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Tetraphenylsilane-containing polyarylates with well-defined functional groups via postpolymerization modification

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ABSTRACT

New tetraphenylsilane-containing polyarylate with two pendant benzyl ester groups was synthesized successfully by direct polycondensation from a new silicon-containing aromatic diacid monomer bis[p-(benzyloxycarbonyl)phenyl]-bis(p-carboxyphenyl)silane (BBCS) with p-dihydroxybenzene in pyridine, using dimethylformamide as the activator and p-tosyl chloride as the condensing agent. Then, the benzyl ester groups were smoothly converted to carboxyl groups by catalytic hydrogenation, obtaining the polyarylate with two carboxyl groups attached on the phenylenes of tetraphenylsilane moiety. The new monomer and polyarylates were characterized by ^{1}H NMR, FTIR, wide angle X-ray diffraction and gel permeation chromatography methods. The carboxyl-containing polyarylate exhibited good solubility in most polar aprotic solvents and had the 5% weight loss over 400 °C. The presence of well-defined carboxyl groups and rigid tetrahedral structure of tetraphenylsilane in the polyarylate provides the feasible routes to the preparation of either hypercrosslinked covalent organic framework materials or optoelectronic materials through the reaction with chromophoric compounds.

1. Introduction

Polymers with well-defined functional groups are of significance for not only basic research but also the postpolymerization modifications for a variety of specific applications ranging from biomedical materials to optoelectronic materials [1–5]. In the past few years, researches have been concentrated on the introduction of pendant functional groups into aliphatic polyesters [6–10], poly(aryl ether ketone)s [11–15] and polyolefins [16,17] to enhance chemical reactivity and to facilitate the further modifications on these polymers. However, a review of literature reveals that, up to now, very few postpolymerization modifications on polyarylates were reported.

A limitation for the preparation of polyarylate with pendant functional groups on the accurate sites is that most of wholly aromatic polyesters are insoluble and infusible by virtue of their dense rigid structures [18]. Various strategies for the incorporation of either kinked structures or bulky pendant groups into the polymer backbone have been approached to circumvent these problems [19–23]. For example, Liaw reported that the introduction of *tert*-butylcyclohexyl effectively improved the solubility of polyarylates [24].

Recently, the silicon-containing polymers have received considerable attention since the silicon can serve as an important bridge between the organic and inorganic materials [25,26]. The solubility and melting processability of the polymer were improved, and meanwhile, the ionic characteristic of Si–C bond and the lower electronegativity of the silicon with respect to the carbon atom increased the thermal stability of the polymer [27]. On the other hand, the silicon having aromatic neighbors is able to give σ–π conjugation, which is advantageous for the electron and hole transport along the polymer chain so that silicon-containing polymers show the potential applications in the field of optoelectronic materials [25,28]. Among them, the tetraphenylsilane-containing polymers have been proven to be effective as light-emitting materials and hole transporting materials in the fabrication of OLEDs [29–32]. In addition, owing to the unique tetrahedral geometry, tetraphenylsilane core has been successfully used as building block for preparing predictably ordered three dimension polymer networks [33,34].

Polyarylates are generally prepared through the interfacial reaction between acid chlorides and bisphenols or by the ester exchange reaction between bisphenols and acetates of the diacid under high temperature and reduced pressure [35,36]. However, interfacial reaction often results in polyarylate with low molecular

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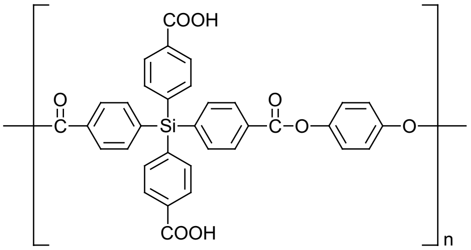
weight due to the insolubility of the polymer in the reaction media, while ester exchange reaction may lead to elimination of ester or ether protecting group, and destroy the well-designed structure. Recently, Higashi reported that polyarylates with high molecular weight and narrow polydispersity could be achieved by the direct polycondensation of hydroxybenzoic acid or isophthalic acid with bisphenols in the presence of condensing agent at mild condition [37–39], but very few polyarylates derived from other aromatic acids in this way appear in the literature.

