Synthesis and characterization of carborane-containing polyester with excellent thermal and ultrahigh char yield

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ABSTRACT: A series of wholly carborane-containing polyesters with high thermostability were successfully synthesized by the catalytic polycondensation of carborane diol monomers with carborane diacid chlorides. They can be used for the preparation of materials of high temperature resistant coatings and adhesive. The influence of solvent, reaction temperature, and reaction time on the molecular weight and yield of the polymers were studied. In comparison with the carborane-free polyester, the carborane-containing polyesters showed higher degradation temperature and char yield and lower degradation rate. The thermal gravimetric analyzer (TGA) curves indicate that the carborane group could effectively reduce the degradation rate of carborane-containing polyesters, which give a char yield of exceeding 64% under air (47% under N_2) at 700 °C. Such data are superior to the carborane-free polyester, which showed a low char yield of around 0.3% under air (5% under N_2) at the same condition. Moreover, the thermal transition mechanism of carborane-containing polyesters was also studied. The FTIR spectra and TG-FTIR analysis indicate that the carborane cage could react with oxygen to form B—O—B and B—C linkages at elevated temperatures, which postpones the thermal decomposition of polyester and accounts for the high char yield. The newly prepared kind of high temperature polyesters have enormous technical and economic value, especially in the high temperature fields. They can be widely used as raw materials to prepare the high temperature resistant coatings or adhesives for automotive engine, aircraft and other equipments worked in high-temperature environments. Under high environmental temperature, the good thermal stability is capable of keeping polyesters stable and expanding their service lives. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44202.

INTRODUCTION

Polyester was one of the earliest families of polymers explored synthetically, and they have been thoroughly investigated and widely applied in practically all major industries such as coatings,[1,2] glass or carbon fibers[3,4] and structural adhesives[5] due to their low cost, ease of processing, and good balance of mechanical and chemical properties.[6,7] In recent years, many efforts have been paid to improving the toughness and thermostability of the polyester resins.[8,9] The thermal behavior of polyester resins over a wide temperature range is an important aspect which determines their potential utility.[10] Generally, the thermal resistance of aliphatic polyesters is poor. To improve thermal stability of polyester, aromatic groups have been introduced to the main chain of polyesters. Until now, a lot of aromatic polyester resins with high melting temperature have been reported.[9] Additionally, introducing organic heterocyclic groups into the polyester backbones also can improve the thermal stability of the polyesters.

Carboranes ($C_2B_{10}H_{12}$) have attracted a great deal of attention for more than 50 years after which were first reported by Shapiro[11] in 1962. Carborane is a remarkably stable icosahedral molecule which consists of two carbon atoms and ten boron atoms, which have three isomers as shown in Chart 1: *o*-carborane, *m*-carborane, and *p*-carborane. Generally, *m*-carborane is more stable than *o*-carborane but less than *p*-carborane. At 450 °C, *o*-arborane undergoes an irreversible thermal rearrangement to produce *m*-carborane. When the temperature increased to over 650 °C, the *m*-carborane rearranges reversibly to the *p*-carborane.[12] The stable large cage structures endows the carborane with excellent thermal and chemical stability.[13–15] Besides, the rich boron contents makes these compounds useful candidates as neutron trapping agents. Owing to these distinctive properties, carboranes have been regarded as one of the most excellent organic groups to improve performance of organic polymers with remarkable thermal stability.[16–18] Therefore, carboranes were incorporated into many traditional polymers to improve their thermal stability including epoxy resins,[19,20] phenolic
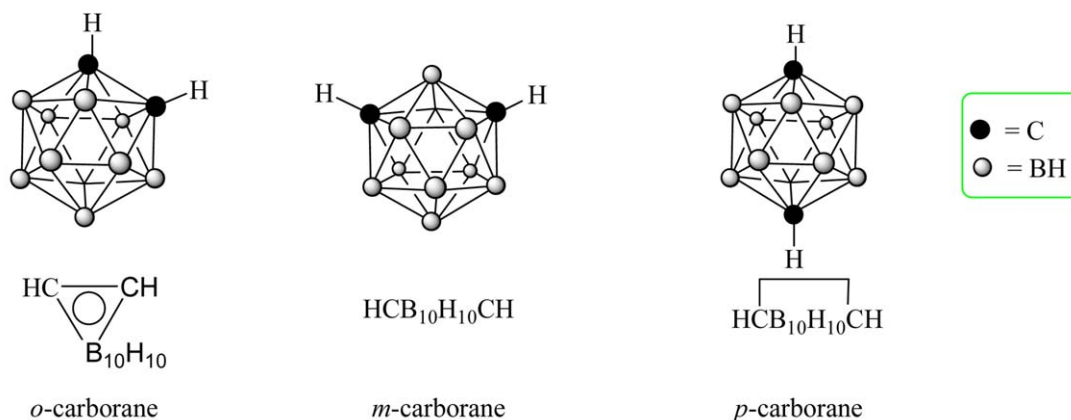
Cha 1. Structures of three carborane isomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resins,[21–23] polyurethanes,[24–27] organic silicone polymers,[28–32] benzoxazine resins,[17,33,34] polyimides,[16] and so forth.

Carborane groups also can be introduced into polyesters to improve the thermal stability of the polyesters. Decades ago, several research groups have prepared the carborane-containing polyester with different molecular weight.[24,35–38] However, few research works about carborane-containing polyester have been reported in recent years. Due to the big steric hindrance and stereostructure of the carborane, the preparation of polyesters containing carborane required tough experiment condition such as high temperature, especially when the monomers all contain carborane groups. Additionally, the thermal degradation mechanism of polyester containing carborane also been rarely studied.

Herein, we introduce carborane groups into the main chain of the aliphatic polyester to improve the thermal stability of aliphatic polyester. The highlight is that a series of wholly carborane polyesters, in which both diol and diacid chloride contain carborane, were prepared and the experiment condition is gentle. The influence of the nature of the solvent, the reaction temperature, the reaction time on the molecular weight, and yield of the polymers were studied. Furthermore, the thermal degradation mechanism of the polyester resins have been studied. The synthesis route of carborane diol precursors (**1**, **2**), diacid chloride precursors (**4**, **7**) and carborane-containing polyesters (PE-m1-m4-C (P1), PE-m1-m7-C (P2), PE-o2-m4-C (P3), PE-o2-m7-C (P4)) were showed in Scheme 1. The carborane-containing polyester PE-m1-m4-C (P1) and PE-m1-m7-C(P2) were prepared form C,C'-bis-hydroxymethyl-1,7-carborane **1** reacting with C,C'-1,7-Carboranyl bis-carboxylic acid chloride **4** and C,C'-1,7-Carboranyl bis(3-propionic acid chloride) **7**, respectively, at room temperature (25 °C) by controlling the molar ratios of diol and dichloride. And the carborane-containing polyester PE-o2-m4-C (P3), PE-o2-m7-C (P4) were prepared form C,C'-bis-hydroxymethyl-1,2-carborane **2** reacting with carborane derivatives **4** and **7**, respectively, under the same condition. The carborane diol monomers **1** and **2** contain different carborane isomers, and the carborane diacid chlorides **4** and **7** contain different carbon chains while the same meta-carborane structure. These carborane derivatives (**1**, **2**, **4**, **7**) are all originated from o-carborane or m-carborane via a series of intermediate reaction. The obtained

carborane-containing polyesters have good thermal stability at the temperatures of up to 500–700 °C. Hence, these kind of polyesters can be used as material of high temperature resistant adhesive and coating, which can be widely used in the field of aerospace, automotive and other equipments worked in high-temperature environments. Under high environmental temperature, the good thermal stability is capable of keeping polyesters stable and expanding their service lives.

EXPERIMENTAL

Materials
Carborane was purchased from Alfa Aesar China (Tian jin). Para-formaldehyde was purchased from Tian jin Chemical Reagent Research Institute. Carbon dioxide was supplied by Beijing Ruyuan Ruquan Technology Company. Phosphorus pentachloride and phosphorus oxychloride were obtained from Chengdu XiYa Chemical Technology. n-BuLi was purchased from J&K Scientific. Sodium hydroxide, sodium chloride, manganese dioxide, and tetrahydrofuran (THF) were purchased from Beijing Chemical Works. THF was dried by refluxing with sodium and the dye of benzophenone.

