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# Synthesis of Branched Silicon-Containing Arylethyleneacetylene Resin and the Performance of Casting

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## Abstract

With good thermal properties, dielectric property and high-temperature ceramics performance, silicon-containing arylacetylene resin (PSA) has opened an attractive alternative to high performance thermosetting resins in application in the area of aircraft and missile. However, it is difficult to introduce silicon into the main chain of organic arylacetylene. In this paper, branched silicon-containing arylethyleneacetylene (BSA) resin was synthesized by methyltrichlorosilane and diethynylbenzene with zinc powder as catalyst. The advantages lie in simple operation, short reaction period and mild heat release. BSA resin exhibits excellent processability with the processing temperature of 20˚C - 150˚C and processing window of 130˚C. The glass transition temperature of the resin casting is over 500˚C. The temperature of 5% weight loss ($T_{d5}$) is up to 575˚C and char yield of thermoset at 800˚C ($Y_{800}$) reaches 91% under nitrogen. Also, the dielectric constant and dielectric loss of casting has no change within 10 - $10^6$ Hz.

## Keywords

Branched Silicon-Containing Arylethyleneacetylene (BSA), Zinc Powder, Processability, Heat-Resistant Material

## 1. Introduction

Since 20th century, many countries have strived to develop aviation industry. The development of aviation technologies can reflect the comprehensive strength of a country. The friction between aviation aircraft and atmosphere while high-speed flying will raise the surface temperature, which leads to high requirements on the thermal property of materials [1]. Many heat resistant materials with special functions are widely used on the aerospace vehicle [2].

In recent years, PSA resin has attracted much attention from international and domestic academics. The introduction of silicon improve the thermal stability [3], high-temperature ceramization performance [4] [5] and dielectric property [6]. The main challenge in the synthesis of PSA is how to introduce the organic silicon into the chain segment of arylacetylene polymer. Itoh M [7] used phenylsilane and 1,3-diethynylbenzene catalyzed by MgO synthesized the poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] (MSP). Jiang H [8] *et al.* used zinc chloride catalyzed polycondensation reaction of diethynylbenzene and aminosilane, and synthesized PSA resin containing terminal amino group. This reaction is quick and has high yield, but the terminal amino group impairs the thermal stability of resin. Zhou Q [9] *et al.* first prepared lithium phenylacetylide from the reaction of phenyl acetylene and butyllithium, then this compound was further reacted with methyltrichlorosilane to obtain MTPES. MTPES has good thermal stability, yet the synthesis has large heat release and the reaction system is unstable.

In this article, we prepared branched silicon-containing arylethyleneacetylene resin (BSA) by diethynylbenzene and methyltrichlorosilane catalyzed by zinc power. The molecular weight of BSA resin is easy to control, the reaction process is simple, and there is no heat released; the crosslinking density of thermoset is higher, and thermoset has better thermal property; terminal olefinic on the molecular chain reduces the viscosity of resin which improving the processability of resin.

## 2. Experimental

### 2.1. Materials

Diethynylbenzene (DEB, purity > 98%, prepared by Shanghai Like Chemical Technology Co., Ltd.); Methyltrichlorosilane (MTS, purity > 98%, purchased by Acros Organics); zinc powder (AR, bought from Sinopharm Group); acetonitrile (AR), toluene (AR), hydrochloric acid (AR), acetone (AR) were purchased by Lingfeng Chemical Reagent Co., Ltd.

### 2.2. Synthesis of BSA

An nitrogen-flushed 250 mL three-necked reaction vessel equipped with a reflux condenser, an addition funnel, and a stirring motor was dried. Added zinc powder (0.3 mol) and 40 mL acetonitrile, then the mixed solution of DEB (0.1 mol) and 20 mL acetonitrile was added slowly with stirring within 10 minutes. When the temperature rose to 56˚C, dropwise added the mixed solution of DEB (0.1 mol) and 20 mL acetonitrile with stirring within 20 minutes. After finished the addition, the mixture was stirred at 80˚C for 10 hours.