The focus of the present work is to synthesize polyarylate with tetraphenylsilane unit and well-defined pendant carboxyl groups by postpolymerization modification. Its typical chemical structure is shown below:



To that end, for the first time we designed and synthesized a new tetraphenylsilane-containing aromatic diacid monomer bis[p-(benzyloxycarbonyl)phenyl]-bis(p-carboxyphenyl)silane (BBCS). Then the polyarylates with benzyl ester protective groups were synthesized by direct polycondensation of BBCS with bisphenols in pyridine solution. The benzyl ester groups were then selectively removed by catalytic hydrogenation with Pd/C, which leads to the formation of a new polymer PARB-C with two carboxylic groups on the benzene ring of tetraphenylsilane per repeat unit along the polymer backbone. This polymer system will afford an important precursor for a wide variety of applications such as hyper-crosslinked polymers and optoelectronic materials. The subsequent works are being undertaken to construct covalently crosslinked polymer networks with permanent microporous structure and high surface by the post-crosslinking of such linear precursor with various rigid crosslinkers.

2. Experimental section

2.1. Materials

Tetrachlorosilane and p-bromotoluene were purchased from J&K-Chemical Co., Ltd. Lithium powder, p-dihydroxybenzene, chromiumtrioxide, p-tosyl chloride and thinoyl chloride were purchased from Shanghai Chemical Reagent Co. Palladium carbon (10 wt%) was purchased from Dalian Toyounger Chemical Co., Ltd. Diethyl ether, benzene and tetrahydrofuran(THF) were purified by refluxing over sodium with the indicator benzophenone complex. Pyridine was purified by distillation under reduced pressure over calcium hydride. Thionyl chloride was distillation prior to use. The other solvents were of reagent grade and used as received.

2.2. Measurement

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet-20DXB IR spectrometer at room temperature with a resolution of 2 cm^{-1}. Samples were prepared by dispersing the sample in KBr and compressing the mixtures to tablets.

Mass spectra were obtained on a Micromass Platform IIconfigured for electrospray ionization in positive and negative modes. The mass-to-charge (m/z) ratios of the ions were determined with a quadrupole mass spectrometer, which was scanned from 65 to 2000 amu. The polarity of the ions detected was rapidly switched between + and −, and the data were recorded.

^1H NMR and ^{29}Si NMR were recorded on a 400-MHz Varian INOVA NMR spectrometer with the tetramethylsilane as an internal reference. The NOESY study was performed at room temperature with a mixing time of 1 s and relaxation time of 2 s.

Elemental analyses were determined with an Elementar Vario EL III elemental analyzer.

TGA was performed on a NETZSCH TG 209 thermal analyzer in a nitrogen atmosphere, and all samples were heated from 50 to 700 °C at a rate of 10 °C/min.

Differential scanning calorimetry (DSC) measurements were conducted with a NETZSCH DSC 204 instrument. The calorimeter was calibrated with indium metal as a standard. About 10–14 mg samples were used at a heating rate of 10 °C/min under a flow of nitrogen (20 ml/min).

A wide angle X-ray diffraction (WAXD) study of the sample was performed using Rigku D/max-2400 X-ray diffractometer (40 kV, 200 mA) with a copper target at a scanning rate of 2°/min, scanned from 5 to 60°.

