Introduction

Polyarylacetylene (PAA) was first synthesized by Hay and co-workers as a family of high-temperature polymers.1-3 PAA is a prepolymer or oligomer, which is derived from diethynylbenzene and possesses excellent properties such as low dielectric constant, low moisture pickup, and high thermal stability. Unfortunately, PAA suffers from problems such as poor process control, low mechanical properties, and the susceptibility to decomposition at elevated temperatures in oxidative environments.

To improve the processability, mechanical properties, and thermo-oxidative stability, more attention has been focused on the modifications of PAA.4-13 Itoh and coworkers have developed a silicon-containing polyarylacetylene.4 The silicon-containing polyarylacetylene, poly[(phenylsilyleneethynylene-1,3-phenyleneethynylene)] (named MSP), was synthesized by dehydrogenative coupling polymerization reactions between phenylsilane and $m$-diethynylbenzene. The cured MSP possesses high decomposition temperature and high residual yield at 1000 °C. Several reports concerning MSP have been published. The potential applications of the MSP materials are considered as composite materials, ceramic materials, and electronic materials.4,5 In 2001, phenylacetylene terminated poly(silyleneethynylenephenyleneethynylene) oligomers abbreviated as BLJ were synthesized by the condensation reaction between dichlorosilane and a mixture of diethynylbenzene and phenyl acetylene magnesium reagents.6 This BLJ resin is an easily processable polymer and cured at elevated temperature to form a crosslinked polymer with high heat resistance and high char yield.

It is well known that siloxane-containing polymers possess some unique properties, including good flexibility, high heat resistance, excellent moisture resistance, and good electrical properties.14,15 Recently, several investigations have been conducted on polymers containing siloxane and acetylene units.16-24 For example, Keller17 and coworkers reported the preparation of linear siloxane-diacetylene polymers by reacting dichlorosiloxanes with dilithiodiacetylene. These linear siloxane-diacylene polymers show excellent thermal and thermo-oxidative stabilities. Beckham21 and coworkers have also reported the synthesis of diacetylene-containing poly(dimethylsiloxane)s. However, there are few reports on the incorporation of dimethylsiloxane units into the polyarylacetylene backbone.25,26

In this report, we have designed and prepared a series of arylacetylene resins with various dimethylsiloxane unit lengths. The resins were characterized by FT-IR, NMR, GPC, DSC, and TGA techniques. The relationship between the structures and properties of the resins was investigated.

Experimental

Materials. Unless otherwise noted, all syntheses were performed under an atmosphere of dry nitrogen. Hexane, tetrahydrofuran (THF), carbon tetrachloride (CCl₄), ethyl bromide (EtBr), ethyl ether, dimethylchlorosilane, palladium dichloride (PdCl₂), silica gel, magnesium powder, and phosphorus pentoxide (P₂O₅) were purchased from Sinopharm Chemical Reagent Co. Ltd. Tetrahydrofuran (THF) was refluxed over sodium with benzophenone and freshly distilled in nitrogen before use. Carbon tetrachloride (CCl₄) was distilled over P₂O₅. Dimethylchlorosilane and ethyl bromide were distilled before use. Dimethylchlorosilane and 1,1,3,3-tetramethyldisiloxane (TMDS) were purchased from Shanghai Sili Gongmao Co. Ltd. and used as received. Octamethylcyclotetrasiloxane (D₄) was purchased from Shanghai Hua Run Chemicals Co. Ltd. and used
as received. \textit{1,1,3,3,5,5,7,7,7-Octamethyltetrasiloxane} (OMTS), \textit{1,1,3,3,5,5,7,7,9,9,11,11-Dodecamethylhexaosiloxane} (DMHS), \textit{1,3-dichlorotetramethyldisiloxane} (DCDTS), \textit{1,5-dichlorohexamethyltrisiloxane} (DCHMTS), and \textit{1,11-dichlorododecamethylhexasiloxane} (DCDMHS) were synthesized according to procedures described in the literatures.\textsuperscript{27-32} \textit{m-Diethynylbenzene} was supplied by Fine Chemical Institute of East China University of Science and Technology and used as received.

