



Synthesis and thermal degradation mechanism of polyorganocarboranesiloxanes containing *m*-carboranylmethyl unit



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ABSTRACT

This paper reports a high-yielding, efficient and facile method in preparing monomers, namely 1,7-bis(hydroxyl(dimethyl)silylmethyl)-*m*-carborane (**M1**), 1,7-bis(diethylamino(dimethyl)silylmethyl)-*m*-carborane (**M2**), 1,3-dimethyl-1,3-diphenyl-siloxanediol (**M3**) and diethylaminomethylphenylsilane (**M4**). The reaction of **M2** and **M3** to get polymer **P1**, and the reaction of **M1** and **M4** to get polymer **P2** which has a promising lead in searching for materials with high-temperature properties. The structure of monomers and linear polymers were characterized by NMR and FTIR. Thermal properties of the polyorganocarboranesiloxane elastomers were characterized by DSC and TGA. The results showed that elastomers **E1** and **E2** have better thermal stability and thermal oxidative stability with 5% weight loss temperatures above 570 °C, 650 °C in nitrogen and 536 °C, 730 °C in air, respectively than that of linear polymers **P1** and **P2**. The highlight was to study the thermal degradation mechanism of polyorganocarboranesiloxane elastomers using XPS and Solid-state ²⁹Si NMR. Carborane and organosiloxane outside of samples were gradually oxidized to B₂O₃ and SiO₂ respectively, the inside only occurred the cleavage of the Si-Ph bond caused by terminal hydroxyl groups which resulted in chain branching and illustrated there was no access for oxygen easy to internal oxidation.

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1. Introduction

Polysiloxanes, which have many excellent properties, such as good resistance to heat and cold, good hydrophobicity and electro-insulating properties, are among the best choices for application whenever a polymer material is required to withstand an unusually wide range of temperatures and still maintain desired properties [1–4]. They have been widely used in many fields, such as aviation, aerospace, automobile industry, and medical fields, to withstand very crucial conditions or environments. With the development of the aviation, aerospace and other fields, the demand for high-performance elastomeric materials is also increasingly urgent especially the properties of resisting higher temperatures which are used in sealing devices for fuel systems, flight control systems and for insulations on cables [5–7]. However, the mainly method to improve the thermal properties of the silicon rubber is changing the main-chain structure by adding the bulky group, such as

arylene [8–10], aryloxide [11], N,N'-bis(diphenylsilyl)tetramethylcyclodisiazane [12–15] and carboranes [16–26] to increase the rigidity of polymer chain and then delay the degradation speed. Carboranes, which are rich boron cluster and high thermal and anti-oxidation stabilities, have attracted significant attention and extensive researches as one of the most excellent inorganic group to improve properties of organic polymers. Carborane containing polymers, such as polyimide, poly-heterocycles, phenol formaldehyde resin, polyethers, polyurethanes, polythiophenes, polyphosphazenes and polysiloxanes have been reported [27–34] to improve the high temperature resistance performance of the intrinsic polymer. However, the most promising for the excellent high-temperature elastomeric performance characteristic was the carborane-siloxane polymers because of incorporation of the carborane moiety into the siloxane backbone significantly enhanced overall thermal stability.

Among the known poly(carborane-siloxane) polymers, which are used in the synthesis of polymers and contain the C_{cb}-Si [35–38] or the system of bonds C_{cb}-(CH₂)_x-Si (x = 1–4, C_{cb} stand for the carbon of carborane). When x = 1, polymer exhibits higher stability even

