

Article

# UV-Cured Coatings Prepared with Sulfhydryl-Terminated Branched Polyurethane and Allyl-Terminated Hyperbranched Polycarbosilane

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**Abstract:** The conventional polyurethane (PU) coatings have poor heat resistance, which will undergo severe pyrolysis when the temperature exceeds 200 °C. To overcome the shortcoming of conventional PU coatings, an ultraviolet (UV)-cured solvent-free hyperbranched polycarbosilane modified PU coatings was prepared by sulfhydryl-terminated polyurethane and allyl-terminated hyperbranched polycarbosilane. The initial decomposition temperature ( $T_d^{5\%}$ ) of the UV-cured coating ranges from 258 to 268 °C, which is obviously higher than those of the conventional PU coatings reported. The coating shows fairly low water absorption in the range of 0.6–1.36 wt% and exhibits grade 1, grade 2 and grade 3 adhesion to glass, tin plate and aluminum sheet, respectively.

**Keywords:** UV cured coating; silicone modified polyurethane; hyperbranched polycarbosilane; thermal stability

## 1. Introduction

Ultraviolet (UV)-cured coatings have drawn much attention because of their advantages such as environment friendliness, rapid curing rates, and optimized energy consumption [1–6]. UV-cured polyurethane (PU) is widely used in coatings to improve the appearance, lifespan, and corrosion resistance of products [7–9]. However, the conventional PU coatings, namely PUs synthesized via diisocyanates and polyols with various chain length, have poor heat resistance, which will undergo severe pyrolysis when the temperature exceeds 200 °C [9–11]. The poor mechanical performance and chemical resistance of conventional PU coatings attributed to the low density and inadequate photosensitive groups of the PU oligomers also limit the application of PU coatings [12]. Therefore, efforts should be made to develop novel PUs coatings with superior performances.

Polycarbosilanes are a class of polymers at the interface between organic and inorganic chemistry; the Si–C bond of carbosilane is less susceptible to nucleophilic attack than the Si–O bonds in siloxanes, which is part attributed to the relative stability of the carbosilane [13]. The crosslinkable carbosilane polymers exhibit excellent heat-resistance [14,15]. Inspired by these works, a polyurethane coating might be modified with polycarbosilanes to improve heat resistance.

Hyperbranched polymers have attracted much attention in the field of UV-curable coatings because of their low viscosity, highly branched structure, and rich functional moieties and many experiments have confirmed that the application of hyperbranched polymers in a UV-curable coating can reduce the content of reactive diluent and solvent, which can reduce the emission of VOC [13,16–18].

Hyperbranched polycarbosilane has both the advantages of polycarbosilane and hyperbranched polymers [17].

The aim of this work is to fabricate a UV-cured solvent-free hyperbranched polycarbosilane modified PU coating. The UV-cured silicone coatings were prepared by sulfhydryl terminated polyurethanes and allyl terminated hyperbranched polycarbosilanes. The thermal stability, hardness, adhesion property, water absorption, surface water contact angle and corrosion resistance to acid, alkali and salt were also explored. The results confirmed that the UV-cured coatings obtained have fairly high thermal stability, low water absorption, and good adhesion to glass.

## 2. Materials and Methods

### 2.1. Materials

The materials used are summarized in Table 1.