\textbf{Characterization.} \textit{1H NMR, 13C NMR, and 29Si NMR} spectra were performed on a BRUKER AVANCE 500 (500Mz) instrument, using tetramethylsilane (TMS) as an external standard in a CDCl$_3$ solution. Fourier transform infrared (FT-IR) spectra were performed on a BRUKER AVANCE 500 (500Mz) instrument, using teramethylsilane (TMS) as an external standard in aqueous) at 0 °C. The resulting two-phase mixture was transferred to a 500-mL separatory funnel and extracted three times with 75 mL each of toluene. The toluene extracts were combined and washed with deionized water until pH of the washed water was neutral. The dark organic phase was poured into a round-bottomed flask and dried over anhydrous Na$_2$SO$_4$. Filtration into a round-bottomed flask was followed by rotary evaporation and then exposure to reduced pressure at room temperature for 5 h. The resin I was obtained in 93\% yield as a brown viscous liquid. FTIR (KBr, cm$^{-1}$) 3297 (C=O-C), 3068 (Ar-H), 2962 (-CH$_3$), 2156 (C=C), 1257 (Si-CH$_3$), 1028-1081 (Si-O-Si), 784-848 (Si-C). \textit{1H NMR} (CDCl$_3$, $\delta$ ppm) 0.38 (Si-CH$_3$), 3.07 (C=O-C), 7.20-7.58 (Ar-H). \textit{13C NMR} (CDCl$_3$, $\delta$ ppm) 2.82 (Si-CH$_3$), 78.7, 83.3 (-C=O-C), 94.8, 103.8 (Si-C=O-C), 123.8, 129.0, 132.8, 136.1 (C=H). \textit{29Si NMR} (CDCl$_3$, $\delta$ ppm) -16.3 (O-Si-C=O-C), respectively.

The resins II-IV were prepared in a similar procedure except for using DCHMTS, DCOMTS, and DCDMHS instead of DCTMDS, respectively.

Resin II was obtained in 91\% yield as a brown viscous liquid. FTIR (KBr, cm$^{-1}$) 3301 (C=O-C), 3068 (Ar-H), 2967 (-CH$_3$), 2156 (C=C), 1258 (Si-CH$_3$), 1018-1105 (Si-O-Si), 780-847 (Si-C). \textit{1H NMR} (CDCl$_3$, $\delta$ ppm) 0.17-0.39 (Si-CH$_3$), 3.07 (C=O-C), 7.20-7.58 (Ar-H). \textit{13C NMR} (CDCl$_3$, $\delta$ ppm) 1.72, 2.82 (Si-CH$_3$), 78.5, 83.7 (-C=O-C), 94.9, 103.4 (Si-C=O-C), 123.7, 129.7, 132.6, 136.3 (C=H). \textit{29Si NMR} (CDCl$_3$, $\delta$ ppm) -16.3 (O-Si-O-Si-C=O-C), -18.6 ~ -19.2 (O-Si-O-Si-O-Si-C=O-C).

Resin III was obtained in 92\% yield as an orange viscous liquid. FTIR (KBr, cm$^{-1}$) 3301 (C=O-C), 3068 (Ar-H), 2967 (-CH$_3$), 2156 (C=C), 1258 (Si-CH$_3$), 1008-1116 (Si-O-Si), 790-850 (Si-C). \textit{1H NMR} (CDCl$_3$, $\delta$ ppm) 0.08-0.37 (Si-CH$_3$), 3.09 (C=O-C), 7.40-7.60 (Ar-H). \textit{13C NMR} (CDCl$_3$, $\delta$ ppm) 1.73, 2.82 (Si-CH$_3$), 77.9, 83.2 (-C=O-C), 94.9, 103.7 (Si-C=O-C), 123.7, 128.9, 132.7, 136.2 (C=H). \textit{29Si NMR} (CDCl$_3$, $\delta$ ppm) -16.3 (O-Si-O-Si-C=O-C), -18.6 ~ -19.5 (O-Si-O-Si-O-Si-C=O-C), -21.4 (O-Si-O).