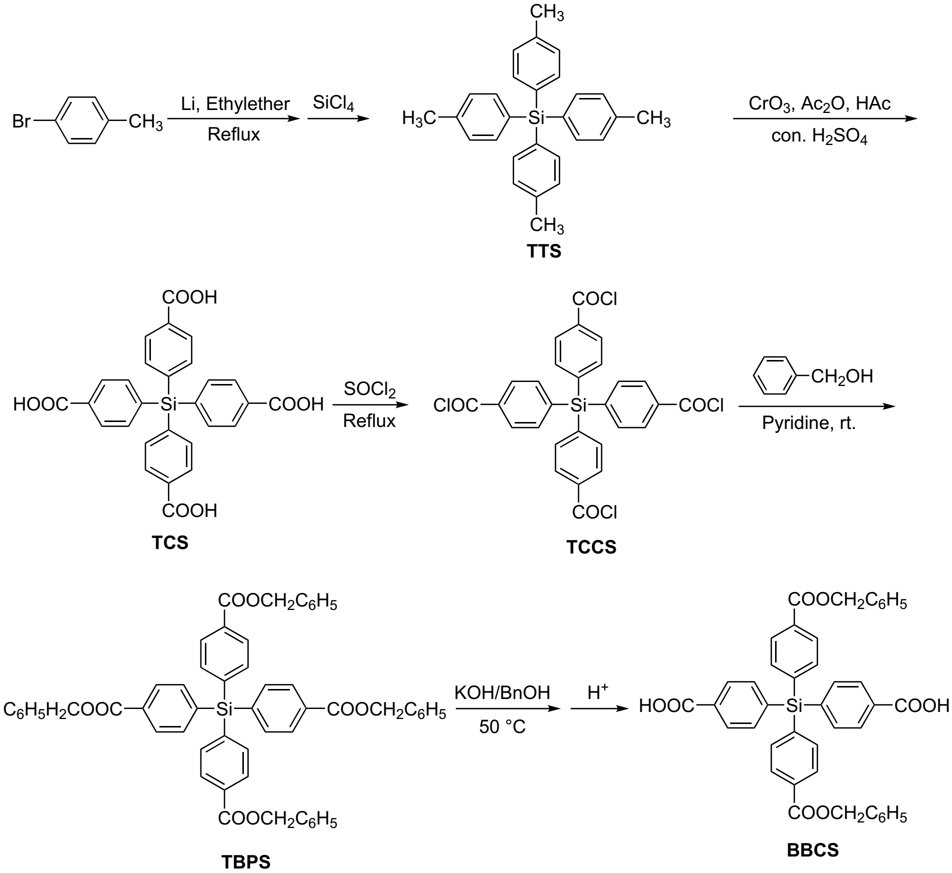
Molecular weight and molecular weight distribution were determined by GPC with a Water Associates Model PL-GPC-220 apparatus at room temperature with chloroform as eluent, at a flow rate of 1 ml/min, calibrated with polystyrene standards.

2.3. Tetra(4-tolyl)silane (TTS)

Tetra(4-tolyl)silane was prepared according to the procedure of literature [40] with some modifications. A 1-L four-necked flask equipped with a mechanical stirrer, nitrogen inlet and outlet, a condenser and a dropper was charged with lithium powder (13.04 g, 1.94 mol) and anhydrous diethyl ether (250 ml). 4-Bromotoluene (159.55 g, 0.933 mol) in anhydrous diethyl ether (200 ml) was added dropwise over a 8-h period under vigorous stirring under the protection of nitrogen atmosphere. An immediate exothermic reaction caused the ether to start boiling. The mixture was stirred for 4 h, and then 17.7 ml tetrachlorosilane in 50 ml anhydrous diethyl ether was added dropwise over a 4-h period. The mixture was stirred for an addition 2 h and quenched by the slow addition of 200 ml 1 N aqueous HCl at 0 °C. Diethyl ether was removed by rotary evaporation, the solid was filtered off, washed with 400 ml methanol and 200 ml 1 N aqueous HCl. The crude product was dissolved in chloroform, and the insoluble fraction was filtered off by filtration. Solvent was evaporated to afford a white solid. The crude product was recrystallized twice in cyclohexane and gave TTS as colorless crystals (53.4 g, 87.6%); mp: 236–236.5 °C. ^1H NMR (400 MHz, $CDCl_3$,): δ (ppm) 2.45 (s, 12H, Ar–CH_3), 7.15 (d, 8H, Ar–H), 7.42 (d, 8H, Ar–H); IR (KBr, cm^{-1}): 3063 and 3010 (arom. C–H), 2972 and 2863 (Ar–CH_3), 1597, 1499 (arom. C=C), 1445, 1107 and 760 (Si–Ph), 803 (arom. p-subst.).

