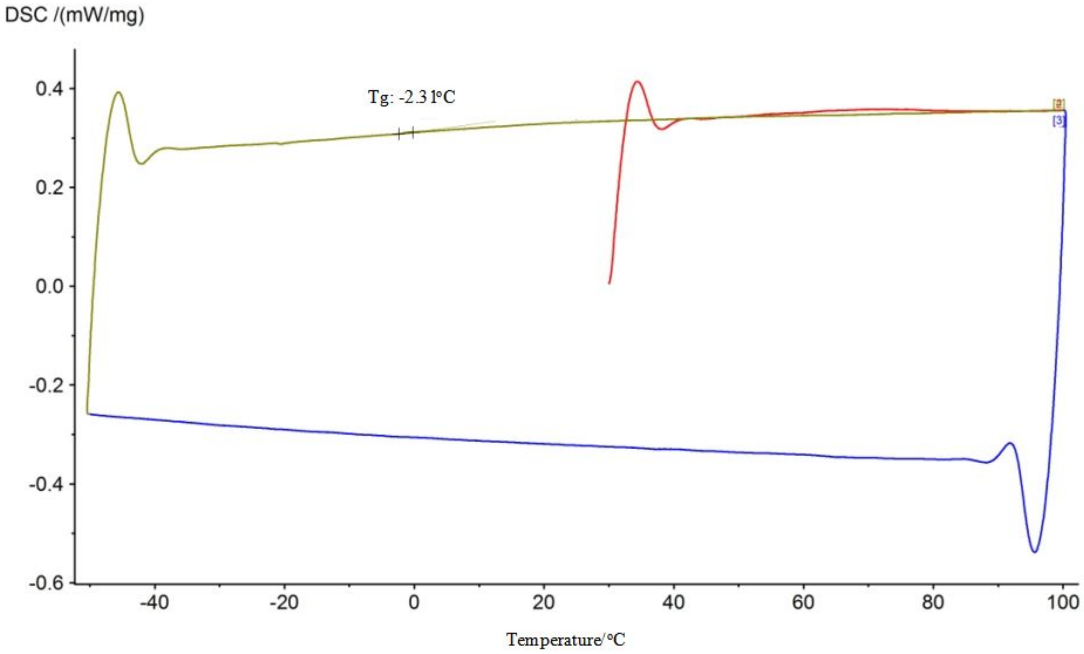
Thiol content is 0.004 mol·g$^{-1}$ Thiol content is 0.005 mol·g$^{-1}$



