

# A Branched Silicon-Containing Arylacetylene Resin

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## Abstract

Silicon-containing arylacetylene resin (PSA) is a new high-performance thermoset resin. PSA possesses not only excellent thermal stability and thermal oxidative stability, but also excellent processing properties, dielectric properties and high temperature ceramization properties. There are potentially important applications for it in the high-tech field. Generally, PSA resin is a linear polymer with less alkynyl groups. In this paper we designed a new low-molecular weight and branched silicon-containing arylacetylene resin with high functionality. The branched silicon-containing arylacetylene resin (BPSA) was successfully gotten through the reaction between the alkyne Grignard reagent and trichloromethylsilane. BPSA was characterized by FTIR, <sup>1</sup>H-NMR, GPC, DSC, TGA analyses. The results showed BPSA is a yellow viscous liquid resin at room temperature. Its initial curing temperature is 195°C. Thermal decomposition T<sub>d5</sub> and the char yields at 800°C of the cured resin are 787°C and 95% in nitrogen, respectively. Flexural strength, flexural modulus and interlaminar shear strength of T300/BPSA composites are 230 MPa, 48 GPa, and 13 MPa, respectively. The resin could be used as a kind of excellent high-temperature resin matrices of composite materials.

**Keyword :** silicon-containing arylacetylene resin , branched arylacetylene resin , high-temperature resistant polymer, polymeric matrix for advanced composites

## 1 Introduction

The silicon-containing arylacetylene resin is a high temperature resistant polymer, possessing extremely high thermal stability, with potential applications as ceramic precursors, heat-resistant materials and matrix of advanced polymer composites in aerospace and astronautics<sup>[1]</sup>.

Itoh<sup>[2]-[3]</sup> prepared poly[(phenylsilylene)-ethynylene-1,3-phenylene-ethynylene] (abbreviated as MSP) by the dehydrogenative coupling polymerization reaction in the presence of magnesia base catalysts. The decomposition temperature at 5% ( $T_{d5}$ ) and residue at 1000°C of the cured MSP was 860°C and 94%, respectively. Buvat<sup>[4]</sup> prepared poly[silyleneethynylene phenyleneethynylene] terminated with phenylacetylene (abbreviated as BLJ) that possessed excellent processing performance. A novel silicon-containing arylacetylene (PSA) resin composed of  $[-Si(CH_3)_2-C\equiv C-Ar-C\equiv C-]$  has been synthesized in our laboratory, which exhibits good processing performance and extremely high heat resistance after cured. Its  $T_{d5}$  and residue at 800°C arrive at 631°C and 90%, respectively<sup>[5]</sup>. The introduction of silicon is not only to maintain excellent high temperature resistance, but also has excellent dielectric properties, mechanical properties and high temperature properties. PSA can form  $SiO_2$  and other inorganic compounds at high temperature. Because the residue has good mechanical and thermal properties, it can be used as the precursor material of high temperature resistant ceramics. The resin shows the unique advantages and potential in the application of aviation and space industry, it is an important milestone in the development of this field.

## 2 Experimental

### 2.1 Materials

Tetrahydrofuran, AR, Shanghai Taitan Co., Ltd; Magnesium powder, AR, Chinese Medicine Group Chemical Reagent Co., Ltd; trimethylchlorosilane, CP, Chinese Medicine Group Chemical Reagent Co., Ltd; trichloromethylsilane, AR, Aladdin reagent; Lithium chloride anhydrous, AR, Shanghai Taitan Co. Ltd; hydrochloric acid, AR, Anhydrous sodium sulfate, AR, Bromoethane, AR, Shanghai Ling Feng Chemical Reagent Co., Ltd.;

diethynylbenzene, Xi'an(Jiaozhou Fine Chemicals Co., Lth; Carbon fiber fabric, T300-3k , Toray Industries Inc., Ltd.

## 2.2 Instruments

<sup>1</sup>H-NMR measurements were carried out on a BRUKER AVANCE 400 (400 MHz) (BRUKER, Switzerland) NMR spectrometer at room temperature in CDCl<sub>3</sub>. Fourier transform infrared (FT-IR) spectra were acquired using a Nicolet 360 FTIR spectrometer (Nicolet, U.S.). Differential scanning calorimetry (DSC) measurements were performed on TA Q2000 DSC (TA, U.S.) at a heating rate of 10 K/min from 40 °C to 400°C for all cases under the nitrogen. Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo TGA/DSC 1 (Mettler-Toledo, Switzerland) at a heating rate of 10 K/min from 400°C to 1000°C in all cases under nitrogen. The mechanical properties of composites were tested as GB/T 1449-2005 and JC/T 773-1982(96).