After the reaction finished, the solution was filtered to separate out the zinc chloride and excess zinc powder. The filtrate was diluted with 80 mL toluene, then added with deionized water to dissolve the $ZnCl_2$ generated in the reaction for three to five times. Then separated water and upper organic phase, after evaporation of solvent, pure BSA resin was isolated by distillation under reduced pressure. The reaction scheme is shown in **Figure 1**.

### 2.3. Synthesis of BSA

To remove any volatile material, the sample was heated at 100˚C. The sample was placed in a furnace and cured at 150˚C/2 h, 170˚C/2 h, 210˚C/2 h, and 250˚C/4 h.

### 2.4. Synthesis of BSA

The viscosity of the resin was analyzed by rotary viscosimeter. Broadband dielectric impedance spectrometer were used to analysis the dielectric properties of thermoset. The dynamic mechanical properties of thermoset were measured by means of dynamic mechanical analysis methods.

## 3. Results and Discussion

### 3.1. Reaction Conditions

Different solvents were used as reaction solvent to explore the influence on this reaction. We used 0.1 mol DEB, 0.033 mol DCMS and 0.3 mol zinc powder in this reaction, and proceed 10 h at 80˚C. The results are shown in **Table 1**. We can know from the table that only when acetonitrile serves as the reaction solvent can the reaction going on, while other solvents cannot.

Acetonitrile as reaction solvent, react 10 h at 80˚C, different dosage of zinc powder were used to explore effect on the reaction yield. The results are shown in **Table 2**. When the dosage of zinc powder was 0.1mol, the yield was 40.1%; when the dosage of zinc powder increased to 0.2 mol, the yield was 49.8%; when

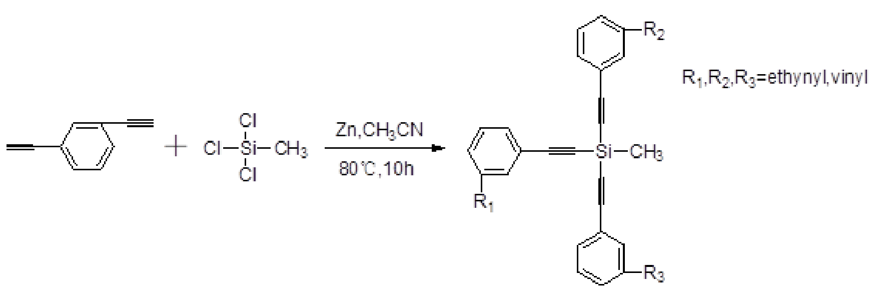


**Figure 1.** The reaction scheme of BSA resin.

**Table 1.** Effects of different solvents on reactions.

| Solvents | Acetonitrile | Tetrahydrofuran | Toluene | Dimethyl sulfoxide | Dimethyl formamide |
|---|---|---|---|---|---|
| Temperature (˚C) | 80 | 66 | 100 | 100 | 100 |
| Reaction result | √ | × | × | × | × |

Note: "×" means no reaction; "√" means has reaction.

**Table 2.** Effects of zinc amounts on reaction yields.

| Zinc (mol) | Temperature (˚C) | Time (h) | Yield (%) |
|---|---|---|---|
| 0.1 | 80 | 10 | 40.1 |
| 0.2 | 80 | 10 | 49.8 |
| 0.3 | 80 | 10 | 78.2 |
| 0.4 | 80 | 10 | 78.8 |

the dosage of zinc powder was 0.3 mol, the yield was 78.2%; and when the dosage of zinc powder was 0.4 mol, the yield was 78.8%, there's no obvious improvement compared with 0.3 mol. Considerate of the reaction yield, the optimal dosage of zinc powder is three times as much as DEB.

### 3.2. Thermal Property

The thermoset was prepared with curing process. The thermal property of thermoset was analysed by TGA, the spectrogram is shown in **Figure 2**. The results shown that the $T_{d5}$ of thermoset is 575˚C in the nitrogen atmosphere, the $Y_{800}$ was 91%, which indicates that BSA resin has high heat-resistant performance. However, BSA resin contains terminal olefinic, which degraded the thermal property of BSA resin. On the other hand, owing to the branched structure of BSA resin, the rate of ring formation was improved, thereby improving the crosslinking density of cured resin and thermal properties of BSA.

