

Synthesis, Characterization, and Pyrolysis of Ferrocenyl Unit Containing Organosilicon Polymers

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Received 21 July 2009; accepted 5 March 2010

DOI 10.1002/app.32392

Published online 14 July 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: New polyferrocenylsiloxanes (PFSXs) and polyferrocenylsilazanes (PFSZs) with linear or linear-cyclic structure were prepared. The ceramic yields of the polymers were estimated by thermogravimetric analysis (TGA) and bulk pyrolysis, which closely depend on molecular structures. Compared with that of their linear counterparts having comparable molecular weights, the ceramic yields of linear-cyclic PFSX and PFSZ were much higher. The pyrolysis process was investigated by lysis character is (TGA) highly depend on their molecular weights and structures, infrared spectra, and pyrolysis-gas chromatog-

raphy-mass spectra (Py-GC-MS) analysis. The results indicated rather amount of ferrocene-based small molecules were formed during the pyrolysis of linear polymers in the range of 25–300°C, whereas the existence of crosslinking or branched structure in the linear-cyclic polymers prohibited this transformation, and therefore, dramatically improved the ceramic yields. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3384–3390, 2010

Key words: synthesis; pyrolysis; structure-property relations; thermogravimetric analysis

INTRODUCTION

Metal-containing polymers are of considerable current interest from a material science perspective.^{1,2} The incorporation of transition metals into polymers is relevant for various applications, such as catalysis,^{3,4} lithography,⁵ redoxactive gels,⁶ molecular and ion recognition,^{7,8} and the formation of liquid crystalline⁹ or supramolecular materials.^{10,11} Beside these applications, ceramic materials with useful mechanical, electrical, and magnetic properties also can be prepared by pyrolysis of transition-metal-containing polymer precursors.^{12–15} Organosilicon polymers, such as polysilane, polycarbosilane, and polysilazane have been used successfully to produce SiC, Si₃N₄, Si–C–N, and so forth, and related ceramic matrix composites. With outstanding thermal and thermal-oxidation stability, organosilicon polymers provide a platform for incorporation of transition metal and adding special electromagnetic functionality. Because ferrocenyl moiety is thermally robust, relatively inexpensive, and readily derivatized, it continues to be an attractive transition metal source, which make polyferrocenylsilanes and their copolymers the hottest research topics in transition-metal-containing organosilicon polymers,¹⁶ not only as magnetic

Fe–Si–C ceramic precursors^{17,18} but also as powerful tools to construct self-assembly nanostructure materials and devices, and so on.¹⁹ Meanwhile, polyferrocenylsiloxanes (PFSXs) and polyferrocenylsilazanes (PFSZs), also draw attentions for their characteristics in possible applications.^{20–22}

Recent years, we have focused our research on iron-containing polysilazane (PSZI) for their potential as a magnetic nanocomposite precursor, as well as an efficient antioxidation additive of polysiloxane materials, such as silicone oil and silicone rubber.²³ In our previous study, an iron-containing hyperbranched polysilazane was prepared by the polycondensation of silazane lithium salts with FeCl₃.²⁴ One drawback of this approach is the difficulty of removing unreacted FeCl₃ and formed lithium chloride completely because of their poor solubility in organic solvents. Aiming at developing iron-containing organosilicon polymers for antioxidation additive via simple synthetic routes that avoid the mentioned disadvantage, we designed and synthesized PFSZ and PFSX through hydrosilylation reactions. Compared with condensation polymerization, an obvious advantage for hydrosilylation reaction is that there is no any byproduct produced. Furthermore, the introduction of ferrocene moiety may provide PFSZ or PFSX better storage stability than the above-mentioned Fe–N bond containing PSZI. In this article, we would like to report our preliminary investigation on synthesis and thermal behavior of new PFSXs and PFSZs with linear or linear-cyclic structures. For

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comparison, linear PFSXs and PFSZs were also prepared via hydrolytic and ammonolytic condensation polymerization, respectively.

