



Thermal curing and degradation behaviour of silicon-containing arylacetylene resins



Kangkang Guo ^{a, b}, Ping Li ^b, Yaping Zhu ^a, Fan Wang ^a, Huimin Qi ^{a, *}

^a Key Laboratory of Specially Functional Polymeric Materials and Related Technology of Ministry of Education, School of Materials Science and Engineering, East China University of Science & Technology, Shanghai 200237, China

^b State Key Laboratory of Chemical Engineering, East China University of Science & Technology, Shanghai 200237, China

ARTICLE INFO

Article history:

Received 15 April 2016

Received in revised form

1 July 2016

Accepted 6 July 2016

Available online 9 July 2016

Keywords:

Silicon

Arylacetylene

Cure

Degradation

ABSTRACT

Silicon-containing arylacetylene resins (PSAs) have already shown potential application as heat-resistant materials due to their excellent thermal stability. The formation and degradation of structures in cured PSAs are very important to evaluate the thermal properties during their applications. Herein, the thermal curing and degradation behavior of PSAs with different substituents were investigated by DSC, FT-IR, Py-GC-MS, TGA and TG-GC-MS. DSC and FT-IR analysis reveals that the curing reaction is dominated by the crosslinking reaction of C≡C–H and Si–C≡C–, meanwhile, the reactive substituents (such as Si–H and Si–CH=CH₂) could promote the C≡C–H and Si–C≡C– reaction with higher conversion. Py-GC-MS was used to detect the pyrolysis products at 650 °C and 750 °C, respectively, and the results could provide important information about the curing reaction and structures of cured PSAs. The curing reaction of PSAs mainly contains cyclotrimerization and Diels-Alder reaction of C≡C–H and Si–C≡C–, and some addition reaction to form polyene structure. The main structures in cured PSAs contain a lot of phenyl rings, some aromatic fused rings and a little of polyene structure, moreover, their contents in cured PSAs are dependent on the substituents of the precursors. The TGA results show that the substituents of Si–H and Si–CH=CH₂ can effectively improve the crosslinking index of the cured PSA-H and PSA-V, and endow them with better thermal stability. Additionally, the degradation behavior of cured PSAs have been well studied by TG-GC-MS. When the temperature is 400 °C, the Si–CH₃ and some aliphatic structure begin to degrade and form CH₄, and with the temperature increasing to 500 °C, the unsaturated and aliphatic structures decompose into C₂H₄ and C₂H₆, and after 600 °C, the aromatic rings and fused rings in cured PSAs are dehydrogenated and release H₂. In addition, the content of the degradation products and their forming temperature are also related with the substituents.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Silicon-containing polymers composed of [–SiR₂–C≡C–Ar–] units have received considerable attention due to their thermally cured resins that possess excellent thermal stability, low dielectric constant and loss factor, and high temperature mechanical properties [1–4]. These polymers have already shown potential applications as ceramic precursors, heat-resistant materials and matrix of advanced composites in aerospace and astronautics [5–7]. Also, these resins thermally cure without the evolution of volatile byproducts, and will form three-dimensional network structures

which could offer the cured resins with excellent thermal stability, solvent resistance, chemical stability, etc [4]. Kuroki and Itoh investigated the curing mechanism of poly[(phenylsilylene) ethynylene-1, 3-phenyleneethynylene] (called as MSP) containing Si–H by the FT-IR, solid-state NMR and computational chemistry. The results showed that the formed three-dimensional network structures contained naphthalene rings from Diels-Alder reaction between Ph–C≡C and C≡C, and styrene structure from hydrosilylation reaction between Si–H and Ph–C≡C [8,9]. Kimura et al. studied the thermal curing behavior of diethynylbenzene-silylene polymers containing vinyl groups by the solid-state NMR method. It was found that the formed three-dimensional network structures involved naphthalene rings from Diels-Alder reaction of alkynyl groups, and aliphatic structure from addition reaction of vinyl groups and Ph–C≡C [4]. Zhang et al. investigated the cross-linking

* Corresponding author.

E-mail address: qihm@ecust.edu.cn (H. Qi).

reaction of poly[(dimethylsilylene ethynylene phenylene ethynylene)] (abbreviated as DMSEPE) containing methyl group by Py-GC-MS. They found several structures in three-dimensional network structures, such as polyene structure from the radical polymerization of $C\equiv C$, phenyl rings structure from cyclotrimerization of $C\equiv C$ and naphthalene rings structure from Diels-Alder reaction between $Ph-C\equiv C$ and $C\equiv C$ [7]. However, to our best knowledge, there are few reports on the detailed and dominated structures in cured resins, especially for the influence of substituents connected to silicon atoms on these three-dimensional network structures. Meanwhile, during the applications of cured resins, the service temperature is very high, which indicate the three-dimensional network structures are exposed to high temperature environment [10]. Therefore, it is necessary to systematically investigate the detailed three-dimensional network structures with different substituents during the curing reaction and thermal degradation behavior of these structures under high temperature.