### 3.3. Viscosity of BSA Resin

The rheological property of resin is an important index reflecting the internal structure and processability. Exploring the rheological behavior has great significance for machining and shaping of resin.

Tested the rheological properties of BSA resin, rheological curve is shown in **Figure 3**. It is observed that when the temperature rose from 40˚C to 150˚C, the viscosity of BSA resin does not change significantly. When the temperature rises to 150˚C, the viscosity of resin increases sharply, which is mainly due to the gelation of resin. BSA resin is flowable at room temperature, so the processing temperature of BSA resin is from 20˚C to 150˚C, and the processing window is 130˚C. Therefore, the BSA resin has prefect processability.

This paper also tested the viscosity of BSA resin at 90˚C as time goes on. The viscosity presented in **Figure 4**. We can see that the viscosity of BSA resin increases slowly over time at 90˚C. In the beginning, the viscosity of BSA resin is 336.2 mPa·s, and then changed to 650.3 mPa·s 3 hours later, which indicates that viscosity of BSA resin is relatively stable, so it can be used in processing temperature for long time.

### 3.4. Properties of Casting

Casting was prepared in a special mould using heating procedure, The diameter size of cylindrical casting is 30 mm. The dielectric property of casting w a s

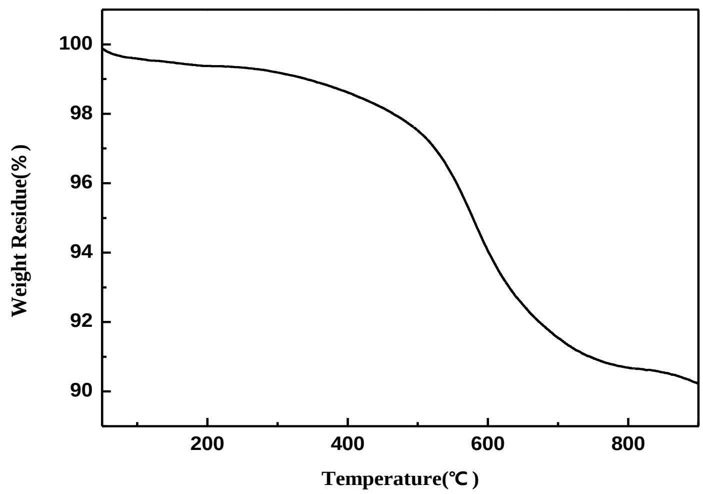


**Figure 2.** TGA curve of cured BSA resin in $N_2$.

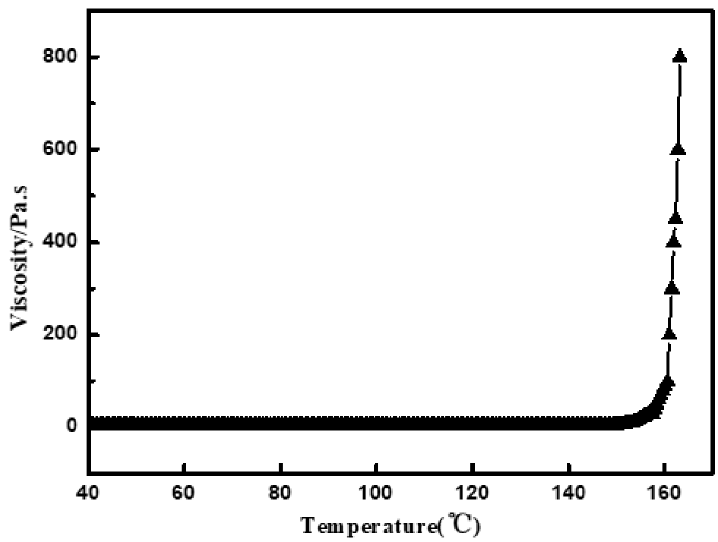


**Figure 3.** Viscosity vs temperature for BSA resin.

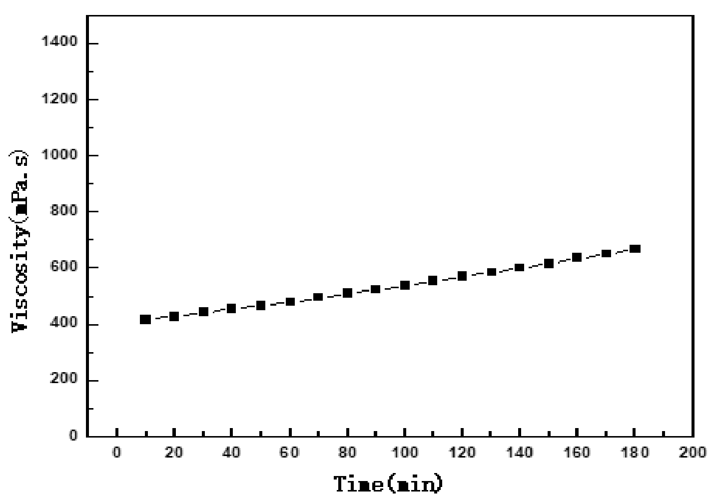


**Figure 4.** Viscosity of BSA resin at different time.

investigated by broadband dielectric impedance spectrometer. The spectrum is shown in **Figure 5**. It is obviously that the dielectric constant ($\varepsilon$) and dielectric loss ($\tan\delta$) is stable in the range of 10 - $10^6$ Hz, which elucidates that casting has good dielectric property as a low-pole polymer.

Casting was prepared in special mould using heating procedure, the size of cuboid casting is 35 mm × 6 mm × 2 mm. The viscoelasticity of casting was determined by DMA. The spectrogram of DMA is shown in **Figure 6**. We can see that within 50˚C - 500˚C, the storage modulus (E) and losses tangent ($\tan\delta$) for the casting were little changed, implying that casting has no glass transition within 50˚C - 500˚C.

