Synthesis and Thermal Stability of Novel Poly(*M*-Carborane-Siloxanes) with Various Pendant Groups

Xiaoxue Yang, Yanyan Zhao, Cuicui Wang, Xiaoa Zhang[*], Shengling Jiang and YafeiLyu

Key Laboratory of Carbon Fiber and Functional Polymers of Ministry of Education, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China
*Email: zhangxiaoa1982@163.com

Abstract. Poly(*m*-carborane-siloxanes) with various pendant groups (**P15**-P**46**) were synthesized via polycondensation of *m*-carborane-containing disilanols (**1**-**4**) and highly active bisureidosilanes (**5** and **6**). The obtained polymers exhibit controlled molecular weight by carefully adjusting the monomer ratio. Standard spectroscopic techniques including FTIR and NMR were utilized to characterize these polymers and satisfactory results were obtained. TGA analysis indicated that the thermal cyclization of polysiloxanes under nitrogen was greatly postponed by the incorporated *m*-carborane cage, since the siloxane bonds within the main chain were strengthened by the inductive effect of the latter. DSC and FTIR results confirmed that both siloxane unit and carborane cage were oxidized at elevated temperature under air, which contributed to the transformation of the polymers into the mixture of SiO_2 and B_2O_3. Therefore, high char yield was obtained. Besides, the electronic effect of pendant groups greatly influenced the degradation behavior of *m*-carborane-containing polysiloxanes, having nothing to do with their position. The initial degradation temperature (T_{d5}) increases with varying substituent in the order: $CH_2CH_2CF_3 < CH_3 \approx Ph < CH = CH_2$.

1. Introduction
Polysiloxane materials have been widely used in various industries including aerospace, construction, electrical and electronics, motor industry, and medicals owing to their unique properties such as high thermal stability, weather resistance, low surface energy, excellent dielectric properties, and biocompatibility[1]. Polysiloxanes are generally composed of inorganic main chain linked by Si-O bonds and organic pendant groups such as methyl, phenyl, and vinyl, therefore their modification approaches can be divided into two types: (1) the attachment of functional pendant groups, and (2) the introduction of special building blocks into the polymer main chain. Systems of the first type can be prepared by direct (co)polymerization of functional organosilicon monomers or postpolymerization of reactive pendant groups[2]. Those of the second type are generally designed to improve the thermal stability of polysiloxanes. For instance, various metallic atoms such as aluminum, titanium, and iron were incorporated into the main chain of polysiloxanes, and the obtained polymers exhibited ultrahigh melting point (T_m) and glass transition temperature (T_g)[3]. Polysiloxanes with arylene in the main chain were also designed and synthesized so that polymers with high degradation temperature and char yield were obtained[4].

Poly(*m*-carborane-siloxanes) with exactly alternating structural units (scheme 1) exhibit excellent thermal stability and elastomeric properties simultaneously, and thus have been intensively studied[5]. It is believed that the carborane cage can inhibit the cyclization of linear polysiloxane at elevated temperature under nitrogen, so the depolymerization process is postponed. The polymers were first synthesized by ferric chloride-catalyzedpolycondensation of dichlorosilane with *m*-carborane-containing dimethoxysilane, nevertheless the obtained polymers showed crosslinked rather than linear structures due to the catalyst-induced crosslinking[6-9]. In order to synthesize linear polymers with satisfactory molecular weight, *m*-carborane-containing dihydroxysilanes were reacted with various reactive monomers such as bisaminosilane, bisureidosilane, and dichlorosilane[10-13]. Recently, the polycondensation of dihydroxysilanes and cyclosilazane was conducted by Chinese scientists, which gave polymers with high thermal stability as well[14].
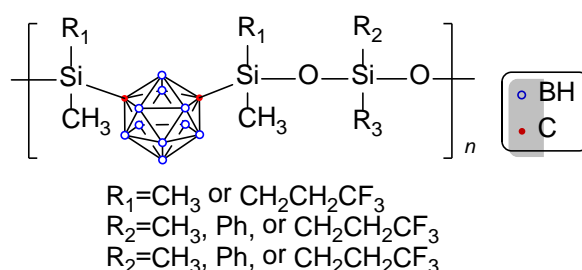

R_1=CH$_3$ or CH$_2$CH$_2$CF$_3$
R_2=CH$_3$, Ph, or CH$_2$CH$_2$CF$_3$
R_2=CH$_3$, Ph, or CH$_2$CH$_2$CF$_3$

Figure 1.Poly(*m*-carborane-siloxanes) with exactly alternating structural units.

It has been more than fifty years since the first poly(m-carborane-siloxane) was developed, however the synergistic effect of carborane moiety and pendant groups on the thermal stability has not been fully studied yet. In this work, four m-carborane-containing disilanols (1-4) with various substituents were designed and synthesized, which further reacted with bisureidosilanes (5 and 6) to give poly(m-carborane-siloxanes) (P15-P46) with various pendant groups and almost the same molecular weight (scheme 2). The obtained polymers were carefully characterized, and the effect of carborane moiety, atmosphere, and pendant groups on their thermal stability was studied.

2. Experimental

2.1. Materials
m-Carborane, tetrahydropyrrole, and *n*-butyllithium in *n*-hexane solution (2.4 M)were purchased from J&K Chemical. Phenyl isocyanate was obtained from Sigma Aldrich. Dimethyldichlorosilane, methylphenyldichlorosilane,methylvinyldichlorosilane, and methyltrifluoropropyldichlorosilane were obtained from TCI Chemical. Anhydrous diethyl ether, dry chlorobenzene, *n*-hexane, *n*-heptane, and acetone were from Sinopharm Chemical Reagent Beijing Co. Ltd. All materials were used without further purification.

2.2. Instrumentation
FTIR spectra were recorded on a Nexus 670 infrared spectrometer. Molecular weight (M_w) and polydispersity indices (M_w/M_n) of the polymers were tested in THF with a Waters 515 gel permeation chromatography system. Tetrahydrofuran (THF) was used as eluent at 30 °C at a flow rate of 1.0 ml/min. ^{1}H and ^{11}B NMR spectra were acquired in deuterated chloroform on a Bruker AV400 at a proton frequency of 400 MHz and the corresponding boron frequency. Tetramethylsilane was used as an internal standard. The melting temperature (T_m) of the *m*-carborane-containing monomers was determined by differential scanning calorimetric (DSC) method, which was conducted using a TA Q1000 DSC operating under nitrogen at a heating rate of 10 °C/min from 30 to 150 °C.Thermogravimetric analysis (TGA) and simultaneous differential scanning calorimetry (DSC) analysis were performed on a TA Instrument SDT-Q600 at a heating rate of 20 °C/min from 50 to 900 °C under nitrogen and air respectively.