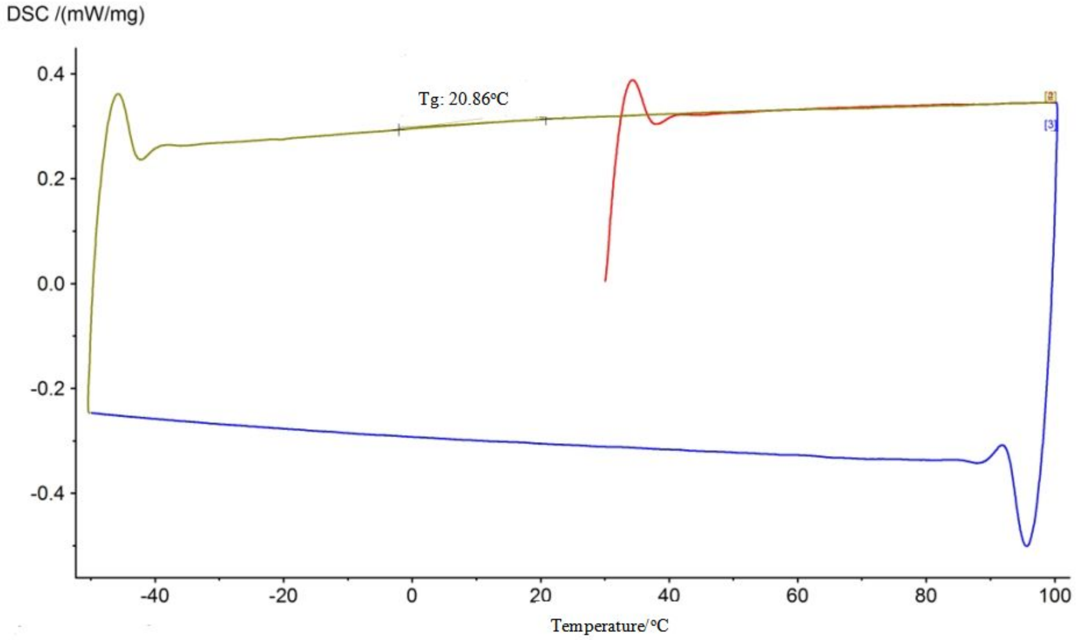
Thiol content is 0.006 mol·g$^{-1}$

Figure S1. Photos for the contact angle for the coatings with various of content of *thiol*
*Conditions: The thiol silicone resin is with* R/Si molar ratio *of 1.4. The terminated hyperbranched polycarbosilane is G1. The molar ratio of* thiol *to allyl is 1.4:1. The coatings were all cured by UV for 30 s.*

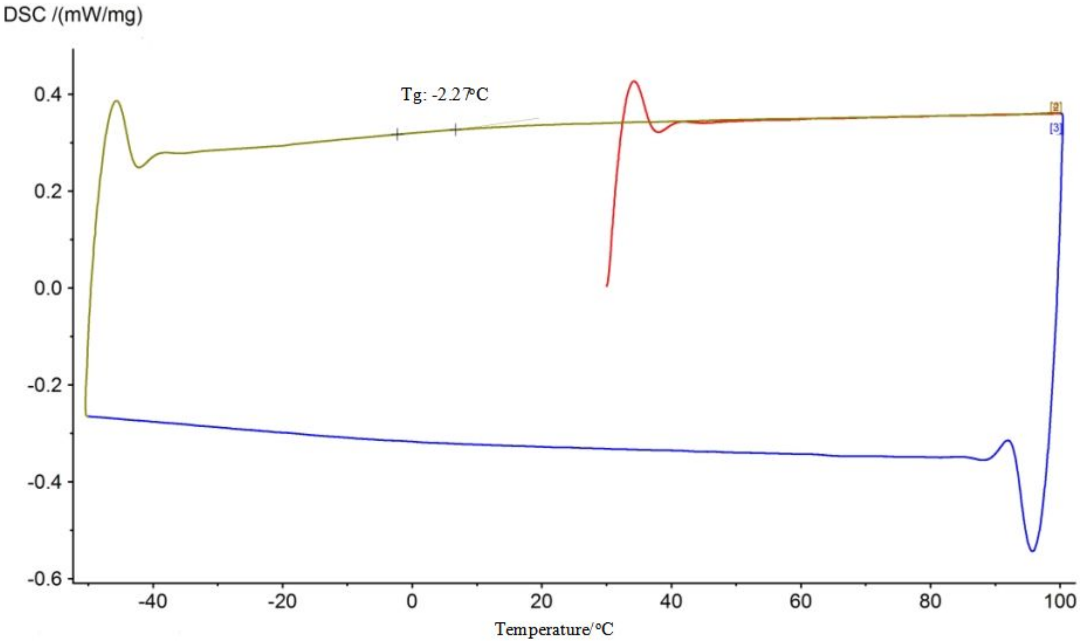
## 2 ***DSC analysis of the coatings prepared with various generations of allyl terminated hyperbranched polycarbosilanes***