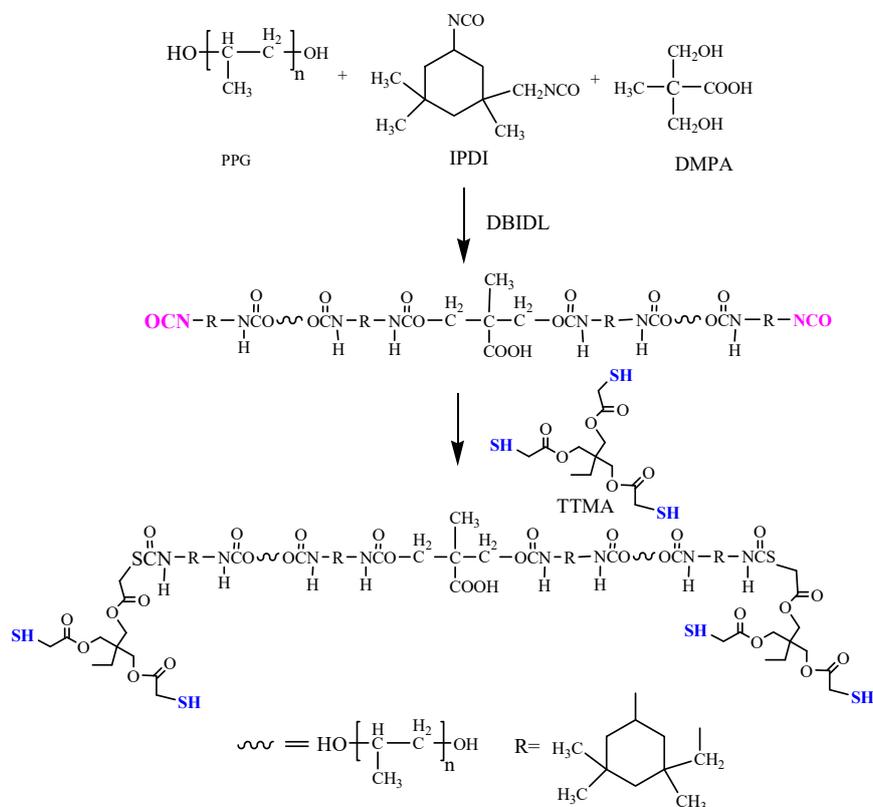
**Table 1.** The materials used.

Materials	Suppliers	Remarks
Polyether diol (PPG-2000, Mn = 2000, A.R.)	9dingchem (Shanghai) Chemical Co., Ltd.	Distilled at 110 °C under 120°/130 mmHg for 1 h before used.
Isophorone diisocyanate (IPDI, A.R.)		
2,2-Bis(hydroxymethyl)propionic acid (DMPA, A.R.)	Energy Chemical (Shanghai) Chemical Co., Ltd.	/
Trimethylolpropane tris(thioglycolate) (TTMA, A.R.)	Tokyo Chemical Industry Co., Ltd.	/
Methyl trimethoxysilane (C.P.)	Shanghai Jiancheng Industry and Trade Co., Ltd.	/
Methyltrichlorosilane (C.P.)		/
Ether (A.R.)	Beijing HWRK Chem Co., Ltd.	Distilled over potassium before used.
tetrahydrofuran (A.R.)		Distilled over potassium before used.
HydroChloric acid (36.5%, A.R.)		
Ditin butyl dilaurate (DBTDL, A.R.)		
sodium chloride (A.R.)	Sinopharm Chemical Reagent Co., Ltd., China.	/
ammonium chloride (A.R.)		
magnesium sulfate anhydrous (A.R.)		
toluene (A.R.)		
Magnesium powder (A.R.)	Shanghai Lingfeng Chemical Reagent Co., Ltd.	/
3-Bromopropene (A.R.)	Adamas Reagent Co., Ltd. (Shanghai)	/
iodine (A.R.)	TCI (Shanghai) Chemical Industrial Development Co., Ltd.	/
Platinum catalyst	Prepared by our group	The content of Pt is 8000 ppm