2.3. Synthesis of 1,7-Bis(Hydroxylmethylorganosilyl)-M-Carborane Monomers(1-4)
1,7-Bis(hydroxylmethylorganosilyl)-*m*-carborane (**1**-**4**) were synthesized according to scheme 2. The detailed procedures for the synthesis of 1,7-bis(hydroxyldimethylsilyl)-*m*-carborane (**1**) were given below as an example. Into a 50 mL baked Schlenk flask with a side arm was added *m*-carborane (**7**, 2.58 g, 17.9 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times through the side arm. Then 10 mL of anhydrous ether was injected into the flask to dissolve **7**. After the flask was cooled below 0 ^{o}C in an ice-salt bath, *n*-butyllithium in *n*-hexane solution (2.4 M, 16.4 mL, 39.4 mmol) was added dropwise, and then the system was intensely stirred for 3 h. After stirring was stopped, the reaction mixture separated into two layers. The upper layer is *n*-hexane, while the lower layer is 1,7-dilithio-*m*-carborane ether solution. After the upper layer was removed by double-ended needle under reduced pressure, the lower layer was washed with 20 mL of *n*-hexane on stirring. *n*-Hexane was removed by the above method. The flask was further cooled in an ice-salt bath, and 10 mL of anhydrous diethyl ether was injected to dilute the solution. Into the flask was added dropwisedimethyldichlorosilane (4.8 mL, 39.4 mmol), and then the system was stirred below 0 ^{o}C for 1 h. Then the reaction proceeded at room temperature for 20 h. The formed solid byproduct lithium chloride (LiCl) was removed by filtration under reduced pressure under nitrogen. The collected filtrate was condensed to remove solvent and excess silane. 1,7-Bis(chlorodimethylsilyl)-*m*-carborane was obtained as a light brown clear liquid. This liquid was transferred to reaction flask, into which 20 mL of anhydrous diethyl ether, 20 mL of acetone, and 5 mL of deionized water were also added. The system was stirred at room temperature for 5 h. After stirring was stopped, the reaction mixture separated into two layers. The upper layer is 1,7-bis(hydroxyldimethylsilyl)-*m*-carborane (**1**) ether solution, while the lower layer is mixed solvent of acetone and water. The upper layer was condensed under reduced pressure, and crude product was obtained. Then the obtained **1** was purified by recrystallization in *n*-hexane three times, and white solid was obtained in a yield of 52.8%. T_{m} = 101.1 ^{o}C (DSC method). FTIR, ν (cm^{-1}, in KBr pellet): 3292 (-OH), 2963 (-CH$_3$-), 2592 (B-H), 1403, 1260, 1103 (Si-O), 994, 866, 811, 781, 659. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 3.50-1.50 (m, 10H), 1.94 (s, 2H), 0.26 (s, 12H).

1,7-Bis(hydroxylmethylphenylsilyl)-m-carborane(2)was synthesized from methylphenyldichlorosilane in a yield of 46.4% by similar method as a white solid. Tm = 87.6 oC (DSC method). FTIR, ν (cm-1, in KBr pellet): 3336 (-OH), 3077 (CH on Ph), 2973 (-CH3-), 2594 (B-H), 1590 (C=C on Ph), 1428, 1260, 1100 (Si-O), 993, 853, 773, 730, 694, 472, 428. 1H NMR (400 MHz, CDCl3), δ (TMS, ppm): 7.46 and 7.37 (m, 10H), 3.10-1.40 (m, 10H), 2.21 (s, 2H), 0.49 (s, 6H).

1,7-Bis(hydroxylmethylvinylsilyl)-*m*-carborane (**3**) was synthesized from methylvinyldichlorosilane in a yield of 58.1% by similar method as a white solid. T_{m} = 113.2 ^{o}C (DSC method). FTIR, ν (cm^{-1}, in KBr pellet): 3299 (-OH), 3060 and 3020 (=CH$_2$), 2958 (-CH$_3$-), 2609 (B-H), 1634 and 1595 (C=C), 1406, 1260, 1103 (Si-O), 968, 858, 802. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 6.11 (m, 2H), 5.89 (m, 4H), 3.30-1.40 (m, 10H), 2.01 (s, 2H), 0.33 (s, 6H).

1,7-Bis(hydroxylmethyltrifluoropropylsilyl)-m-carborane (4) was synthesized from methyltrifluoropropyldichlorosilane in a yield of 28.7% by similar method as a white solid. Tm = 82.0 oC (DSC method). FTIR, ν (cm-1, in KBr pellet): 3299 (-OH), 2973 (-CH3-), 2911 (-CH2-), 2609 (B-H), 1421 (Si-CH3), 1266, 1212, 1135, 1069, 1029, 898 (Si-CH2CH2CF3), 1103 (Si-O), 860, 807. 1H NMR (400 MHz, CDCl3), δ (TMS, ppm): 3.30-1.40 (m, 10H), 2.20-2.00 (s, 4H, Si-CH2CH2CF3), 1.95 (hidden by peak at 2.20-2.00, Si-OH), 1.10-0.80 (m, 4H, Si-CH2CH2CF3), 0.30 (s, 6H, Si-CH3).

