

Synthesis and Properties of Arylacetylene Resins with Siloxane Units

Fei Gao, Lingling Zhang, Leming Tang, Jian Zhang, Yan Zhou, Farong Huang,* and Lei Du

Key Laboratory for Specially Functional Polymeric Materials and Related Technology of the Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China. *E-mail: fhuanglab@ecust.edu.cn
Received October 23, 2009, Accepted December 15, 2009

A series of arylacetylene resins with siloxane units were synthesized by the condensation reactions of *m*-diethynylbenzene magnesium reagents with various α,ω -bis(chloro)dimethylsiloxanes. These resins are liquids and are miscible with common organic solvents at room temperature. The structures of the resins were characterized by FT-IR, ^1H NMR, ^{13}C NMR, ^{29}Si NMR, and gel permeation chromatography (GPC). The thermal behaviors of the resins were examined with differential scanning calorimetry (DSC). These resins have good processability. They can be thermally cross-linked through the ethynyl groups to produce cured resins. The thermal and thermooxidative stabilities of the cured resins were studied by thermogravimetric analysis (TGA). The cured resins possess high thermal and thermooxidative stability. Their decomposition occurs at above 500 °C in both N_2 and air. With increasing the length of siloxane units in the resins, the thermal stability of the cured resins decreases in N_2 . When the cured resins were sintered above 1450 °C under argon, hard and glassy SiOC ceramics were obtained. These SiOC ceramics have the decomposition temperatures at 5% weight loss above 800 °C in air.

Key Words: Arylacetylene resin with siloxane units, Diethynylbenzene, Siloxane, Organic-inorganic polymer, Ceramic

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 thermooxidative 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 residue 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.⁴⁻⁷ In 2001, phenylacetylene terminated poly(silyleneethynylene)phenyleneethynylene oligomers abbreviated as BLJ were synthesized by the condensation reaction between dichlorosilane and a mixture of diethynylbenzene and phenyl acetylene magnesium reagents.⁸ 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-diacetylene polymers show excellent thermal and thermooxidative 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 (CCl_4), ethyl bromide (EtBr), ethyl ether, dimethyldichlorosilane, palladium dichloride (PdCl_2), silica gel, magnesium powder, and phosphorus pentoxide (P_2O_5) 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 (CCl_4) was distilled over P_2O_5 . Dimethyldichlorosilane 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 (D_4) was purchased from Shanghai Hua Run Chemicals Co. Ltd. and used

as received. 1,1,3,3,5,5-Hexamethyltrisiloxane (HMETS), 1,3-dihydroxytetramethyldisiloxane (DHTMDS), 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane (OMTS), 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethylhexasiloxane (DMHS), 1,3-dichlorotetramethyldisiloxane (DCTMDS), 1,5-dichlorohexamethyltrisiloxane (DC-HMETS), 1,7-dichloroocta methyltetrasiloxane (DCOMTS), and 1,11-dichlorododecamethylhexasiloxane (DCDMHS) were synthesized according to procedures described in the literatures.²⁷⁻³² *m*-Diethynylbenzene was supplied by Fine Chemical Institute of East China University of Science and Technology and used as received.

Characterization. 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 CDCl₃ solution. Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet 550 spectrometer. The molecular weights of the resins were determined by gel permeation chromatography (GPC) using a Waters GPC system equipped with a DAWN HELEOS static laser scattering detector and an Optilab Rex refractive index detector. GPC was performed using THF as an eluent at a flow rate of 1 mL/min. Differential scanning calorimetric analyses (DSC) were performed on a NETZSCH 200 PC module at the heating rate of 10 °C/min under nitrogen. Thermogravimetric analyses (TGA) were performed on a TA Instruments SDT Q600 analyzer. All thermal analyses were performed at the heating rate of 10 °C/min under nitrogen or air with the flow rate of 15 cm³/min. XRD spectrum was obtained on a Rigaku (Japan) D/max 2550 VB/PC diffractometer.

