Thermal curing and Degradation Behaviour of Silicon-containing Arylacetylene Resins

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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 $\text{C}\equiv\text{C-H}$ and $\text{Si-C}\equiv\text{C-}$, meanwhile, the reactive substituents (such as Si-H and Si-CH=CH_2) could promote the $\text{C}\equiv\text{C-H}$ and $\text{Si-C}\equiv\text{C-}$ 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 $\text{C}\equiv\text{C-H}$ and $\text{Si-C}\equiv\text{C-}$, 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=CH_2 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-CH_3 and some aliphatic structure begin to degrade and form CH_4 , and with the temperature increasing to 500°C , the unsaturated and aliphatic structures decompose into C_2H_4 and C_2H_6 , and after 600°C , the aromatic rings and fused rings in cured PSAs are dehydrogenated and release H_2 . In addition, the content of the degradation products and their forming temperature are also related with the substituents.

Key words:

Silicon, arylacetylene, cure, degradation

1. Introduction

Silicon-containing polymers composed of $[-\text{SiR}_2-\text{C}\equiv\text{C}-\text{Ar}-]$ 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 $\text{Ph}-\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{C}$, and styrene structure from hydrosilylation reaction between Si-H and $\text{Ph}-\text{C}\equiv\text{C}$ [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 $\text{Ph}-\text{C}\equiv\text{C}$ [4]. Zhang *et al.* investigated the cross-linking 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 $\text{C}\equiv\text{C}$, phenyl rings structure from cyclotrimerization of $\text{C}\equiv\text{C}$ and naphthalene rings structure from Diels-Alder reaction between $\text{Ph}-\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{C}$ [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,

1 during the applications of cured resins, the service temperature is very high, which
2 indicate the three-dimensional network structures are exposed to high temperature
3 environment [10]. Therefore, it is necessary to systematically investigate the detailed
4 three-dimensional network structures with different substituents during the curing
5 reaction and thermal degradation behavior of these structures under high temperature.

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

18 In this contribution, three kinds of silicon-containing arylacetylene resins (PSAs),
19 poly[(methylvinylsilylene)ethynylene-1, 3-phenyleneethynylene] (PSA-V) ,
20 poly[(methylhydrosilylene)ethynylene-1, 3-phenyleneethynylene] (PSA-H),
21 poly[(dimethylvinylsilylene)ethynylene-1, 3-phenyleneethynylene] (PSA-M) were
22 chosen to be model polymers. The thermal curing behavior and structure of cured
23 resins were systematically investigated by DSC, FT-IR and Py-GC-MS. TGA and
24 TG-GC-MS were used to investigate the thermal stability and degradation pathway of
25 the cured resins by analysis of the gases evolved during the degradation. Also, the
26 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.

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

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]:

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

where T is the curing temperature, $(A_i/A_r)_T$ and $(A_i/A_r)_{T=25^\circ\text{C}}$ 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 Thermostar quadrupolar 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 reveal the heat-resistant structural information and its formation mechanism in cured PSAs. The type and composition of the pyrolysis products could give direct information about the structure of cured PSAs. Herein, DSC, FTIR and Py-GC-MS were used to investigate the thermal curing behavior of the three kinds of PSAs with different substituents, such as Si-H for PSA-H, Si-CH=CH₂ for PSA-V, Si-CH₃ for PSA-M.

3.1.1 DSC analysis

Figure 1. DSC thermogram (10°C/min in N₂) of cured PSAs.

Figure 1 shows the DSC thermogram of the thermal polymerization of PSAs with different substituent groups. A DSC thermogram of PSA-H exhibits an exotherm peaking at 214°C, an initial curing temperature at 140°C and a final temperature at 262°C. A thermogram of PSA-V shows an exotherm peaking at 229°C, an initial curing temperature at 160°C and a final temperature at 268°C. However, for the PSA-M, an exotherm onset can be observed at about 170°C, the T_{max} (the maximum of the curing exotherms) at 239°C and the final temperature at 273°C. These indicate that the substituent groups on silicon atom have a great influence on the curing reaction, which can be explained that the Si-H and Si-CH=CH₂ could be involved in the curing reaction, but the Si-CH₃ shows a certain inertness [3-5, 7]. Also, it can be seen that the curing reaction of PSA-H occur at lower temperature than those of the PSA-V and PSA-M, which is attributed to the higher activity of Si-H than Si-CH=CH₂ and Si-CH₃. Besides, the PSA-V exhibits higher reactivity than PSA-M due to the reactivity of Si-CH=CH₂.