2.4. Synthesis of bis(1,1-tetramethylene-3-phenylureido)methylorganosilane monomers(5 and 6)
Bis(1,1-tetramethylene-3-phenylureido)methylorganosilane monomers (5 and 6) were synthesized according to scheme 2. The detailed procedures for the synthesis of bis(1,1-tetramethylene-3-phenylureido)dimethylsilane (5) were given below as an example. A 50 mL Schlenk flask with a side arm was evacuated under vacuum and flushed with dry nitrogen three times through the side arm. Then into the flask were added n-heptane (20 mL) and dimethyldichlorosilane (6.10 mL, 50 mmol). The flask was cooled to -10 oC in an ice-salt bath, and then tetrahydropyrrole (17.7 mL, 200 mmol) was added dropwise. The system was intensely stirred at -10 oC for 3 h, and white solid byproduct was generated. The reaction proceeded at room temperature for another 15 h. Then the solid byproducttetrahydropyrrole hydrochloride was removed by filtration under reduced pressure under

nitrogen. The collected filtrate was evaporated under reduced pressure to remove solvent. The obtained crude product was further dissolved in 8 mL of anhydrous diethyl ether, and then the solvent was once again removed under reduced pressure. The dissolution and removal processes were conducted three times, and bis(tetramethyleneamino)dimethylsilane was obtained as a light brown liquid. The flask was once again cooled to -10 oC, and 25 mL of anhydrous diethyl ether was added. The system was stirred and phenyl isocyanate (10.8 mL, 98.3 mmol) was added dropwise. The reaction was conducted at -10 oC for 3 h, and plenty of white solid was generated. The reaction was further conducted at room temperature for 2 h. After stirring was stopped, the upper liquid layer was removed by double-ended needle under reduced pressure. The lower solid was washed with 10 mL of anhydrous diethyl ether, and the solvent was removed by the above method. After being washed three times, white solid 5 was obtain in a yield of 86.4%. FTIR, ν (cm-1, in KBr pellet): 3300, 3056, 2970 (-CH3-), 2877 (-CH2-), 1665, 1645 (C=O), 1597 (Ph), 1531, 1488, 1445, 1395, 1296, 1238, 1181, 1074, 1024, 958 (Si-N), 909, 845, 802 (Si-C), 752, 695, 659, 550, 501. 1H NMR (400 MHz, CDCl3), δ (TMS, ppm): 7.41 (d, 4H, aromatic protons ortho to N), 7.27 (d, 4H, aromatic protons meta to N), 7.01 (m, 2H, aromatic protons para to N), 3.46 (s, 4H), 1.97 (s, 4H), 0.09 (s, 6H).

Bis(1,1-tetramethylene-3-phenylureido)methyltrifluoropropylsilane (**6**) was synthesized from methyltrifluoropropyldichlorosilane in a yield of 98.3% by similar method as a white solid. FTIR, ν (cm^{-1}, in KBr pellet): 3300, 3064, 2970 (-CH$_3$-), 2876 (-CH$_2$-), 1667 (C=O), 1595 (Ph), 1538, 1482, 1418, 1307, 1267, 1201, 1123, 1074, 1024, 966, 902, 836, 758, 701, 552, 509. ^{1}H NMR (400 MHz, acetone-d_6), δ (TMS, ppm): 7.56 (d, 4H, aromatic protons *ortho* to N), 7.28 (d, 4H, aromatic protons *meta* to N), 7.00 (m, 2H, aromatic protons *para* to N), 3.43 (s, 4H), 2.39 (m, 2H), 1.91 (s, 4H), 1.40-1.20 (m, 2H), 0.27 (s, 3H).

2.5. Synthetic Routes to Poly(M-Carborane-Siloxanes) (P15-P46)
Poly(*m*-carborane-siloxanes) with various pendant groups (P**15**-P**46**) were synthesized according to scheme 2. The detailed procedures for the synthesis of poly(*m*-carborane-dimethylsiloxane) (P**15**) were given below as an example. Into a 50 mL baked Schlenk flask with a side arm was added 1,7-bis(hydroxyldimethylsilyl)-*m*-carborane (**1**, 731.3 mg, 2.5 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times through the side arm. Then 5 mL of dry chlorobenzene was injected into the flask to dissolve **1**. In another dry schlenk flask bis(1,1-tetramethylene-3-phenylureido)dimethylsilane (**5**, 1.146 g, 2.625mmol) was dissolved in 10 mL of dry chlorobenzene.After the first flask containing **1** was cooled to -10 ^{o}C in an ice-salt bath, the solution of **5** was added dropwise to the flask on stirring. The system was intensely stirred at -10 ^{o}C for 3 h, and then at room temperature for another 10 h. The solid byproduct was removed by filtration under reduced pressure under nitrogen, and then the filtrate was transferred to reaction flask. **1** (51.5 mg, 0.176mmol) was dissolved in 2 mL of dry chlorobenzene, and then this solution was added dropwise to the reaction flask at -10 ^{o}C under nitrogen. The reaction was conducted at -10 ^{o}C for 2 h and at room temperature for 3 h. The solid was removed by filtration, and the collected filtrate was condensed and added to a large amount of methanol on stirring. A white sticky product of polymer P**15** was precipitated in a yield of 68.2%. M_w: 11200; M_w/M_n: 2.05 (GPC, polystyrene calibration). FTIR, ν (cm^{-1}, in KBr pellet): 2963, 2597, 1410, 1262, 1100, 1046, 858, 802. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 3.10-1.50 (B-*H*), 0.19, 0.08.

P**25** was synthesized from **2** and **5** by a similar method in a yield of 71.9%. M_w: 12900; M_w/M_n: 2.12 (GPC, polystyrene calibration). FTIR, ν (cm^{-1}, in KBr pellet): 3317, 3133, 3071, 2965, 2873, 2596, 1957, 1886, 1650, 1595, 1534, 1500, 1444, 1393, 1305, 1262, 1177, 1100-1000, 845, 803, 733, 695, 474, 429. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.50-7.10 (aromatic protons), 3.30-1.50, 0.29, 0.06.

P**35** was synthesized from **3** and **5** by a similar method in a yield of 50.9%. M_w: 8800; M_w/M_n: 2.22 (GPC, polystyrene calibration). FTIR, ν (cm^{-1}, in KBr pellet): 3060, 3017, 2962, 2596, 1595, 1444, 1405, 1262, 1100-1000, 963, 848, 803, 770. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 6.06 (C*H$_2$*=CH-), 5.77(CH$_2$=C*H*-), 3.30-1.50, 0.26, 0.11.

P**45** was synthesized from **4** and **5** by a similar method in a yield of 44.1%. M_w: 9500; M_w/M_n: 1.63 (GPC, polystyrene calibration). FTIR, ν (cm^{-1}, in KBr pellet): 2964, 2910, 2600, 1444, 1419, 1368,

1316, 1266, 1211, 1130, 1100-1000, 1070, 1025, 900, 802, 768. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 3.10-1.50, 2.10-2.00 (CH_2CF$_3$), 1.00-0.80 (CH_2CH$_2$CF$_3$), 0.26, 0.15.

