

NOVEL PHENYLACETYLENE-TERMINATED POLY (SILYLENE-ACETYLENE): SYNTHESIS AND THERMAL AND OXIDATIVE PROPERTIES

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Introduction

During the past 30 years considerable research efforts have been expended on the development of high temperature polymers for microelectronics and aerospace application as high performance matrix, coatings and sealants [1-3]. Until recently, silylene-acetylene hybrid polymers with $[-\text{SiR}_2-\text{C}\equiv\text{C}-]_n$ (R=alkyl, aryl) unit have been under intense investigation and development due to their unique properties such as high thermal stability, low dielectric constants, radar transparency and low water absorption [4-6]. Incorporating inorganic element silicon into a polymeric material improves the thermo-oxidative stability relative to carbon which was corresponding to the formation of thermally stable inorganic structure (SiC or SiO₂).

In this paper, we offer a convenient method to prepare a novel silylene-acetylene hybrid polymer which possesses excellent heat resistance, especially thermal oxidative property, linear phenylacetylene-terminated poly (silylene-acetylene) (PTSA, Scheme 1). We also investigate cure behavior, thermal and oxidative properties, which will give important information for the design of heat resistant materials and efficient precursors of silicon carbide. No related literature has been reported.

Experimental

Materials

Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled under a nitrogen atmosphere from deep purple solutions of sodium/benzophenone immediately prior to use. All other chemicals were purchased from Aldrich Chemical Company and used as receive.

Synthesis

To a flame-dried three-necked reaction vessel containing 40ml of a 1:1 mixture of THF and Et₂O and n-butyllithium **3** (n-BuLi, 10.4ml of a 2.5M hexane solution, 26mmol) at -78°C, was added trichloroethylene **1** (TCE, 0.56ml, 6mmol) and phenylacetylene **2** (0.88ml,

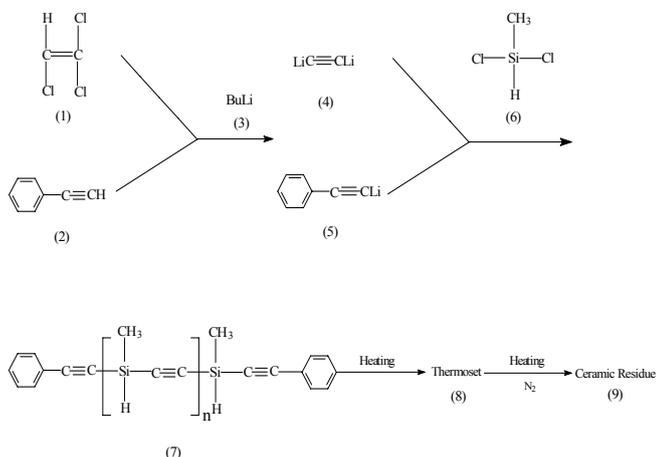
8mmol) in a dropwise fashion over 30 minutes to generate dilithioacetylene **4** and lithium phenylacetylide **5** in situ. Then -78°C bath was removed and the resulting mixture was stirred at room temperature for 3h and recooled to -78°C. A THF solution containing methyldichlorosilane **6** (1.07ml, 10mmol) was added using a cannula over 30 minutes under vigorous stirring. After complete addition, the reaction mixture was allowed to warm to room temperature and stirred for 6h. The reaction mixture was poured into cold aqueous ammonium chloride and extracted with ether. The organic layer was combined, washed with water until neutral, dried over sodium sulfate, and the solvent removed by rotary evaporation to a yellowish viscous polymer. IR (cm⁻¹): 3060 (w), 2964 (w), 2167 (s), 1597 (w), 1574 (w), 1489 (s), 1258 (s). ¹H NMR (δ, TMS, ppm): 0.71 (s, CH₂-H), 4.21 (s, Si-H), 7.30-7.53 (m, Ph-H). ¹³C NMR (δ, CDCl₃, ppm): 2.42 (s, Si-CH₃), 87.92 (s, Si-C≡C), 106.82 (s, Ph-C≡C), 123.04 (s, Ph), 128.86 (s, Ph), 129.48 (s, Ph), 132.90 (s, Ph).

Characterization

FT-IR spectroscopic characterization was carried out with Nicolet Magna-IR550. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance 500 spectrometer. Thermogravimetric analysis (TGA) was performed on PerkinElmer Pyris Diamond from room temperature to 900°C at heating rate of 10°C/min under nitrogen and air atmosphere. The differential scanning calorimetry (DSC) study was performed on NETZSCH DSC 200PC at heating rate of 10°C/min. Gel permeation chromatography (GPC) analysis was performed on a Waters 1515 using THF as eluent.