Characterization
FTIR spectra were measured by a Nicolet Nexus 670 FTIRspectrophotometer with a scanning range from 4000 to 400 cm^{-1}. And the solid samples were prepared as pellets using spectroscopic grade KBr. ^{1}H and ^{11}B NMR spectra were measured on a Bruker ARX 400 NMR spectrometer with CDCl$_3$ and and acetone - d6 as the solvent and tetramethylsilane (TMS; δ = 0 ppm) as internal standard. Molecular weights (M_w and M_n) and polydispersity indexes (PDI, M_w/M_n) of the polymers were estimated in THF by a Waters gel permeation chromatography (GPC) system (Waters, 515 HPLC Pump) using THF as an eluent and refractive index detector. The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGS 2 thermogravimetric analyzer, in which a sample of ~1.5 mg was heated to 800 °C at a fixed heating rate of 10 °C/min under nitrogen or air ambience. Elemental analysis (C, H) was performed with a Perkin-Elemer 2400 II Elemental Analyzer. Melting point was measured by the XT4B micro melting point apparatus (Beijing department instrument optical instrument factory).

Synthesis
The synthesis route of carborane precursors and carborane-containing polyesters were showed in Scheme 1.
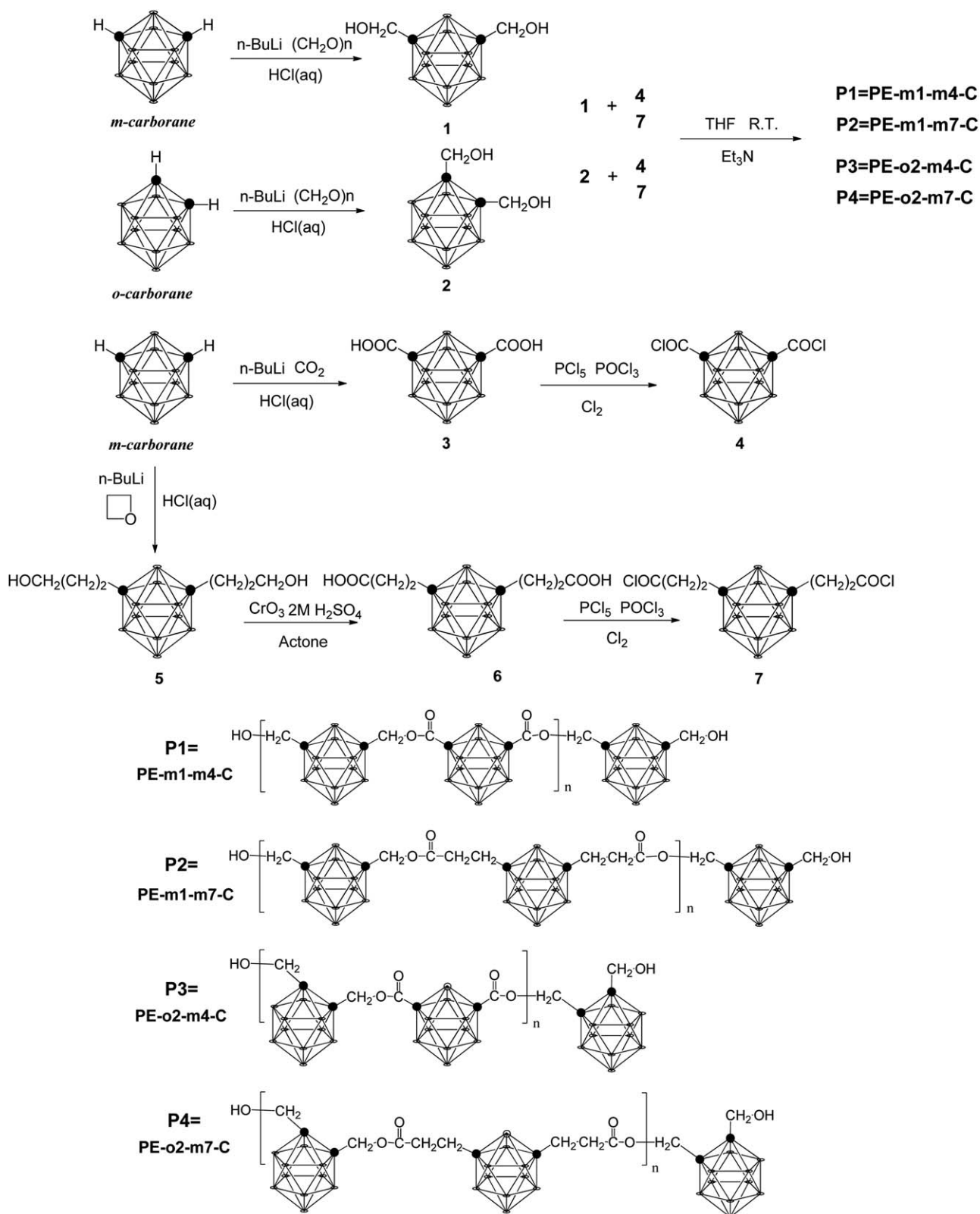
Scheme 1. The synthesis route of carborane derivatives (**1**, **2**, **4**, **7**) and carborane-containing polyesters (PE-m1-m4-C (P1), PE-m1-m7-C (P2), PE-o2-m4-C (P3), PE-o2-m7-C (P4)).

Synthesis of C,C′-bis-Hydroxymethyl-1,7-Carborane (1). 1 was synthesized according to the synthetic route shown in Scheme 1. *m*-Carborane (585.2 mg, 4.057 mmol) was dissolved in

16 mL anhydrous THF, and then a solution of 2.4 *M n*-BuLi in hexane (3.80 mL) was added dropwise to the above carborane solution at 0 °C under the protection of nitrogen and stirred for

2 h. Then, paraformaldehyde (272.5 mg, 9.08 mmol) was added into the above mixture solution in one portion. The reaction system was stirred for 3 h at room temperature (25 °C). And the reaction was quenched with 10% HCl aqueous solution. After evaporation of the solvent and water by a rotary evaporator, the residue was extracted with diethyl ether. The organic layer was washed with deionized water for three times and dried over anhydrous $MgSO_4$. After remove the solvent, the residue was purified by column chromatography on silica gel using a mixture solvent of petroleum ether and ethyl acetate as the eluent (1:1, v/v) to give a light yellow solid **1** with 87% yield[39] m. p. 150 °C.

Anal. Calcd for FTIR (ν, cm^{-1}, KBr): 3287, 1374 and 656 (-OH), 2943 and 2885 (—CH_2), 2595 (B–H), 1460 and 732 (—CH_2), 1074 (CH_2—OH). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.8-3.50 (10H, br m), 3.84 (4H, s), 1.93 (2H, s).^{13}C-NMR [$(CD_3)_2CO$] δ (ppm): 65.5, 79.4.

Synthesis of C,C′-bis-Hydroxymethyl-1,2-Carborane (2). Compound **2** was synthesized from *o*-Carborane by a procedure similar to that used for preparation of **1**. A light yellow solid with a yield of 85% and m. p. 207 °C was obtained as the target product.

Anal. Calcd for FTIR (ν, cm^{-1}, KBr): 3313, 1383 and 655 (—OH), 2947 and 2886 (—CH_2), 2599 (B-H), 1461 and 728 (—CH_2), 1078(CH_2—OH). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.8–3.50 (10H, br m), 4.26 (4H, d), 2.86 (2H, s).[13]C—NMR [$(CD_3)_2CO$] δ (ppm): 61.0, 81.6.

Synthesis of C,C′-1,7-Carboranyl-bis-Carboxylic Acid (3). Compound **3** was synthesized according to the synthetic route shown in Scheme 1. *n*-BuLi of 2.4 *M* in hexane (2.80 mL) was added dropwise to a stirred solution of *m*-carborane (439.2 mg, 3.00 mmol) in 12 mL anhydrous THF under nitrogen. The mixture was stirred for 0.5 h at 0 °C. Gaseous carbon dioxide was passed into the solution rapidly for 1 h. The reaction was quenched with 1 *M* HCl aqueous solution. After removing THF, the residue was extracted with diethyl ether. The organic layer was washed with deionized water and brine three times, respectively, and dry over anhydrous $MgSO_4$. The solvent was removed under vacuum and the solid residue was recrystallized several times from ethylene dichloride to give a colorless crystal solid **3** with 80% yield.[38,40]

Anal. Calcd for FTIR (ν, cm^{-1}, KBr): 3023, 1415 and 624 (—OH), 2618 (B-H), 1720 (C=O), 1273 [C(O)O]. ^{1}H NMR (400 MHz, Acetone) δ (ppm): 0.8-3.50 (10H, br m), 5.42 (2H, s). [13]C—NMR [Acetone] δ (ppm): 73.8, 162.3.