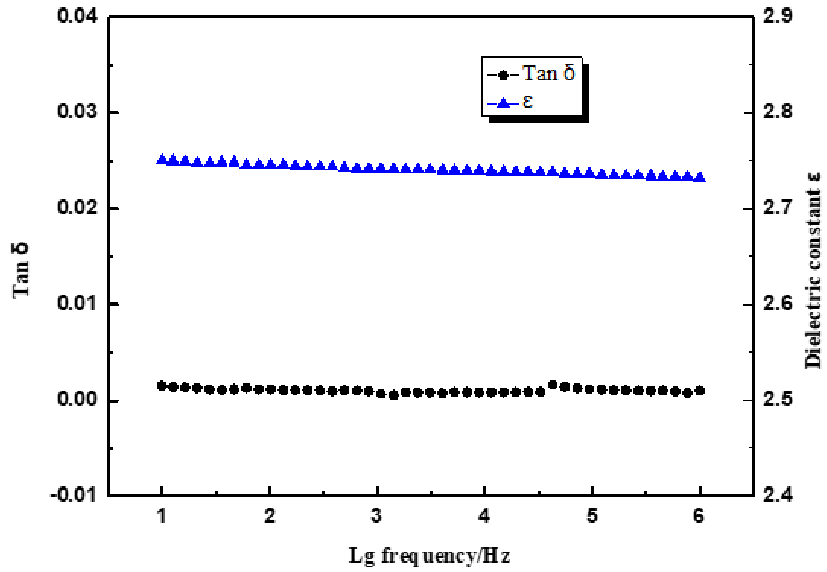


**Figure 5.** Dielectric curve of cured BSA resin.

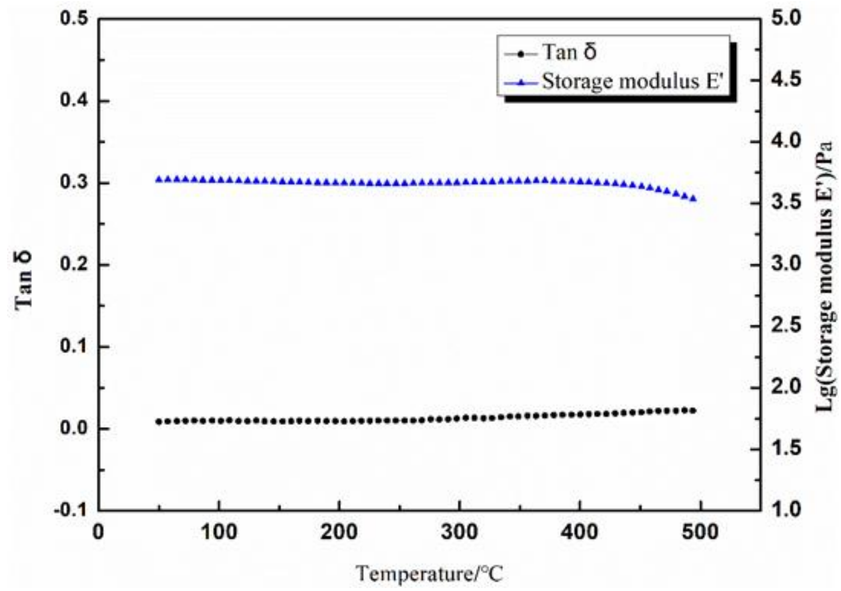


**Figure 6.** DMA curve of cured BSA.

## 4. Conclusion

In this article, branched silicon-containing arylethyleneacetylene resin was synthesized by methyltrichlorosilane and diethynylbenzene catalyzed by zinc powder. The optimum conditions: acetonitrile as the reaction solvent, the amount of zinc overdosed 200%. The reaction has advantages of simple operation, short reaction period and mild heat release. BSA resin has good thermal properties: $T_{d5}$ of thermoset reaches up to 575˚C, and $Y_{800}$ is 91%. BSA resin has excellent processability. The dielectric constant and dielectric loss of the casting are stable within 10 - $10^6$ Hz, which implies good dielectric properties, the glass transition temperature of the resin casting is over 500 ˚C.

## References


[1] Meador, M.A. (1995) High Temperature Polymer Matrix Composite for Aeropropulsion Appications. *Materials Challenge Diversification and the Future*, 268-276.

[2] Lin, S.C. and Pearce, E.M. (1994) High Performance Thermosets. Hanser, New York, 108.

[3] Zhang, J., Huang, J. and Du, W. (2011) Thermal Stability of the Copolymers of Silicon-Containing Arylacetylene Resin and Acetylene-Functional Benzoxazine. *Polymer Degradation & Stability*, **96**, 2276-2283. https://doi.org/10.1016/j.polymdegradstab.2011.04.022