Resin IV was obtained in 90% yield as an orange liquid. FTIR (KBr, cm$^{-1}$) 3303 (C=O-C), 3068 (Ar-H), 2967 (-CH$_3$), 2156 (C=C), 1259 (Si-CH$_3$), 1008-1130 (Si-O-Si), 775-872 (Si-C). \textit{1H NMR} (CDCl$_3$, $\delta$ ppm) 0.07-0.38 (Si-CH$_3$), 3.07 (C=O-C), 7.20-7.58 (Ar-H). \textit{13C NMR} (CDCl$_3$, $\delta$ ppm) 1.74, 2.85 (Si-CH$_3$), 78.7, 83.6 (-C=O-C), 95.8, 103.8 (Si-C=O-C), 123.6, 129.1, 132.6, 136.2 (C=H). \textit{29Si NMR} (CDCl$_3$, $\delta$ ppm) -16.3 (O-Si-O-Si-C=O-C), -18.6 ~ -19.5 (O-Si-O-Si-C=O-C), -21.4 (O-Si-O).

\textbf{Thermal curing of the resins.} Prior to cure, the resins I-IV were degassed at 100 °C/15 mmHg. The resins I-IV were thermally cured according to the procedure: 2 h at 150 °C, 170 °C, 210 °C, 250 °C, and 300 °C, respectively. Thereafter, the resins were allowed to cool slowly to room temperature. Shiny void-free and dark cured resins L$_n$-IV$_n$ were obtained.

\textbf{Thermal pyrolysis of the cured resins.} The cured resins L$_n$-IV$_n$ were weighed in an alumina crucible and placed into tube furnace. After three purges of argon, the cured resins were heated under argon according to the procedure: 2 h at 400 °C, 600 °C, 800 °C, 1000 °C, 1200 °C, and 1450 °C, respectively, and then cooled to room temperature. Hard and black ceramics L$_n$-IV$_n$ were obtained.

\textbf{Results and Discussion}

\textbf{Synthesis and characterization of the resins.} The synthesis reactions of arylacetylene resins with siloxane units I-IV are
shown in Scheme 1. The resins with various siloxane units length were synthesized by the reactions of the bismagnesium derivative of \( m \)-diethynylbenzene with various \( \alpha,\omega \)-bis(chloro)dimethylsiloxanes. The synthetic yields of the resins I-IV are higher than 92%. The GPC measurement shows the resins have the number-average molecular weight between 747 and 1630, and the polydispersity index between 1.64 and 2.11.