Synthesis of C,C′-1,7-Carboranyl-bis-Carboxylic Acid Chloride (4). **3** (220.2 mg, 0.949 mmol), PCl_5 (1680.2 mg) and 2 mL of $POCl_3$ were added into a three-neck flask equipped with a water condenser which connected to a drying tube and tail gas absorbed equipment and chlorine inlet below the surface of the liquid, then stirred for 2 h at 90 °C. Chlorine was then bubbled through for 1 h at the same temperature. After removing $POCl_3$ by a rotary evaporator, the residue was extracted with *n*-pentane, filtered. The *n*-pentane was removed and the residue was sublimed under reduced pressure. A white solid with a yield of 75% was obtained as the target product **4**.[35,40]

Synthesis of C,C′-bis-Hydroxypropyl-1,7-Carborane (5). **5** was synthesized according to the synthetic route shown in Scheme 1. *m*-Carborane (1590 mg, 11.00 mmol) was dissolved in 40 mL anhydrous THF, and then a solution of 2.4 *M* *n*-BuLi in hexane (10.10 mL) was added dropwise to the above carborane solution at 0 °C under the protection of nitrogen and stirred for 0.5 h. Trimethylene oxide (1.60 mL, 24.60 mmol) was dropped slowly, and the whole mixture was stirred for 5 h at room temperature. And the reaction was quenched with 10% HCl aqueous solution. After evaporation of the solvent and water by a rotary evaporator, the residue was extracted with diethyl ether. The organic layer was washed with deionized water for three times and dried over anhydrous $MgSO_4$. After remove the solvent, the residue was purified by column chromatography on silica gel using a mixture solvent of petroleum ether and ethyl acetate as the eluent (1:1, v/v) to give **5**[41] as a lucid solid with yield 90% and melt point of 88 °C.

Anal. Calcd for FTIR (ν, cm^{-1}, KBr): 3290, 1375, and 669 (—OH), 2939 and 2879 (—CH_2), 2592 (B-H), 1451 and 734 (—CH_2), 1064(CH_2—OH). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.8–3.50 (10H, br m), 3.57 (4H, t), 2.03 (4H, m), 1.64 (4H, m), 1.30 (2H, s).[13]C—NMR [$(CD_3)_2CO$] δ (ppm): 32.8, 33.5, 61.9, 77.5.

Synthesis of C,C′-1,7-Carboranyl-bis(3-propionic acid) (6). **5** (1140 mg, 4.38 mmol) was dissolved in 25 mL acetone and the solution was cooled down to 0 °C. Meanwhile, CrO_3 (3850 mg, 38.5 mmol) dissolved into 30 mL 2 *M* H_2SO_4 solution, and then the CrO_3 solution was added dropwise into the above solution during 0.5 h. The mixture was stirred for 10 h at room temperature (25 °C). After evaporation of the solvent and water by a rotary evaporator, the residue was extracted with CH_2Cl_2. And after removing CH_2Cl_2, the residue was treated with 10% NaOH, extracted with diethyl ether. The aqueous solution was treated with 1 *M* HCl for precipitation. And the precipitate was isolated by filtration and washed with deionized water, recrystallized from a mixture solvent of acetone and ether (1:2, v/v) to give a white crystal solid **6**[42] with 74% yield, m. p. 130 °C.

Anal. Calcd for FTIR (ν, cm^{-1}, KBr): 3047, 1314, and 654 (—OH), 2929 and 2869 (—CH_2), 2598 (B-H), 1707 (C=O), 1431 and 738 (—CH_2), 1230 [C(O)O]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.8–3.50 (10H, br m), 4.01 (2H, t), 2.46 (4H, t), 2.33 (4H, t). ^{13}C-NMR [DMSO] δ (ppm): 31.1, 33.6, 75.2, 172.4.

Synthesis of C,C′-1,7-Carboranyl-bis(3-propionic acid chloride) (7). **7** was synthesized from **6** by a procedure similar to that used for preparation of **4** from **3**. A white solid with a yield of 65% was obtained as the target product **7**.

Synthesis of PE-m1-m4-C (P1). C,C′-1,7-carboranyl-bis-carboxylic acid chloride (**4**, 161.0 mg, 0.594 mmol) was dissolved in 4 mL anhydrous THF, and then, a solution of C,C′-bis-hydroxymethyl-1,7-carborane (**1**, 121.1 mg, 0.594 mmol) in 2 mL THF and 2 mL triethylamine were added dropwise to the above solution under nitrogen at room temperature (25 °C). The mixture was stirred for 48 h at the same temperature. Then small amount of C,C′-bis-hydroxymethyl-1,7-carborane (**1**, 6.116 mg, 0.03 mmol) was added into reaction system,again and continue to stirred for 1 h. After filtering, the solvent of the filtrate was

remove by reduced pressure distillation again. Then, the product was washed repeatedly with deionized water and dried at 50 °C in a vacuum oven for 10 h. After extracting with diethyl ether, a light yellow solid powder PE-m1-m4-C (P1) was obtained with yield of 65%.

ANAL. Calcd for GPC: $M_w = 7334$, PDI = 2.17. FTIR (ν, cm^{-1}, KBr): 3388 (—OH), 2959 and 2900 (—CH$_2$), 2595 (B—H), 1719 (C=O), 1461 and 735 (CH$_2$), 1252 [C(O)O]. ^{1}H NMR (400 MHz, Acetone) δ (ppm): 0.8–3.50 (B—H, m), 1.41 (—OH, s), 3.36 (COO—CH$_2$—, s), 3.84 (HO—CH$_2$—, s). Elemental analysis calculated (%) for PE-m1-m4-C (P1): C, 23.99; H, 6.05. Found (%): C, 23.96; H, 5.99.

Synthesis of PE-m1-m7-C (P2). PE-m1-m7-C (P2) was synthesized by polycondensation of **1** with **7** and the procedure is similar to that used for preparation of PE-m1-m4-C (P1). A light yellow solid powder with a yield of 58% was obtained as the target product PE-m1-m7-C (P2).

ANAL. Calcd for GPC: $M_w = 7907$, PDI = 1.50. FTIR (ν, cm^{-1}, KBr): 3375 (—OH), 2935 and 2880 (—CH$_2$), 2594 (B—H), 1742 (C=O), 1400 and 737 (CH$_2$), 1158 [C(O)O]. ^{1}H NMR (400 MHz, Acetone) δ (ppm): 0.8–3.50 (B—H, m), 1.13 (—OH, t), 2.43 (—CH$_2$—CH$_2$COO, m), 2.86 (CH$_2$-COO, m), 3.35 (COO—CH$_2$—, s), 3.79 (HO—CH$_2$—, s). Elemental analysis calculated (%) for PE-m1-m7-C (P2): C, 31.37; H, 7.04. Found (%): C, 31.28; H, 7.02.

Synthesis of PE-o2-m4-C (P3). PE-o2-m4-C(P3) was synthesized by polycondensation of **2** with **4** and the procedure is similar to that used for preparation of PE-m1-m4-C (P1). A brown solid powder with a yield of 43% was obtained as the target product PE-o2-m4-C (P3).

ANAL. Calcd for GPC: $M_w = 5443$, PDI = 1.75. IR (ν, cm^{-1}, KBr): 3391 (-OH), 2981 and 2940 (—CH$_2$), 2588(B—H), 1724 (C=O), 1464 and 727 (CH$_2$), 1264 [C(O)O]. ^{1}H NMR (400 MHz, Acetone) δ (ppm): 0.8–3.50 (B-H, m), 3.23 (OH, s), 3.41 (COO—CH$_2$—, s), 4.54 (HO—CH$_2$—, s). Elemental analysis calculated (%) for PE-o2-m4-C (P3): C, 23.98; H, 6.07. Found (%): C, 23.93; H, 6.02.

Synthesis of PE-o2-m7-C (P4). PE-o2-m7-C (P4) was synthesized by polycondensation of **2** with **7** and the procedure is similar to that used for preparation of PE-m1-m4-C (P4). A brown solid powder with a yield of 49% was obtained as the target product PE-o2-m7-C (P4).