### 2.2. Preparation of Sulfhydryl-Terminated Polyurethanes (Sulf-PU)s

The sulfhydryl-terminated polyurethanes (sulf-PU)s were synthesized according to Scheme 1 [19,20] and the raw materials feed ratios were collected in Table 2. To a typical procedure for synthesis sulf-PU-4 in Table 2, 22.22 g IPDI (0.1 mol) and 1.34 g DMPA (0.01 mol) were added into a 500 mL three-necked flask. Subsequently, 20.00 g PPG-2000 (0.01 mol) was dripped slowly into the three-necked flask for about 30 min and then 0.17 g DBTDL was added. The mixture was kept at 60 °C for 3 h and then 90 mL tetrahydrofuran was added into it. Then, the mixture was introduced into a mixture of 57.0 g TTMA (0.16 mol) and 57.02 g tetrahydrofuran at 40 °C for about 2 h. Later, the mixture was heated to 65 °C and reacted for 3 h. Finally, the residuals of the raw materials and tetrahydrogen were removed by a rotary evaporator and a pale yellow viscous solid product of sulf-PU-4 was obtained. Because the reaction for synthesis of sulf-PU was not selective, the products obtained are mixtures of polyurethanes end-capped with multiple sulfhydryl groups. Fourier-transform infrared (FT-IR) spectroscopic analysis of sulf-PU-4 was conducted as shown in

Figure S1. The characteristic absorption at  $2530\text{--}2590\text{ cm}^{-1}$  was ascribed to  $\text{-SH}$ . Obviously, there are no characteristic absorption of isocyanate group and OH of polyether in the range of  $2260\text{--}2280\text{ cm}^{-1}$  and  $3500\text{ cm}^{-1}$  respectively, which denotes that the isocyanate group and  $\text{-OH}$  reacted completely.



**Scheme 1.** The ideal diagram for the synthesis of Sulf-PU.

**Table 2.** The feed ratios for the preparation of sulfhydryl-terminated polyurethanes (Sulf-PU).

Sulf-PU	The Molar Ratio of NCO to OH	The Amount of the Raw Materials/mol			
		IPDI	DMPA	PPG-2000	TTMA
Sulf-PU-1	2:1	0.04	0.01	0.01	0.04
Sulf-PU-2	3:1	0.06	0.01	0.01	0.08
Sulf-PU-3	4:1	0.08	0.01	0.01	0.12
Sulf-PU-4	5:1	0.1	0.01	0.01	0.16
Sulf-PU-5	6:1	0.12	0.01	0.01	0.20
Sulf-PU-6	7:1	0.14	0.01	0.01	0.24

### 2.3. Synthesis of Allyl-Terminated Hyperbranched Polycarbosilanes

Various generations of allyl-terminated hyperbranched polycarbosilanes shown in Figure S2 were synthesized according to the procedure given by Scheme S1. The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of the allyl terminated hyperbranched polycarbosilanes were exhibited in Figure S3 and Figure S4 respectively.

### 2.4. Preparation of Ultraviolet (UV)-Cured Coatings

The mixtures of sulf-PU and allyl-terminated hyperbranched polycarbosilane were deposited on slides with thickness about 0.5 mm by spin-coating under a rotation speed of 3000 r/s for 30 s, and then cured by UV (ZB1000, Changzhou Zibo Electron Technology Co., Ltd., Changzhou, China) with laser wavelength 365 nm, radiation Intensity  $10.6\text{ mw}\cdot\text{cm}^{-2}$ , and a distance of the slides to the light of

20 cm. A typical procedure for preparation UV-cured coatings, sulf-PU-4 mixed with G2 according to molar ratio of 3-mercaptopropyl to acrylate with 2:1 and cured for 40 s.