Synthesis of arylacetylene resins with siloxane units. A 250 mL roundbottomed flask was equipped with a dropping funnel, a reflux condenser, a three-way stopcock, and a mechanical stirring bar. The flask was then evacuated and back-filled three times with dry nitrogen. Magnesium powder (6.00 g, 0.25 mol) and anhydrous THF (100 mL) were transferred into the flask. The reaction flask was then immersed in an ice/water bath. While stirring, a solution of ethyl bromide (23.98 g, 0.22 mol) in 100 mL anhydrous THF was added dropwise over 40 min, forming a gray black solution. The ice/water bath was removed and the reaction mixture was heated to 45 °C with an oil bath with stirring over 1 h, resulting in the formation of a dark solution. The reaction flask was then cooled with an ice/water bath and a solution of *m*-diethynylbenzene (13.86 g, 0.11 mol) in anhydrous THF (100 mL) was added dropwise over 40 min. After complete addition, the ice/water bath was removed and the reaction mixture was heated to 65 °C with an oil bath with stirring over 1 h. The reaction mixture was thick slurry with a white precipitate. The flask was then cooled with an ice/water bath and a solution of DCTMDS (14.21 g, 0.07 mol) in anhydrous THF (100 mL) was added dropwise over 40 min. As the addition proceeded, the white precipitate of the organic magnesium reagent gradually disappeared. After complete addition, the ice/water bath was removed and the reaction mixture was heated to 75 °C with an oil bath. The reaction was allowed to proceed overnight at 75 °C. After cooling to room temperature, the reaction mixture was then poured into a 2% solution of hydrochloric acid (300 mL, 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 Na₂SO₄. Filtration into a roundbottomed 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≡C-H), 3068 (Ar-H), 2962 (-CH₃), 2156 (C≡C), 1257 (Si-CH₃), 1028-1081 (Si-O-Si), 784-848 (Si-C). ¹H NMR (CDCl₃, δ, ppm) 0.38 (Si-CH₃), 3.07 (C≡C-H), 7.20-7.58 (Ar-H). ¹³C NMR (CDCl₃, δ, ppm) 2.82 (Si-CH₃), 78.7, 83.3 (-C≡C-H), 94.8, 103.8 (Si-C≡C-), 123.8, 129.0, 132.8, 136.1 (C₆H₄). ²⁹Si NMR (CDCl₃, δ, ppm) -16.3 (O-Si-C≡C-).

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

Resin II was obtained in 91% yield as a brown viscous liquid. FTIR (KBr, cm⁻¹) 3299 (C≡C-H), 3068 (Ar-H), 2967 (-CH₃), 2156 (C≡C), 1258 (Si-CH₃), 1018-1105 (Si-O-Si), 780-847 (Si-C). ¹H NMR (CDCl₃, δ, ppm) 0.17-0.38 (Si-CH₃), 3.07 (C≡C-H), 7.20-7.58 (Ar-H). ¹³C NMR (CDCl₃, δ, ppm) 1.72, 2.82 (Si-CH₃), 78.5, 83.7 (-C≡C-H), 94.9, 103.4 (Si-C≡C-), 123.2, 129.7, 132.6, 136.3 (C₆H₄). ²⁹Si NMR (CDCl₃, δ, ppm) -16.3 (O-Si-C≡C-), -18.6 ~ -19.2 (O-Si-O-Si-C≡C-).

Resin III was obtained in 92% yield as an orange viscous liquid. FTIR (KBr, cm⁻¹) 3301 (C≡C-H), 3068 (Ar-H), 2967 (-CH₃), 2156 (C≡C), 1258 (Si-CH₃), 1008-1116 (Si-O-Si), 790-850 (Si-C). ¹H NMR (CDCl₃, δ, ppm) 0.08-0.37 (Si-CH₃), 3.09 (C≡C-H), 7.40-7.60 (Ar-H). ¹³C NMR (CDCl₃, δ, ppm) 1.73, 2.82 (Si-CH₃), 77.9, 83.2 (-C≡C-H), 94.9, 103.7 (Si-C≡C-), 123.7, 128.9, 132.7, 136.2 (C₆H₄). ²⁹Si NMR (CDCl₃, δ, ppm) -16.3 (O-Si-C≡C-), -18.6 ~ -19.5 (O-Si-O-Si-C≡C-), -21.4 (O-Si-O).