P16 was synthesized from **1** and **6** by a similar method in a yield of 61.1%. M_w: 9200; M_w/M_n: 1.78 (GPC, polystyrene calibration). FTIR, ν (cm^{-1}, in KBr pellet): 2964, 2597, 1444, 1410, 1368, 1314, 1264, 1210, 1100-1000, 900, 858, 812. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 3.20-1.50, 2.10-2.00, 0.90-0.70, 0.23, 0.13.

P36 was synthesized from **3** and **6** by a similar method in a yield of 65.6%. M_w: 16000; M_w/M_n: 2.05 (GPC, polystyrene calibration). FTIR, ν (cm^{-1}, in KBr pellet): 3060, 3010, 2961, 1596, 1444, 1406, 1368, 1315, 1264, 1211, 1130, 1100-1000, 1068, 966, 900, 850, 806, 767. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 6.20-5.70, 3.30-1.50, 2.10-1.90, 0.90-0.70, 0.28, 0.13.

P46 was synthesized from **4** and **6** by a similar method in a yield of 52.4%. M_w: 12000; M_w/M_n: 2.11 (GPC, polystyrene calibration). FTIR, ν (cm^{-1}, in KBr pellet): 2964, 2910, 2600, 1444, 1419, 1368, 1316, 1266, 1211, 1130, 1100-1000, 1070, 1025, 900, 802, 768. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 3.20-1.50, 2.20-2.00, 1.26, 0.79, 0.28, 0.19.

3. Results and Discussion

3.1. Synthesis of Poly(M-Carborane-Siloxanes) (P15-P46)

Poly(*m*-carborane-siloxanes) with various pendant groups (**P15**-**P46**) were synthesized via polycondensation of *m*-carborane-containing disilanols (**1**-**4**) and bisureidosilanes (**5** and **6**) according to scheme 2. The reactions and polymerizations proceeded smoothly, and desired polysiloxanes were obtained in acceptable yields (~ 41-71 %). It is worth noting that the bisureidosilane monomers are very sensitive to the moisture in the air, so they must be kept and dealt with under dry nitrogen in the glove box. The polycondensation is a nucleophilic substitution on bisureidosilane by disilanol as the nucleophile. The substitution can proceed rapidly below 0 ^{o}C, at which temperature the possible self-condensation side reaction of silanol can be greatly restrained. Chlorobenzene was selected as the polymerization solvent, for it is a good solvent for the polymer but cannot dissolve the urea byproduct, providing a driving force for the complete polycondensation and enabling an easy purification method of polymer from the byproduct.
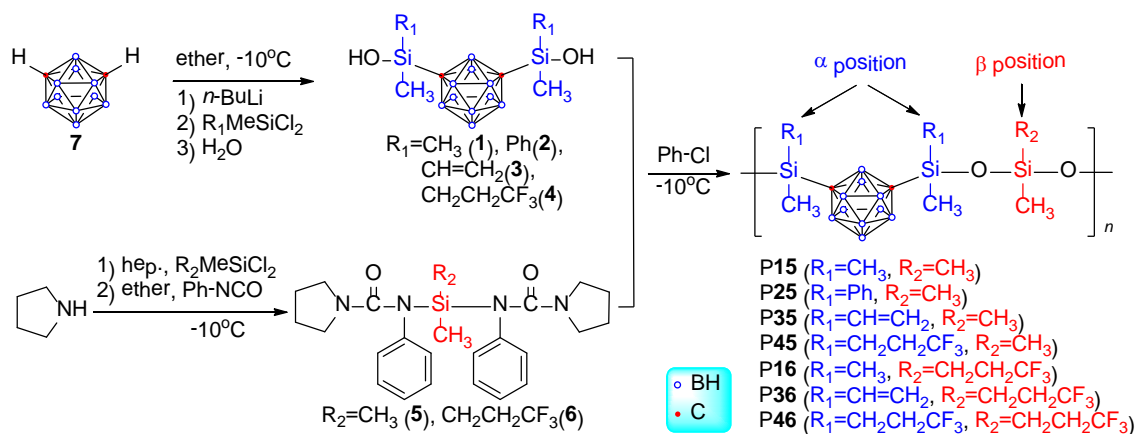

Figure 2. Synthetic routes to poly(*m*-carborane-siloxanes) with various pendant groups (**P15**-**P46**).

Considering the step-growth character of the polycondensation, the monomer ratio should be carefully adjusted so as to acquire polymers with high molecular weight. The synthetic process of poly(*m*-carborane-dimethylsiloxane) (**P15**) is taken as an example, and the results are shown in Table 1. The two monomers, 1,7-bis(hydroxyldimethylsilyl)-*m*-carborane (**1**) and bis(1,1-tetramethylene-3-phenylureido)dimethylsilane (**5**), were introduced to the reaction system by a semicontinuous charging, and thus the monomer ratio (r = [**5**] / [**1**]) was well regulated. Stoichiometric **1** was first placed in the flask, and then the chlorobenzene solution of **5** was added dropwise at -10 ^{o}C. During the addition, r increased from 0 to 1.05, while polymers with low molecular weight were obtained (Table 1, nos 1-3).

In order to increase the molecular weight of the product, additional **1** was introduced slowly to adjust the molar ratio, and polymer with the highest M_w was obtained when r is 0.98 (Table 1, no 6).

Table 1.The synthesis of poly(*m*-carborane-dimethylsiloxane) (**P15**) [a]

no.	t, h [b]	r [c]	yield, %	M_w [d]	M_w/M_n [d]
1	0	0	0	-	-
2	3	1.05	20.4	2940	1.58
3	13	1.05	39.6	3200	1.62
4	14	1.02	32.7	5030	1.60
5	15	1.00	41.1	7400	1.72
6	16	0.98	68.2	11200	2.05
7	17	0.96	66.5	8600	2.01

[a] Carried out in chlorobenzene at -10 °C under nitrogen; [b] t is the reaction time; [c] r is the molar ratio of **5** to **1**, r = [**5**] / [**1**]; [d] Estimated by gel permeation chromatograph (GPC) in THF on the basis of polystyrene calibration.

