

Ethynyl Aromatic Siliconhybridized Resin: Synthesis, Characterizations, and Thermal Properties

Ming Yang,^{1,2} Song Shi,³ Mingcun Wang,¹ Yuhui Wang,³ Zhenhua Luo,¹
Zhihai Feng,³ Tong Zhao¹

¹Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

²Graduate School of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China

³National Key Laboratory of Advanced Functional Composite Materials, Aerospace Research Institute of Materials and Processing Technology, Beijing 100076, People's Republic of China

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ABSTRACT: A novel silicon-containing resin (ESA resin) was successfully synthesized by the condensation reaction of lithium arylacetylide with chlorosilane in high yields. The resin was characterized by the techniques of FTIR, ¹H-NMR, ²⁹Si-NMR, and gel permeation chromatography. Thermal cure process was monitored by DSC and FTIR methods. This resin could melt at around 100°C and thermally cured at 200–250°C with low exothermal enthalpy. Owing to the high aryl groups containing and the complete crosslinking of

ethynyl groups, the cured ESA resin exhibited excellent thermal stability and high char yield. The decomposition temperature T_{d5} of the cured resin was at 510°C, and the residue yield at 900°C was 82.9% in N₂. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 714–719, 2010

Key words: ethynyl; aromatic; silicones; thermosets; thermal properties

INTRODUCTION

High temperature resistant resins have been used as matrices of composites for thermostructural and ablative materials for several decades, and they are still gaining a great attention to date. Upto now, many kinds of high performance resins have been explored and their applications were found.¹ For example, phenolic resins are considered to have several desirable characteristics, such as thermal resistance, flame retardance, and superior ablative properties. However, the shortcomings originating from their brittle structure and volatile emitting cure mechanism dispel their application as a high temperature resin for advanced engineering materials.² Polyimides have been extensively used as structural or substructural materials in aeronautic and astronautic industry for their good thermal and dimensional stability, but they are still limited due to difficulties in processability and solubility in common organic solvents.³ Acetylene-terminated resins

(AT-resins) have been developed for decades in view of their good processability, thermal stability, and matrix suitability. On thermal curing, they provide a three-dimensional network exhibiting an excellent comprehensive properties including high glass transition temperature, good thermal stability, moisture and solvent resistance, and promising mechanical properties.⁴ Polyarylacetylene (PAA) resin as a highly cross-linked AT-resin that contains only carbon and hydrogen. It has marvelous ablative properties, which have been regarded as the best alternative to phenolic resin for matrices in high temperature composite materials, but its curing speed is so fast that the a potential runaway reaction may exist during processing, and the mechanical properties of PAA composites are comparably poor.⁵

The introduction of a polymerizable group as an end cap for low molecular weight oligomers has received much attention, because the oligomer usually has good processability compared with the higher molecular weight polymers.⁶ Combination of inorganic and organic units in a polymer chain, i.e. an inorganic–organic hybrid polymer, is a relatively new approach to develop heat-resistant polymeric materials. One of the potential candidates would be a hybrid polymer containing silane and ethynyl with low molecular weight, and it is believed that the flexibility of silicon–carbon bond renders good processability for the resin. So many scientists have paid

Correspondence to: T. Zhao (tzhao@iccas.ac.cn).

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attention to introduce silicon to carbon backbone, to prepare novel high performance thermosetting resins.^{7–10} For example poly(phenylsilyleneethynylene-1,3-phenyleneethynylene) (MSP)⁷ and poly{[bis(diethynylphenyl)silylene]phenylene}s⁸ were synthesized and reported. The results showed that the polymer had an extremely high thermal stability after cured.

In this study, a novel ethynyl silicon-containing aromatic resin (ESA) was synthesized and characterized. It was designed as a kind of high aromatic thermosetting resins that have a broad processing window which can be easily polymerized. The processability, thermal cure property, and thermal stability were evaluated in detail.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone before use. Diphenyldichlorosilane was obtained from Alfa Aesar. *N*-butyl lithium (2.5M solution in *n*-hexane) was obtained from J&K chemical. All other chemicals were purchased from Beijing Chemical Reagent Company and used as received.