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facing both nucleophilic and electrophilic reagents compared to polymer when $x = 0$; Meanwhile, it also shows higher thermal stability compared to the polymer when $x = 2, 3, 4$ [39]. Hence it is particular important to synthesize this kind of reactive silicon derivatives of carboranes ($x = 1$). However, serious fabrication in the preparation of high-performance elastomers having long-term thermal and oxidative stability to the synthetic polymer chemist is a current challenge that has prevented exploitation of previously reported carboranesiloxane and there were a few reports [40–42] about the synthesis of the compounds when $x = 1$ and the pioneering processes for synthesizing polyorgano-carboranesiloxanes containing 1,7-bis(dimethylsilylmethyl)-*m*-carborane ($x = 1$) in main chain involved difficult procedures and low yields in preparing monomers. Izmailov [43] investigated the synthesis of polyorgano-carboranesiloxanes by condensation of 1,7-bis(hydroxyl(dimethyl)silylmethyl)-*m*-carborane with the α, ω -bis(dimethylamino)diorgano-siloxanes which having a methylene group between the silicon atom and carborane. And they reported that polydiorganosiloxanes containing 1,7-bis(dimethyl-silylmethyl)-*m*-carborane unit have higher thermal stability especially when the diorganosiloxane block is methylphenylsiloxane than the diorganosiloxane block is dimethylsiloxane. Therefore, it is indispensable to give further study of this kind of polymer ($x = 1$) which furnished a promising lead in searching for materials with high-temperature properties. Nevertheless, the yield of synthesis the monomers is too low and the methods are complicated and difficult to repeat and they didn't research the properties of elastomers cured by the above mentioned polymers. Recently our group has made some attempts to incorporate carborane moiety into the siloxane backbone to improve the overall thermal stability. And our previous investigations have demonstrated that a novel and facile synthetic method utilizing *p*-methoxyphenyl as protecting group and Br₂ as deprotecting reagent was developed to prepare functional organosilicone compounds contain *m*-carboranyl methyl group ($x = 1$) [44].

This work investigated the reaction of 1,7-bis (diethylamino(dimethyl)silylmethyl)-*m*-carborane (**M2**) with the 1,3-dimethyl-1,3-diphenylsiloxanediol (**M3**) to get the same polymer (**P1**) and the reaction of 1,7-bis(hydroxy(dimethyl)silylmethyl)-*m*-carborane (**M1**) with diethylaminomethylphenylsilane (**M4**) to get another polymer (**P2**) with good thermooxidative stability. The difference between **P1** and **P2** is variation the repeat units in the backbone. According to previous research [39], repeat units longer or shorter is not good for thermal properties so we designed the structure of **P1** and **P2**. In addition, the methods of synthesis **M2** and **M3** were more efficient, higher productivity and easy to repeat than the monomers reported by Izmailov, also the methods of synthesis **M1** and **M4** were high-yielding, simple and convenient. There are few reports about the four monomers which play an essential role in organic silicon chemistry. The highlight was to study the thermal stability and thermal degradation mechanism of polyorgano-carboranesiloxane elastomers under air which were cured by polysilazane curing agent (KH-CL) [45] using XPS and Solid-state ²⁹Si NMR to examine residues after degradation at 400 °C, 450 °C and 500 °C for 30 min under air, respectively.

The research on degradation mechanism will guide further investigations on polyorganocarboranesiloxanes, ceramics precursors and high temperature resistant resins which introducing carborane to modify thermal properties of polymers.

2. Experimental

2.1. Materials

All manipulations in the experiments were performed in flame-

dried glassware under nitrogen atmosphere. The solvents used were purified by distillation over the drying agents indicated and were transferred under nitrogen: Et₂O (Na), THF (Na), THP (Na), Hexane (Na), CH₂Cl₂ (CaH₂). Sodium (Na), magnesium (Mg), iodine (I₂), liquid bromine, calcium hydride (CaH₂), diethyl amine (Et₂NH), triethylamine (Et₃N) and all solvents were purchased from Beijing Chemical Works (Beijing, China). *N*-butyl lithium (2.5 M in hexane) was purchased from Acros, dichloromethylphenylsilane (98%; J&K Chemical) and used as received. Carborane was synthesized by our laboratory. 1,7-bis(4-methoxyphenyl(dimethyl)silylmethyl)-*m*-carborane (**1**) and 1,7-bis(hydroxyl-(dimethyl)-silylmethyl)-*m*-carborane **M1** were synthesized according to our previous work [44].