2.4. Tetrakis(4-carboxyphenyl)silane (TCS)

Tetrakis(4-carboxyphenyl)silane was prepared according to the procedure of literature [41] with some modifications. A 2-L three-necked round-bottom flask in an ice bath was equipped with a thermometer, a mechanical stirrer and a dropper. To this flask was charged 960 ml glacial acetic acid and 400 ml acetic anhydride. Maintaining the temperature below 10 °C, sulphuric acid (60 ml) and TTS (20.8 g) was added successively with stirring. After that, the temperature was raised to 25 °C, and Cr_2O_3 (160 g) was charged in four portions over a 2-h period. The mixture was stirred for addition 1 h. Then the product was decomposed with ice-cold water (1.6 L) and filtered. The green solid was dissolved in dilute



Scheme 1. The synthesis route of silicon-containing aromatic diacid monomer BBCS.

aqueous NaOH, and the solution was acidified with 1 N aqueous HCl until the pH reached 1. The resultant white solid was washed with dilute aqueous HCl and distilled water for several times. The crude product was recrystallized from acetic acid three times to give tetraacid TCS (17.44 g, 67%); mp: >300 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.12 (d, 8H, Ar–H), 7.75 (d, 8H, Ar–H); ^{29}Si NMR (acetone-d_6 400 MHz, acetone-d_6): δ (ppm) −10.4; IR (KBr, cm^{-1}): 3025 (arom. C–H), 2300–3400, 2666, 2552 (–CO–OH), 1694 (–C=O, carboxyl), 1600, 1498 (arom. C=C), 1093, 759 (Si–Ph), 708 (arom. p-subst.).

2.5. Tetrakis(4-chlorocarbonylphenyl)silane (TCCS)

A 100-ml three-necked round-bottom flask was equipped with a thermometer, a mechanical stirrer and a condenser. A bubbler trap containing aqueous NaOH solution was attached to the end of a condenser to absorb the released SO_2 gas. TCS (2.0 g, 3.9 mmol) and thionyl chloride (50 ml, 685.5 mmol) was charged into the flask and the mixture was refluxed for about 8 h. Then DMF (0.5 ml) was added to terminate the reaction and the refluxing was continued for another 3 h. Finally, the excess thionyl chloride was removed by vacuum distillation. The remained white product was recrystallized from benzene twice to give tetraacid chloride TCCS (1.94 g, 84.7%); mp: >300 °C. IR (KBr, cm^{-1}): 1777, 1739 (–C=O, acid chloride), 1590, 1492 (arom. C=C), 1018, 785 (Si–Ph), 878 (arom. p-subst.), 716 (C–Cl, acid chloride).

2.6. Tetrakis[p-(benzyloxycarbonyl)phenyl]silane (TBPS)

A 200-ml three-necked flask equipped with a mechanical stirrer, dry nitrogen inlet and outlet, a condenser and a dropper was placed in an ice bath and cooled. To this flask was added benzyl alcohol (23.27 ml, 234.38 mmol) and pyridine (19.3 ml, 234.38 mmol). A solution of tetraacid chloride TCCS (11.4 g, 19.53 mmol) in dry tetrahydrofuran (60 ml) was added dropwise under stirring to the above mixture over a 1-h period. After reacting overnight at room temperature, half of the solvent was removed by distillation and the residue was poured into 400 ml 5% Na_2CO_3 at 0 °C. The precipitate was filtered and washed with 1 N aqueous HCl and distilled water for several times. The cured product was recrystallized twice from acetic acid to give tetrabenzylated ester TBPS (12 g,