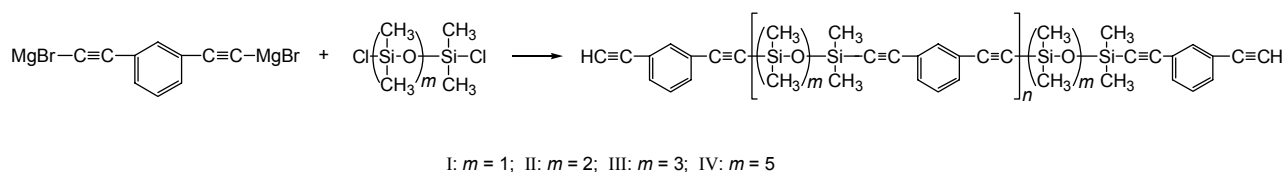
Resin IV was obtained in 90% yield as an orange liquid. FTIR (KBr, cm⁻¹) 3303 (C≡C-H), 3068 (Ar-H), 2967 (-CH₃), 2156 (C≡C), 1259 (Si-CH₃), 1008-1130 (Si-O-Si), 775-872 (Si-C). ¹H NMR (CDCl₃, δ, ppm) 0.07-0.38 (Si-CH₃), 3.07 (C≡C-H), 7.20-7.58 (Ar-H). ¹³C NMR (CDCl₃, δ, ppm) 1.74, 2.85 (Si-CH₃), 78.7, 83.6 (-C≡C-H), 95.8, 103.8 (Si-C≡C-), 123.6, 129.1, 132.6, 136.2 (C₆H₄). ²⁹Si NMR (CDCl₃, δ, ppm) -16.33 (O-Si-C≡C-), -18.6 ~ -19.5 (O-Si-O-Si-C≡C-), -21.4 (O-Si-O).

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 I_c-IV_c were obtained.

Thermal pyrolysis of the cured resins. The cured resins I_c-IV_c 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 I_{cc}-IV_{cc} were obtained.

Results and Discussion

Synthesis and characterization of the resins. The synthesis reactions of arylacetylene resins with siloxane units I-IV are



Scheme 1

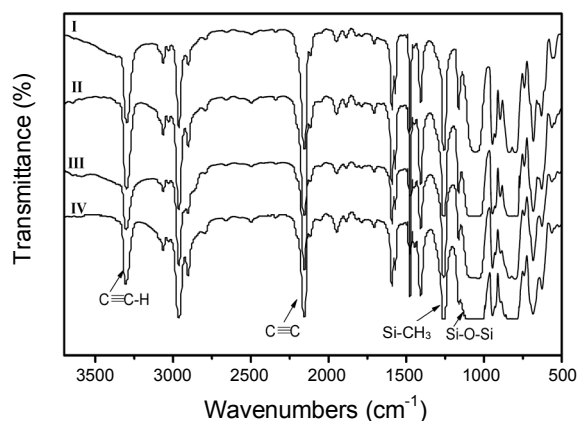


Figure 1. FT-IR spectra of the resins I-IV.

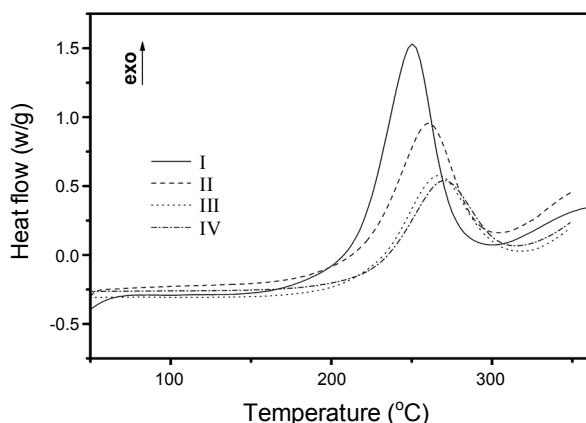


Figure 2. DSC curves of the resins I-IV.