## 2.3 Synthesis of mono-substituted diethynylbenzene Grignard reagent

The synthesis route of mono-substituted diethynylbenzene Grignard reagent is shown in figure 1. The entire synthesis process was carried out in dry nitrogen. Magnesium powder (2.88 g, 0.12 mol), 4.20g LiCl<sup>[6]-[9]</sup> and THF (40 ml) were added to a 250-ml four-necked round-bottomed flask equipped with a condenser, a thermometer, a constant pressure dropping funnel and a mechanical stirring bar. And then, ethyl bromide (10.9 g, 0.10 mol) in THF (40 ml) was added dropwise in 20 min, and then, remove the ice/water bath and the mixture was refluxed for 1 h to get ethylmagnesium bromide lithium chloride. The reaction system was then cooled with an ice/water bath, and a solution of diethynylbenzene(12.6 g, 0.10 mol) in THF (20 ml) was added over 10 min with stirring(temperature isn't above 40°C). The reaction refluxed an additional 1.5 h to produce mono-substituted diethynylbenzene magnesium Grignard reagent. Then, a solution of trimethylchlorosilane in THF(20ml) was dropwise added to the mixture at room temperature over 1h, After the dropping process, the temperature is heated up to 70°C and the mixture was refluxed for 2h. Thereafter, most of THF was removed by distillation and toluene (80 ml) was added into the flask. Afterwards, 30 ml 10% aqueous hydrochloric acid were dropwise added to the flask, cooled in an ice/water bath. The resulting organic phase was separated out, washed with water and then dried by using anhydrous sodium sulphate. The solvent was distilled off from the solution to obtain a yellow liquid at room temperature with 60%.

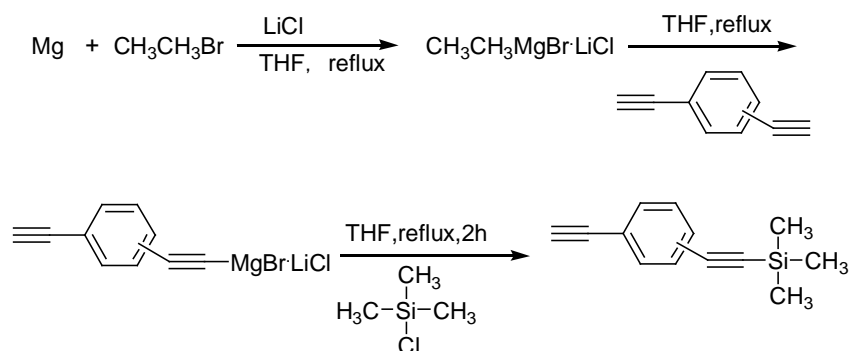


Figure 1 Synthesis of mono-substituted diethynylbenzene Grignard reagent

## 2.4 Synthesis of branched silicon-containing arylacetylene resin

Branched silicon-containing arylacetylene resin was synthesised by figure 2. The reaction system was cooled with an ice/water bath to make the temperature less than 25 °C. A solution of trichloromethylsilane (5.01 g, 0.033 mol) in THF (20 ml) was dropwise added to mono-substituted diethynylbenzene magnesium Grignard reagent at room temperature over 1h. After the dropping process, the temperature is heated up to 70 °C and the mixture was refluxed for 2h. Thereafter, most of THF was removed by distillation and toluene (100 ml) was added into the flask. Afterwards, 60 ml 10% aqueous hydrochloric acid were dropwise added to the flask, cooled in an ice/water bath. The resulting organic phase was separated out, washed with water and then dried by using anhydrous sodium sulphate. The solvent was distilled off from the solution to obtain a yellow viscous liquid at room temperature.

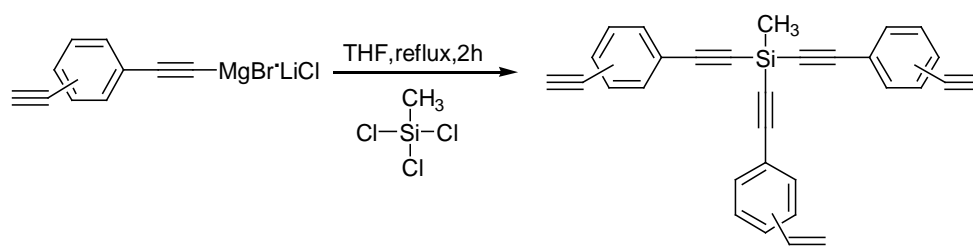


Fig. 2 Synthesis of branched silicon-containing arylacetylene resin

## 2.5 Preparation of carbon fiber reinforced composites

Carbon fiber reinforced BPSA composites were prepared by molding. T300 carbon fiber fabric prepreg was prepared from 12 layers T300 carbon fabric and a resin solution with a 35 wt% BPSA resin in THF. The prepreg was dried in a vacuum at 60 °C. The prepreg stack was pressed in a mold with a cure procedure :2h at 150 °C, 2 h at 170 °C, 2 h at 210 °C and 4 h at 250 °C under the pressure of 6 MPa . T300 carbon fabric reinforced BPSA resin composites was obtained and the content of the resin in the composite sample was about 30 wt% .