[4] Wang, C., Huang, F., Jiang, Y., Zhou, Y. and Du, L. (2012) A Novel Oxidation Resistant SiC/B4, C/C, Nanocomposite Derived from a Carborane-Containing Conjugated Polycarbosilane. *Journal of the American Ceramic Society*, **95**, 71-74. https://doi.org/10.1111/j.1551-2916.2011.04972.x

[5] Brefort, J.L., Corriu, R.J.P., Gerbier, P., Guerin, G. and Henner, B.J.L. (1992) New Poly[(Silylene)Diacetylenes]and Poly[(Germylene)Diacetylenes]: Synthesis and Conductive Properties. *Orga-nometallics*, **11**, 2500-2506. https://doi.org/10.1021/om00043a037

[6] Yan, L., Zhang, X., Li, H. and Gui, H. (2007) Carbon Cloth Reinforced Polyarylacetylene Ablative Materials. *Journal of Advanced Materials*, **39**, 22-25.

[7] Itoh, M. (1999) A Novel Synthesis of a Highly Heat-Resistant Organosilicon Polymer Using Base Catalysts. *Catalysis Surveys*, **3**, 61-69. https://doi.org/10.1023/A:1019051113699

[8] Jiang, H., Deng, S.F. and Ruan, X.Z. (2017) Zinc Chloride Catalyzes Synthesis of Silicon-Containing Arylacetylene Resin. *Polymer Materials Science and Engineering*, **33**, 18-21.

[9] Zhou, Q., Feng, X., Ni, L.Z. and Chen, J.D. (2006) Novel Heat Resistant Methyl -Tri(Phenylethynyl)Silane Resin: Synthesis, Characterization and Thermal Properties. *Applied Polymer Science*, **102**, 2488-2492. https://doi.org/10.1002/app.24605