Figure 1 shows FT-IR spectra of resins I-IV. All resins are featured by absorptions at 3300 cm\(^{-1}\) (\( \equiv \)C-H), 3068 cm\(^{-1}\) (Ar-H), 2156 cm\(^{-1}\) (C=\( \equiv \)C), 1258 cm\(^{-1}\) (Si-CH\(_3\)), 1008 - 1130 cm\(^{-1}\) (Si-O-Si), and 770 - 850 cm\(^{-1}\) (Si-C). The intensity of the Si-O stretching at 1000 - 1100 cm\(^{-1}\) of the resins increases with the increase in the length of the siloxane units. As for \(^1\)H NMR analysis of the resins, the dimethylsiloxy protons by peak resonances with chemical shift are observed in the 0.07 - 0.38 ppm range and the protons of the terminal acetylene groups by peak resonances with chemical shift appear at 3.07 ppm. In addition, the aromatic hydrogens by peak resonances with chemical shifts resonate in the 7.20 - 7.58 ppm range. The \(^{13}\)C NMR spectrum confirms aromatic carbons by peak resonances with chemical shifts in the 123.7 - 136.1 ppm range. The internal acetylenic carbons appear as a pair of peak resonances at 94.8 ppm and 103.8 ppm when attached to silicon atom and aromatic ring, respectively. The terminal acetylenic carbons appear as a pair of peak resonances at 78.7 ppm and 83.3 ppm. In addition, dimethylsiloxio carbons by peak resonances with chemical shifts are observed at 2.82 ppm. The \(^{29}\)Si NMR resonances for each Si nuclei [O-Si-C=\( \equiv \)C- at ~ -16.3 ppm, O-Si-O-Si-C=\( \equiv \)C- in the range from ~ -18.6 ppm to ~ -19.5 ppm, and O-Si-O at ~ -21.4 ppm] appear. The characterization by \(^1\)H NMR, \(^{13}\)C NMR and \(^{29}\)Si NMR confirms that the resins have the expected chemical structures as shown in Scheme 1.

**Miscibility of the resins.** The miscibility of the resins I-IV was investigated in various organic solvents. The resins I-IV are miscible with common organic solvents such as benzene, toluene, chloroform, THF, acetone, butanone, and dimethylformamide (DMF) at room temperature. However, the resins I-IV are immiscible in petroleum ether and methanol at room temperature. The good miscibility of the resins I-IV is probably due to the effect of the siloxane units in the main chain.

**Thermal behavior of the resins.** Figure 2 shows the DSC curves of the resins I-IV at a heating rate of 10 °C/min in the temperature range from 100 to 350 °C in N\(_2\). It is observed that the resins I-IV show a similar curing behavior. As shown in Figure 2, there are sharp exotherms for the resins in the temperature range from 150 to 300 °C. The temperatures at peak top for the resins I-IV are 256, 261, 267, and 270 °C, respectively. The enthalpies of the resins I-IV are 367.3, 225.1, 176.9 and 142.3 J/g, respectively. These exotherms are attributed to the crosslinking reaction of the ethynyl and ethynylene groups. As shown in Figure 2, the reactions take place at the temperature above 150 °C. The peak temperatures top and peak width increase from the resin I to IV with the increase in the length of siloxane units. This indicates that the reactivity of the resins reduces with the increase in the length of siloxane units. Small broad exotherms in the high temperature range are also observed and are attributed to the reaction of ethynylene groups.

**Thermal and thermooxidative stabilities of the cured resins.** The thermal stabilities of the cured resins I\(_c\)-IV\(_c\) were determined by thermogravimetric analysis (TGA) in N\(_2\) and air up to 1000 °C. Figure 3 shows the TGA curves of the cured resins I\(_c\)-IV\(_c\) in N\(_2\) at a heating rate of 10 °C/min. The cured resins I\(_c\)-IV\(_c\) have high onset degradation temperatures ranging from 483 to 510 °C. The cured resins I\(_c\)-IV\(_c\) are high in the N\(_2\) and air up to 1000 °C.
The degradation temperatures at 5% weight loss for the cured resins Ic-IVc are 602, 550, 532, and 505 °C, respectively. The residue yields at 1000 °C for the cured resins Ic-IVc are 86, 85, 81, and 72%, respectively. As the length of the siloxane units increases, the degradation temperatures and the residue yields at 1000 °C for the cured resins Ic-IVc decrease. This is consistent with reported trends that the increase in the siloxane units length leads to decrease the thermal stability of thermosets derived siloxane-containing polymers. The high thermal stability results from the highly crosslinked structures. As the length of the siloxane unit increases, the crosslinking density of the cured resins decreases. Therefore, the thermal stability of the cured resins Ic-IVc decreases with the increase in the length of siloxane units.