## 3 Results and Discussion

### 3.1 The structure of BPSA resin

The structure of BPSA resin were characterized by  $^1\text{H-NMR}$  and FT-IR. The  $^1\text{H-NMR}$  spectra of BPSA resins is shown in Fig.3. As shown in the figure, According to the law of chemical shift, The chemical shift for  $-\text{C}\equiv\text{C-H}$  occurs at 3.0(a) ppm,  $\text{Si-CH}_3$  occurs at 0.62(b) ppm, for methyl hydrogen peak of toluene at 2.28(c) ppm is present.

The FT-IR of spectra BPSA resins is Fig.4. As shown in the figure, the band for stretching vibration peak of  $\equiv\text{C-H}$  occurs at  $3293\text{ cm}^{-1}$ . the absorption bands for  $-\text{Si}(\text{CH}_3)_3$  group at  $2967\text{ cm}^{-1}$ , for  $-\text{C}\equiv\text{C}-$  group at  $2157\text{ cm}^{-1}$ , for bending vibration absorption kurtosis of C-H of benzene ring at  $799\text{ cm}^{-1}$ . It didn't have absorption of Si-Cl and Si-OH.

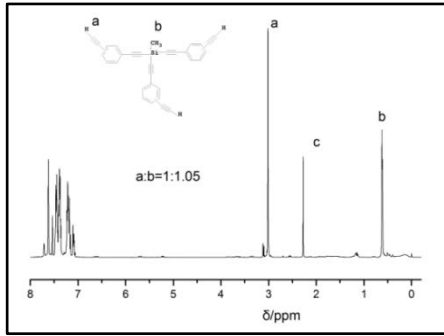


Fig. 3  $^1\text{H-NMR}$  spectra of BPSA resins

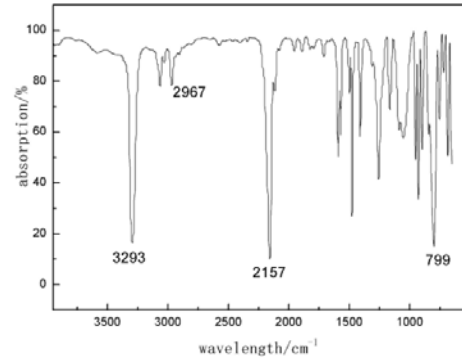


Fig. 4 FT-IR spectra of BPSA resins

### 3.2 Curing behavior of BPSA resin

The thermal curing behaviors of BPSA resins were traced by DSC analysis and the results are shown in Fig.5 and Table 1. PSA and BPSA showed a exothermic peak about 200°C, that indicate the curing reactions of  $\text{C}\equiv\text{C-H}$ . BPSA resin has fast curing speed and high heat release rate. The  $\Delta\text{H}$ (Heat change) of BPSA is two times more than PSA. In the BPSA, the content of the  $\text{C}\equiv\text{C-H}$  is much more than that of PSA resin. Curing process is more complete, which lead to the initial exothermic temperature and the exothermic peak temperature of the curing process of the resin in advance.

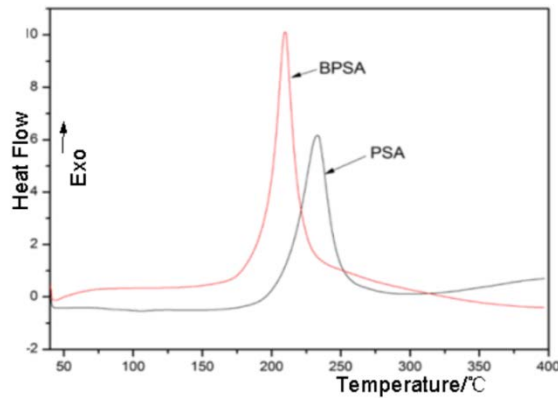


Fig.5 DSC curve of BPSA and PSA resin

sample	$T_i/^\circ\text{C}$	$T_p/^\circ\text{C}$	$\Delta\text{H}(\text{J/g})$
BPSA	196	210	1115
PSA	210	232	468

Table 1 DSC analysis of BPSA and PSA resin

### 3.3 TGA analysis of BPSA thermosets

The thermal-stabilities of BPSA thermosets are traced by TGA analysis under nitrogen and air atmosphere at the heating rate of 10 K/min. TGA curves of PSA and BPSA thermosets are shown in Fig. 6 and Fig.7 correspondingly and the results are in Table 2. The mass loss of BPSA resin was faster than that of PSA resin before 450°C. The decomposition temperatures at 5% ( $T_{d5}$ ) of PSA is 625°C and the residue yield at 800°C ( $Y_{800^\circ\text{C}}$ ) is 93.1%. BPSA resin has a higher content of acetylene, which makes the curing degree is higher, the solidification structure is compact, and the gas erosion is slow.  $T_{d5}$  of BPSA is 787°C and the residue yield at 800°C ( $Y_{800^\circ\text{C}}$ ) is 94.8% in nitrogen atmosphere. these is higher than PSA resin.