EXPERIMENTAL

Materials

Me₂HSiCl was purchased from Alfa Aesar. 1,1'-bis(dimethylvinylsilyl)ferrocene (**1**) and 1,1'-bis(dimethylhydrosilyl)ferrocene (**2**) were synthesized according to literature procedures.²⁵ 1,1,3,3-tetramethyldisiloxane (MM^H) and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D₄^{Vi}) were purchased from Jilin Haoyou Industrial Company and fractionated before use. 1,1,3,3-tetramethyldisilazane (MM^{NH}) and 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane (D₃^{NVi}) were synthesized according to literature procedures.^{26,27} Karstedt's catalyst (platinum-divinyltetramethyldisiloxane complex in divinyltetramethyldisiloxane, MM^{Vi}, 1.5 wt % Pt) was prepared by general procedure.²⁸ All solvents were distilled from sodium benzophenone ketyl. All reactions were carried out under an atmosphere of nitrogen.

Synthesis

Synthesis of compound **3**

To a solution of **1** (0.96 g, 2.71 mmol), 64 μL of Karstedt's catalyst (34 ppm) in 25 mL anhydrous toluene was added HMe₂SiCl (1.00 mL, 8.71 mmol) at room temperature. The mixture was stirred at 50°C for 1 h. After cooling to room temperature, the mixture was evaporated under reduced pressure to afford 1.44 g (2.65 mmol) compound **3** in 98% yield as moisture-sensitive viscous oil. ¹H-NMR (CDCl₃, 300 Hz): δ0.14 (s, 12H, -Si(CH₃)₂CH₂), δ0.39 (m, 12H, -CH₂Si(CH₃)₂Cl), δ0.60 (m, 4H, -Si(CH₃)₂CH₂), δ0.73 (m, 4H, -CH₂Si(CH₃)₂Cl), 4.17 (m, 4H, C₅H₄), δ4.40 (m, 4H, C₅H₄). ²⁹Si-NMR (CDCl₃, 59.62 Hz): δ-0.16 (-Si(CH₃)₂CH₂), δ32.86 (-CH₂Si(CH₃)₂Cl). Anal. Calcd. C 58.85, H 8.02, Cl 15.83; found: C 58.49, H 8.04, Cl 15.51.

Synthesis of PFSXs **IP-1** and **IP-3**

Procedure a: To a mixture of **3** (1.44 g, 2.65 mmol) and NaHCO₃ (1.01 g, 10 mmol) in 20 mL ethanol were added 97 μL H₂O at 25°C. The mixture was stirred for 10 h at the temperature. After filtration, the filtrate was condensed *in vacuo* to produce 1.24 g (2.54 mmol) **IP-1** in 96% yield as a viscous liquid. ¹H-NMR (CDCl₃, 300 Hz): δ0.12 (s, 12H, -Si(CH₃)₂CH₂), δ0.31 (m, 12H, -CH₂Si(CH₃)₂O), δ0.56 (m, 4H, -Si(CH₃)₂CH₂), δ0.68 (m, 4H, -CH₂Si(CH₃)₂O), δ4.10 (m, 4H, C₅H₄), δ4.38 (m, 4H, C₅H₄). ²⁹Si-NMR (CDCl₃, 59.62 Hz): δ-0.18

(-Si(CH₃)₂CH₂), δ8.20 (-CH₂Si(CH₃)₂O). GPC M_n = 11,000, PDI = 2.17. Anal. Calcd. C 54.10, H 8.20; found: C 53.91, H 8.22.

Procedure b: To a solution of **1** (2.98 g, 8.42 mmol), Karstedt's catalyst (192 μL, 34 ppm) in 75 mL anhydrous toluene was added MM^H (1.13 g, 8.42 mmol). The mixture was stirred at 50°C for 1 h and then another 12 h at room temperature. After removing the volatiles *in vacuo*, 4.03 g (8.25 mmol) **IP-3** was received as a viscous liquid in 98% yield. ¹H-NMR (CDCl₃, 300 Hz): δ0.14 (s, 12H, -Si(CH₃)₂CH₂), δ0.33 (m, 12H, -CH₂Si(CH₃)₂O), δ0.55 (m, 4H, -Si(CH₃)₂CH₂), δ0.65 (m, 4H, -CH₂Si(CH₃)₂O), δ4.14 (m, 4H, C₅H₄), δ4.37 (m, 4H, C₅H₄). ²⁹Si-NMR (CDCl₃, 59.62 Hz): δ-0.34 (-Si(CH₃)₂CH₂), δ8.15 (-CH₂Si(CH₃)₂O). GPC M_n = 27,000, PDI = 1.85. Anal. Calcd. C 54.10, H 8.20; found: C 53.94, H 8.17.