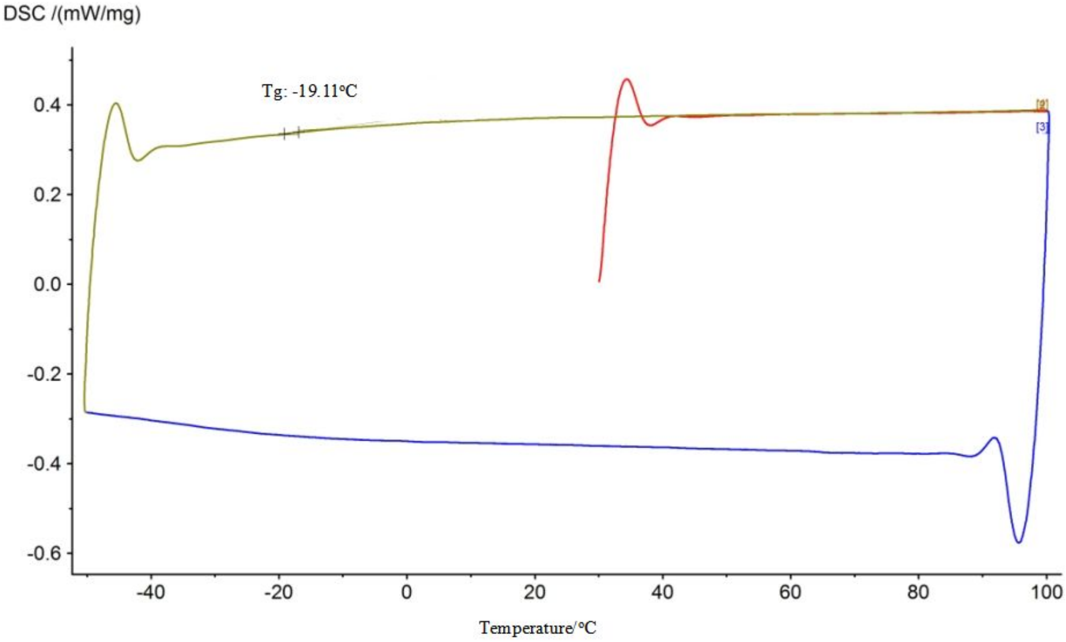
*The coating prepared with G0*



*The coating prepared with G1*



*The coating prepared with G2*



*The coating prepared with G3*

*Figure S2. The DSC curves of the coatings prepared with various generations of allyl terminated hyperbranched polycarbosilanes*

### *3 The $^1$H–NMR characterization of thiol silicone resin*

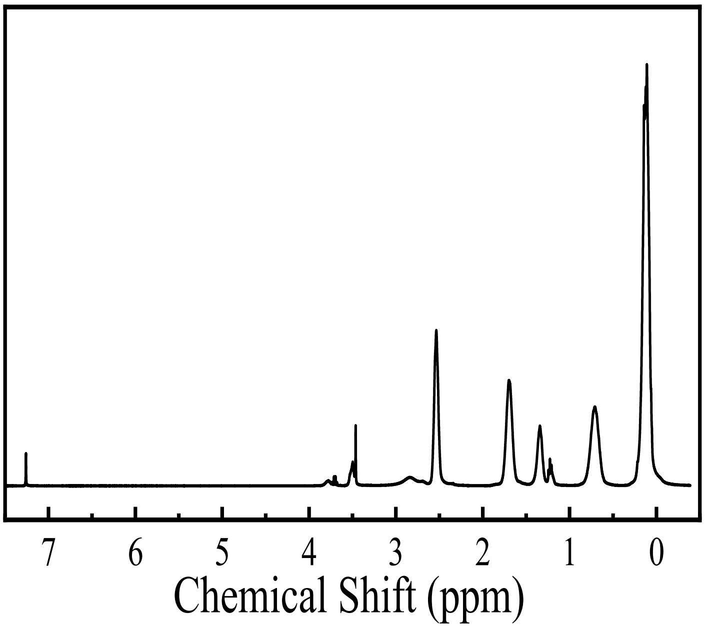


*Figure S3. The $^1$H–NMR spectrum of the thiol silicone resin*

-0.36~0.18ppm:$–SiC\boldsymbol{H}_3$,

1.12~1.34ppm:$\boldsymbol{H}SCH_2CH_2CH_2Si–$,

2.28~2.55ppm:$HSC\boldsymbol{H}_2CH_2CH_2Si–$,

3.28~3.55ppm:$–OC\boldsymbol{H}_3$,

0.37~0.76ppm:$HSCH_2CH_2C\boldsymbol{H}_2Si–$,

1.43~1.74ppm:$HSCH_2C\boldsymbol{H}_2CH_2Si–$,

1.02~1.14ppm:$–OCH_2C\boldsymbol{H}_3$,

3.50~3.78ppm:$–OC\boldsymbol{H}_2CH_3$.