### 2.5. Characterization

The  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker AVANCE AV400 (400 MHz) (Bruker, Billerica, MA, USA) spectrometer in  $\text{CDCl}_3$  at room temperature without tetramethylsilane (TMS) as internal reference. FT-IR analysis was carried out using a Nicolet 700 spectrometer (Nicolet Co., Ltd., Madison, WI, USA) over the frequency range  $4000\text{--}650\text{ cm}^{-1}$  with ATR attachment. The pencil hardness of the cured samples was measured with a BGD-562 Pencil hardness meter (Zhenwei Testing Machinery Co Ltd, Jiangdu, China) according to GB/T6739-2006. Thermogravimetric analysis (TGA) was carried out using a TG 209C apparatus (NETZSCH-Gerätebau GmbH, Selb, Germany), in which samples were heated from ambient temperature to  $800\text{ }^\circ\text{C}$  at a rate of  $10\text{ }^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. The cured samples were washed with toluene by Soxhlet extraction at  $150\text{ }^\circ\text{C}$  for 4 h and then the degree of curing contents were calculated as a percentage of the residual mass in the original mass of the cured coatings. The adhesion was measured with a BGD-502 paint film according to ISO 2409-2007 by a cross cut test (see Table S1). The water absorption was measured after the coatings were immersed in water for 24 h according to "Determination of water absorption rate of insullac films" HGT 3856-2006. The surface water contact angle was measured according to "Measurement of water-contact angle of plastic films", GB/T 30693-2014 on a KRÜSS DSA30 water contact angle meter (KRÜSS, Hamburg, Germany).

## 3. Results and Discussion

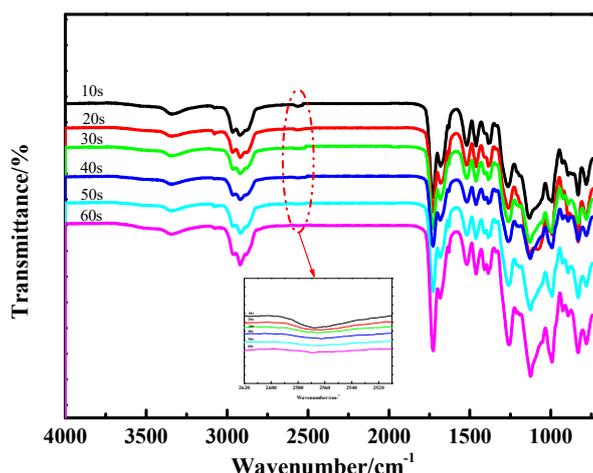
### 3.1. The Influence of Curing Time

The influence of curing time on the performances of the coatings prepared is summarized in Table 3. When the curing time was in the range of 10–40 s, the degree of curing content, pencil hardness and surface water contact angle of the coatings increased while the water absorption of the coatings decreased with the increase of the curing time. A further increment of the curing time had almost no effect on these properties of the coatings, which may be explained by the fact that the mixture was cured completely by UV for 40 s. This is proved by the FT-IR spectra of the cured films shown by Figure 1. The characteristic vibration absorption peak of  $\text{C}=\text{C}$  in the allyl group at  $1627\text{ cm}^{-1}$  disappeared and the weak characteristic absorption peak of HS at  $2550\text{ cm}^{-1}$  becomes smaller and smaller with the prolongation of the curing time and vanished when the curing time is 40 s. The coatings prepared exhibit hydrophobic properties because the contact angle of water is greater than  $90^\circ$ . The coatings show fairly low water absorption in the range of 0.59–1.36wt%, which is lower than the traditional UV-cured PU coatings [21]. This is consistent with the coatings reported previously that the high contact angle of water results in low water absorption [22,23].

**Table 3.** The influence of curing time on the silicone coatings prepared.

Entry	Curing Time/s	Degree of Curing Content /%	Pencil Hardness	Surface Water Contact Angle/ $^\circ$	Water Absorption/(wt%)
1	10	63.0	5B	89.6	1.36
2	20	72.8	2B	93.2	1.06
3	30	82.0	B	95.8	0.75
4	40	85.6	HB	102.2	0.60
5	50	85.8	HB	102.1	0.62
6	60	86.2	HB	102.8	0.59

Conditions: sulf-PU was the sulf-PU-4 in the Table 2 and allyl-terminated hyperbranched polycarbosilane was G2. The molar ratio of 3-mercaptopropyl to acrylate is 2:1. The water absorption was measured after the coatings being immersed in water for 24 h.