Similarly, the above semicontinuous charging was also utilized in order to synthesize poly(*m*-carborane-siloxane)s with various pendant groups. The optimal molar ratio of bisureidosilane to disilanol (r) was obtainted and the results are shown in Table 2. It is seen that polymers with relatively consistent M_w were obtain by carefully regulating r. These polymers will be chosen to study the effect of pendant group on their thermal stability, without considering the effect of molecular weight.

Table 2.The synthesis of poly(*m*-carborane-siloxane)s (**P25**-**P36**) [a]

no.	polymer	t, h [b]	r [c]	yield, %	M_w [d]	M_w/M_n [d]
1	**P25**	16	0.98	71.9	12900	2.12
2	**P25**	17	0.96	68.3	29400	2.50
3	**P35**	16	0.98	50.9	8800	2.22
4	**P45**	17	0.96	44.1	9500	1.63
5	**P16**	16	0.98	61.1	9200	1.78
6	**P36**	17	0.96	60.8	30400	2.55
7	**P36**	18	0.94	65.6	16000	2.05
8	**P46**	17	0.96	52.4	12000	2.11

[a] Carried out in chlorobenzene at -10 °C under nitrogen; [b] t is the reaction time; [c] r is the molar ratio of bisureidosilane to disilanol; [d] Estimated by gel permeation chromatograph (GPC) in THF on the basis of polystyrene calibration.

3.2. Structure Characterization

The structures of the obtained poly(*m*-carborane-siloxane)s (**P15**-**P46**) were characterized by standard spectroscopic methods such as FTIR and NMR. The analysis data were quite satisfactory corresponding to the expected molecular structures (see Experimental section for details). An example of the FTIR spectrum of poly(*m*-carborane-dimethylsiloxane) (**P15**) is shown in Fig. 1; the spectra of its corresponding monomers, 1,7-bis(hydroxyldimethylsilyl)-*m*-carborane (**1**) and bis(1,1-tetramethylene-3-phenylureido)dimethylsilane (**5**), are also given in the same figure for comparison. It is seen from Figure 1 that monomer **1** shows strong absorption band at 2592 cm^{-1}, which is assigned to the stretching vibrations of B-H bonds. This band is also present in the spectrum of **P15**, indicating that the carborane cage is successfully incorporated into the polymer structure. Besides, both monomers show medium absorption peaks at 2963 cm^{-1}, ascribing to the asymmetry stretching vibrations of methyl attached to silicon atoms. This peak is also seen in the spectrum of **P15**, which

may be attributed to the polymerization process that dimethyl silyl from the two monomers will constitute the polymer main chain. Furthermore, the broad double-peak appears in the range of 1100-1048 cm^{-1} attributed to the characteristic absorption of Si-O-Si structure, which indicates the formation of polydimethylsiloxane main chain.
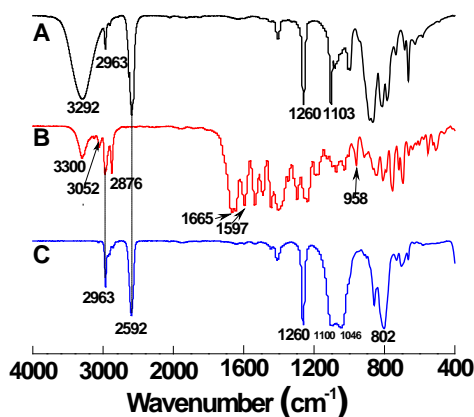

Figure3. FTIR spectra of (A) 1,7-bis(hydroxyldimethylsilyl)-*m*-carborane (**1**), (B) bis(1,1-tetramethylene -3-phenylureido)dimethylsilane (**5**), and (C) poly(*m*-carborane-dimethylsiloxane) (**P15**, Table 1 no. 6).

Figure 2 shows the ^{1}H NMR spectra of **P15** and their starting monomers (**1** and **5**). It is seen that monomer **1** shows three kinds of protons, which is well consistent with its molecular structure. Hydroxyl protons show their resonance peak at δ 1.94, while methyl protons resonate at δ 0.26. Baseline prominence and unrecognized peaks at δ 3.50-1.50 are ascribed to protons on the carborane cage. Monomer **5** also shows resonance peaks well associated with its expected structures. The aromatic protons resonate at δ 7.41, 7.27, and 7.01, and methyl protons resonate at δ 0.09, while the peaks associated with the resonance of methylene protons appear at δ 3.46 and 1.97. During the polymerization, dimethylsilane structures from both monomers are connected together to constitute the polymer chain, therefore **P15** shows two resonance peaks of methyl protons at δ 0.19 and 0.08. Besides, similar to monomer **1**, **P15** also shows baseline prominence at δ 3.50-1.50 ascribed to the resonance of protons on carborane cage.
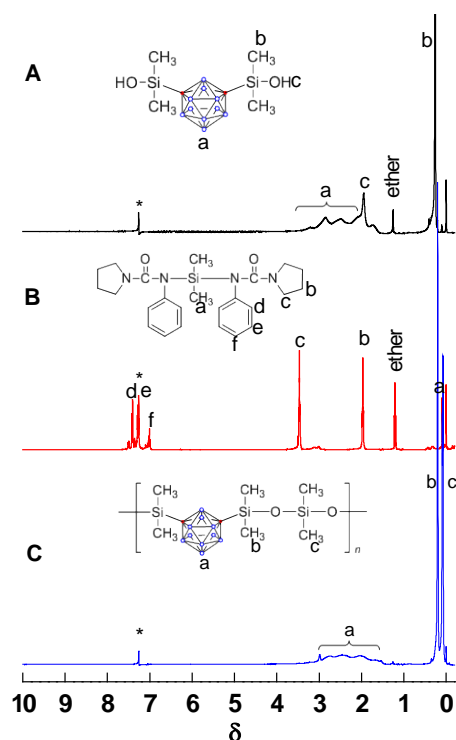
Figure4.^{1}H NMR spectra of (A) 1,7-bis(hydroxyldimethylsilyl)-*m*-carborane (**1**), (B) bis(1,1-tetramethylene -3-phenylureido)dimethylsilane (**5**), and (C) poly(*m*-carborane-dimethylsiloxane) (P**15**, Table 1 no. 6) in CDCl₃. The solvent peaks are marked with asterisks.