## 4 Synthesize various generations for allyl terminated hyperbranched polycarbosilanes

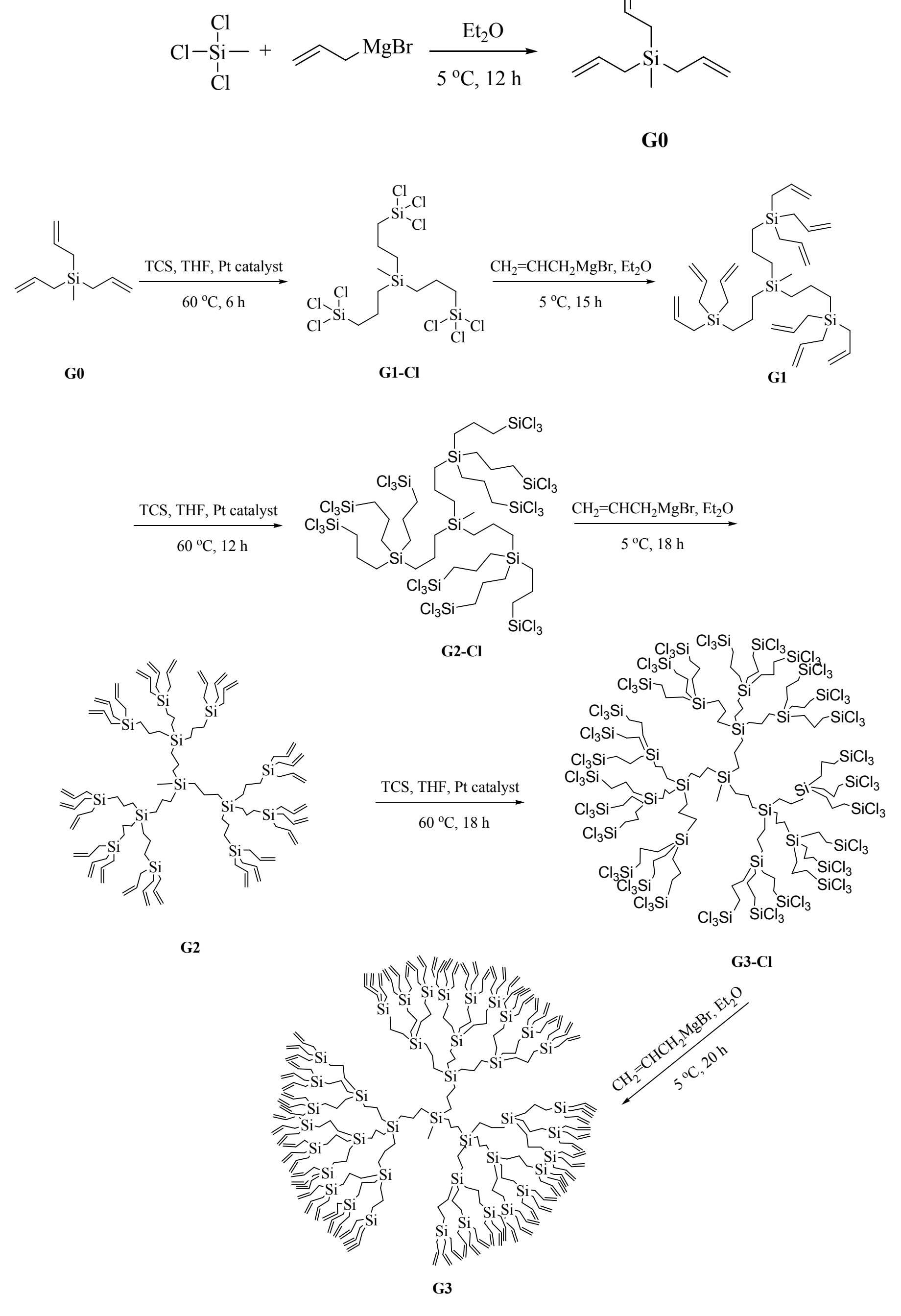


Figure S4. The scheme for synthesis of various generations allyl terminated hyperbranched polycarbosilanes