Synthesis of PFSZs **IP-2** and **IP-4**

Procedure a: To a saturated solution of NH₃ in 10 mL toluene was slowly added **3** (1.24 g, 2.28 mmol) over 45 min at room temperature. After stirred for 5 h, the mixture was filtered. The filtrate was evaporated to give 1.19 g (2.19 mmol) of **IP-2** as a viscous liquid in 96% yield. ¹H-NMR (CDCl₃, 300 Hz): δ0.10 (s, 12H, -Si(CH₃)₂CH₂), δ0.23 (m, 12H, -CH₂Si(CH₃)₂N), δ0.40 (m, 4H, -Si(CH₃)₂CH₂), δ0.54 (m, 4H, -CH₂Si(CH₃)₂N), δ4.05 (m, 4H, C₅H₄), δ4.30 (m, 4H, C₅H₄). ²⁹Si-NMR (CDCl₃, 59.62 Hz): δ-0.90 (-Si(CH₃)₂CH₂), δ4.02 (-CH₂Si(CH₃)₂NH). GPC M_n = 5400, PDI = 1.36. Anal. Calcd. C 54.10, H 8.40, N 3.07; found: C 53.89, H 8.31, N 2.98.

Procedure b: To a solution of **1** (2.97 g, 8.40 mmol) and 192 μL (34 ppm) of Karstedt's catalyst in 75 mL anhydrous toluene was added MM^{NH} (1.12 g, 8.40 mmol) within 2 min at room temperature. The mixture was stirred at 90°C for 1.5 h and then another 12 h at room temperature. After removing the volatiles, 4.01 g (8.23 mmol) **IP-4** was obtained as a viscous liquid in 98% yield. ¹H-NMR (CDCl₃, 300 Hz): δ0.09 (s, 12H, -Si(CH₃)₂CH₂), δ0.22 (m, 12H, -CH₂Si(CH₃)₂N), δ0.37 (m, 4H, -Si(CH₃)₂CH₂), δ0.53 (m, 4H, -CH₂Si(CH₃)₂N), δ4.04 (m, 4H, C₅H₄), δ4.28 (m, 4H, C₅H₄). ²⁹Si-NMR (CDCl₃, 59.62 Hz): δ-0.87 (-Si(CH₃)₂CH₂), δ3.99 (-CH₂Si(CH₃)₂N). GPC M_n = 64,000, PDI = 1.41. Anal. Calcd. C 54.10, H 8.40, N 3.07; found: C 53.91, H 8.36, N 3.00.

Synthesis of PFSX **cP-1**

PFSX **cP-1** was prepared as a very viscous liquid in 98% yield from reaction of **2** with D₄^{Vi} (the molar ratio of **2** : D₄^{Vi} is 2 : 1), essentially in the same manner as described for **IP-3**. ¹H-NMR (CDCl₃, 300 Hz, ppm): δ0.10–0.22 (m, 12H, -Si(CH₃)₂CH₂; 6H,

$-\text{CH}_2\text{CH}_3\text{SiO}$; 6H, $-(\text{CH}=\text{CH}_2)\text{CH}_3\text{SiO}$, δ 0.40–0.50 (m, 4H, $-\text{Si}(\text{CH}_3)_2\text{CH}_2$; 4H, $-\text{CH}_2\text{CH}_3\text{SiO}$), δ 4.18 (m, 4H, C_5H_4), δ 4.78 (m, 4H, C_5H_4). ^{29}Si -NMR (CDCl_3 , 59.62 Hz, ppm): δ -18.90 ($-\text{CH}_2(\text{CH}_3)\text{SiO}$), δ -0.14 ($-\text{Si}(\text{CH}_3)_2\text{CH}_2$). GPC $M_n = 21,000$, PDI = 2.0. Anal. Calcd. C 50.63, H 7.17; found: C 50.39, H 7.09.