The heat resistance of PSA resin is excellent in air atmosphere. BPSA resin has a lower silicon content, the  $T_{d5}$  is 473°C, and the char yield of BPSA thermosets is about 20% at 800°C in the air atmosphere. However, The general PSA resin,  $T_{d5}$  is 485°C, char yield of PSA thermosets is about 24.6% at 800°C. In the air, the heat resistance of BPSA resin is slightly worse than that of PSA resin. Silicon was oxidized above 450°C, Fig.8 showed that the mass of BPSA thermosets increased above 400°C. And then, Residual decreased gradually.

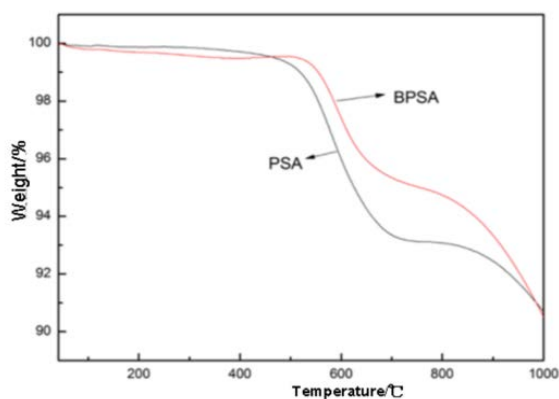


Fig.6 TGA curve of BPSA and PSA resins at  $\text{N}_2$  atmosphere

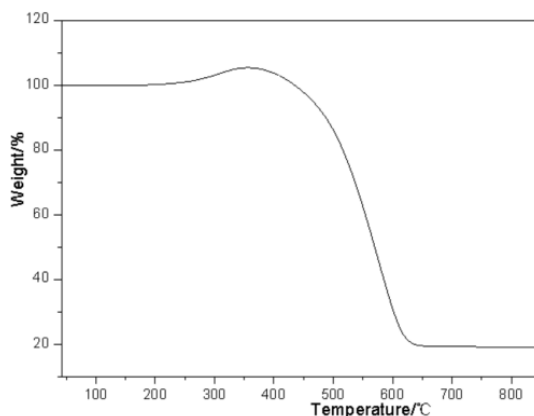


Fig.7 TGA curve of BPSA resins at  $\text{O}_2$  atmosphere

resin	N <sub>2</sub>		Air	
	T <sub>d5</sub> /°C	residual at 800°C/%	T <sub>d5</sub> /°C	residual at 800°C/%
PSA	625	93.1	473	24.6
BPSA	787	94.8	485	20

Table 2 TGA analysis of BPSA resins

### 3.4 The mechanical properties of BPSA composites

The mechanical behavior of T300/BPSA resin composites are shown in Table 3. The branched silicon-containing arylacetylene resin has a higher proportion of the acetylene groups, which makes the curing degree is higher, the cured structure is compact. It shows that composites has higher modulus, improved 59% compared with T300/PSA composites. However, Flexural strength and ILSS are close to these of PSA composites. The data indicate that the composite material has high mechanical properties, and can be used in the field of high performance materials.

resin	Flexural Strength/MPa	Flexural Modulus/GPa	ILSS/MPa
PSA	240.0±2.0	29.6±1.2	15.7±1.0
BPSA	230.0±1.0	47.0±2.2	12.2±2.0

Table 3 Properties of T300/BPSA composites

## 4 Conclusions

According to Knochel works, we synthesized mono-substituted diethynylbenzene Grignard reagent, LiCl as catalyst to decrease coupling of diethynylbenzene Grignard reagent by interaction Grignard reagent with LiCl. The mono-substituted Grignard reagent reacted with trichloromethylsilane to get BPSA. The BPSA has a higher content of acetylene, which makes the curing degree is higher, the cured structure is compact, and the gas erosion is slow. These show that cured product of BPSA has excellent thermal properties. Initial curing temperature of BPSA were 195°C, T<sub>d5</sub> were of 787°C, and the char yields at 800°C were of 95% in nitrogen. T<sub>d5</sub> were of 485°C, the char yields at 800°C were of 25% in air. The

T300/BPSA composites has better mechanical properties. Flexural modulus increases 59% compared with T300/PSA composites. However, Flexural strength and ILSS are close to these of PSA composites. The BPSA resin can be used as a kind of excellent high-temperature and high modulus materials, it will have a great application in the field of Aerospace.

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