ANAL. Calcd for GPC: $M_w = 5867$, PDI = 1.33. IR (ν, cm^{-1}, KBr): 3399 (-OH), 2979 and 2945 (—CH$_2$), 2599 (B-H), 1752 (C=O), 1474 and 736 (CH$_2$), 1158 [C(O)O]. ^{1}H NMR (400 MHz, Acetone) δ (ppm): 0.8–3.50 (B—H, m), 2.43 (—CH$_2$—Carborane, m), 2.61 (CH$_2$—COO, m), 3.14 (OH, s), 3.59 (COO—CH$_2$—, s), 4.87 (HO—CH$_2$—, s). Elemental analysis calculated (%) for PE-o2-m7-C (P3): C, 31.29; H, 7.05. Found (%): C, 31.26; H, 7.02.

RESULTS AND DISCUSSION

Synthesis of Carborane-Containing Polyester

Carborane-containing polyesters [PE-m1-m4-C (P1), PE-m1-m7-C(P2), PE-o2-m4-C (P3), and PE-o2-m7-C (P4)] were

Table I. Yield and Molecular Weight (M_w) of PE-m1-m4-C (P1) while Using Different Solvents[a]

No.	Solvent	Yield (%)	M_w[b]	M_w[b]/M_n
1	THF	65	7334	2.17
2	Acetone	70	4839	2.00
3	THF/DMF	64	6168	1.67

[a] Carried out at room temperature (25 °C) for 48 h with Et$_3$N as acid binding agent.
[b] Estimated by GPC in THF on the basis of polystyrene calibration.

synthesized via the polycondensation reaction of carborane diols (**1** and **2**) with *m*-carboranyl diacid chlorides (**4** and **7**) according to synthetic routes shown in Scheme 1. And triethylamine (Et$_3$N) was used as the acid binding agent. The molar ratio of hydroxy to acyl chloride was 1. However, Different reaction conditions could influence the yield and molecular weight of the final products, so the influence of the nature of the solvent, the reaction temperature, the reaction time on the molecular weight and yield of the polymers were studied.

Solvents. While using different solvents, PE-m1-m4-C (P1) as the example, the yield and molecular weight (M_w) of the final product PE-m1-m4-C (P1) were showed in Table I.

From Table I, it is obvious that the product PE-m1-m4-C (P1) showed a highest M_w and comparable yield when using THF as solvent. The reason are as followed. The solubility of carborane derivatives in organic solvent was DMF > THF > acetone, respectively. The by-product Et$_3$N-HCl of polymerization follows the same rule, which was insoluble in acetone, slight soluble in THF and DMF. When using acetone as solvent, the precipitation of the Et$_3$N-HCl promotes the reaction, so the yield of polyester PE-m1-m4-C (P1) in acetone is high and the M_w is low. Using THF/DMF, PE-m1-m4-C (P1) had a low M_w/M_n while its yield and M_w were not the best.

Reaction Temperature. Take PE-m1-m4-C (P1) as the example, the yield and molecular weight (M_w) of the final product PE-m1-m4-C (P1) at different temperature were showed in Table II.

From Table II, the polymerization was feasible at room temperature, as PE-m1-m4-C (P1) has the highest M_w and yield. The polymerization of **1** with **4** is a exothermic reaction. So when increasing the temperature (25 °C), the polymerization would be hindered and some side reactions maybe occur. Moreover, with the increasing of the temperature, the by-product HCl could not be tied by the acid-binding agent Et$_3$N to produce precipitate of Et$_3$N-HCl. So the yield and M_w of the polyester PE-m1-m4-C (P1) prepared in high temperature is low.

Reaction Time. As different reaction time would affect the yield and molecular weight (M_w) of the product directly, four different time, 12 h, 24 h, 48 h, and 72 h were chosen to study the reaction time effect on the yield and molecular weight of the product, and the results are showed in Table III.

From Table III, when polymerization reaction carried out at room temperature (25 °C) in THF with the acid binding agent

Table II. Yield and Molecular Weight (M_w) of PE-m1-m4-C (P1) at the Different Temperature[a]

No.	Temperature (°C)	Yield (%)	M_w[b]	M_w[b]/M_n
1	0	60	7099	2.19
2	r.t.	65	7334	2.17
3	60	56	4600	1.67
4	100	41	4075	2.21

[a] Carried out in THF for 48 h, and the polymerization with Et$_3$N as acid binding agent.
[b] Estimated by GPC in THF on the basis of polystyrene calibration.

of triethylamine at different reaction time, PE-m1-m4-C (P1), as the example, its yield and M_w improved as extended as the reaction time. And after 48 h, the yield and M_w of PE-m1-m4-C (P1) only have slight change. The same rule also could be found in the preparation of other polyesters (PE-m1-m7-C (P2), PE-o2-m4-C (P3), and PE-o2-m7-C (P4)). So the optimal reaction time of polymerization is 48 h. During the initial polymerization process, the product molecular weight increases as time extends. Comparing with PE-m1-m4-C (P1), PE-m1-m7-C (P2) had higher polymerization degree at the same reaction time. The possible reasons are as follows. In precursor **4**, the carbon chains connecting to the carborane directly are much longer than that in precursor **7**. With the increase of the carbon chain, the reaction activity and the chain flexibility are enhanced. The same reason could be used to explain PE-o2-m4-C (P3) and PE-o2-m7-C (P4) as well. Additionally, PE-o2-m4-C (P3) has a lower polymerization degree than PE-m1-m4-C (P1) at the same reaction time. The reason is that the steric hindrance and stereostructure of the ortho-carboranyl group in precursor **2** were larger than the meta-carboranyl group in

Table III. Yield and Molecular Weight (M_w) of PE-m1-m4-C (P1), PE-m1-m7-C (P2), PE-o2-m4-C (P3), and PE-o2-m7-C (P4) with Different Reaction Time[a]

No.	Polymer	Time (h)	Yield (%)	M_w[b]	M_w[b]/M_n
1	PE-m1-m4-C (P1)	12	14	3411	1.30
2	PE-m1-m4-C (P1)	24	49	4693	1.38
3	PE-m1-m4-C (P1)	48	65	7334	2.17
4	PE-m1-m4-C (P1)	72	67	7301	2.29
5	PE-m1-m7-C (P2)	12	23	3645	1.45
6	PE-m1-m7-C (P2)	24	45	5498	1.50
7	PE-m1-m7-C (P2)	48	58	7907	1.50
8	PE-m1-m7-C (P2)	72	59	7956	1.99
9	PE-o2-m4-C (P3)	24	27	2807	2.50
10	PE-o2-m4-C (P3)	48	43	5443	1.75
11	PE-o2-m4-C (P3)	72	44	5451	1.67
12	PE-o2-m7-C (P4)	24	26	3071	1.43
13	PE-o2-m7-C (P4)	48	49	5867	1.33
14	PE-o2-m7-C (P4)	72	49	5899	1.30

[a] Carried out in THF at room temperature (25 °C), and the polymerization with Et$_3$N as acid binding agent.
[b] Estimated by GPC in THF on the basis of polystyrene calibration.

precursor **1**, and so the reaction activity of PE-o2-m4-C (P3) is lower than PE-m1-m4-C (P1). The same reason could be used to explain PE-m1-m7-C (P2) and PE-o2-m7-C (P4) as well.

Structural Characterization

The structures of the precursors (**1**, **2**, **4**, and **7**) and polyesters (PE-m1-m4-C (P1), PE-m1-m7-C(P2), PE-o2-m4-C (P3), and PE-o2-m7-C (P4)) were well characterized by standard spectroscopic methods such as FTIR and NMR. The analysis data were quite satisfactory corresponding to their expected molecular structures (see Experimental section for details). The FTIR spectra of polyesters PE-m1-m4-C (P1) and PE-m1-m7-C (P2) are showed in Figure 1. PE-m1-m4-C (P1) was illustrated in detail below as an example. The spectrum of the precursor **1** is also given in the same figure for comparison. The strong absorption peak at 2595 cm^{-1} is ascribed to the stretching vibration of B-H bonds on the carborane cage which exists both in the FTIR spectra of the precursor **1** and polyester PE-m1-m4-C (P1). Moreover, the peaks of the -CH$_2$- symmetric and antisymmetric stretching vibration at 2943 and 2885 cm^{-1} and the peaks of —CH$_2$— flexural vibrations at 1460 and 732 cm^{-1} in the precursor **1** are also exist in the FTIR spectrum of polyester PE-m1-m4-C (P1). These above peaks show that PE-m1-m4-C (P1) has the same backbone structure with its precursor **1**. Expect for these peaks, two new peaks at 1719 and 1252 cm^{-1} appear in the FTIR spectrum of polyester PE-m1-m4-C (P1), which ascribe to the stretching vibration peak of C=O and antisymmetric stretching vibration peak of —COO—, respectively. These new peaks indicate that the expected m-carborane-containing polyester PE-m1-m4-C (P1) is successfully prepared.