Synthesis of PFSZ cP-2

PFSZ cP-2 was prepared as a very viscous liquid in 99% yield from reaction of **2** with D_3^{NVi} (the molar ratio of **2** : D_3^{NVi} is 3 : 2), essentially in the same manner as described for IP-4. ^1H -NMR (CDCl_3 , 300 Hz, ppm): δ 0.09–0.18 (m, 9H, $-\text{Si}(\text{CH}_3)_2\text{CH}_2$; 4.5H, $-\text{CH}_2\text{CH}_3\text{SiNH}$; 4.5H, $-(\text{CH}=\text{CH}_2)\text{CH}_3\text{SiNH}$), δ 0.40–0.50 (m, 3H, $-\text{Si}(\text{CH}_3)_2\text{CH}_2$; 3H, $-\text{CH}_2\text{CH}_3\text{SiNH}$), δ 4.04 (m, 4H, C_5H_4), δ 4.27 (m, 4H, C_5H_4). ^{29}Si -NMR (CDCl_3 , 59.62 Hz, ppm): δ -3.43 ($-\text{CH}_2(\text{CH}_3)\text{SiNH}$), δ -0.81 ($-\text{Si}(\text{CH}_3)_2\text{CH}_2$). GPC $M_n = 76,000$, PDI = 1.46. Anal. Calcd. C 50.85, H 7.63, N 6.36; found: C 50.57, H 7.58, N 6.29.

Pyrolysis of PFSXs and PFSZs

Pyrolysis of the samples was performed using an SK-1-10 tube furnace equipped with an Intelligent Universes PID controller and quartz tube. Alumina ceramics boats were used to contain the precursors in the quartz tube. After the samples were placed into the tube, an initial furnace purge of 200 mL min^{-1} was run for 15 min to remove oxygen before heating. Then the gas flow was decreased, and a flow of 50 mL min^{-1} was used during the pyrolysis. To collect the residues produced at 200, 300, and 800°C for structure characterization, the furnace temperature is increased at a rate of 5°C min^{-1} from ambient temperature, and hold at these temperatures respectively for 2 h.

Characterization

IR spectra were recorded on a Bruker tensor 27 spectrophotometer. ^1H -NMR and ^{29}Si -NMR spectra were obtained on a Bruker DMX 300 spectrometer. The molecular weight and distribution was measured by a gel permeation chromatograph (GPC) analysis with polystyrene standard calibration using a WATERS 2690D Separation Module and Waters 2410 Refractive Index Detector equipped with TSK-GEL GMHHR-M and TSK column at 30°C in toluene. Analyses of Fe content for the polymeric and the pyrolyzed samples were performed on inductively coupled plasma spectroscopy. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris 1 TGA, at a heating rate of 10°C min^{-1} in a nitrogen flow with a rate of 20 mL min^{-1} . Py-

GC-MS was recorded on CDS 500 pyrolysis unit and SHIMADZU GCMS-2010 mass spectrometer.