3.1.2 FT-IR analysis

Figure 2. FT-IR spectra of PSAs after each cure cycle: (a) PSA-H, (b) PSA-V, (c) PSA-M.

FT-IR spectra of the PSAs at each curing cycle are shown in **Figure 2**. The intensity of the absorption peaks at 3300 cm^{-1} and 2160 cm^{-1} assigned to $\text{C}\equiv\text{C-H}$ and $-\text{C}\equiv\text{C-Si(Me)R-}$ (Si-H and $\text{Si-C}\equiv\text{C-}$ in the same position for PSA-H) decreases gradually with the curing temperature increasing. Meanwhile, the vinyl group ($1404\sim1407\text{ cm}^{-1}$) has the same tendency as $\text{Si-C}\equiv\text{C-}$ for PSA-V. Additionally, the absorption peaks of $\text{Si-C}\equiv\text{C-}$ still can be seen after curing at 350°C for the cured

1 PSAs, indicating that the curing reactions of PSAs are incomplete. Great changes can
2 be observed during the curing reaction for reactive groups (such as internal alkynes,
3 terminal alkynes, vinyl group and Si-H), which suggest that the curing reaction is
4 mainly the reaction of these reactive groups. However, the intensity of the absorption
5 peaks for Si-CH₃ in cured PSAs has no changes during the curing reaction, which can
6 be used as an internal standard to obtain the IR relative intensity of reactive groups for
7 measuring the conversion (a) of the reactive groups as equation (1) shown [2]. Thus,
8 the dependence of the conversion of the reactive groups with the curing temperature
9 are shown in **Figure 3**. It can be observed that the C≡C-H and Si-C≡C- of PSA-H
10 and PSA-V exhibit higher conversion than those of PSA-M. This can be explained
11 that the Si-H and Si-CH=CH₂ involve in the cross-linking reaction of Si-C≡C and C
12 ≡C-H, and increase their conversions, which could be confirmed by the lower curing
13 temperature of PSA-H and PSA-V as shown in DSC thermogram.

Figure 3. Conversion of reactive groups after each cure cycle for PSAs: (a) PSA-H, (b) PSA-V, (c) PSA-M.

Figure 3(c) shows that the conversion of C≡C-H is higher than Si-C≡C- for the PSA-M at the same curing condition (time and temperature), which indicate the terminal alkynes have higher reaction activity. Also, it can be observed that the conversion of C≡C-H and Si-C≡C- for PSA-V is higher than those of PSA-M at the same curing condition from Figure 3(b), which confirm the vinyl group involving the curing reaction and improve the conversion. Figure 3(a) shows that the absorption

bands at 2150-2160 cm^{-1} (Si-H and Si-C $\equiv$ C-) exhibit higher conversion than 3300 cm^{-1} (C $\equiv$ C-H) for PSA-H, which indicate the Si-H involves in the curing reaction and improve the conversion [8]. Besides, the Si-CH=CH₂ exhibits lower conversion than the Si-C $\equiv$ C and C $\equiv$ C-H at low curing temperature from the **Figure 3(b)**, which indicate that Si-CH=CH₂ have lower reaction activity than Si-C $\equiv$ C and C $\equiv$ C-H at this temperature [4].

3.1.3 PY-GC-MS analysis

Py-GC-MS is an effective method to investigate the possible structures of the different cured PSAs from the pyrolysis products. **Figure 4** shows the GC spectra for pyrolysis products of the cured PSAs at 650°C and 750°C and the pyrolysis products are summarized in **Table 1**.

Figure 4. Py-GC-MS detection of gas products evolved from pyrolysis of cured PSAs: (a) PSA-H, (b) PSA-V, (c) PSA-M.