The thermooxidative stability of the cured resins Ic-IVc were determined by thermogravimetric analysis (TGA) in air up to 1000 °C. Figure 4 shows the TGA curves of the cured resins Ic-IVc in air. As expected, the stability in air is generally less than the corresponding stability in N₂. The decomposition temperatures at 5% weight loss for the cured resins Ic-IVc are 548, 535, 522, and 514 °C, respectively. The residue yields at 1000 °C for the cured resins Ic-IVc are 36, 45, 47, and 49%, respectively. As the length of the siloxane units increases, the decomposition temperatures decrease whereas the residue yields at 1000 °C increase for the cured resins Ic-IVc. Unusual change in the residue yields for the cured resins Ic-IVc in air could be probably attributed to the content of siloxane units in the resins.

Characterization of the ceramics. Figure 5 shows the X-ray diffraction spectra of the ceramics Ic-IVc obtained from the cured resins Ic-IVc pyrolyzed at 1450 °C under argon. All the diffraction peaks have been identified and indexed on the basis of free carbon, β-SiC, and SiO₂. The peak at 2θ angle of 21.86 degree is attributed to free carbon. The peaks at 2θ angle of 35.54, 60.42, and 71.8 degrees are attributed to β-SiC. The peak at 2θ angle of 43.60 degree is attributed to SiO₂. The ceramics Ic-IVc are composed of free carbon, β-SiC, and SiO₂. The FT-IR spectra of the ceramics show two major peaks: one at 1100 cm⁻¹ attributed to Si-O-Si stretching mode, another at about 830 cm⁻¹ assigned to Si-C stretching (pure crystalline SiC at 850 cm⁻¹). The FT-IR analyses of the ceramics illustrate that SiC and SiO₂ exist in the ceramics, which is in agreement with the XRD analysis results of these ceramics.

The thermooxidative stability of the ceramics Ic-IVc were determined by thermogravimetric analysis (TGA) in air up to 1000 °C. Figure 6 shows the TGA curves of the ceramics Ic-IVc in air at the heating rate of 10 °C/min. As shown in the Figure 6, there is a one-step decomposition process. The ceramics Ic-IVc have high onset decomposition temperatures. The decomposition temperatures at 5% weight loss are 842, 852, 804, and
861 °C, respectively. The residue yields at 1000 °C for the ceramics \( \text{Ic} - \text{IVc} \) are 86, 87, 83, and 89%, respectively. The good thermooxidative stability for the ceramics is probably attributed to the synergistic effects of \( \beta \)-SiC and \( \text{SiO}_2 \) in the SiOC ceramics.

**Conclusions**

A series of arylacetylene resins with various siloxane unit lengths have been synthesized and characterized. The resulted resins are liquids and miscible with common organic solvents at room temperature. These resins exhibit good processing capability. At elevated temperatures, these resins can be thermally transformed into highly crosslinked structures. TGA results show that the cured resins have high thermal and thermooxidative stability. With the increase in the length of siloxane units, the decomposition temperatures at 5% weight loss for the cured resins decrease from 602 to 505 °C, and the residue yields at 1000 °C decrease from 85 to 72% in \( \text{N}_2 \). By contrast, the decomposition temperatures at 5% weight loss for the cured resins decrease from 535 to 514 °C, and the residue yields at 1000 °C decrease from 85 to 72% in \( \text{N}_2 \). At elevated temperatures, these resins can be thermally transformed into highly crosslinked structures. TGA results show that the cured resins have high thermal and thermooxidative stability. With the increase in the length of siloxane units, the decomposition temperatures at 5% weight loss for the cured resins decrease from 602 to 505 °C, and the residue yields at 1000 °C decrease from 85 to 72% in \( \text{N}_2 \). By contrast, the decomposition temperatures at 5% weight loss for the cured resins decrease from 535 to 514 °C, and the residue yields at 1000 °C decrease from 85 to 72% in \( \text{N}_2 \).

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**References**