Condition: The amount of the Spiere's platinum catalyst is 20 ppm of the total amount of allyl terminated hyperbranced polycarbosilanes and trimethylsilane

### 4.1 preparation of allyl bromine Grignard reagent in ether

All the operations were carried out under the atmosphere of $N_2$. 3 g(125 mmol) magnesium, a grain of iodine and 50 mL ether were added in to a three–necked bottle and cooled down to 0–5 $^{o}$C and stirred quickly. Subsequently, a solution of 20ml ether and 12.6 g(105 mmol) allyl bromide was slowly dripped into the three-necked bottle for about 30 min. The reaction mixture was kept at 0–5 $^{o}$C for 2 h and a solution of allyl bromine Grignard reagent in ether was prepared.

### *4.2 The synthesis of G0*

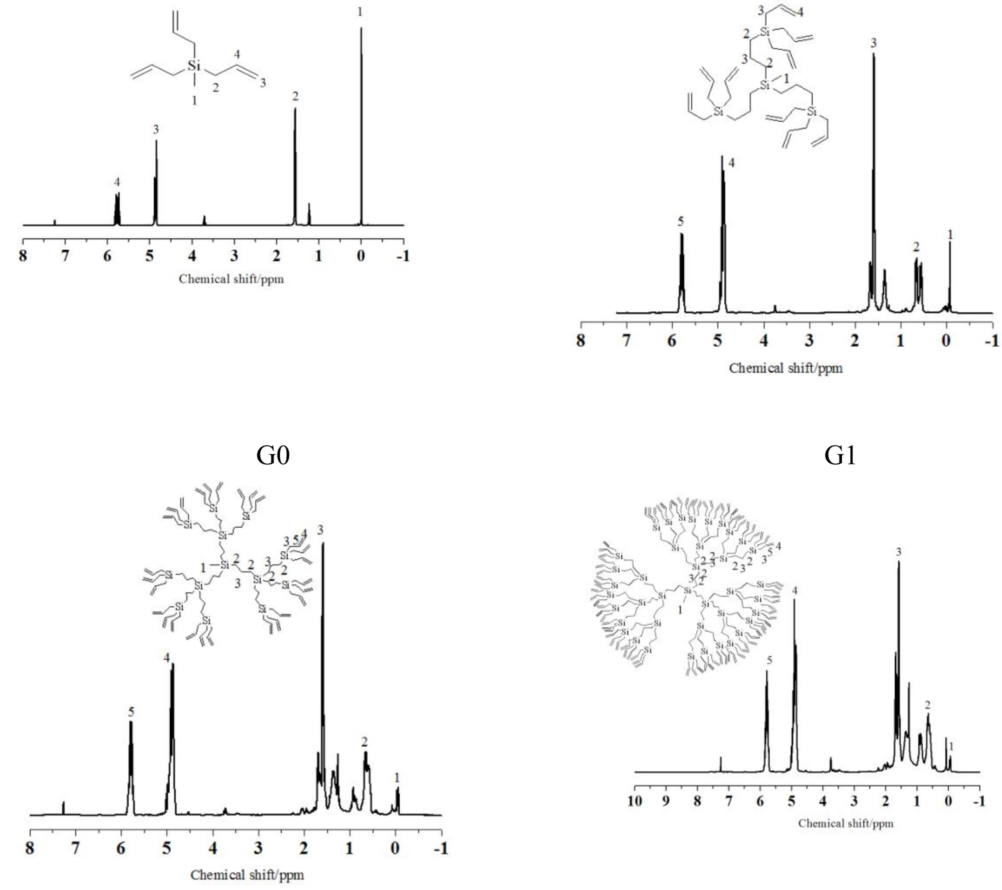
All the operations were carried out under the atmosphere of $N_2$. The solution of 3.5 g(23.4 mmol) methyl trichlorosilane in 30 mL ether was added into a three–necked bottle containing the solution of allyl bromine Grignard reagent in ether prepared at 0–5 $^{o}$C for about 30 min. The mixture was stirred quickly and kept at room temperature for about 12 h. Then, the mixture was filtered with Buchner funnel and the precipitate was washed with 60 mL ether for three times. 200 mL 0–5$^{o}$C saturated ammonium chloride aqueous solution was added into the cake of the precipitate to quench the reaction. The solution of ether was collected and washed with saturated sodium chloride aqueous solution and the mixture of ice and water for three times, then driedwith anhydrous magnesium sulfate overnight. Finally the solution of ether was distilled at 95 $^{o}$C/130 mmHg and a colorless transparent liquid of G0 with purity of 96.0 % and yield of 83.0 % was produced.