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Table 1. Percentage of pyrolysis products of cured PSAs.

Retention time (min)	M _w	Structure	PSA-H		PSA-V		PSA-M	
			Area (%)		Area (%)		Area (%)	
			650°C	750°C	650°C	750°C	650°C	750°C
1.92	68			0.22		0.22		0.51
2.34	84			0.14		0.14		0.15
3.07	78		37.52	42.19	28.30	31.73	37.31	43.78
4.65	92		34.84	33.41	36.89	35.5	38.79	35.1
6.47	106		8.88	7.96	10.84	10.39	8.89	7.52
7.06	104		5.62	5.95	4.19	5.43	3.71	3.53
8.47	120		1.36	0.96	1.91	1.76	1.21	0.92
12.53	128		4.59	4.23	6.32	6.07	4.64	4.81
14.31	142		1.83	1.42	3.36	2.73	2.61	1.28
15.56	154		0.95	0.91	2.46	2.21	1.02	
15.77	156		0.19		0.50	0.30	0.11	
16.63	152		0.16		0.33	0.23	0.13	
17.05	168		0.34		0.89	0.77	0.38	
20.94	178		0.30		0.96	0.48	0.25	

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3 The identified products can be divided into three kinds: (1) olefin volatiles, i.e. 1,
4 4-pentadiene, cyclopentene and 1-hexene, (2) phenyl ring volatiles, i.e. benzene,
5 biphenyl, and their derivatives, and (3) aromatic fused ring volatiles, i.e. naphthalene,
6 phenanthrene, and their derivatives. The olefin volatiles only appear in the products at
7 750°C, and cannot be found in products at 650°C. It can be proposed that the olefin
8 volatiles are from the further pyrolysis of aromatic rings at higher temperature.
9 Accordingly, the products at 650°C seem more effective to investigate the structure of

1 the cured PSAs than those at 750°C. The dominant products of cured PSAs are phenyl
2 ring volatiles, which are far higher than the aromatic fused ring volatiles. The phenyl
3 rings in products far exceed the phenyl ring in PSAs as designed in its synthesis
4 (**Scheme 1**), which indicates that some phenyl rings could be from the curing reaction
5 or cyclization during the pyrolysis [23]. Therefore, it is presumed that there are two
6 possible sources for the observed extra phenyl rings: (1) The phenyl rings are formed
7 by the cyclotrimerization (**Scheme 2(a)**) of $C\equiv C$ group during the thermal curing [24,
8 25], (2) polyene structure (**Scheme 2(b)**) obtained during curing reaction would
9 cyclize and produce the phenyl rings during the pyrolysis [11, 23]. The absorption
10 peaks of the polyene structure cannot be found from FT-IR spectra of cured PSAs
11 (**Figure 2**), but the signal of $CH_2=CH_2$ in the results of TG-GC-MS and styrene with
12 content less than 6% in the Py-GC-MS products can be observed, which could
13 indicate that the curing reaction contain a little of reaction as shown in **Scheme 2(b)**.
14 Therefore, it could be concluded that the phenyl rings in the products cured PSAs are
15 mainly from the cyclotrimerization of $-C\equiv C-$ group during the thermal curing
16 reaction of PSAs. The aromatic fused ring volatiles detected in products should be
17 from the aromatic fused ring structure formed by Diels-Alder reaction (**Scheme 2(c)**
18 and **(d)**) in cured PSAs [4, 7, 8, 11, 23]. Based on the analysis above, the main
19 structure of the cured PSAs could be described as shown in **Scheme 3**.

Scheme 2. Schematic illustration of the thermal cure reaction of PSAs: (a) cyclotrimerization of $-C\equiv C-$ group, (b) addition reaction of $-C\equiv C-$ group, (c) Diels-Alder reaction of forming naphthalene ring, (d) Diels-Alder reaction of forming phenanthrene ring.

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Scheme 3. Schematic illustration of structures for cured PSAs.