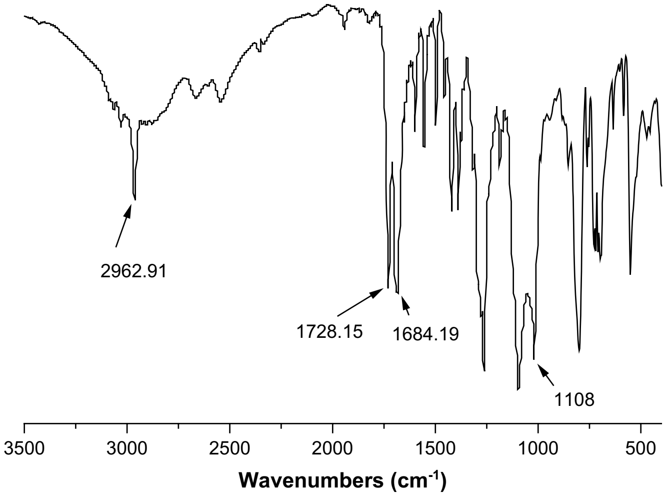


Fig. 1. FTIR spectra of silicon-containing diacid monomer BBCS.

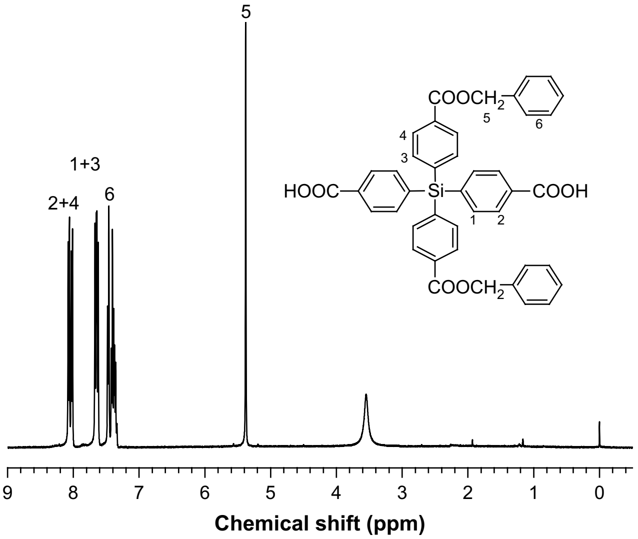


Fig. 2. ^{1}H NMR spectrum of silicon-containing aromatic diacid monomer BBCS.

70.3%). mp: 118–120 °C. IR (KBr, cm^{-1}): 3065, 3032 (arom. C–H), 2956, 2871 (–CH$_2$–, benzyl ester), 1720 (–C=O, benzyl ester), 1598, 1497 (arom. C=C), 1455, 1019, 755 (Si–Ph), 1275 (–C–O–C–, benzyl ester), 725 (arom. p-subst.). Anal. calcd for $C_{56}H_{442}O_8Si$ (873.06): C 77.04, H 5.08; Found: C 77.10, H 5.01.

2.7. *Bis[p-(benzyloxycarbonyl)phenyl]-bis(p-carboxyphenyl)-silane (BBCS)*

A 160 ml benzyl alcohol solution of KOH (8.96 g, 0.16 mol) was added to a solution of TBPS (70 g, 0.08 mol) in benzyl alcohol (700 ml) over a 2-h period under vigorous stirring. The reaction mixture was kept at room temperature for 2 h. Then the system was warmed to 50 °C and stirred for addition 12 h. Finally, most of the solvent was removed by distillation, and the residue was cooled to 0 °C and 60 ml toluene was added. The precipitate was filtered, washed several times with toluene, and dried under a vacuum at 80 °C. The salt was purified by first dissolving it in excess water, filtering the insoluble residue, and titrating the solution with 0.1 N aqueous HCl solution to pH 4.8, and the solution was settled overnight at 0 °C. The white precipitate was vacuum dried and recrystallized twice from acetic acid to give diacid BBCS (20 g, 36.1%). mp: >300 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.12 (q, 8H, Ar–*H*), 7.6 (q, 8H, Ar–*H*), 7.3–7.5(m, 10H, Ar–*H*), 5.4 (s, 4H, –C*H*$_2$–); IR (KBr, cm^{-1}): 3069, 3027 (arom. C–H), 2300–3400, 2666, 2545 (–CO–OH), 2962, 2879 (–CH$_2$–, benzyl ester), 1728 (–C=O, benzyl ester), 1684 (–C=O, carboxyl), 1599, 1496 (arom. C=C), 1455, 1018, 761 (Si–Ph), 1262 (–C–O–C–, ester), 800 (arom. p-subst., aromatic acid). EIMS (*m/z*): Calcd for $C_{42}H_{32}O_8Si$, 692.80; found, 727.20 $[M+Cl]^+$. Anal. calcd for $C_{42}H_{32}O_8Si$ (692.72): C 72.65, H 4.71; Found: C 72.72, H 4.66.