Similar to FTIR spectrum of PE-m1-m4-C (P1), PE-m1-m7-C (P2) only has a little difference which has a much stronger absorption at 2935 and 2880 cm^{-1} (—CH$_2$) than PE-m1-m4-C (P1). Polyesters PE-o2-m4-C (P3) and PE-o2-m7-C (P4) exhibit
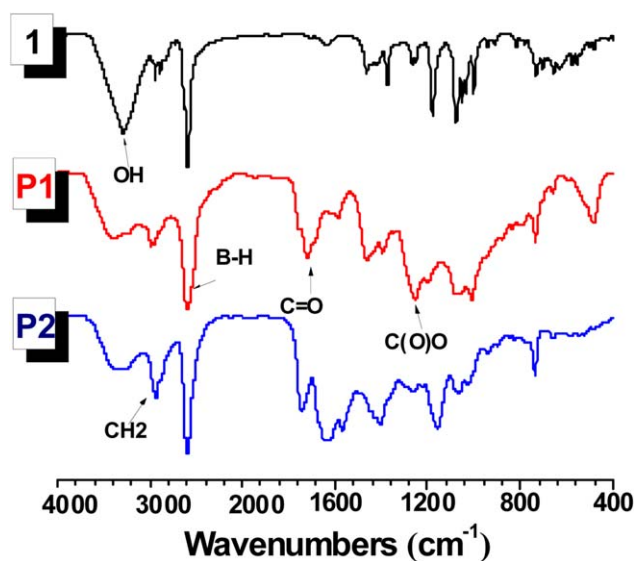

Figure 1. FTIR spectra of precursor monomer **1** and polyester PE-m1-m4-C (P1) and PE-m1-m7-C (P2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
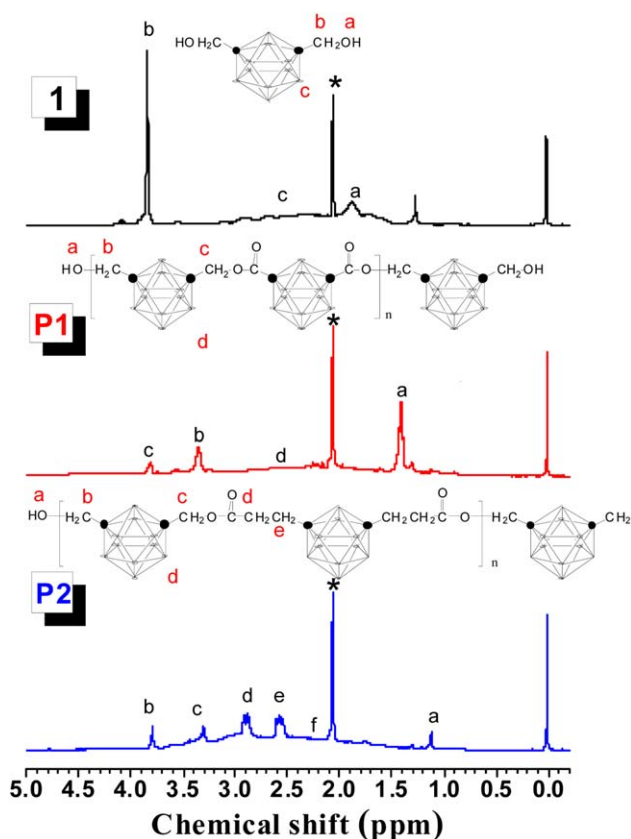
Figure 2. ^{1}H NMR spectra of precursor monomer **1** and polyester PE-m1-m4-C (P1) and PE-m1-m7-C (P2). The solvent peaks are marked with asterisks. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

almost the same characteristic peaks as PE-m1-m4-C (P1) and PE-m1-m7-C (P2), respectively, which identify themselves as polyesters in the similar way.

To further characterize the carborane-containing polyesters, NMR spectroscopy is an effective method. ^{1}H NMR spectra of PE-m1-m4-C (P1) and PE-m1-m7-C (P2) can be found in Figure 2. The spectrum of precursor **1** is also given in the same figure for comparison. For precursor **1** and polyester PE-m1-m4-C (P1), a same multiple broad peak at $\delta = 0.8$–3.50 ppm ascribes to the protons which connect to the boron atoms on the carborane cage. And the peak at $\delta = 3.84$ ascribes to the peak of the methylene (CH_2) protons connecting with —OH group. As for PE-m1-m4-C (P1), a new peak around at $\delta = 3.36$ appears which associates with the methylene (CH_2) protons connecting with —COO— group. The new peak confirms the successful formation of PE-m1-m4-C (P1).

Similar to PE-m1-m4-C (P1), the polyester PE-m1-m7-C (P2) also exhibits the multiple broad peak at $\delta = 0.8$–3.50 ppm (B-H) and the peak at $\delta = 3.84$ ascribes to the peak of the methylene (CH_2) protons connecting with —OH group. Additionally, three new peaks appear around at $\delta = 3.35$, 2.86, and 2.43 ppm which ascribes to the methylene protons (CH_2, Hc—He), respectively. These new peaks also confirmed PE-m1-m7-C (P2) has been successfully prepared. The analysis data of polyesters PE-o2-m4-C

(P3) and PE-o2-m7-C (P4) were quite satisfactory corresponding to their expected molecular structures (see Experimental section for details). Polyesters PE-o2-m4-C (P3) and PE-o2-m7-C (P4) exhibit almost the same characteristic peaks as PE-m1-m4-C (P1) and PE-m1-m7-C (P2), respectively, which identify themselves as polyesters in the similar way.

The ^{11}B NMR spectra of **1** and PE-m1-m4-C (P1) are shown in Figure 3. In the carborane cage, there are three kinds of boron atoms: (i) connecting with two carbon atoms, (ii) connecting with one carbon atom, (iii) not connecting with carbon atom which only connect with boron atoms. These three kinds of boron atoms are marked as a, b and c, respectively. The peak at $\delta = 0$–9.17 was assigned to the first kind of boron atoms. The peaks at $\delta = 10.11$ and $\delta = 12.19$ correspond to boron atoms b and boron atoms c. From the Figure 3, the characteristic peaks of boron atoms of carborane-containing polyester PE-m1-m4-C (P1) are well consistent with their precursor **1**.

Thermal Stability of Carborane-Containing Polyester

TGA Analysis. Until now, carborane-containing polyester is one of the best heat-resistant synthetic polymers. Therefore, it is significant to study the thermal stability of the obtained carborane-containing polyester resins [PE-m1-m4-C (P1), PE-m1-m7-C (P2), PE-o2-m4-C (P3), and PE-o2-m7-C (P4)]. TGA technique was utilized to study the thermal resistance of the carborane-containing polyester resins under nitrogen and air. Their TGA curves were showed Figures 4 and 5. The TGA curve of a carborane-free polyester resin (CFP) is also given for comparison.