RESULTS AND DISCUSSION

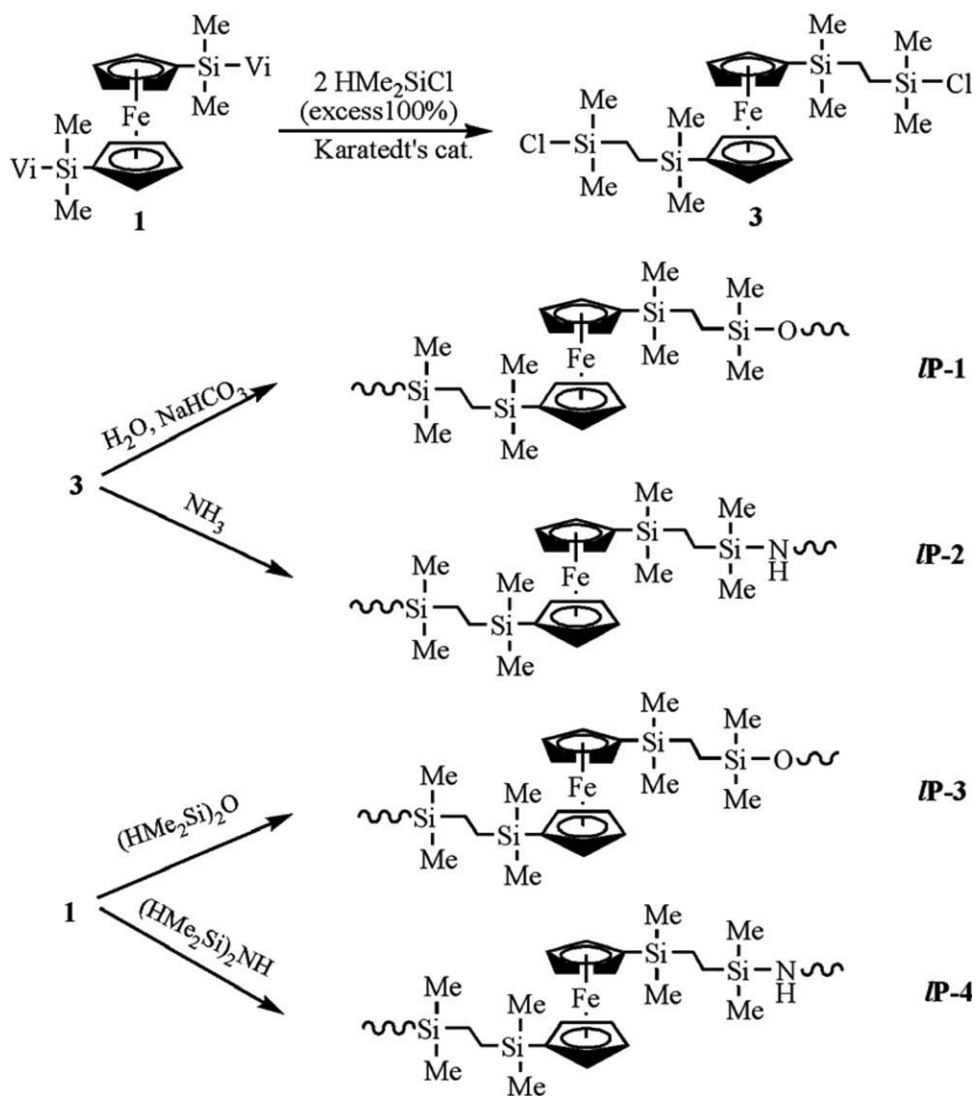
Synthesis

Compound **3** was synthesized via hydrosilylation reaction²⁵ of **1** with excess chlorodimethylsilane in toluene at 50°C in the presence of Karstedt's catalyst. The ^1H -NMR and ^{29}Si -NMR spectra of **3** indicated only β -hydrosilylation products formed under the described reaction conditions.

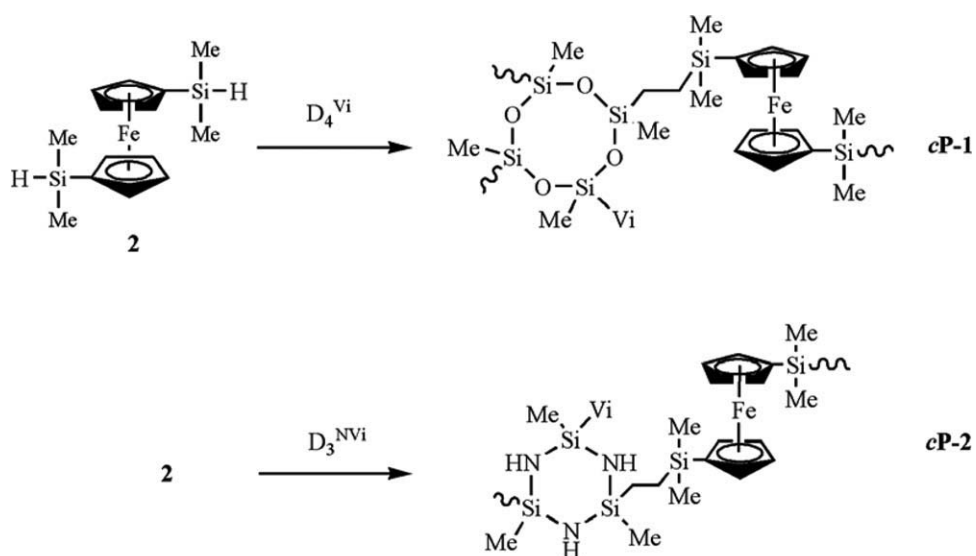
Six polymers, IP-1, IP-2, IP-3, IP-4, cP-1, and cP-2 were prepared. Among them, IP-1~IP-4 have linear structures, and cP-1 ~ 2 have linear-cyclic structures. Thus, IP-1 and IP-2 were produced from the hydrolytic reaction and ammonolytic reaction of **3**, respectively, whereas IP-3 and IP-4 were synthesized by hydrosilylation reaction of **1** with 1,1,3,3-tetramethyldisiloxane and 1,1,3,3-tetramethyldisilazane, respectively (Scheme 1). The hydrosilylation reaction of **2** with 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane produced cyclotetrasiloxane-unit containing polymer cP-1, whereas the use of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane instead of tetravinylcyclotetrasiloxane resulted in cyclotrisilazane-unit containing cP-2 (Scheme 2).