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 α,ω -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} ($\equiv\text{C-H}$), 3068 cm^{-1} (Ar-H), 2156 cm^{-1} ($\text{C}\equiv\text{C}$), 1258 cm^{-1} (Si-CH₃), $1008 - 1130\text{ cm}^{-1}$ (Si-O-Si), and $770 - 850\text{ cm}^{-1}$ (Si-C). The intensity of the Si-O stretching at $1000 - 1100\text{ cm}^{-1}$ of the resins increases with the increase in the length of the siloxane units. As for ^1H NMR analysis of the resins, the dimethylsiloxy protons by peak resonances with chemical shift are observed in the $0.07 - 0.38\text{ ppm}$ 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 $7.20 - 7.58\text{ ppm}$ range. The ^{13}C NMR spectrum confirms aromatic carbons by peak resonances with chemical shifts in the $123.7 - 136.1\text{ ppm}$ 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, dimethylsiloxy 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 $\sim -16.3\text{ ppm}$, O-Si-O-Si-C \equiv C- in the range from $\sim -18.6\text{ ppm}$ to $\sim -19.5\text{ ppm}$, and O-Si-O at $\sim -21.4\text{ ppm}$] appear. The characterization by ^1H 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 $10\text{ }^\circ\text{C}/\text{min}$ in the temperature range from 100 to $350\text{ }^\circ\text{C}$ 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 $300\text{ }^\circ\text{C}$. The temperatures at peak top for the resins I-IV are 256 , 261 , 267 , and $270\text{ }^\circ\text{C}$, 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 $150\text{ }^\circ\text{C}$. 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 $1000\text{ }^\circ\text{C}$. Figure 3 shows the TGA curves of the cured resins I_c-IV_c in N_2 at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The cured resins I_c-IV_c have high onset degradation temperatures ranging from 483 to $510\text{ }^\circ\text{C}$.

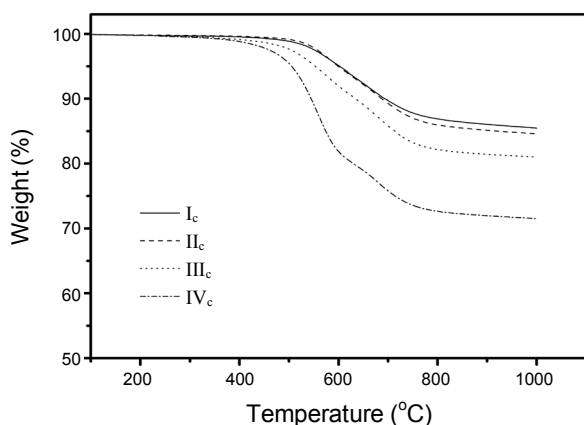


Figure 3. TGA curves of the cured resins I_c-IV_c in nitrogen.

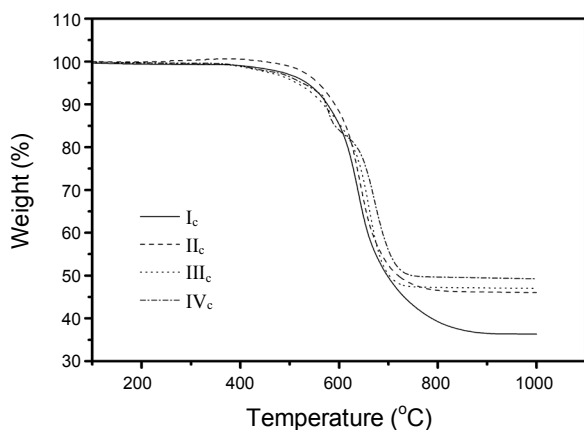


Figure 4. TGA curves of the cured resins I_c-IV_c in air.

The degradation temperatures at 5% weight loss for the cured resins I_c-IV_c are 602, 550, 532, and 505 °C, respectively. The residue yields at 1000 °C for the cured resins I_c-IV_c 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 I_c-IV_c 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.³³ 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 I_c-IV_c decreases with the increase in the length of siloxane units.