PAA resin was kindly provided by Aerospace Research Institute of Aerospace Materials and Processing Technology, China Aerospace Science and Technology. PAA (Fig. 1) resin is a kind of high performance addition curable resin made up of nonpolar ethynyl aromatic hydrocarbons, such as *m*-diethynylbenzene, *p*-diethynylbenzene and their prepolymers (30%), which can be cured to a highly cross-linked aromatic polymer that contains only carbon and hydrogen by means of addition polymerization without any elimination of low molecules.

Instruments

The resin and compounds were characterized by the techniques of FTIR, NMR, gel permeation chromatography (GPC), and Mass spectra. FTIR was recorded on IR spectrometer 4000 (Perkin-Elmer, US) in the wave number range of 4000–400 cm^{-1} using standard procedures. In all cases, 32 scans at a resolution of 4 cm^{-1} were used to record the spectra. ¹H-NMR spectra were recorded at room temperature on Bruker AV400 spectrometer using DMSO-*d*₆ as solvent and TMS as internal standard. The following conditions were used: data points, 65,536; sweep width, 11,990.407 Hz; acquisition time, 2.73 sec; relaxation delay, 2 sec. ²⁹Si-NMR spectra was recorded at room temperature on a Bruker WM 300 spectrometer using DMSO as solvent. The following conditions were used: data points, 65,536; sweep width, 23,809.523 Hz; acquisition time,

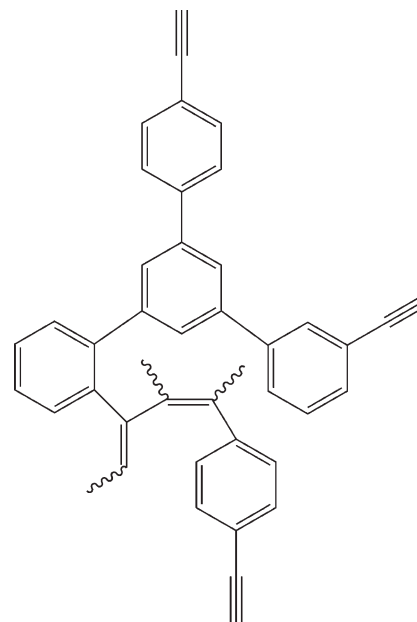


Figure 1 Molecular structures of the PAA resin.

1.38 sec; relaxation delay, 2 sec. GPC analysis was done on waters (515 HPLC pump, 2410 refractive index detector) using THF as eluent and polyethylene glycol as standards for calibration. Mass spectra were recorded on an AEI MS-50 mass spectrometer. The characteristics of thermal cure were monitored by DSC technique using Mettler-toledo DSC822^e at a heating rate of 10°C/min under nitrogen atmosphere. Thermal stability was evaluated by TGA on STA409pc (Netzsch, Germany) at a heating rate of 10°C/min. Rheological experiments were carried out on a TA Instruments AD2000 rheometer with a 25-mm diameter parallel-plate fixture from R.T. to 160°C at a heating rate of 3°C/min.

Synthesis of 1,3,5-tri(4-bromophenyl)benzene (1)¹¹

This compound was prepared in an analogous manner to the literature procedure with some modifications. SiCl_4 (100 mL, 0.87 mol) was added slowly by syringe to a stirred solution of 4-bromoacetophenone (50 g, 0.25 mol) in dry ethanol (500 mL). The mixture was stirred for 12 h at room temperature to give a yellow mixture containing large amount of precipitates, then poured into water and filtered. The precipitate was washed with ethanol until only one product spot could be detected by TLC, and dried in a vacuum stove at 100°C for 4 h to give 37 g (yield 82%).

MS (EI, *m/z*): 544, 542 (M^+ , 100%). Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{Br}_3$: C, 53.07%; H, 2.78%; Br, 44.14%. Found: C, 53.48%; H, 3.08%; Br, 43.66%.