**Figure 1.** The Fourier transform infrared (FT-IR) spectra of the films cured for various periods.

Sulf-PU was the sulf-PU-4 in Table 1 and allyl-terminated hyperbranched polycarbosilane was G2. The molar ratio of 3-mercaptopropyl to acrylate is 2:1.

### 3.2. The Influence of Various Sulf-PUs

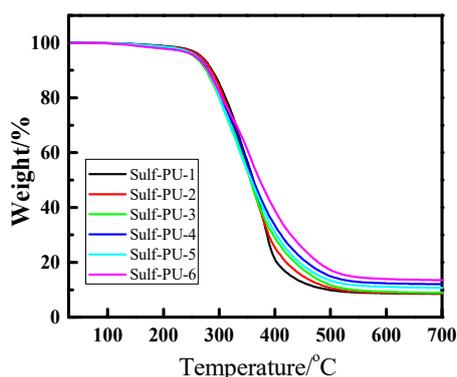
The influence of various sulf-PU (In Table 2) was investigated and the results were collected in Table 4. It can be seen that the pencil hardness of the coatings is the highest when the coating is prepared with sulf-PU-4 and the pencil hardness of all the coatings prepared is in the range of 5B-HB, which is similar to those UV-cured polyurethane coatings reported previously [24–26]. The surface water contact angle is still not very high, which is in the range of 88.5–102.2° (Figure S5). The water absorption is in the range of 0.73–1.06 wt%, which denotes the coating prepared with fairly low water absorption.

**Table 4.** The influence of various sulf-PU on the cure materials.

Entry	Sulf-PU	The Pencil Hardness	The Surface Water Contact Angle/°	Water Absorption/(wt%)
1	Sulf-PU-1	5B	88.5°	1.06
2	Sulf-PU-2	3B	93.4	0.95
3	Sulf-PU-3	3B	95.1	0.97
4	Sulf-PU-4	HB	102.2	0.60
5	Sulf-PU-5	2B	96.4	0.70
6	Sulf-PU-6	2B	96.8	0.73

Conditions: Allyl-terminated hyperbranched polycarbosilane was G2. The molar ratio of 3-mercaptopropyl to allyl is 2:1. The coatings were cured for 40 s. The water absorption was measured after the coatings were immersed in water for 24 h.

As reported by previous work, the conventional PU coatings have poor heat resistance which will undergo severe pyrolysis when the temperature exceeds 200 °C [9–11]. To investigate the thermal stability of the UV-cured coatings obtained, the materials prepared with various sulf-PU were analyzed by TGA (Figure 2). As can be seen from the TGA curves presented in Figure 2, the initial decomposition temperature ( $T_d5\%$ ) ranges from 258 °C to 268 °C, which is obviously much higher than those of the conventional PU coatings reported [9–11].



**Figure 2.** Thermogravimetric analysis (TGA) curves of the coatings prepared with various of sulf-PU.

### 3.3. The Influence of Molar Ratio of 3-Mercaptopropyl to Allyl

The influence of the molar ratio of 3-mercaptopropyl to allyl on the UV-cured coatings is shown in Table 5. It can be seen that the pencil hardness of the coatings was in the range of 4B–HB, which was obviously effected by the molar ratio of 3-mercaptopropyl to allyl. When the molar ratio of 3-mercaptopropyl to allyl is 1.4, the pencil hardness and surface water contact angle of the coating is the highest (Figure S6), which may be ascribed to the highest cross-linking density [16]. The water absorption is in the range of 0.60–1.03 wt%, which still remains quite low.

**Table 5.** The influence of molar ratio of 3-mercaptopropyl to allyl on the cure materials.

Entry	Molar ratio of 3-Mercaptopropyl to Allyl	Pencil Hardness	Surface Water Contact Angle/°	Water Absorption/(wt%)
1	0.8	4B	85.5	1.03
2	1.0	3B	91.4	0.87
3	1.2	B	96.8	0.64
4	1.4	HB	102.2	0.60
5	1.6	2B	87.1	0.75
6	1.8	3B	72.1	0.82

Conditions: sulf-PU was the sulf-PU-4 in the Table 2 and allyl-terminated hyperbranched polycarbosilane was G2. The coatings were cured for 40 s. The water absorption was measured after the coatings being immersed in water for 24 h.