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The relative contents of benzene in products of cured PSA-V (28.30% at 650°C) are less than PSA-M (37.31% at 650°C) and PSA-H (37.52% at 650°C), but cured PSA-V has a highest content of the volatiles containing aromatic fused rings in three cured resins. This reveals the cured PSA-V containing more structure of aromatic fused rings. It is well known that the aromatic fused rings could be produced by Diels-Alder reaction, where phenyl rings are necessary in this reaction. The vinyl group in PSA-V is advantageous to rotation of molecule chains to form the *syn-out* conformation prone to Diels-Alder reaction [8]. However, this *syn-out* conformation is not easy to form in the curing process of the PSA-M, because the methyl group is shorter than the vinyl group, and not good for the motion of the molecular chains. Also, the molecular chains of PSA-H could be limited by the hydrosilation reaction of alkynyl groups at lower temperature as shown in **Figure 2(a)**. Besides, **Table 1** shows that the relative contents of styrene for cured PSA-V and PSA-H are higher than that of the cured PSA-M. This can be interpreted that the Si-H and Si-CH=CH₂ could react with alkynyl groups to form the structure containing styrene as shown in **Scheme 4**.

Scheme 4. (a) Schematic illustration of addition reaction of Si-H and -C≡C- group, (b) Schematic illustration of addition reaction of Si-CH=CH₂ and -C≡C- group.

3.2 Thermal degradation behavior

The investigation of the thermal degradation behavior is very important to understand the thermal degradation mechanism and determine the limit of their service temperature. The thermal degradation behavior of cured PSAs is examined by TGA and TG-GC-MS from ambient temperature to 1000°C.

3.2.1 TGA analysis

Figure 5. TGA thermogram (10°C/min in N₂) of cured PSAs.

Table 2. Thermal property of the cured PSAs.

	T_{d5} (°C)	Residue (%) at 1000°C
PSA-H	715	93
PSA-V	650	91
PSA-M	583	87

To evaluate the thermal stability of cured PSAs, TGA was carried out from ambient temperature to 1000°C under nitrogen atmosphere. **Figure 5** shows the TGA curves of cured PSAs with different substituent groups, and **Table 2** lists the degradation temperature of 5% weight loss (T_{d5}) and the residual yield at 1000°C. As shown in **Figure 5** and **Table 2**, it could be observed that the cured PSA-H, PSA-V and PSA-M offer excellent thermal stability and give residual yield 93%, 91% and 87% when heated to 1000°C, and the T_{d5} reach to 715°C, 583°C and 650°C, respectively. Obviously, the cured PSA-H and PSA-V exhibit a better thermal stability than cured PSA-M, which indicate that the substituent groups on silicon atom have a great influence on the thermal stability of cured PSAs, and the reactive substituents (such as

1 Si-H and Si-CH=CH₂) could improve their thermal stability. This can be explained
2 that Si-H and Si-CH=CH₂ involve in the curing reaction and improve the crosslinking
3 index of cured PSAs, which is also confirmed by the higher conversion of C≡C-H
4 and Si-C≡C- for PSA-H and PSA-V from **Figure 3a** and **3b**. Besides, it can be also
5 seen that PSA-H has a higher T_{d5} and residual yield than PSA-V, which is attributed
6 to the difference in crosslinking reaction of Si-H and Si-CH=CH₂ as shown in
7 **Scheme 4**. It can be seen that the Si-CH=CH₂ of PSA-V is prone to forming the
8 aliphatic chain, which is not stable during the process of thermal degradation.

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11 *3.2.2 TG-GC-MS analysis*
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Figure 6. TG/GC/MS spectra of the gases evolved from cured PSAs: (a) PSA-H, (b) PSA-V, (c) PSA-M.

Scheme 5. Schematic illustration of thermal degradation of structures for cured PSAs.