2.8. *Polyarylates with pendant benzyl ester groups*

The polyarylates with benzyl ester protective groups were synthesized in the similar procedure, so only the detailed synthesis of PARB was described here as an example: a mixture of p-tosyl chloride (2.9742 g, 15.6 mmol), dimethylforamide (0.2628 g, 36 mmol) and BBCS (4.1529 g, 6 mol) in 20 ml dry pyridine was stirred at room temperature for 30 min and then at 80 °C for 10 min. To the above mixture, p-dihydroxybenzene (0.6606 g, 6 mol) in 6 ml pyridine was added dropwise over a 20-min period. The system reacted at 80 °C for an additional 5 h. Then the product was precipitated in 60 ml methanol. Filtered and washed with 1 N aqueous HCl solution, distilled water and methanol successively, and finally precipitated from a chloroform solution into methanol. The polymer obtained was dried at 100 °C under a vacuum to constant weight. Yield: 91%. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.15–8.30 (d, 4H, Ar–*H*), 8.00–8.15 (d, 4H, Ar–*H*), 7.66–7.75 (d, 4H, Ar–*H*), 7.60–7.66 (d, 4H, Ar–*H*), 7.30–7.50(m, 10H, Ar–*H*), 7.29 (s, 4H, Ar–*H*), 5.40 (s, 4H, –C*H*$_2$–). IR (KBr, cm^{-1}): 3065, 3030 (arom. C–H), 2949, 2886 (–CH$_2$–, benzyl ester), 1739 (–C=O, aromatic ester), 1722 (–C=O, benzyl ester), 1598, 1500 (arom. C=C), 1455, 1017, 754 (Si–Ph), 1273 (–C–O–C–), 722 (arom. p-subst., aromatic ester).

2.9. *Polyarylate with pendant carboxyl groups*

Into a hydrogenator containing 40 ml tetrahydrofuran and 10 ml of formic acid, 0.2 g of PARB and small amount of Pd/C (10 wt%) was added. After purging with nitrogen three times, the reaction mixture was stirred under 1.2 MPa hydrogen pressure at 60 °C for 5 days. After removal of the Pd/C powders, the solution was poured into an excess of methanol. The precipitate was dried under a vacuum at 100 °C for 24 h. Yield: 77%. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) 8.22–8.35 (d, 4H, Ar–*H*), 8.13–8.22 (d, 4H, Ar–*H*), 7.73–7.82 (d, 4H, Ar–*H*), 7.62–7.73 (d, 4H, Ar–*H*), 7.3 (s, 4H, Ar–*H*). IR (KBr, cm^{-1}): 3062, 3034 (arom. C–H), 2300–3400, 2666, 2545 (–CO–OH), 1735(–C=O, aromatic ester), 1690 (–C=O, benzoic acid), 1602, 1500 (arom. C=C), 1455, 1017, 761 (Si–Ph), 1256 (–C–O–C–), 829 (arom. p-subst., benzoic acid), 717 (arom. p-subst., aromatic ester).