### *4.3 The synthesis of G1, G2 and G3*

All the operations were carried out under the atmosphere of $N_2$. 1.6 g G0(9.62 mmol), 7.22 g TCS(53.3 mmol), 60 mL THF and 0.2 μL Karstedt’s catalyst were added into an 250 mL three–necked bottle. The mixture was stirred quickly and kept at 60 $^{o}$C for 6 h. Subsequently, the tetrahydrofuran and excess trichlorosilane were removed by being distilled at 95 $^{o}$C/130 mmHg and the liquid of G1–Cl was synthesized. The obtained G1–Cl was dissolved in 20 mL anhydrous ether and slowly dripped into 125 mmol 0–5$^{o}$C allyl bromine Grignard reagent in ether for about 2 h. The reaction system was stirred overnight at room temperature. The following procedure was similar to that of G0 and the transparent liquid of G1 with purity of 95.0 % and yield of 80.0 % was produced.

The synthesis of G2 and G3 was similar to that of G1.

## *5 The characterization of various generations for allyl terminated hyperbranched polycarbosilanes*

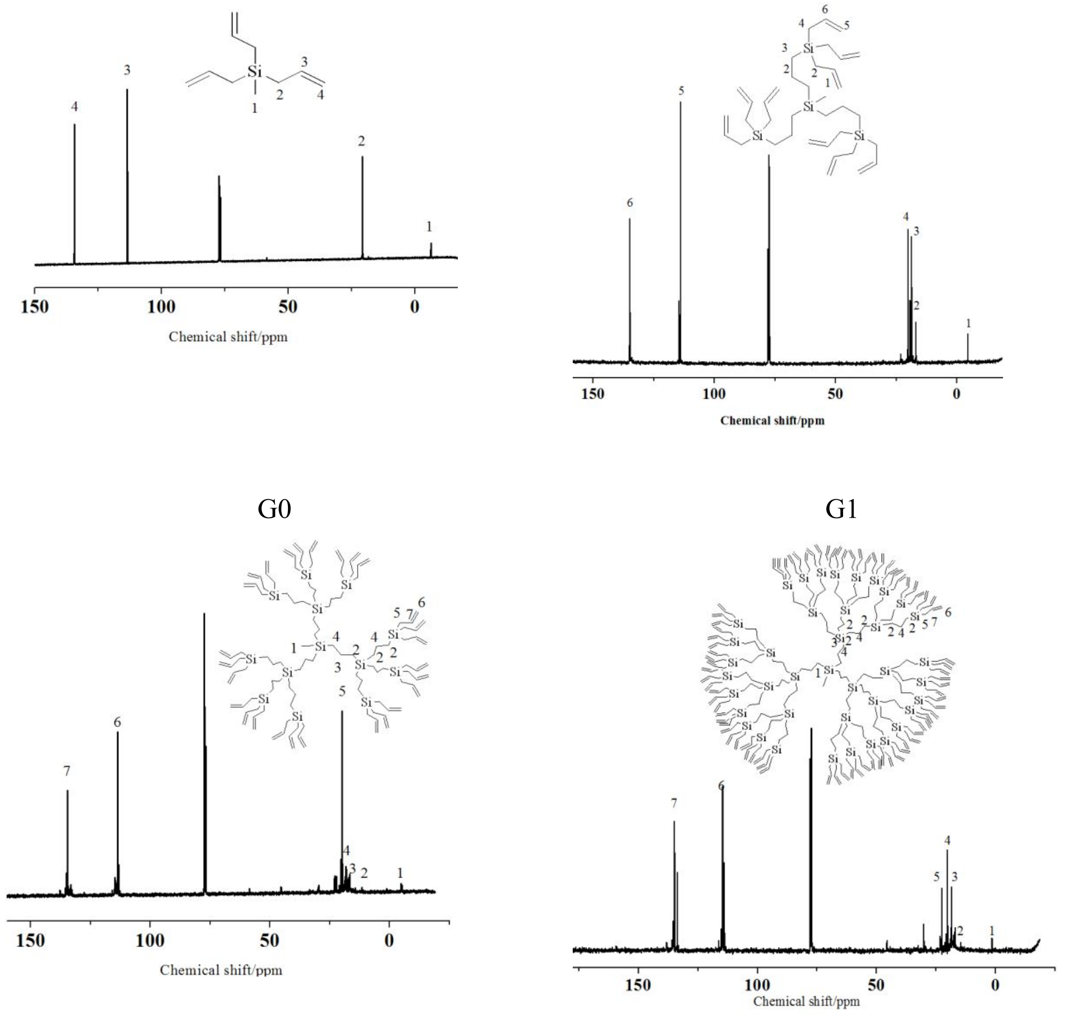


G0 G1

G2 G3

*Figure S5. The $^1$H–NMR spectra of various generation of allyl terminated hyperbranched polycarbosilanes*

5.67–5.92 ppm: $-C\boldsymbol{H}{=}CH_2-CH_2-$, 4.70–5.20 ppm: $-CH{=}C\boldsymbol{H}_2$, 1.49–1.66 ppm:$SiC\boldsymbol{H}_2-$, -0.2–0.2 ppm:$-SiC\boldsymbol{H}_3$, 1.49–1.66 ppm $SiC\boldsymbol{H}_2-$



G0 G1

G2 G3

*Figure S6. ${}^{13}$C–NMR spectra of of various generation of allyl terminated hyperbranched polycarbosilanes*