The most attractive point of this work lies in the introduction of carborane cage into the main chain of polysiloxanes with various pendant groups. Considering the existence of boron, ^{11}B NMR spectroscopy was also utilized to characterize the obtained polymers. The ^{11}B NMR spectrum of P**15** is shown in Figure 3. It is clear that theborons on carborane cage resonate in the range of δ -2 to -18, which is well consistent with the NMR data of *m*-carborane.
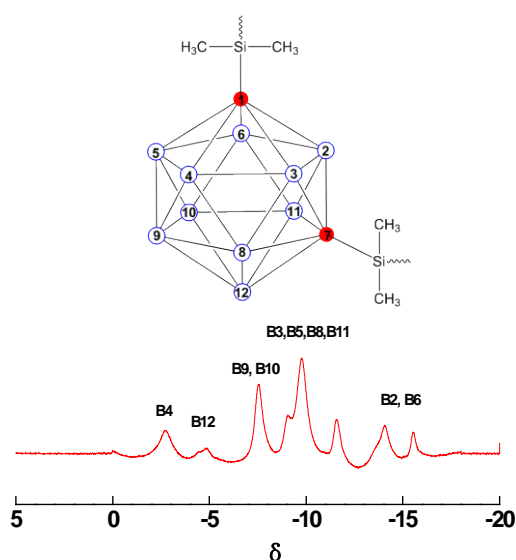

Figure5.^{11}B NMR spectrum of poly(*m*-carborane-dimethylsiloxane) (P**15**, Table 1 no. 6) in CDCl₃.

3.3. Thermal Stability

Carborane cage can serve as a heat resistant structural unit within the inorganic main chain of polysiloxane, therefore it is of great importance to carefully study the thermal stability of poly(*m*-carborane-siloxanes). Firstly, thermal gravimetric analysis (TGA) technique was utilized to evaluate the thermal stability of poly(*m*-carborane-dimethylsiloxane) (**P15**) under nitrogen and air, and the recorded TGA and DTG thermograms are shown in Figure6. The thermograms of a commercially available polydimethylsiloxane (PDMS, $M_w \approx 10000$) is also given for comparison. The initial decomposition temperature (T_{d5}) is defined as the temperature at which the polymers lose 5% of its original weight. T_{d5} values and char yield of the polymers are picked up from the TGA curves and shown in Table 3.
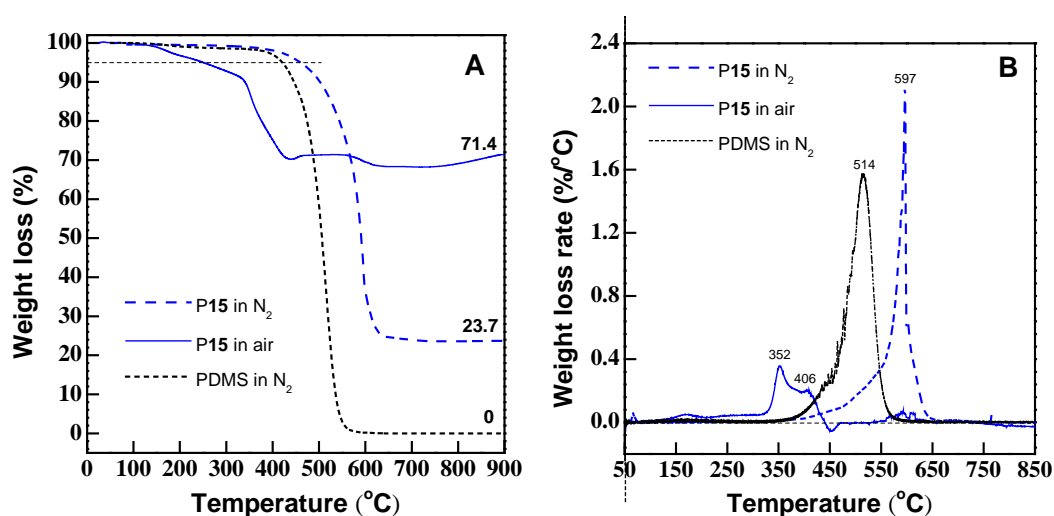

Figure6. TGA (A) and DTG (B) curves of poly(*m*-carborane- dimethylsiloxane) (**P15**, Table 1 no. 6) under nitrogen and air; TGA and DTG curves of carborane-free polydimethylsiloxane (PDMS, $M_w \approx 10000$) are also given for comparison.

Table 3.Effect of pendant groups on the thermal stability of poly(*m*-carborane-siloxane)s

no.	polymer	R_1	R_2	T_{d5}[a], ^{o}C	char yield at 900 ^{o}C, %
1	PDMS	-	-	421	0
2	P15	CH_3	CH_3	460	23.7
3[b]	P15	CH_3	CH_3	250	71.4
4	P25[c]	Ph	CH_3	476	81.6
5	P35	$CH=CH_2$	CH_3	555	87.6
6	P45	$CH_2CH_2CF_3$	CH_3	402	12.6
7[b]	P45	$CH_2CH_2CF_3$	CH_3	371	44.7
8	P16	CH_3	$CH_2CH_2CF_3$	381	12.5
9	P36[d]	$CH=CH_2$	$CH_2CH_2CF_3$	507	61.4
10[b]	P46	$CH_2CH_2CF_3$	$CH_2CH_2CF_3$	326	42.6

[a] T_{d5} is defined as the temperature at which the polymers lose 5% of its original weight; [b] TGA analysis was conducted under air; [c] Sample from Table 2 no. 1; [d] Sample from Table 2 no. 7.

It is seen that, heated under nitrogen, **P15** shows much higher T_{d5} value (460 ^{o}C) than that of carborane-free PDMS (421 ^{o}C). We are also surprised to find that **P15** owns char yield of 23.7% at 900 ^{o}C under nitrogen, which is hard to explain by the usual degradation mechanism of linear polysiloxane. It has been well established that linear polysiloxane undergoes depolymerization via a cyclization mechanism under inert atmosphere, which gives rise to low molecular weight volatile

cyclosiloxane, without forming any residue[15]. However, the introduced$m$-carborane cage within the main chain can serve to prevent the above extensive cyclization reaction, therefore the depolymerization process is postponed to higher temperature. DTG thermograms (Fig. 6B) provide more information on the depolymerization process. It is obvious that PDMS shows maximum weight loss rate (1.57%/^{o}C) at 514 ^{o}C, indicating that at this temperature the highest cyclization rate is obtained. As for **P15**, this temperature transferred to 597 ^{o}C and the corresponding weight loss rate is 2.12%/^{o}C. It is postulated that the siloxane bond can be strengthened by the inductive effect of electron-deficient m-carborane, thus the activation energy of the cyclization increases accordingly[16,17]. Additionally, the high char yield of **P15** can be attributed to the formation of boron oxide (B_2O_3), which is well confirmed by recent studies on carborane-containing polymers[18-20].