### 3.4. The Influence of Generations of Allyl-Terminated Hyperbranched Polycarbosilanes

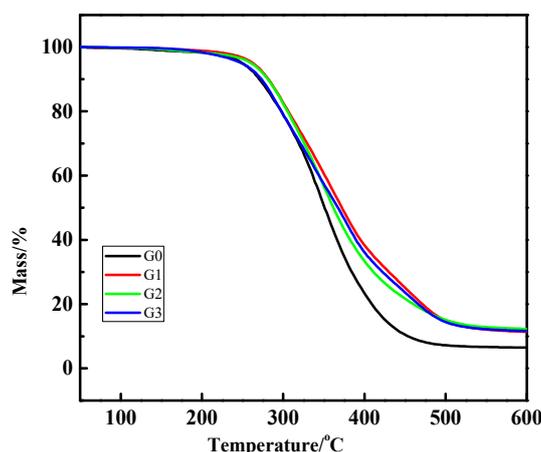
The influence of generations of allyl-terminated hyperbranched polycarbosilanes was explored as shown in Table 6, and the generations of allyl-terminated hyperbranched polycarbosilanes have significant impact on the pencil hardness of the silicone coatings. The pencil hardness of the coating is the highest when the generation of the hyperbranched polycarbosilanes is G2. A preferable generation of the hyperbranched polycarbosilanes will result in an optimal cross linking network of the molecular structure, which may be attributed to the optimal cross-linking density [27].

**Table 6.** The influence of generations of allyl-terminated hyperbranched polycarbosilanes.

Entry	Generations of Allyl-Terminated Hyperbranched Polycarbosilanes	Pencil Hardness	Surface Water Contact Angle/°	Water Absorption/(wt%)
1	G0	5B	75.8	1.07
2	G1	3B	87.9	0.64
3	G2	HB	102.2	0.60
4	G3	B	98.2	0.63

Conditions: sulf-PU was the sulf-PU-4 in the Table 2 and The molar ratio of 3-mercaptopropyl to allyl is 2:1. The coatings were cured for 40 s. The water absorption was measured after the coatings were immersed in water for 24 h.

Figure 3 shows the TGA curves of UV-cured silicone modified coatings with various generations of allyl-terminated hyperbranched polycarbosilanes. As can be seen, the start thermal decomposition temperature ( $T_{d5\%}$ ) of the cured coatings is in the range of 248–263 °C. It also can be concluded that the UV-cured coatings with various generations of allyl-terminated hyperbranched polycarbosilanes have good thermal stability, which is obviously higher than those of the conventional PU coatings reported [9–11].

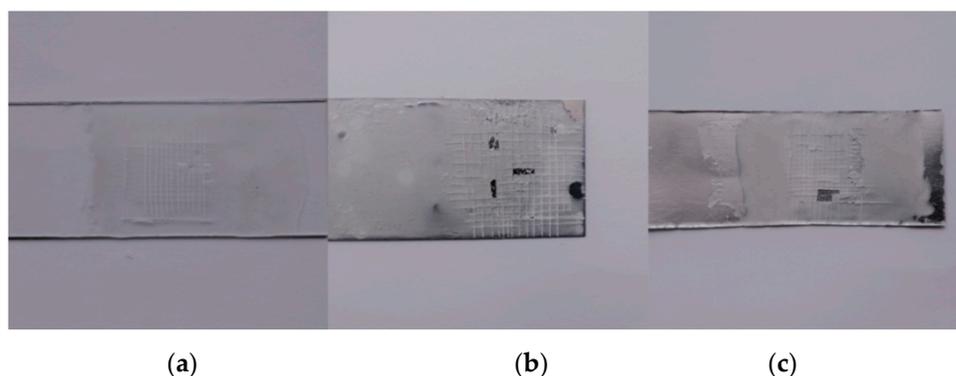
**Figure 3.** TGA curves of the coatings prepared with various generations of allyl-terminated hyperbranched polycarbosilanes.