To evaluate the initial decomposition behavior of polymers, the decomposition temperature (T_d) is defined as the temperature at which the resin loses 5% of its original weight. The T_d values and the char yields at 700 °C of the four carborane-containing polyesters and the carborane free polyester CFP have been concluded in the Figure 4 and Table IV. Obviously, PE-m1-m4-C (P1) > PE-m1-m7-C (P2) $\approx$ PE-o2-m4-C (P3) > PE-o2-m7-C
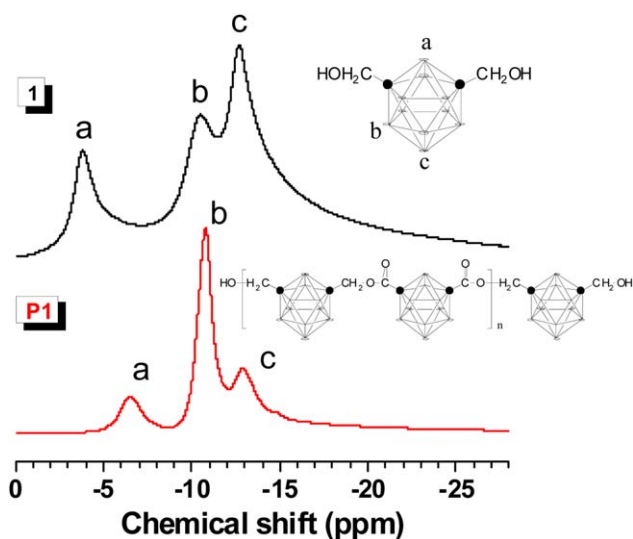

Figure 3. ^{11}B NMR spectra of precursor monomer **1** and polyester PE-m1-m4-C (P1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
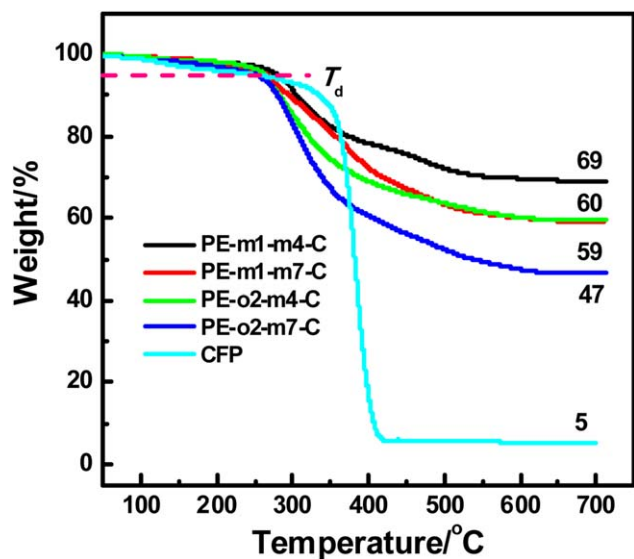
Figure 4. Thermo-gravimetric curves of PE-m1-m4-C (P1, sample from Table III, No.3), PE-m1-m7-C (P2, sample from Table III, No.7), PE-o2-m4-C (P3, sample from Table III, No.10), PE-o2-m7-C (P4, sample from Table III, No.13), and CFP in N_2 at a heating rate of 10 °C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(P4) > CFP, no matter the T_d values or the ultimate char yields. It is noting that the char yield of the PE-m1-m4-C (P1) is up to 69%, which is far higher than that of CFP (5%). The high char yield could be regarded as the "shining point" of carborane containing polyesters. The high char yield and T_d of the carborane containing polyesters indicate that the carborane groups could effectively reduce the degradation rate of carborane-
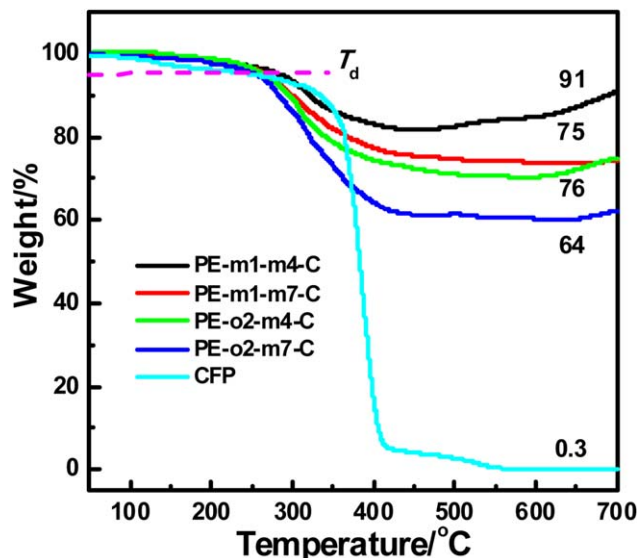

Figure 5. Thermo-gravimetric curves of PE-m1-m4-C (P1, sample from Table III, No. 3), PE-m1-m7-C (P2, sample from Table III, No. 7), PE-o2-m4-C (P3, sample from Table III, No. 10), PE-o2-m7-C (P4, sample from Table III, No. 13), and CFP in air at a heating rate of 10 °C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Thermal Properties of PE-m1-m4-C (P1), PE-m1-m7-C(P2), PE-o2-m4-C (P3), and PE-o2-m7-C (P4) in N_2

No.	Polyester	T_d (°C)	Coke formation of 700 °C in the N_2 (%)
1	PE-m1-m4-C (P1)	289	69
2	PE-m1-m7-C (P2)	269	59
3	PE-o2-m4-C (P3)	264	60
4	PE-o2-m7-C (P4)	253	47
5	CFP	251	5

containing polyesters. On the other hand, based on T_d values and char yields (700 °C) of the four carborane-containing polyesters, it can be concluded as PE-m1-m4-C (P1) > PE-m1-m7-C (P2) and PE-o2-m4-C (P3) > PE-o2-m7-C (P4), respectively. These results demonstrate that the length of carbon chain connecting to the carborane group relates to the thermal resistance of carborane-containing polyester. The shorter the carbon chain length, the better the thermal resistance of carborane-containing polyester. Moreover, form the T_d values and the char yields (700 °C) of the four carborane-containing polyesters, it also can be concluded as PE-m1-m4-C (P1) > PE-o2-m4-C (P3) and PE-m1-m7-C (P2) > PE-o2-m7-C (P4), respectively. These results indicate that the polyesters which contain meta-carborane group (P1 and P2) have better thermal resistance than the polyester which contain ortho-carborane group (P3 and P4).

In air, the T_d value and the char yield of the carborane-containing polyester showed the same trend as in N_2 as shown in Table V. It is worth noting that the char yield of the carborane free polyester CFP in air is only 0.3%, which is far lower the carborane containing polyesters. Therefore, the thermal stability of the carborane containing polyesters are far more excellent compared to the carborane free polyester CFP.

For further research, the thermal transition mechanism of carborane-containing polyesters under nitrogen and air, respectively, the TG-FTIR combination analyzer was utilized. And the polyester PE-m1-m4-C (P1) was illustrated in detail as an example as shown in Figures 6–9.

As Figure 6 shown, there are three stages in the process of decomposition of PE-m1-m4-C (P1) under nitrogen: (i) rm ~ 225 °C, the weight loss of atmospheric moisture and volatiles, (ii) 225–480 °C, the disintegration of the carborane-free

Table V. Thermal Properties of PE-m1-m4-C (P1), PE-m1-m7-C(P2), PE-o2-m4-C (P3), and PE-o2-m7-C (P4) in Air

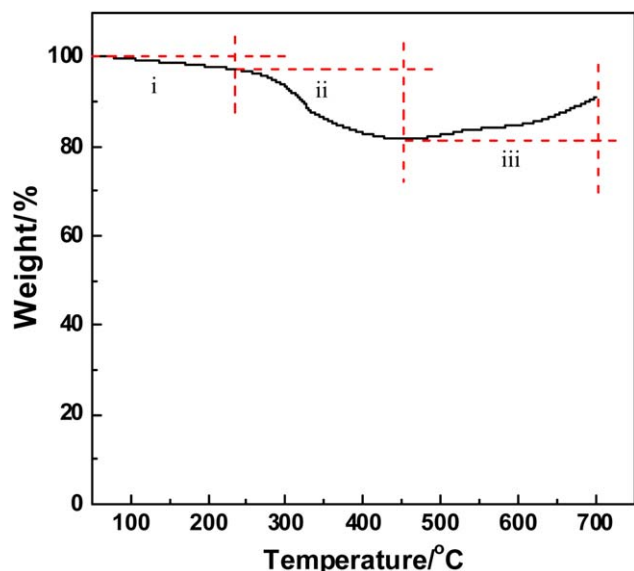| No.	Polyester	T_d (°C)	Coke formation of 700 °C in the air (%)
1	PE-m1-m4-C (P1)	281	91
2	PE-m1-m7-C (P2)	259	75
3	PE-o2-m4-C (P3)	260	76
4	PE-o2-m7-C (P4)	253	64
5	CFP	249	0.3

Figure 6. Thermo-gravimetric curves of PE-m1-m4-C (P1) in N_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. Thermo-gravimetric curves of PE-m1-m4-C in air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

groups, (iii) 480°–700 °C, the thermal transformation of carborane group.