Synthesis of 1,3,5-tris-(4-ethynylphenyl)benzene (3)¹²

A 1000 mL three-necked round-bottomed flask equipped with a reflux condenser, nitrogen inlet, and calcium chloride guard tube was charged with 800 mL of triethylamine, triphenylphosphine (840 mg, 3.2 mmol), copper iodide (624 mg, 3.28 mmol), 1,3,5-Tri(4-bromophenyl)benzene (22 g, 40.5 mmol), and 2-methyl-3-butyn-2-ol (27.78 g, 330.7 mmol) under magnetic stirring. Nitrogen was then bubbled through this stirred mixture for 20 min. Dichlorobis(triphenylphosphine)palladium(II) (1152 mg, 1.64 mmol) was then added under a flow of nitrogen. The mixture was heated with stirring at 110°C (bath temperature) under a slow flow of nitrogen for 12 h. The reaction mixture was allowed to cool to room temperature, and was filtered to remove insoluble salts (triethylamine hydrobromide) formed during the reaction. The filtrate was diluted with 400 mL of ethyl acetate and washed with distilled water (3 × 200 mL) and dried over anhydrous magnesium sulfate. The organic solvents were removed under reduced pressure on a rotary evaporator and the residue was recrystallized from toluene as colorless needles in 90% yield (20.1 g), which was characterized to be 1,3,5-tris-[4-(3-hydroxy-3-methyl-but-1-ynyl)phenyl]benzene.⁽²⁾

1,3,5-tris-[4-(3-hydroxy-3-methyl-but-1-ynyl)phenyl]benzene (8 g, 14.5 mmol) was dissolved in 120 mL of toluene in a single-necked, 250 mL round-bottomed flask. Potassium hydroxide (3.36 g, 60 mmol) dissolved in 24 mL of anhydrous methanol was added and a Dean-Stark trap fitted with a reflux condenser was attached. The mixture was heated at 120°C (bath temperature) for 3 h and about 40 mL of a toluene-methanol-acetone mixture was collected at that time. The reaction mixture was cooled to room temperature, washed with water (3 × 1600 mL), and dried over magnesium sulfate and the toluene was removed on a rotary evaporator to give 8 g of 1,3,5-tris-(4-ethynylphenyl)benzene (yield 58%).

FTIR (KBr, cm^{-1}): 3286, 2950, 2108. ¹H-NMR (DMSO- d_6 , ppm): 7.2–8.0 (multi, aromatic protons, 5H), 4.3 (single, ethynyl protons, 1H). Anal. Calcd for $\text{C}_{30}\text{H}_{18}$: C, 95.24%; H, 4.76%. Found: C, 94.65%; H, 4.83%.

Synthesis of ESA resin (4)

A N_2 flushed 100 mL three-necked reaction vessel equipped with a reflux condenser, an addition funnel, and a stirring motor was charged with 1,3,5-tris-(4-ethynylphenyl)benzene (0.945 g, 2.5 mmol) and dry THF (15 mL). The solution was cooled to -30°C , then 2 mL *n*-BuLi (5 mmol, 2.5M in hexane) was added dropwise over 50 min, and the mixture turned green. The solution was then stirred for

another 3 h. Subsequently diphenyldichlorosilane (0.6325 g, 2.5 mmol) was added slowly over 30 min, and the reaction solution turned yellow and transparent. The reaction was allowed to warm to room temperature and kept stirring for another 12 h. The product was extracted with toluene-water system, washed with water, dried over MgSO_4 , and evaporated in vacuum to give 1.2 g pale yellowish solid (yield 86%).

FTIR (KBr, cm^{-1}): 3290, 3046, 2156, 2106, 1595. ¹H-NMR (DMSO- d_6 , ppm): 7.2–8.0 (broad, aromatic protons, 23H), 4.3 (single, ethynyl protons, 1H). ²⁹Si-NMR (THF, ppm): -48.05 ($\text{C}\equiv\text{C}-\text{SiPh}_2-\text{C}\equiv\text{C}$)