Cure procedure

In order to remove any volatile material, the sample was heated at 100°C. The sample was placed in a furnace and cured under an atmosphere of dry argon at 150°C/2h, 180°C/4h, 200°C/4h, 250°C/4h and 300°C/2h. Then, thermoset was cooled slowly to room temperature in order to prevent cracking to get required specimens.



Scheme 1 Synthesis of PTSA

Results and Discussions

Synthesis

The preparation of PTSA, 7, was illustrated in Scheme 1. The couple reaction of dichloro-oligosilanes with dimetalated π -conjugated compounds was a typical way to synthesize the polymer of oligosilylene units and π -units. The synthetic method used was a simple one pot, two-step reaction. The synthesis of 7, by the reaction of methylchlorosilane 6 with dilithioacetylene 4 and phenylacetylide 5, which could be generated in situ from TCE 1 and phenylacetylene 2 with *n*-BuLi 3, with the formation of LiCl and *n*-chlorobutane. GPC analysis indicated that the average weight molecular mass and polydisperse was 14640 and 4.1, respectively.

Cure Behavior

The DSC curve (figure 1) indicated that bulk thermal crosslinking reaction to form a network system occurred. The presence of exothermic transitions in the 110-300 °C with peak temperature at 232 °C indicated both hydrosilation reaction attributing to $C\equiv C$ and Si-H and addition reaction of the internal acetylene group.

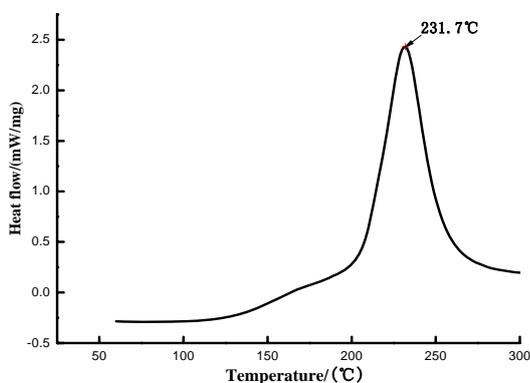


Fig.1 DSC curve of PTSA

Thermal and Oxidative Properties

Thermal and oxidative properties were evaluated by TGA analysis, as shown in figure 2. TGA analysis exhibited the temperature of 5% weight loss (T_{d5}) was

652 °C and char yield at 900 °C was 90.0% in nitrogen. In air, surprisingly, both T_{d5} and char yield at 900 °C showed slightly increase, which was 671 °C and 90.7%, respectively. This slight weight increase was attributed to the oxidation of silicon to SiO_2 upon exposure to oxidizing atmosphere at elevated temperatures and the formation of a protective layer on the sample. However, most organic based systems are usually observed to undergo weight losses in the 500 to 600 °C temperature range upon exposure to air.

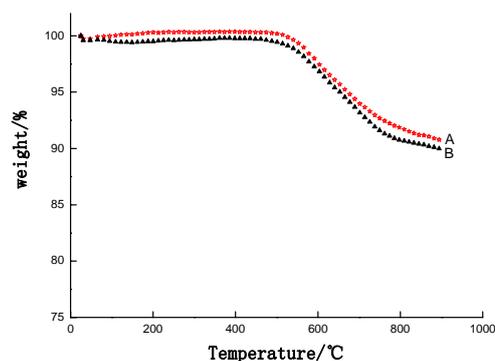


Fig.2 TGA curves of PTSA (A: N_2 , B: Air)

Conclusions

PTSA was synthesized by a simple one pot, two step reaction and characterized using FT-IR, 1H -NMR and ^{13}C -NMR. Cure behaviors were studied by DSC and showed broad prominent exotherm with peaks at 232 °C. Thermoset exhibited extremely high heat-resistance and TGA curves showed T_{d5} was 652 °C and char yield at 900 °C was 90.0% in nitrogen. In air, however, thermoset showed a slightly increase both in T_{d5} (671 °C) and in char yield (90.7%). Thus, PTSA exhibited outstanding potential as matrix materials for high temperature composite applications.

Acknowledgements

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Reference

- [1] Hergenrother PM. High. Perform. Polym. 2003, 15: 3-45.
- [2] Ding MX. Prog. Polym. Sci. 2007, 32: 623-628.
- [3] Ren H, Sun JZ, Zhao Q, Zhou QY, Lin QC. Polym. 2008, 49: 5249-5253.
- [4] Kwak G, Masuda T. Macromolecules 2003, 35: 4138-4142.
- [5] Ijadi MS, Barton TJ. Macromolecules 1990, 23, 4485-4492.
- [6] Corriu RJP, Gerbier P, Guérin C, Henner, B. Chem. Mater. 2000, 12: 805-811.