For the three stages of the decomposition of PE-m1-m4-C (P1), the corresponding pyrolysis time and strength of the volatile component are showed in Figure 7. During the first two stages under nitrogen, carborane groups have not been pyrolyzed, but the carborane-free groups have been disintegrated into small molecules, such as H_2O, CO_2 and CO, and so forth. The absorption peaks around 3453 and 1634 cm^{-1} are ascribed to H_2O and the absorption peaks around 2349 and 667 cm^{-1} corresponds to CO_2. During the process of the disintegration of
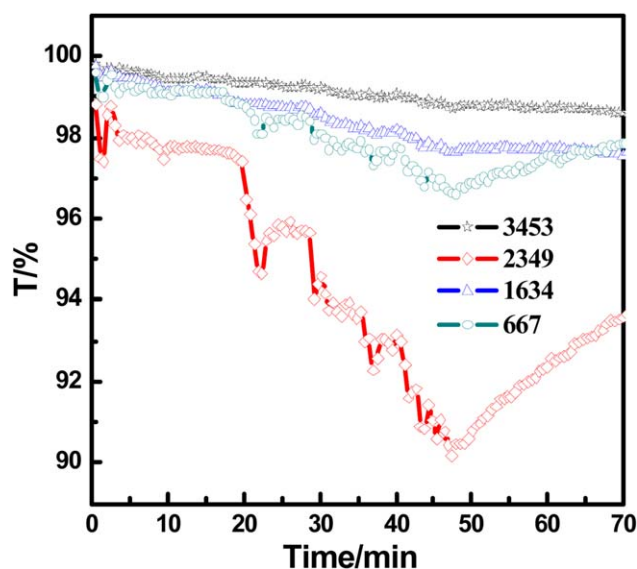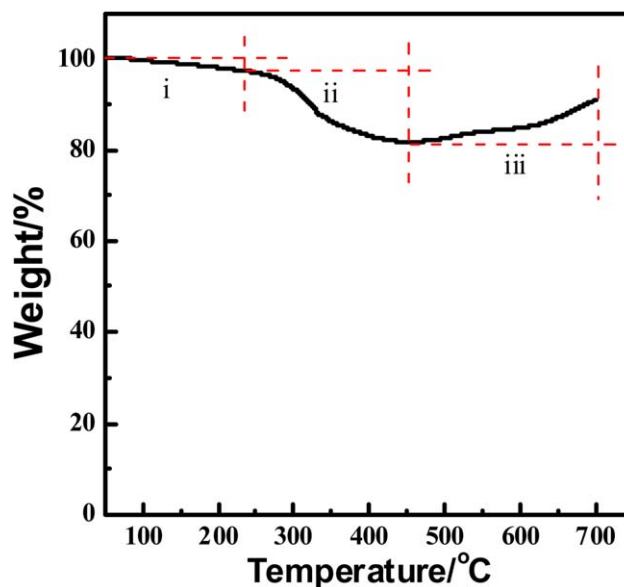
the carborane-free groups, with the consuming of the chemical oxygen, the ratio of chemical oxygen in polyester system decreased gradually, and so the disintegration of the carborane-free groups tends to slow sown, so the release of CO_2 reduce gradually. At the third stage, the carborane groups come into pyrolysis and the carbon atoms on the carbrane cage would be oxidized to CO_2 or CO. So the release of CO_2 increases to some extent.

The TG-FTIR analysis of PE-m1-m4-C (P1) was further conducted under air and the results are showed in Figures 8 and 9.
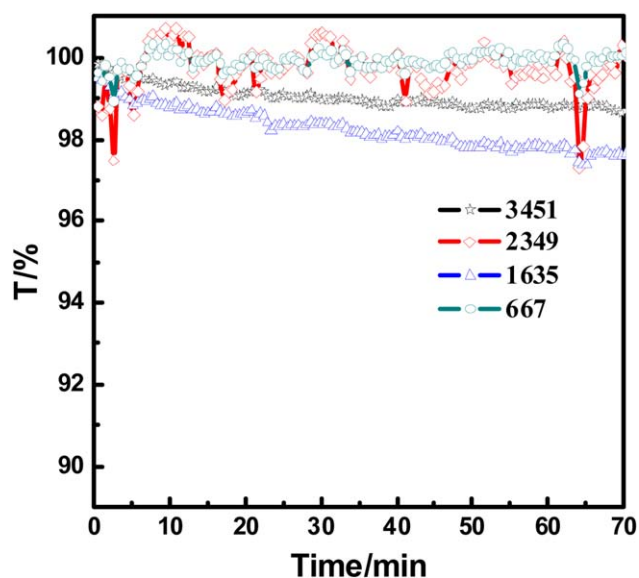

Figure 7. Curves of absorption intensity of CO_2 (2349 and 667 cm^{-1}) release and H_2O (3453 and 1634 cm^{-1}) absorption-time of PE-m1-m4-C (P1) in the heating process in N_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. Curves of absorption intensity of CO_2 (2349 and 667 cm^{-1}) release and H_2O (3451 and 1635 cm^{-1}) absorption-time of PE-m1-m4-C (P1) in the heating process in air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
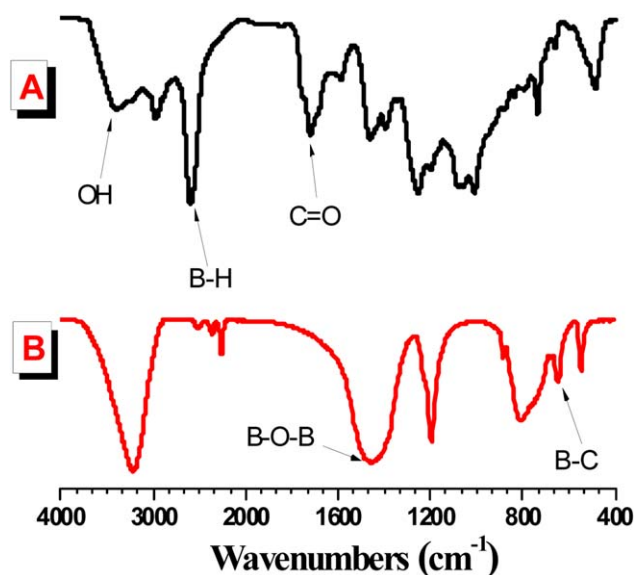
Figure 10. FTIR spectra of carborane-containing polyester (PE-m1-m4-C, P1) before (A) and after (B) TGA test under air at 700 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

The trend of the first two stages in air is similar to that in N_2. However, the third stage both in N_2 and air is different. As Figure 8 shown, the carborane-containing polyester PE-m1-m4-C (P1) had a weight gain after 450 °C under air showed in TGA curve which also can be found in other crborane-containing polyester PE-m1-m7-C (P2), PE-o2-m4-C (P3) and PE-o2-m7-C (P4) under the same condition as shown in Figure 5, while could not be found under nitrogen (Figure 4). It could be explained as followed. On the one hand, with the temperature increasing, especially after the temperature over 450 °C, the B—H bonds in the carborane fragments were oxidized gradually to form the strong B—O—B, B—B, and possible B—C linkages by oxygen which came from the oxygen-containing groups or air. While forming the B—O—B and B—B by the thermal oxidization of B—H under nitrogen, the oxygen came from only the oxygen-containing groups in the polyester. However, while testing the thermal resistance of the polyester under air, the oxygen not only came from the oxygen-containing groups in the polyester but also came from the air. As a consequence, the weight of PE-m1-m4-C (P1) increase after 450 °C under air. On the other hand, at high temperatures, the B-H bonds would generate protons, which could be combined with free radicals delivered by the decomposition of polyester resins. So the decomposition process of the carborane-containing polyester could be postponed to a certain extent. Finally, the carborane-containing polyester appeared obvious weight increment showed in TGA curve at the third stage.

To further research the structural variation of carborane-containing polyester at elevated temperature, the FTIR spectroscopy was utilized and the spectra of PE-m1-m4-C (P1) before and after TGA test under air are showed in Figure 10. As the Figure 10 shown, it was found that the stretching vibration peak of B-H bonds at 2600 cm^{-1} almost disappeared, which indicated that the B-H bonds on carborane cage have been consumed completely at elevated

temperature. Besides, the absorption peaks at 1700 cm^{-1} also disappeared, attributing to the destruction of carborane-free fragments of the polyester. Absorption peaks around 1450 and 643 cm^{-1} are ascribed to the stretching vibrations of B—O—B and B—C, respectively. The above result indicates that the carborane cage is destroyed and the B-H bonds in the carborane fragments are oxidized gradually to form the strong B-O-B and possible B-C linkages by oxygen at high temperatures. And the oxidized polyester would further crosslink by these strong B-O-B linkages. And the crosslinked systems containing B-O-B linkages are more thermally stable which may be one of the causes of the large amount of coked residue given by polyester containing the carborane structure. The high char yield of the obtained carborane-containing polyesters is desirable because high temperature resistance and high ablation resistance are required by many high-tech applications, especially in the high temperature fields. This kind of carborane-containing polyesters can be widely used as raw materials to prepare the high temperature resistant coatings or adhesives for automotive engines, aircraft and other equipments worked in high-temperature environments. Under high environmental temperature, the good thermal stability is capable of keeping polyester stable and expanding their service lives.