Thermal cure

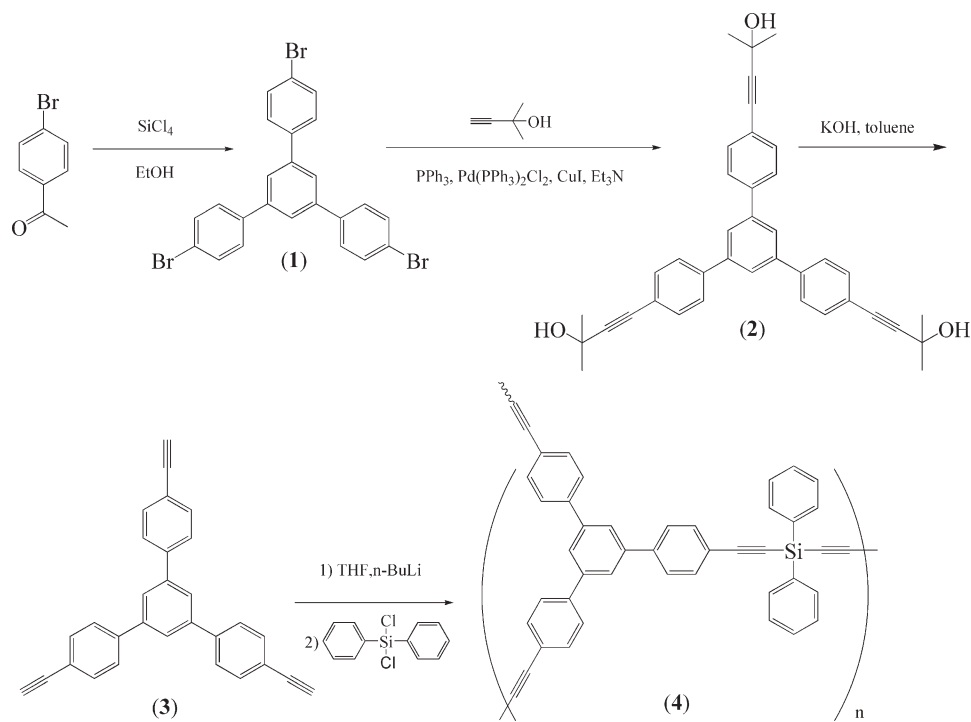
The ESA resin was thermally cured by heating in an electric oven in air atmosphere according to the following schedule: 120°C, 1 h/160°C, 1 h/180°C, 1 h/200°C, 1 h/220°C, 4 h.

RESULTS AND DISCUSSION

Synthesis and structure characterization of ESA resin

The parent monomer 1,3,5-tri(4-bromophenyl)benzene (1) was prepared by acid-catalyzed condensation of 4-bromoacetophenone, then the 1,3,5-tri(4-bromophenyl)benzene (1) was treated with 2-methyl-3-butyn-2-ol in refluxing triethylamine, the reaction being catalyzed by dichlorobis(triphenylphosphine)palladium and copper iodide together with triphenylphosphine. The protecting group was removed by heating under reflux, a solution in toluene together with KOH, the acetone formed being distilled out. The 1,3,5-tris-(4-ethynylphenyl)benzene (3) was white crystal, and it did not melt before cure temperature. Microanalysis showed 1,3,5-tris-(4-ethynylphenyl)benzene (3) to be essentially free of Br-terminated material.

The methods for the synthesis of multiple ethynylsilanes reported so far include three types of reactions: the Grignard reaction, the reaction of lithium acetylide, and the reaction of sodium acetylide. The ESA resin was prepared by the condensation polymerization of 1,3,5-tris-(4-ethynylphenyl)benzene lithium and chlorosilane. (Scheme 1) The acetylene was easily lithiated to form corresponding carbon ions with enough reactivity to react with Si–Cl bond. It was believed that the flexibility of silicon–carbon bond rendered the character of viscous fluid and favorable processing properties of ESA resin. As expected, the formed oligomer turned into a brown fluid with good mobility, when it was heated to 120°C.



Scheme 1 Synthetic protocol for the ESA resin.

The GPC curves of the ESA resin and monomer **3** as comparison were shown in Figure 2. The ESA resin exhibited six peaks with different relative intensities in the retention time range of 21–30 min located at about 23, 23.5, 24, 25, 27, and 29 min. The retention time at 29 min was monomer **3**. The high molar mass products appeared as separated peaks were expected to be dimer, trimer, and other high polymerization degree oligomers, which were combined by silicon. The resin had a molecular weight (M_w) about 1588 and a polydispersity of 2.2.