3. Results and discussion

3.1. *Preparation of BBCS*

The synthesis route to the silicon-containing diacid monomer of BBCS is shown in Scheme 1. Firstly, p-bromotoluene was converted to p-tolyllithium and then reacted with tetrachlorosilane to produce the TTS. The oxidation of the latter with chromiumtrioxide

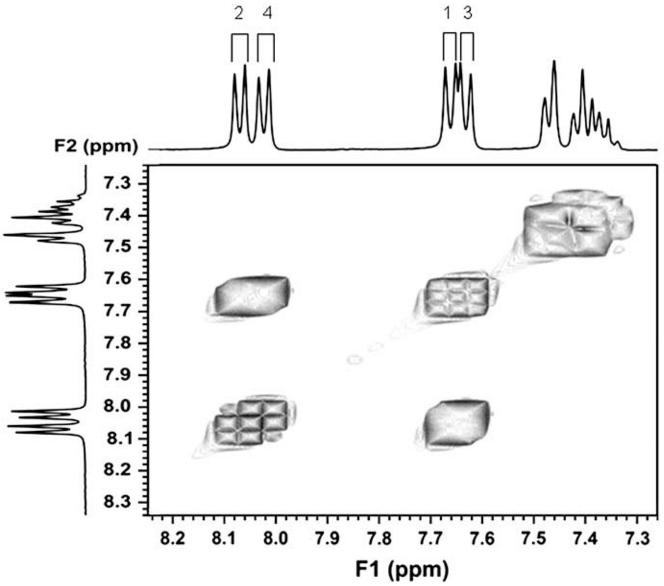
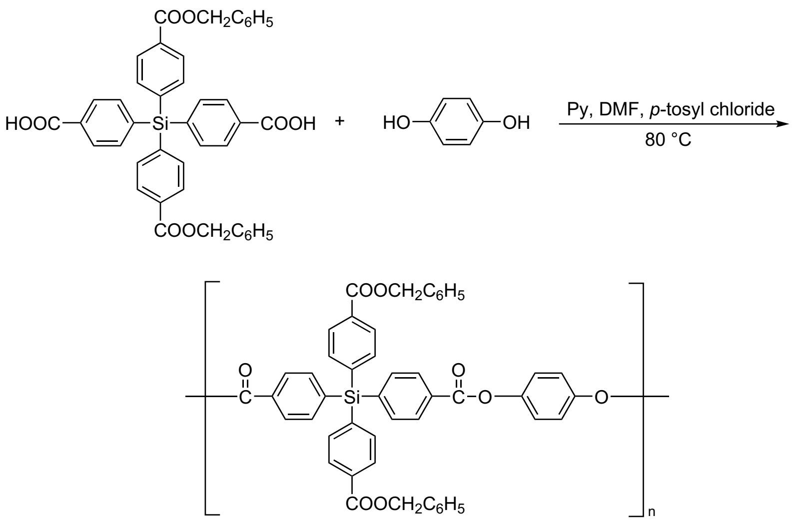


Fig. 3. ^{1}H–^{1}H COSY of silicon-containing aromatic diacid monomer BBCS (7.2–8.3 ppm).



Scheme 2. The direct polycondensation routes for polyarylates PARB.

gave the corresponding tetraacid TCS in good yield (58.7% overall yield). After that, the TCS was readily converted to the tetraacid chloride TCCS by reaction with thionyl chloride and the tetraacid chloride was esterified with benzyl alcohol to afford the TBPS. Finally, the TBPS was controllably hydrolyzed with the aqueous potassium hydroxide solution, and acidized to give the diacid monomer of BBCS.

It is important to note that the target diacid monomer is not easy to be synthesized by partial esterification of tetraacid chloride. Fortunately, the controlled hydrolysis of the tetrabenzylated ester TBPS by alkali under a certain pH was almost quantitative, and the triacid byproduct was facilely removed by titration (pH = 4.8) and precipitation method. The crude product (containing a little amount of monoacid byproduct) was then purified by recrystallization from acetic acid to achieve the high-purity sample required for its use in the subsequent polycondensation reaction.