For the polymers having the same backbone synthesized from different routes, *viz.*, IP-1 versus IP-3, and IP-2 versus IP-4, the molecular weights are very different. (Table I) The molecular weight of IP-1 is far lower than that of IP-3, and IP-2 lower than that of IP-4. That is, in each case, the polymer synthesized through hydrosilylation reaction has higher molecular weight. IP-1 and IP-2 were synthesized through ammonolytic and hydrolytic reaction of **3**, respectively, and both reactions belong to condensation polymerization, whereas IP-3 and IP-4 were prepared via addition polymerization. The difference of molecular weights between IP-1 and IP-3, as well as that of between IP-2 and IP-4, may be caused by different polymerization reaction mechanism. The polymers cP-1 and cP-2 synthesized from hydrosilylation reaction of **2** with corresponding cyclosiloxane and cyclosilazane, respectively, have high molecular weights.

It is also noteworthy that the hydrosilylation reaction of ferrocenyl-containing monomers with siloxanes proceeded in milder conditions than with silazanes.²⁹ The reaction of **1** with MM^{H} as well as that of **2** with D_4^{Vi} proceeded well at 50°C, but the higher temperature was needed for the reaction of **1** with MM^{NH} or **2** with D_3^{NVi} . The initial attempt on the hydrosilylation of **1** with MM^{NH} or **2** with D_3^{NVi} under the same condition for the reaction of 1,1,3,3-tetramethyldisilazane and 1,3-divinyl-1,1,3,3-



Scheme 1



D_4^{Vi} = 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane

D_3^{NVi} = 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane

Scheme 2

TABLE I
GPC Results and Ceramic Yields at 800°C of
PFSXs and PFSZs

| samples | M_n | PDI | Ceramic yield (%) |
|-------------|--------|-----|-------------------|
| <i>IP-1</i> | 11,000 | 2.2 | 7.2 |
| <i>IP-2</i> | 5400 | 1.4 | 1.3 |
| <i>IP-3</i> | 27,000 | 1.9 | 16.4 |
| <i>IP-4</i> | 64,000 | 1.4 | 17.2 |
| <i>cP-1</i> | 21,000 | 2.0 | 55.9 |
| <i>cP-2</i> | 76,000 | 1.5 | 57.8 |

tetramethyldisilazane that adopted by Son³⁰ failed, and the increase of reaction temperature and catalyst concentration gave satisfactory results.

Pyrolysis of PFSXs and PFSZs

To examine the pyrolysis characteristics of the synthesized polymers, a series of bulk pyrolysis and TGA experiments on these samples were performed. The TGA curves between room temperature and 800°C, as shown in Figure 1, basically exhibit a three-step mass loss, and the mass loss for all six samples was observed in the first and second steps with the temperature range of 100–500°C. That is the decomposition of the organic groups was mainly took place below 500°C. No marked weight loss was observed at temperature above 600°C for all samples.