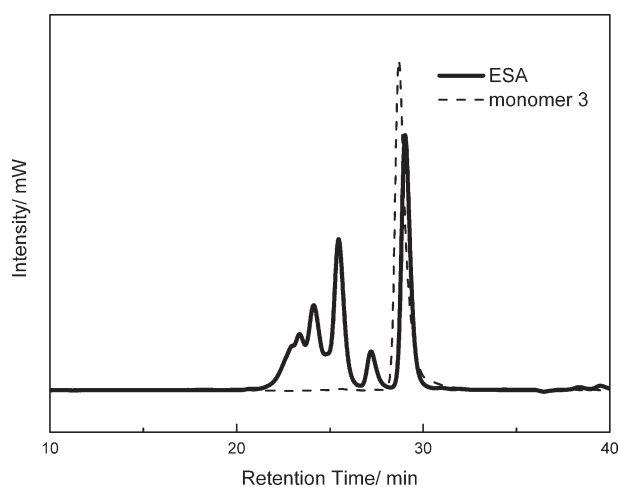


Figure 2 GPC profiles of the ESA resin together with the starting monomer **3** (THF eluent, PS standard).

The structure of the ESA resin could be elucidated by its $^1\text{H-NMR}$ spectrum (Fig. 3). There were only two kinds of signals that belong to the ESA resin in the spectrum. The multiple signals at regions 7.2–8.0 for Ph-H and 4.3 for $\text{C}\equiv\text{C-H}$, and their ratio was 22.6 : 1, which meant that the resin was a complex mixture and the $\text{C}\equiv\text{C-H}$ reduced with the condensation polymerization of 1,3,5-tris-(4-ethynylphenyl)benzene lithium and chlorosilane. (The monomer **3**'s ratio was 5.4 : 1). There was only one kind of signal

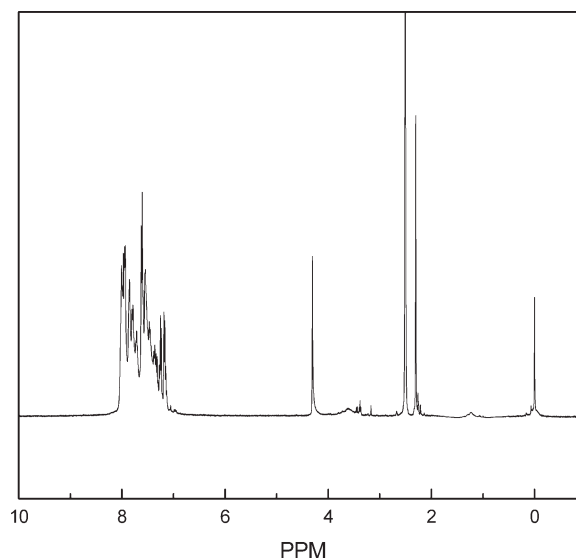


Figure 3 $^1\text{H-NMR}$ spectrum of the ESA resin.

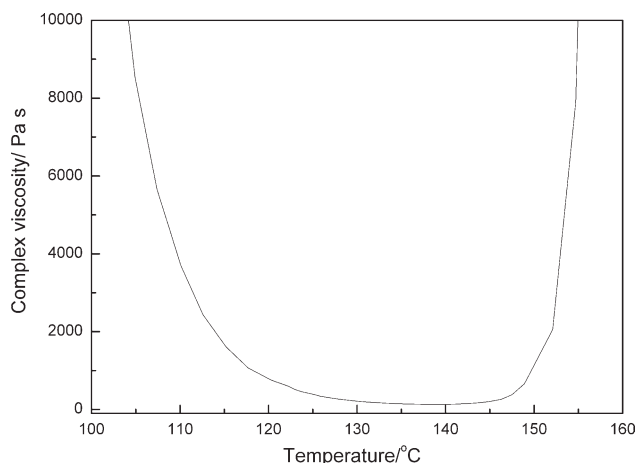


Figure 4 Viscosity-temperature relationship of the ESA resin.

at -48 for Si-Ph in ^{29}Si -NMR, which indicated the complete reaction of lithide and chlorosilane.

FTIR (Fig. 6) confirmed the molecular structure of ESA resin, with $\text{C}-\text{C}\equiv\text{C}-\text{C}$ triple bond stretching at 2106 cm^{-1} , $\text{C}-\text{C}\equiv\text{C}-\text{Si}$ triple bond stretching at 2156 cm^{-1} , $\equiv\text{C}-\text{H}$ stretching at 3286 cm^{-1} and $\text{Si}-\text{C}$ stretching at 1260 cm^{-1} .