### 3.5. The Adhesive Properties

The adhesion properties of the coating on various substrates were measured with a BGD-502 paint film according to GB/T 9286-88 by a cross cut test as shown by Table 7 and Figure 4. The coatings obtained exhibit grade 1 (Figure 4a), grade 2 (Figure 4b) and grade 3 (Figure 4c), adhesion to the glass, tin plate and aluminum sheet, respectively. When it comes to the coating on glass, although there is a little slice separation, the separated area is obviously no more than 5%. The coating partially peels off the tin plate in the test area and the adhesion of the coating on the aluminum sheet is worst because a large area of coating falls off in the test area. This denotes that the UV-cured materials obtained can be used as coating for substrates such as glass and tin plate, but not suitable for aluminum.

**Table 7.** The adhesive properties of the coatings on various substrates.

Substrates	Glass Slide	Tin plate	Aluminum Sheet
Adhesive grade	Grade 1	Grade 2	Grade 3



**Figure 4.** The photos for the adhesive experiments of the coatings on various substrates. (a) Glass slide; (b) tin plate; (c) aluminum sheet.

#### 4. Conclusions

To overcome the shortcoming of poor heat resistance for conventional PU coatings, UV-cured solvent-free hyperbranched polycarbosilane modified PU coatings were prepared by sulfhydryl-terminated polyurethanes and allyl-terminated hyperbranched polycarbosilanes. The coatings show fairly low water absorption in the range of 0.6–1.36 wt%. The coatings obtained exhibit grade 1, grade 2 and grade 3 adhesion to glass, tin plate and aluminum sheet, respectively. This denotes that the UV-cured materials obtained can be used as coating for substrates such as glass and tin plate, but are not suitable for aluminum. When sulf-PU-4 was mixed with G2 according to a molar ratio of 3-mercaptopropyl to acrylate of 2:1 and cured for 40 s, initial decomposition temperature ( $T_{d5\%}$ ) of the UV-cured coating was 268 °C and water absorption was 0.60wt%. Compared with the conventional PU coatings with decomposition temperature lower than 200 °C, the hyperbranched polycarbosilane-modified PU coatings prepared show obvious superior thermal stability. This implies that modification of PU with hyperbranched polycarbosilanes may be an effective method to improve the thermal stability of PU.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2079-6412/10/4/350/s1>, Figure S1: FT-IR analysis of Sulf-PU; Figure S2: The structure of various generations for allyl terminated hyperbranched polycarbosilanes; Figure S3: The  $^1\text{H-NMR}$  spectra of various generation of allyl terminated hyperbranched polycarbosilanes; Figure S4:  $^{13}\text{C-NMR}$  spectra of various generation of allyl terminated hyperbranched polycarbosilanes; Figure S5: Photos for the surface water contact angle of coatings prepared with various of Sulf-PU; Figure S6: Photos for the surface water contact angle of coatings prepared with various of molar ratio of 3-mercaptopropyl to allyl; Table S1: The adhesion grade, corresponding peel off ratio and sample drawings; Scheme S1: The scheme for the synthesis of various generations allyl terminated hyperbranched polycarbosilanes; Scheme S2: Scheme of the cross-linking reaction of G2 with Sulf-PU.

**Author Contributions:** Conceptualization, X.Y.; formal analysis X.J., T.Z., F.C. and X.Y.; investigation, X.J., Y.F., J.L.; data curation, X.J., J.L. and Y.W.; writing—Original draft preparation, X.Y.; writing—Review and editing, X.Y.; project administration, G.L. and X.Y.; funding acquisition, X.Y. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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