The gas products from the thermal degradation process could further disclose the thermal degradation behavior. TG-GC-MS was used to analyze the evolved gas by a mass spectrometer. The results obtained at a heating rate of 10°C/min were chosen to analyze all the possible degradation mechanisms. The evolved gases were analyzed as a function of the temperature as shown in **Figure 6**. The strong signals are observed from the m/z fragments 2, 16 and 18 corresponding to the H_2 , CH_4 and H_2O , respectively. Besides, weak signals appear from the m/z fragments 28 and 30 assigned to the C_2H_4/CO and C_2H_6 . According to the analyses of fragments above, the structure of cured PSAs producing these ionic fragments is presumed as follow: (1) The methane from the elimination of $Si-CH_3$ and aliphatic structure, (2) The ethylene and ethane from the decomposition of unsaturated and aliphatic structure, (3) The hydrogen from the carbonization of aromatic rings and fused rings, (4) H_2O from the product of reaction between hydrogen and oxygen used as an auxiliary gas. Therefore, the thermal degradation process for the structure of cured PSAs is concluded as **Scheme 5** according to the **Figure 6**. When the temperature up to 400°C, the $Si-CH_3$ and some aliphatic structure begin to degrade and form CH_4 . With the temperature increasing to 500°C, the unsaturated and aliphatic structure decomposes into C_2H_4 and C_2H_6 . After 600°C, the aromatic rings and fused rings in cured PSAs are dehydrogenated and release H_2 . Meanwhile, the thermal degradation process is accompanied by H_2O from the reaction between the H_2 and O_2 used as an auxiliary

gas. Also, it can be clearly observed that the substituent groups have a great influence on the thermal degradation behavior from **Figure 6**. The initial formation temperature of CH_4 and H_2 for cured PSA-H is higher than cured PSA-V and PSA-M, which indicate the decomposition temperature of Si-CH_3 and the carbonization temperature of aromatic and fused rings for cured PSA-H is higher than cured PSA-V and PSA-M. This behavior is caused by the higher crosslinking index of cured PSA-H as discussed in TGA. In addition, the current intensity of CH_4 for cured PSA-M is highest among three kinds of resins and the terminal temperature of CH_4 is lowest, which can be interpreted that the cured PSA-M contains more Si-CH_3 prone to producing CH_4 during thermal degradation. This indicate the cured PSA-M have lower thermal stability than PSA-V and PSA-H. Cured PSA-V and PSA-M exhibit more obvious current intensity of C_2H_4 and C_2H_6 than cured PSA-H. This can be explained that the cured PSA-M contain more unsaturated structures as shown in **Figure 3(c)**, and the cured PSA-V contain the structure as shown in **Scheme 4(b)** which could decompose into C_2H_4 and C_2H_6 . This confirm the highest thermal stability of cured PSA-H as discussed in TGA. Also, the current intensity of m/z fragments for cured PSA-M is obviously higher than cured PSA-V except for C_2H_6 a little lower than cured PSA-V. This indicate the cured PSA-V have higher thermal stability than cured PSA-M, which has been confirmed by TGA.

4. Conclusion

The thermal curing and degradation behavior of PSAs with different substituents has been investigated, and the influence on the curing and degradation behavior from substituents has been discussed. DSC and FT-IR analysis shows that the curing reaction of PSAs is mainly the crosslinking reaction of $\text{C}\equiv\text{C-H}$ and $\text{Si-C}\equiv\text{C-}$. Meanwhile, the reactive substituents (such as Si-H and Si-CH=CH_2) could involve in the curing reaction and endow the $\text{C}\equiv\text{C-H}$ and $\text{Si-C}\equiv\text{C-}$ with higher conversions. Py-GC-MS results provide important information about the curing reaction and structure of cured PSAs. The curing reaction of PSAs is dominated by

cyclotrimerization and Diels-Alder reaction, and also contains a little addition reaction to form polyene structure. The main structures of cured PSAs contain phenyl rings, aromatic fused rings and a little polyene structure, and their contents have some dependence on the substituents. The TGA analysis shows that the reactive substituents (such as Si-H and Si-CH=CH₂) could improve the crosslinking index of cured PSAs, and endow cured PSA-H and PSA-V with better thermal stability than PSA-M. TG-GC-MS is used to investigate the degradation process of cured PSAs, which further give degradation behaviors of the structure of cured PSAs. When the temperature up to 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. Besides, the content of the degradation products and their forming temperature also are related with the substituents.

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