Furthermore, the data of the MS and elemental analyses mentioned in experimental section coincide with the analysis results from GPC, ^1H -NMR, and FTIR spectra, in other words, from the above results we can conclude that it was prepared for a novel thermosetting ethynyl resin of silicon hybridized aromatics.

Processability and thermal cure properties of ESA resin

The melt viscosity of ESA resin was shown in Figure 4. The viscosity was low enough for melt

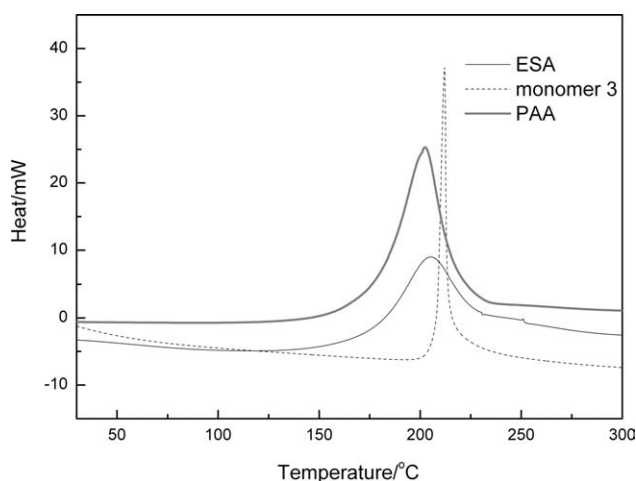


Figure 5 DSC profiles of the ESA resin, PAA resin and monomer 3 (N_2 , $10^\circ\text{C}/\text{min}$).

TABLE I
Characteristic Parameters of Thermal Cure (by DSC) of the ESA, PAA resins, and Monomer 3

	$T_{\text{onset}}(^{\circ}\text{C})^{\text{a}}$	$T_{\text{peak}}(^{\circ}\text{C})^{\text{b}}$	$T_{\text{endset}}(^{\circ}\text{C})^{\text{c}}$	$\Delta H(\text{J/g})$
Monomer 3	206	210	212	760
PAA resin	179	203	218	1031
ESA resin	178	207	243	319

^a Onset temperature of the exothermic peak.

^b Peak temperature of the exothermic peak.

^c Endset temperature of the exothermic peak.

prepreg preparation (lower than 400 Pa s between $120\text{--}160^\circ\text{C}$). Furthermore, the ESA resin could dissolve in a variety of solvents such as THF, toluene, acetone, butanone, and chloroform, etc., which means it would be easier to be processed in solution prepreg.

The cure behaviors of the ESA resin were traced by DSC technique. Figure 5 showed the typical DSC curve of the ESA resin, and PAA resin, monomer 3 were also given as comparison (Table 1). The ESA resin had an exothermic transition attributable to acetylene polymerization reaction peaking at approximate 200°C . In comparison to PAA resin, which cure enthalpy is 1031 J/g , the cure enthalpy of ESA resin was only 319 J/g . The low enthalpy was sometimes important and favorable to the control of heat release during the processability of the resin. While the DSC curve of monomer 3 showed that there was a single exothermic peak located at a narrow temperature range of $200\text{--}230^\circ\text{C}$. The monomer 3 was white crystal and the cured monomer 3 has a very high char yield *ca* 90% , but the monomer 3 did not melt before cure temperature that means it's hard to be processed. Upon heating, the ESA resin melted and gradually turned black and solidified above

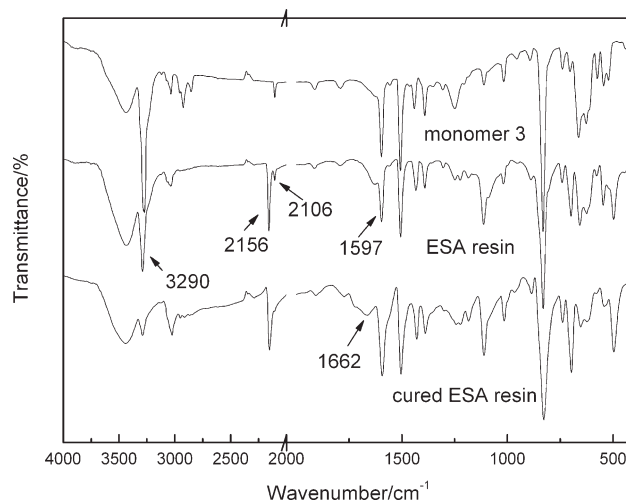


Figure 6 FTIR spectra of the ESA resin and its cured material.