CONCLUSIONS

Four carborane-containing polyesters were successfully synthesized by the catalytic polycondensation of carborane diol monomers with carborane diacid chlorides in THF, and the experiment condition is gentle. The structures of these carborane-containing polyesters have been well characterized with spectroscopic characterization techniques including GPC, FTIR, ^{1}H NMR, and ^{11}B NMR. TGA analyses manifested that the introduction of carborane cages into the main chain of polyesters endowed the obtained polyesters with excellent thermal stability. The carborane-containing polyesters own higher degradation temperature and char yield and lower degradation rate. Furthermore, the thermal transition mechanism of carborane-containing polyesters also was studied by TG-FTIR combination analyzer. At elevated temperatures, the carborane cage could react with oxygen to form B-O-B and B-C linkages, which postpones the thermal decomposition of polyester and accounts for the high char yield. Consequently, carborane-containing polyester is successfully synthesized as a product with excellent thermal stability. This kind of high temperature polyesters have enormous technical and economic value in the fields of adhesives, especially in the high temperature fields. They can be widely used as raw materials to prepare the high temperature resistant coatings or adhesives for automotive engines, aircraft and other equipments worked in high-temperature environments. Under high environmental temperature, the good thermal stability is capable of keeping polyester stable and expanding their service lives.

ACKNOWLEDGMENTS

REFERENCES

1. Atta, A. M.; Elsaeed, A. M.; Farag, R. K.; El-Saeed, S. M. *React. Funct. Polym.* **2007**, *67*, 549.

2. Prabu, A. A.; Alagar, M. *Prog. Org. Coat.* **2004**, *49*, 236.

3. Wambua, P.; Ivens, J.; Verpoest, I. *Compos. Sci. Technol.* **2003**, *63*, 1259.

4. Mishra, S.; Mohanty, A. K.; Drzal, L. T.; Misra, M.; Parija, S.; Nayak, S. K.; Tripathy, S. S. *Compos. Sci. Technol.* **2003**, *63*, 1377.

5. Lausund, K. B.; Johnsen, B. B.; Rahbek, D. B.; Hansen, F. K. *Int. J. Adhes. Adhes.* **2015**, *63*, 34.

6. Manfredi, L. B.; Rodríguez, E. S.; Wladyka-Przybylak, M.; Vázquez, A. *Polym. Degrad. Stab.* **2006**, *91*, 255.

7. Hager, W. G.; Ramey, T. W.; Krumlauf, R.; Beckman, J. J. U.S. Pat. 5,373,058 (**1994**).

8. Teli, M. D.; Kale, R. D. *Polym. Eng. Sci.* **2012**, *52*, 1148.

9. Levchik, S. V.; Weil, E. D. *Polym. Adv. Technol.* **2004**, *15*, 691.

10. Bansal, R. K.; Mittal, J. *J. Appl. Polym. Sci* **1989**, *37*, 1901.

11. Shapiro, I.; Good, C. D.; Williams, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 3837.

12. Sugden, I. J.; Plantb, D. F.; Bell, R. G. *Chem. Commun.* **2013**, *49*, 975.

13. Tsuji, M. *J. Org. Chem.* **2003**, *68*, 9589.

14. Grimes, R. N. Carboranes, 2nd ed.; Elsevier: New York, **2011**; Chapter 9, pPE-o2-m4-C01-540, Chapter 10, p 541.

15. Armstrong, A. F.; Valliant, J. F. *Dalton Trans.* **2007**, *38*, 4240.

16. Xing, T.; Zhang, K. *Polym. Int.* **2015**, *64*, 1715.

17. Huang, X.; Zhang, Q.; Meng, Z.; Gu, J.; Jia, X.; Xi, K. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 973.

18. Parrott, M.; Valliant, C.; Adronov, J. F. A. *Langmuir* **2006**, *22*, 5251.

19. Qi, S.; Wang, Y.; Han, G.; Yang, Z.; Zhang, X.; Jiang, S.; Lv, Y. *Acta Polym. Sin.* **2015**, *8*, 921.

20. Men, X.; Cheng, Y.; Chen, G.; Bao, J.; Yang, J. *High. Perform. Polym.* **2014**, *27*, 497.

21. Qi, S.; Han, G.; Wang, H.; Li, N.; Zhang, X. A.; Jiang, S.; Lu, Y. *Chin. J. Polym. Sci.* **2015**, *33*, 1606.

22. Abramova, T. M.; Alekseyeva, S. G.; Valetskii, P. M.; Golubenkova, L. I.; Makarova, I. M.; Slonim, I. Y.; Urman, Y. G.; Shabadash, A. N. *Vysokomol. Soyed.* **1980**, *22*, 1637.

23. Ohta, K.; Ogawa, T.; Kaise, A.; Oda, A.; Endo, Y. *Chem. Pharm. Bull.* **2014**, *62*, 386.

24. Luo, Y.; Lu, Y.; Li, N.; Li, Y.; Zhang, X.; Qi, S. *J. Appl. Polym. Sci.* **2015**, *132*, DOI: 10.1002/app.42227.

25. Petrova, A. P. *Polym. Sci., Ser. C* **2007**, *49*, 251.

26. Lewicki, J. P.; Eastwood, E.; Albo, R. L. F.; Harley, S. J.; Lampe, M.; Maxwell, R. S. *Polym. Preprints* **2012**, *53*, 64.

27. Zhao, F. M.; Wang, X. *Zhanjie* **2014**, *35*, 33, 41.

28. Wang, C.; Zhou, Y.; Huang, F.; Du, L. *React. Funct. Polym.* **2011**, *71*, 899.

29. Jiang, Y. M.; Lv, Y. F.; Li, Y.; Qi, S. C. *Polym. Mater. Sci. Eng.* **2014**, *30*, 1.

30. Patel, M.; Swain, A. C. *Polm. Degrad. Stab.* **2004**, *83*, 539.

31. Patel, M.; Swain, A. C.; Cunningham, J. L.; Maxwell, R. S.; Chinn, S. C. *Polym. Degrad. Stab.* **2006**, *91*, 548.

32. Zhang, X.; Kong, L.; Dai, L.; Zhang, X.; Wang, Q.; Tan, Y.; Zhang, Z. *Polymer* **2011**, *52*, 4777.

33. Liu, Y.-L.; Chang, C.-Y.; Hsu, C.-Y.; Tseng, M.-C.; Chou, C.-I. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 4010.

34. Qi, S.; Wang, H.; Han, G.; Yang, Z.; Zhang, X. A.; Jiang, S.; Lu, Y. *J. Appl. Polym. Sci.* **2016**, *133*, DOI: 10.1002/app.43488.

35. Vinogradova, S. V.; Valetskii, P. M.; Kabachii, Y. A. *Russ. Chem. Rev.* **1995**, *64*, 365.

36. Korshak, V. V.; Sarishvili, I. G.; Zhigach, A. F. *Russ. Chem. Rev.* **1967**, *36*, 903.

37. Korshak, V. V.; Bekasova, N. I.; Solomatina, A. I.; Vagina, Zh P.; Klimentova, N. V.; Suprun, A. P. *Vysokomol. Soyed., Ser. A* **1983**, *25*, 989.

38. Bekasova, N. I.; Komarova, N. G. *Russ. Chem. Rev.* **1992**, *61*, 352.

39. Ohta, K.; Konno, S.; Endo, Y. *Chem. Pharm. Bull.* **2009**, *57*, 307.

40. Alexander, R. P.; Killingworth; Heying, T. L; Haven, N. U.S. Pat. 3,258,479 (**1966**).

41. Gratton, S. E. A.; Parrott, M. C.; Adronov, A. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 469.

42. Ghaneolhosseini, H.; Tjarks, W.; Sjoberg, S. *Tetrahedron* **1998**, *54*, 3877.