The ceramic yields obtained from TGA and the molecular weights estimated by GPC measurements for the polymers are listed in Table I. For the polymers having the same backbone but different molecular weights, namely *IP-1* versus *IP-3*, and *IP-2* versus *IP-4*, the polymers with higher molecular weights have higher ceramic yields. The ceramic yields for *IP-3* and *IP-4* are 16.4 and 17.2%, whereas those of *IP-1* and *IP-2*, their analogs with lower molecular weights, are only 7.3 and 1.3%, respectively.

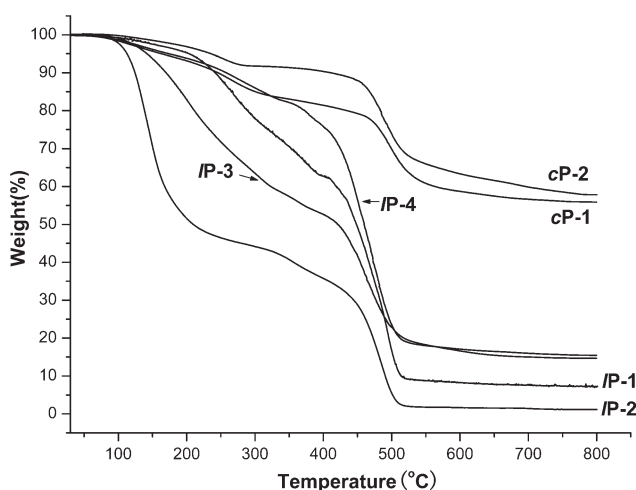


Figure 1 TGA curves of PFSXs and PFSZs.

TABLE II
Fe Contents of the PFSXs, PFSZs, and their Residues
After Pyrolysis at 800°C

| Samples | Fe content (%) | |
|-------------|------------------|-----------------|
| | Before pyrolysis | After pyrolysis |
| <i>IP-3</i> | 11.10 | 10.4 |
| <i>IP-4</i> | 11.05 | 10.8 |
| <i>cP-1</i> | 11.6 | 11.8 |
| <i>cP-2</i> | 11.9 | 12.0 |

The ceramic yields were also affected by molecular structures. Compared with those of *IP-3* and *IP-4*, the ceramic yields of *cP-1* and *cP-2*, which consist of cyclic units and linear linkages in their backbones, are much higher. This phenomenon confirms the general empirical rule that the existence of cages or rings in polymer precursors is helpful to decrease the polymer degradation and to give higher ceramic residues because of relatively high degree of branching or crosslinking resulted by cages or rings.³¹

Fe contents of four precursors, *IP-3*, *IP-4*, *cP-1*, and *cP-2* are shown in Table II, as well as those of their ceramic residues after pyrolysis at 800°C. Though there is only slight difference for the Fe contents of each precursor and its pyrolytic residue, considering the relative low ceramic yield, a certain amount of mass loss on Fe took place during the process of pyrolysis.

To understand the effect of molecular structure on pyrolytic character in detail, bulk pyrolysis experiment and Py-GC-MS were performed for *IP-3*, *IP-4*, *cP-1*, and *cP-2*, respectively. In the bulk pyrolysis experiment, each sample was set in a furnace and progressively heated at 5°C/min⁻¹ up to the appointed temperature and held for 2 h. The IR analysis for pyrolytic residues collected at different temperature was performed, and the spectra of pyrolytic residues of *IP-3* and *cP-1* are shown in Figures 2 and 3, respectively, together with that of precursors, for comparison. As to *IP-3*, the ferrocenyl stretch (1407 cm⁻¹) gradually decreased relative to the absorption of Si-Me (1256 cm⁻¹) as the temperature rose from 200 to 300°C (Fig. 2), whereas the ferrocenyl stretch changed little when compared with the Si-Me stretch in the spectrum of *cP-1* (Fig. 3). During the pyrolysis of *IP-3*, the orange sublimation products condensed on the cold part of quartz tube, including a small amount of crystal ferrocene (identified by ¹H-NMR) and some orange liquid. Py-GC-MS studies on *IP-3* showed that the volatiles formed in the range of 25–300°C were mainly consisted of two parts: ferrocene (m/z 186), (methylvinylsilyl)ferrocene (m/z 270). However, there was no any ferrocene-based product detected when *cP-1* was examined by Py-GC-MS at the same condition, though some orange sublimation products were also formed