Differential scanning calorimetric analyses (DSC) and Fourier transform infrared (FT-IR) are effective techniques to analyze the curing mechanism, and important structural information can be obtained by these methods [11,12]. Recently, pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) has become a very important technique for the analysis of polymer structures [12–14]. Despite the complexity of pyrolysis process, a wealth of information about the polymer structures is present in the pyrolysis products [15,16]. Thermogravimetric analysis (TGA) is one of the most commonly used thermal analysis technique. It can provide quantitative results regarding the thermal properties [17]. Thermogravimetry-gas chromatography-mass spectrometry (TG-GC-MS) is commonly used to investigate the thermal behavior of polymers, which could reveal a much more complex degradation pathway of polymers [18,19].

In this contribution, three kinds of silicon-containing arylacetylene resins (PSAs), poly[(methylvinylsilylene)ethynylene-1, 3-phenyleneethynylene] (PSA-V), poly[(methylhydrosilylene)ethynylene-1, 3-phenyleneethynylene] (PSA-H), poly[(dimethylvinylsilylene)ethynylene-1, 3-phenyleneethynylene] (PSA-M) were chosen to be model polymers. The thermal curing behavior and structure of cured resins were systematically investigated by DSC, FT-IR and Py-GC-MS. TGA and TG-GC-MS were used to investigate the thermal stability and degradation pathway of the cured resins by analysis of the gases evolved during the degradation. Also, the substitute effects on the curing and degradation behavior will be discussed.

2. Experiment

2.1. Materials

Diethynylbenzene was supplied by Fine Chemical Institute of East China University of Science and Technology and distilled on a vacuum line before use. Dichloromethylsilane, dimethyldichlorosilane, dichloromethylvinylsilane, toluene, tetrahydrofuran (THF), ethyl bromide (EtBr), silica gel, and magnesium powder were

purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Preparation and curing of PSA-V, PSA-M and PSA-H

PSA-V, PSA-M and PSA-H were prepared by the condensation reactions between diethynylbenzene Grignard reagents and dichlorosilane in tetrahydrofuran as solvent (Scheme 1) according to the reported method [20,21]. The PSAs were thermally cured according to the following procedures: 170 °C for 2 h, 210 °C for 2 h, 250 °C for 2 h, 300 °C for 2 h, and 350 °C for 4 h.

2.3. Characterization

Differential scanning calorimetric analyses (DSC) were performed on a NETZSCH 200 PC module with a heating rate of 10 °C/min from ambient temperature to 300 °C under nitrogen atmosphere. Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet 550 spectrometer. The powder samples were previously milled and dried at 100 °C for at least 2 h. In order to analyze the absorption intensity changes of reactive groups in the FT-IR spectra, some absorptions were normalized and their relative conversions (a) at various curing temperatures were determined as follow [22]:

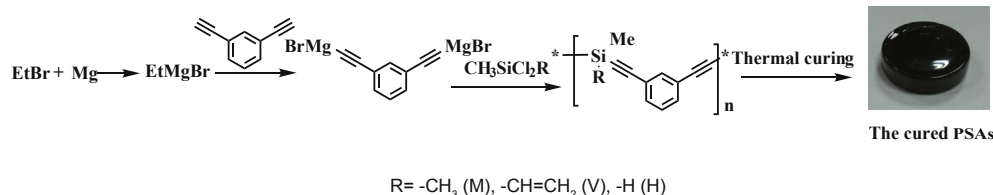
$$a = 1 - \frac{(A_i/A_r)_T}{(A_i/A_r)_{T=25^\circ C}} \quad (1)$$

where T is the curing temperature, $(A_i/A_r)_T$ and $(A_i/A_r)_{T=25^\circ C}$ are the ratios of integrated intensity of the specified band to the integrated intensity of the internal standard band at the curing temperature T and at the ambient temperature, respectively. The band of Si-CH₃ at 1255 cm⁻¹ was used as an internal standard. The pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) analyses were conducted on a Frontier Lab Single-shot Pyrolyzer PY-2020i (PY Single-shot Pyrolyzer, quartz tube) and a Shimadzu GCMS-QP2010 chromatograph/mass spectrometer (Chromatographic column, 30 m × 0.25 mm i.d. × 0.25 μm; carrier gas, helium gas; pressure, 34.0 kPa; total flow, 84.3 mL/min; column flow, 0.80 mL/min). Pyrolyses were carried out at 650 °C and 750 °C, respectively. Thermogravimetric analyses (TGA) were performed on a TA Instruments SDT Q600 analyzer. All thermal analyses were conducted under nitrogen atmosphere at a heating rate of 10 °C/min from ambient temperature up to 1000 °C. Evolved gas analyses were performed on a TG-GC-MS (INFICON Transpector 2) at a heating rate of 10 °C/min from ambient temperature up to 1000 °C in a controlled dry helium flow of 50 mL/min. The evolved gases were analyzed by mass spectrometry on a Thermostat quadrupole apparatus from Balzers instruments covering a mass range from 0 to 300 amu.

3. Results and discussion

3.1. Thermal curing behavior

The study of thermal curing behavior is important, which can



Scheme 1. Schematic illustration of the preparation and curing of silicon-containing arylacetylene resins (PSAs).

Download English Version:

<https://daneshyari.com/en/article/5201047>

Download Persian Version:

<https://daneshyari.com/article/5201047>

[Daneshyari.com](https://daneshyari.com)