P15 owns different degradation behavior when it is heated under air. As is well-known, during the thermo-oxidative degradation of polysiloxane, the pendant group undergoes oxidation at lower temperature than depolymerization and gives rise to volatile materials such as carbon dioxide and water, and the polymer finally transforms into pure silicon dioxide (SiO_2) at elevated temperature [21]. Therefore, it is reasonable that **P15** owns lower T_{d5} (250 ^{o}C) and higher char yield (71.4%) under air. Moreover, it is believed that the polymer transforms into the mixture of SiO_2 and B_2O_3 at elevated temperature under air, since silicon and boron in the polymer structure were oxidized simultaneously. The formation of these oxides is further confirmed by FTIR analysis (Fig. 8) which will be discussed below.

Figure 5 shows the simultaneous differential scanning calorimetry (DSC) curve of **P15** under air, which gives two exothermic peaks at 406 and 579 ^{o}C. The first peak is ascribed to the oxidation of pendant methyl, indicating relatively high weight loss rate (0.21%/^{o}C, Fig. 6B). The peak at 579 ^{o}C is associated with the cleavage and oxidation of m-carborane cage, which is consistent with significant energy release and tiny weight loss (Fig. 6B). Indeed, the oxidation of carborane cage absorbs oxygen from the environment, retarding the weight loss rate to some extent.
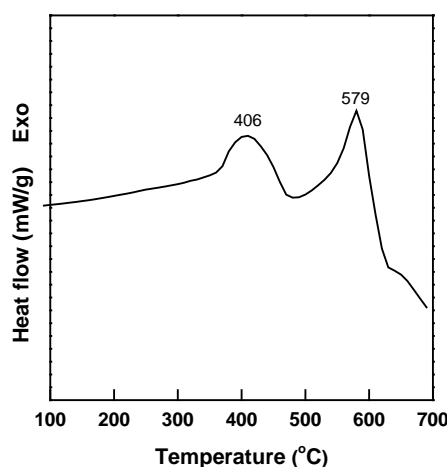

Figure7.Simultaneous differential scanning calorimetry (DSC) curve of **P15** (Table 1 no. 6) under air.

The oxidation behavior of poly(m-carborane-siloxanes) is further studied by FTIR technique. **P15** was first thermally treated under air at 450 and 650 ^{o}C for 20 min, and then the samples were analyzed by FTIR. It can be seen from Figure 6A that, after thermal treatment at 450 ^{o}C, **P15** owns similar characteristic absorption peaks as the original polymer (Fig. 1C), which indicates that both the siloxane chain and the carborane cage remain intact and only the pendant methyl is partly oxidized. Thus, it is again confirmed that the weight loss of **P15** below 450 ^{o}C under air (Fig. 4B) is caused by the oxidation of pendant methyl. However, both polymer main chain and carborane cage were damaged when **P15** was thermally treated at 650 ^{o}C. It is seen from Fig. 6B that the characteristic absorption band around 1100cm^{-1} disappears, indicating the breakdown of polymer main chain linked

by Si-O-Si. Besides, the intensity of band at 2592 cm^{-1} attributed to B-H sharply decreases due to the cleavage and oxidation of carborane cage. A broad characteristic absorption band around 1440 cm^{-1} appears in the spectrum, corresponding to B-O-B asymmetric stretching vibration, indicating the formation of boron oxide (B_2O_3). New absorption peaks appear at 1055 and 800 cm^{-1}, corresponding to asymmetrical and symmetrical stretching vibrations of silicon dioxide (SiO_2) respectively.
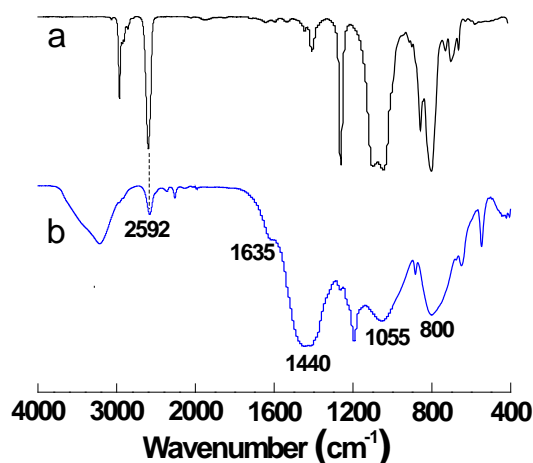

Figure8.FTIR spectra of **P15** after thermal treatment at different temperatures under air for 20 min: (A) 450 ^{o}C, and (B) 650°C.