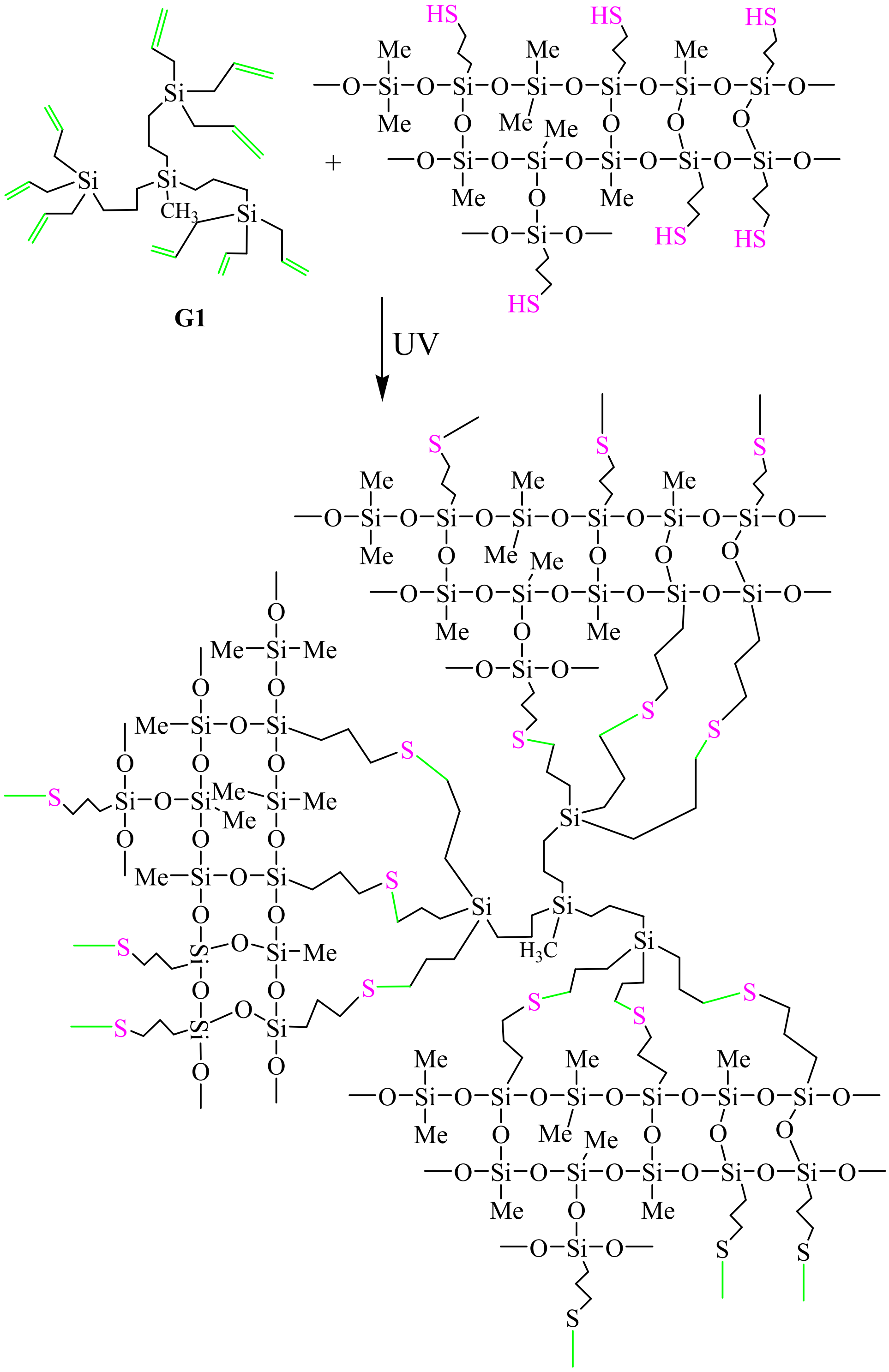
~3.4ppppm:**C**$H_3$Si–, 19~27ppm: –Si**C**$H_2$–**C**$H_2$–**C**$H_2$, ~116ppm:–CH=**C**$H_2$, ~135ppm:–**C**H=$CH_2$

Table S1 MALDI–TOF–MS of various generations for allyl terminated hyperbranched polycarbosilanes

| Various generations | Theoretical value of molecular weight | molecular weight caculatedwith [M + Na]+ | Theoretical number of terminal groups | Caculated number of terminal groups |
|---|---|---|---|---|
| G0 | 166.34 | -- | 3 | 3 |
| G1 | 623.27 | 657.2 | 9 | 8.0 |
| G2 | 1994.08 | 2033.9 | 27 | 22.1 |
| G3 | 6105.51 | 6037.9 | 81 | 62.7 |

MALDI-TOF MS analysis of various generations for allyl terminated hyperbranched polycarbosilanes showed that the molecular ion peak (M Na) of G1 and G2 had good resolution ratio. However, the molecular ion peak (M Na) of G3 reduced. The molecular ion peak (M Na) of G3 is indistinguishable for the very high noise, whih may be attibuted to the relatively high molecular weight of G3. The m/z values of G1 is very closed to the theoretical value, and there is no obvious miscellaneous peak. There is a relatively small molecular peak in the m/z values of G2 and the difference of 153.6 amu from the main molecular ion peak at 2033.9 denoted that a Si–allyl group on G1 did not take place in the reaction during the course of preparation of G2. Therefore, G2 has 25 allyl terminal groups instead of 27 allyl terminal groups. The m/z value of G3 is approximate to 6000, which is not completely consistent with the theoretical mass value of 6105.5. These results implied that G3 is not perfect branched hyperbranched polymer.

## ***Scheme for preparation of the UV cured transparent solvent-free silicone coatings***



*Scheme S1*. The scheme for UV curing process of thiol *silicone resins and G1*