2.2. Synthesis of monomers

2.2.1. Synthesis of 1,7-bis(diethylamino(dimethyl)silylmethyl)-*m*-carborane (**M2**)

To a solution of 1,7-bis(4-methoxyphenyl-(dimethyl)silylmethyl)-*m*-carborane (3 g, 6 mmol) in dry CH₂Cl₂ (20 mL) was added drop wise to a solution of bromine (4.75 g, 26.4 mmol) in dry CH₂Cl₂ (10 mL) at 0 °C. After dropwise added, the reaction mixture was stirred at room temperature for about 10 h. Intermediate (**2**) was obtained after removing CH₂Cl₂ under reduced pressure. Subsequently, the obtained orange oily liquid (**2**) was dissolved in anhydrous hexane (200 mL) under nitrogen atmosphere and then added Et₂NH (4 g, 54.79 mmol) at one time at room temperature. Subsequently, the mixture was refluxed for 3 h, and the hydrochloride salts were removed by centrifuging. The product of **M2** was acquired after removing solvent under reduced pressure and nitrogen atmosphere. ²⁹Si NMR (300 MHz, Toluene, δ): 1.43 (Si(CH₃)₂NEt₂).

2.2.2. Synthesis of 1,3-dimethyl-1,3-diphenylsiloxane-diol (**M3**)

The freshly distilled Cl₂SiMePh (15 g, 78.53 mmol) in 10 mL anhydrous hexane was added slowly to a mixture of sodium hydrogen carbonate (25 g, 0.3 mol) and 200 g distilled water under nitrogen atmosphere at 0 °C with vigorous stirring. The mixture was extracted with dichloromethane and then the combined extracts were washed with distilled water.

The solvent was removed under reduced pressure, and the residue was purified by recrystallization (from *n*-hexane) to afford **M3** (9.5 g, 85.07%). ¹H NMR (400 MHz, CD₂Cl₂, δ): 0.42 (s, 6H), 2.35 (br, 2H), 7.38–7.43 (m, 6H), 7.62 and 7.63 (2d, $J = 6.50$ Hz, 4H); ¹³C NMR (400 MHz, CDCl₂, δ): 138.7, 135.2, 131.8, 129.5, 0.96. ²⁹Si NMR (300 MHz, CDCl₃, δ): -24.31 (SiOH). HRMS (ESI, m/z): [M+Na]⁺ calcd for C₁₄H₁₈NaO₃Si₂, 313.0694; found, 313.0687.

2.2.3. Synthesis of diethylaminomethylphenylsilane (**M4**)

The freshly distilled Cl₂SiMePh (10 g, 52.36 mmol) was added at one time to a mixture of Et₂NH (11 g, 0.15 mol) and 200 mL anhydrous hexane under nitrogen atmosphere at room temperature with vigorous stirring. Subsequently, the mixture was refluxed for 3 h, and the hydrochloride salts were removed by centrifuging. The product of **M4** was acquired after removing solvent under reduced pressure and nitrogen atmosphere. ¹H NMR (400 MHz, CDCl₂, δ): 0.47 (s, 3H), 1.13 (t, 12H), 2.34–3.03 (q, $J = 2.63$ Hz 8H), 7.15–7.25 (2d, $J = 7.20$ Hz 2H), 7.37 and 7.70 (m, 3H); ¹³C NMR (400 MHz, CD₂Cl₂, δ): 134.44, 129.15, 128.09, 127.5, 39.5, 15.42, -2.22. ²⁹Si NMR (300 MHz, Toluene, δ): -11.09 (SiMePhNEt₂).

2.3. Synthesis of polymers (**P1** and **P2**)

The polyorganocarboranesiloxane **P1** and **P2** were prepared in a similar procedure only the different positions of monomer

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