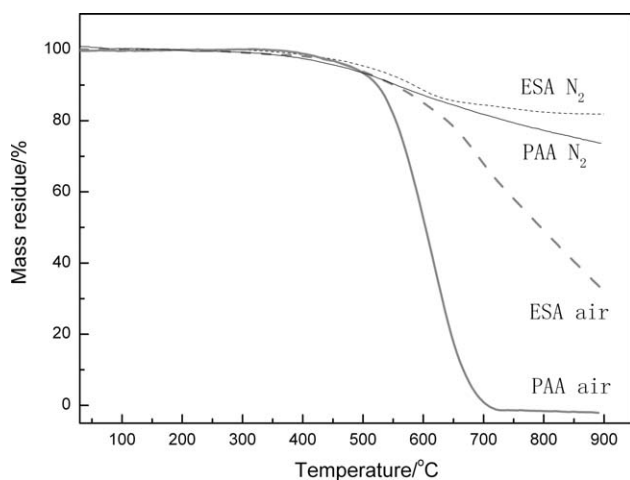


Figure 7 TGA curves of the cured ESA resin and cured PAA resin (N₂, 10°C/min; air, 10°C/min).

200°C. After DSC measurement, the sticky ESA resin formed a black dense brittle solid.

FTIR spectra (Fig. 6) of the ESA resin and cured resin showed the weakening of the acetylenic stretching band at 3290 cm⁻¹ (≡C–H stretch) and strengthening in the relative intensities of the absorption at 1662 cm⁻¹ (C=C stretch). This was due to addition polymerization of ethynyl groups during thermal cure.

The polymerization reactions in the thermal cure of ESA resin seemed to be very complex, and the exact mechanism is not elucidated owing to the lack of powerful techniques for such thermosetting resins. Many previous studies, based on the analysis of compounds formed during thermal polymerization of monofunctional model compounds confirmed that low molar mass species are formed initially by ways of Strauss coupling, Glaser coupling and diene-diene dimers. In the second stage, species with higher molar mass are formed by chained conjugated dienes.¹³ The ESA resin, as a kind of acetylene-functional resin, was expected to cure in a similar way.

Thermal stability

Figure 7 shows the TGA profiles for the cured ESA resin with the cured PAA resin for a comparison. For the ESA resin there was very little weight loss in thermal cracking under N₂ below 500°C, and most of the weight loss occurred between 500–700°C, attributing to carbon–carbon and silicon–carbon cleavages. *T*_{d5} of the cured ESA resin was 510°C and the char yield at 900°C was 80% under N₂. It should be pointed out that the char yield of ESA resin at 900°C under nitrogen did not show a significant difference

from that of the PAA resin. But differences were observed under air. While the cured PAA resin completely decomposed with 0% char yield at 900°C, the ESA resin showed a residue of 31.6% at 900°C, demonstrating the importance of silicon in the resin for oxidative stability. Char yield is correlated to the polymer's flame retardancy.¹⁴ Therefore the ESA resin was expected to have good flame retardant properties.

CONCLUSIONS

A novel ESA was prepared by the condensation reaction between diphenyldichlorosilane and lithium arylacetylide. The ESA resin possessed good processability, whose viscosity was low enough for melt processing and it could dissolve in common solvents such as THF. The cure reaction of this resin occurred above 150°C, and a peak with low exothermal heat at 220°C was observed in DSC curve. The decomposition temperature *T*_{d5} of the cured resin were at 483°C and 510°C in air and nitrogen; meanwhile, the residue yields at 900°C were 31.6% and 82.9% under air and nitrogen, respectively. The ESA resin is an ideal candidate for matrices of high performance composite materials.

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