The thermooxidative stability of the cured resins I_c-IV_c were determined by thermogravimetric analysis (TGA) in air up to 1000 °C. Figure 4 shows the TGA curves of the cured resins I_c-IV_c in air at a heating rate of 10 °C/min. 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 I_c-IV_c are 548, 535, 522, and 514 °C, respectively. The residue yields at 1000 °C for the cured resins I_c-IV_c 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

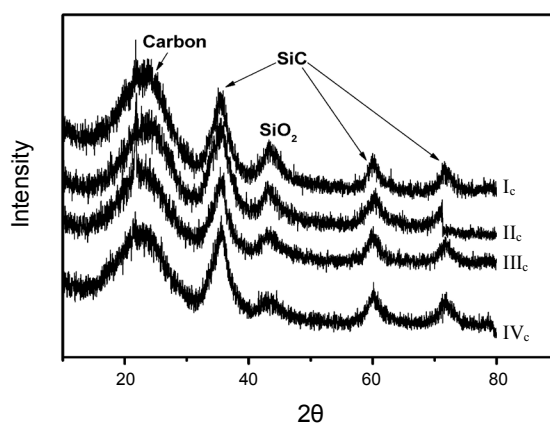


Figure 5. X-ray diffraction spectra of the ceramics I_{cc}-IV_{cc}.

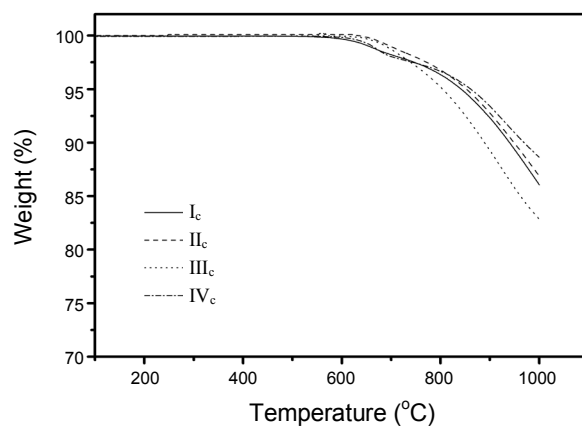


Figure 6. TGA curves of the ceramics I_{cc}-IV_{cc} in air.

resins I_c-IV_c. Unusual change in the residue yields for the cured resins I_c-IV_c 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 I_{cc}-IV_{cc} obtained from the cured resins I_c-IV_c 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 I_{cc}-IV_{cc} 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 I_{cc}-IV_{cc} were determined by thermogravimetric analysis (TGA) in air up to 1000 °C. Figure 6 shows the TGA curves of the ceramics I_{cc}-IV_{cc} 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 I_{cc}-IV_{cc} 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 I_{cc}-IV_{cc} are 86, 87, 83, and 89%, respectively. The good thermooxidative stability for the ceramics is probably attributed to the synergistic effects of β-SiC and SiO₂ 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 N₂. 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 increase from 36 to 49% in air. When these cured resins were heated above 1450 °C under argon, hard and glassy SiOC ceramics composed of β-SiC, SiO₂, and carbon were obtained. These SiOC ceramics exhibit better thermooxidative stability than the relative cured resins.

Acknowledgments. We gratefully acknowledge the financial support from the National High Technology Research and Development Program of China (Grant No.2002305205) and the National Basic Research Program of China (Grant No. 18020006).