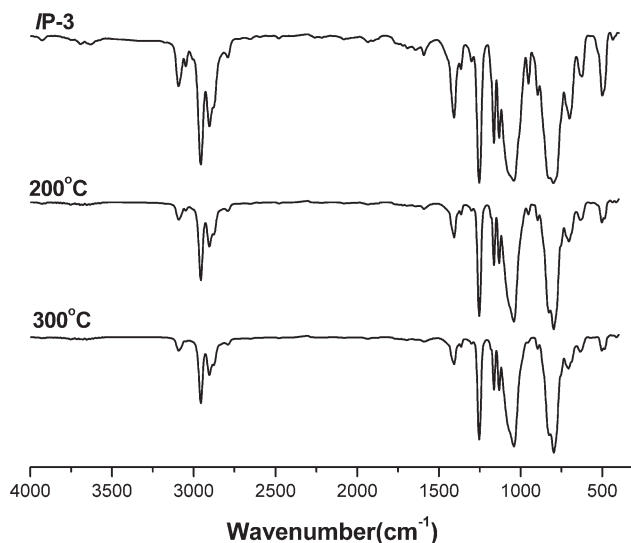


Figure 2 IR spectra of linear PFSX *IP-3* (a) and the residues after pyrolysis at different temperature for 2 h: (b) 200°C, (c) 300°C.

during its pyrolysis. Bulk pyrolysis experiment and Py-GC-MS investigation on *IP-4* and *cP-2* disclosed the similar phenomenon. The formation of ferrocene or ferrocenyl-based compounds was also observed by Manners and co-workers in the pyrolysis of linear polyferrocenylsilanes.^{17,32} The two linear polymers, *IP-3* and *IP-4*, degraded promptly and resulted in a great deal of volatile ferrocenyl-based byproducts in the range of 25–300°C, which led to the higher mass loss than the linear-cyclic ones. Although the linear-cyclic polymers didn't produce detected ferrocene or ferrocenyl-based compounds in the range of 25–300°C, their contents of Fe decreased after pyrolysis at 800°C, which suggests that the "escaping" of Fe took place above 300°C.

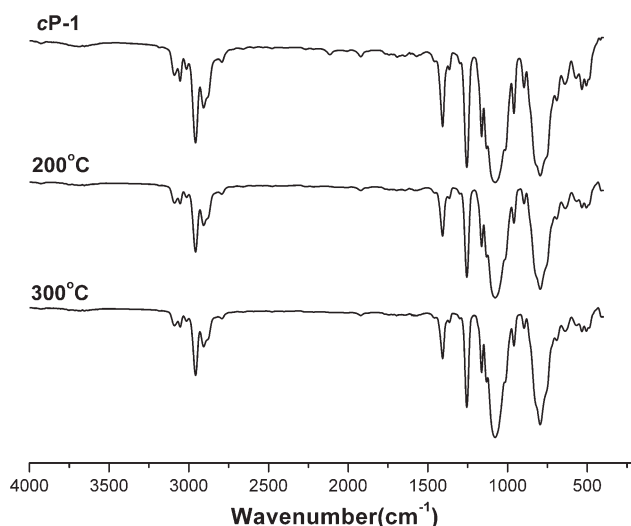


Figure 3 IR spectra of linear-cyclic PFSX *cP-1* (a) and the residues after pyrolysis at different temperature for 2h: (b) 200°C, (c) 300°C.

CONCLUSIONS

New ferrocenyl-based polymers including linear and linear-cyclic PFSXs and PFSZs were synthesized. Investigation on pyrolytic behavior of the polymers indicated that the ceramic yield was affected by molecular weight as well as structure. For the polymers with same structures, higher ceramic yield was observed for that with higher molecular weight. The introduction of cyclic structures into polymers provides branching or crosslinking, which are also helpful for increasing ceramic yields. The ferrocenyl-based compounds escaped in the range of 25–300°C during pyrolysis of linear polymers, whereas the loss of iron-containing moiety took place above 300°C for linear cyclic polymers.

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