   TGA analysis was also utilized to study other poly(*m*-carborane-siloxanes) under nitrogen, and the results are given in Figure 7. The initial decomposition temperature (T_{d5}) and char yield are picked up and shown in Table 3. On basis of their distance from *m*-carborane cage, pendant groups are divided into two kinds of substituents, i.e., R_1 and R_2, which are located on α- and β-positions respectively (scheme 2). When β-substituent (R_2) is selected as methyl, the effect of α-substituent (R_1) on the thermal stability of the polymers is studied in detail. It is seen that the T_{d5} values increase with varying α-substituent in the order: $CH_2CH_2CF_3 < CH_3 \approx$ Ph$<$CH=CH$_2$. This result is well consistent with the electronic effect of the substituents. Researches show that electron-donating substituent can increase the electron availability at oxygen, thereby facilitating the formation of cyclosiloxane and reducing the initial degradation temperature[22].Just like methyl, phenyl exhibits slight electron-donating rather than electron-withdrawing ability, on account of silicon *d*-orbital participation in the delocalized π-electronic system of phenyl. **P45** with pendant trifluoropropyl owns comparatively low T_{d5} value, probably because γ-fluoro elimination reaction occurs at a lower temperature, in which a fluorine atom migrates to the silicon atom in the main chain, generating 1,1-difluoropropene[23]. As an electron-withdrawing group, vinyl reduces electronic density of oxygen in the main chain, and thus increases the T_{d5} value of **P35**. Further analyses of TGA data give more useful information. It is seen that **P45** and **P16** exhibit quite close T_{d5} value and char yield, which indicates that the effect of pendant substituent on thermal stability mainly depends on its electronic effect, having nothing to do with its position. Besides, it is obvious from TGA data of these polymers that the effect of substituents on α- and β-positions satisfies superposition principle.
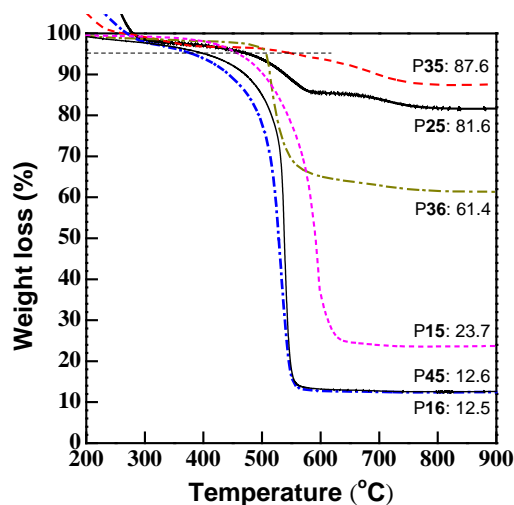
Figure9. TGA curves of poly(*m*-carborane-dimethylsiloxanes) under nitrogen.

4. Conclusion

In summary, *m*-carborane-containing disilanols (**1-4**) were reacted and condensed with highly active bisureidosilanes (**5** and **6**) to give a series of poly(*m*-carborane-siloxanes) with various pendant groups such as methyl, phenyl, vinyl, and trifluoropropyl (P**15**-P**46**). The monomer ratio was carefully adjusted by semicontinuous charging in order to obtain polymers with controlled molecular weight, which were selected to study their thermal stability. The obtained polymers were characterized with spectroscopic techniques including FTIR and NMR, which give satisfactory results. TGA analysis indicated that the thermal cyclization of polysiloxanes under nitrogen was greatly postponed by the incorporated *m*-carborane cage, since the siloxane bonds within the main chain were strengthened by the inductive effect of the latter. DSC and FTIR results confirmed that both siloxane unit and carborane cage were oxidized at elevated temperature under air, which contributed to the transformation of the polymers into the mixture of SiO_2 and B_2O_3. Therefore, high char yield was obtained. Besides, the electronic effect of pendant groups greatly influenced the degradation behavior of *m*-carborane-containing polysiloxanes, having nothing to do with their position. The initial degradation temperature (T_{d5}) increases with varying substituent in the order: $CH_2CH_2CF_3 < CH_3 \approx$ Ph<$CH=CH_2$.

5.Acknowledgments

6.References

[1]   LaiGQ and Xing SM 2010*Silicone products: synthesis process and application(in Chinese),second edition, Chemical Industry Press, Beijing* p.312
[2]   Jones R G, Ando W and Chojnowski J2000 *"Silicon-containing polymers: the science and technology of their synthesis and application", Kluwer academic publishers, London* p.79
[3]   Andrianov K A 1965 *"Metalorganic polymers", John Wiley & Sons, Inc., New York*p.276
[4]   Dvornic, PR and Lenz, RW 1983 *Polymer***24** 763
[5]   PetersEN1984*IndEng Chem. Prod. Res. Dev***23** 28
[6]   Papetti S, Schaeffer BB, Gray AP andHeying TL1966*J PolymSci***Part A-14** 1623
[7]   Dietrich HJ, Alexander RP, Heying TL, Kwasnlk H, Obenland CO,Schroeder HA 1974*MakromolChem***175**425
[8]   Patel M, Swain AC, Skinner AR, Mallinson LG and Hayes GF 2003 *MacromolSymp***202** 47
[9]   Patel M., Swain AC, Cunningham JL, Maxwell RS and Chinn SC 2006*Polym. Degrad. Stab***91**548

[10] Peters EN, Hedaya E, Kawakami JH, Kopf PW, Kwiatkowski GT, Mcneil DW and Owen DA 1977 *J Polym. Sci.: Polym. Chem. Ed***15** 2229

[11] Peters EN, Kawakami JH, Kwiatkowski GT, Hedaya E, Joesten BL, Mcneil DW and Owen DA 1977*J Polym. Sci.: Polym. Phys. Ed.***15** 723

[12] Stewart DD, Peters EN, Beard CD, Dunks GB, hedaya E, Kwiatkowski GT, Moffitt RB and Bohan JJ 1979*Macromolecules***12** 373

[13] Lai YC, Dvornic PR and Lenz RW 1982*J Polym. Sci.: Polym. Chem. Ed.***20** 2277

[14] ZhangX, Kong L, Dai L, Zhang X, Wang Q, Tan Y and Zhang Z 2011*Polymer***52** 4777

[15] Kendrick TC, Parbhoo B and White JW 1991*"The Silicon-heteroatom bond", John Wiley & Sons Ltd., London* p.97

[16] kesting RE, Jackson KF and Klusmann EB 1970*J Appl. Polym. Sci.***14** 2525

[17] Patel M and Swain AC2004 *Polym. Degrad. Stab.* **83** 539

[18] Bekasova NI1984 *Russ. Chem. Rev.***53** 61

[19] Qi S, Han G, Wang H, Li N, Zhang X, Jiang S and Lu Y 2015 *J Polym. Sci.***33** 1606

[20] Qi S, Han G, Wang H, Li N, Zhang X, Jiang S and Lu Y 2016*J Appl. Polym. Sci.*DOI: 10.1002/App.43488

[21] Jones RG, Ando W and Chojnowski J 2000 *'Silicon-containing polymers: the science and technology of their synthesis and application", Kluwer academic publishers, London*p.201

[22] Thomas TH and Kendrick TC 1970 *J Polym. Sci.***Part A-2, 8** 1823

[23] Knight GJ and Wright WW 1982*Polym. Degrad. Stab.***4** 465