References

- Hay, A. S. *J. Org. Chem.* **1960**, *25*, 637.
- Zaldivar, R. J.; Rellick, G. S.; Yang, J. M. *SAMPE* **1991**, *27*, 29.
- Katzman, H. A.; Mallon, J. J.; Barry, W. T. *J. Adv. Mater.* **1995**, *26*, 21.
- Itoh, M.; Mitsuzuka, M.; Iwata, K.; Inoue, K. *Macromolecules* **1994**, *27*, 7917.
- Itoh, M.; Inoue, K.; Iwata, K.; Ishikawa, J.; Takenaka, Y. *Adv. Mater.* **1997**, *9*, 1187.
- Itoh, M.; Inoue, K.; Iwata, K.; Mitsuzuka, M.; Kakigano, T. *Macromolecules* **1997**, *30*, 694.
- Itoh, M.; Iwata, K.; Ishikawa, J.; Sukawa, H.; Kimura, H. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 2658.
- Buvat, P.; Jousse, F.; Delnaud, L.; Levassort, C. *International SAMPE Symposium and Exhibition* **2001**, *46*, 134.
- Wang, F.; Zhang, J.; Huang, J. X.; Yan, H.; Huang, F. R.; Du, L. *Polym. Bull.* **2006**, *56*, 19.
- Yin, G. G.; Zhang, J.; Wang, C. F.; Huang, F. R.; Du, L. *e-Polymers* **2008**, No. 067.
- Li, Q.; Zhou, Y.; Hang, X. D.; Deng, S. F.; Huang, F. R.; Du, L.; Li, Z. P. *Eur. Polym. J.* **2008**, *44*, 2538.
- Zhang, L. L.; Gao, F.; Wang, C. F.; Zhang, J.; Huang, F. R.; Du, L. *Chin. J. Polym. Sci.* **2009**, Accepted.
- Lee, I. S.; Lee, C. G.; Kwak, Y. W.; Gal, Y. S. *Bull. Korean Chem. Soc.* **2009**, *30*, 309.
- Zeigler, J. M.; Fearon, F. W. *Silicon-Based Polymer Science: A Comprehensive Resource*; ACS Symposium Series 224, American Chemical Society: Washington, DC, 1990.
- Dvornic, P. R.; Lenz, R. W. *High Temperature Siloxane Elastomers*; Hüthig & Wepf: Heidelberg, 1990.
- Suzuki, T.; Mita, I. *Eur. Polym. J.* **1992**, *28*, 1373.
- Son, D. Y.; Keller, T. M. *Macromolecules* **1995**, *28*, 399.
- Son, D. Y.; Keller, T. M. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 2969.
- Sundar, R. A.; Keller, T. M. *J. Polym. Sci. Part A: Polym. Chem.* **1997**, *35*, 2387.
- Homrighausen, C. L.; Keller, T. M. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 1334.
- Beckham, H. W.; Keller, T. M. *J. Mater. Chem.* **2002**, *12*, 3363.
- Homrighausen, C. L.; Keller, T. M. *Polymer* **2002**, *43*, 2619.
- Kolel-Veetil, M. K.; Beckham, H.; Keller, T. M. *Chem. Mater.* **2004**, *16*, 3162.
- Kolel-Veetil, M. K.; Keller, T. M. *J. Mater. Chem.* **2003**, *13*, 1652.
- Yamaguchi, B.; Fujisaka, T.; Okada, K. Japanese Patent 8151447, 1996.
- Huang, F. R.; Du, L.; Wang, F.; Gao, F. Chinese Patent 1709928, 2005.
- Mirskov, R. G.; Rakhlin, V. I.; Voronkov, M. G.; Gendin, D. V. *Russ. J. Gen. Chem.* **2003**, *73*, 165.
- Teng, C. J.; Weber, W. P.; Cai, G. *Macromolecules* **2003**, *36*, 5126.
- Beckmann, J.; Dakternieks, D.; Duthie, A.; Foitzik, R. C. *Silicon Chem.* **2003**, *2*, 27.
- Yoshino, K.; Kawamata, A.; Uchida, H.; Kabe, Y. *Chem. Lett.* **1990**, 2133.
- Uchida, H.; Kabe, Y.; Yoshino, K.; Tsumuraya, T.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 7077.
- Ishikawa, M.; Toyoda, E.; Ishii, M.; Kunai, A.; Yamamoto, Y.; Yamamoto, M. *Organometallics* **1994**, *13*, 808.
- Maya, E. M.; Snow, A. W.; Buckley, L. J. *Macromolecules* **2002**, *35*, 460.