Fig. 1 shows the FTIR spectrum of BBCS. The wide absorption peak between 2500–3400 cm^{-1} is assigned to the vibration of OH in the carboxyl group. The peak at 2962 cm^{-1} corresponds to ν_{CH2} stretching vibration of benzyl ester groups. The peaks at 1728 cm^{-1} and 1684 cm^{-1} and (ν_{CO}) are characteristics of the benzyl ester group and carboxyl group, respectively. Absorption bands at 1445, 1108, and 761 cm^{-1} are characteristics of C–Si bond. The absorption at 3030–3060 cm^{-1} is attributed to C–H aromatic bonds.

The structure of the diacid monomer BBCS was also identified by ^{1}H NMR method (Fig. 2). The peaks 7.6–8.1 ppm are assigned to the characteristic aromatic rings attached to the silicon atom. The peaks at 7.3–7.5 ppm are attributed to the benzene ring of the benzyl group. The peak at 5.4 ppm is assigned to the hydrogen (–CH_2–). As an aided method, the aromatic hydrogen atoms labeled as 1, 3 and 2, 4 are clearly assigned in the ^{1}H–^{1}H homonuclear correlation COSY NMR spectrum (Fig. 3). The aromatic signal at δ 8.08 ppm (protons in position 2 in Fig. 2) is correlated to the aromatic signal at δ 7.67 ppm (protons in position 1 in Fig. 2). The aromatic signal at δ 8.02 ppm (protons in position 4 in Fig. 2) is correlated to the aromatic signal at δ 7.63 ppm (protons in position 3 in Fig. 2).

3.2. *Syntheses of polyarylate with benzyl ester protective groups (PARB)*

Diacid chlorides are often used monomers in the synthesis of polyesters. Nevertheless, they have a number of limitations

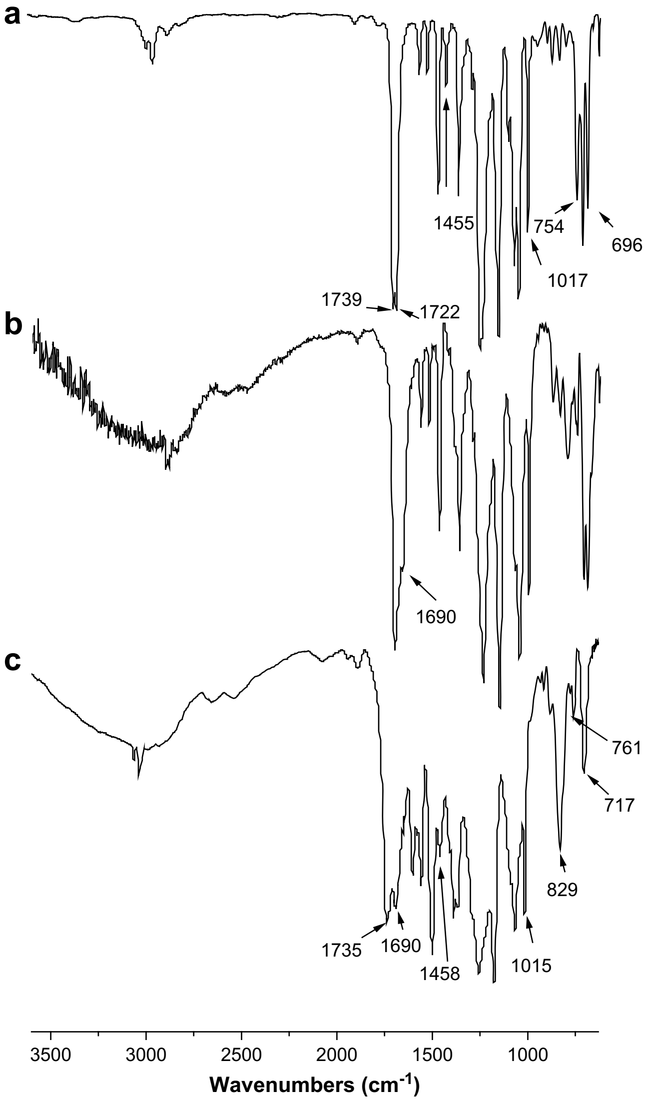


Fig. 4. FTIR spectra of PARB at different hydrogenolysis time (a) 0 h; (b) 72 h; (c) 192 h.

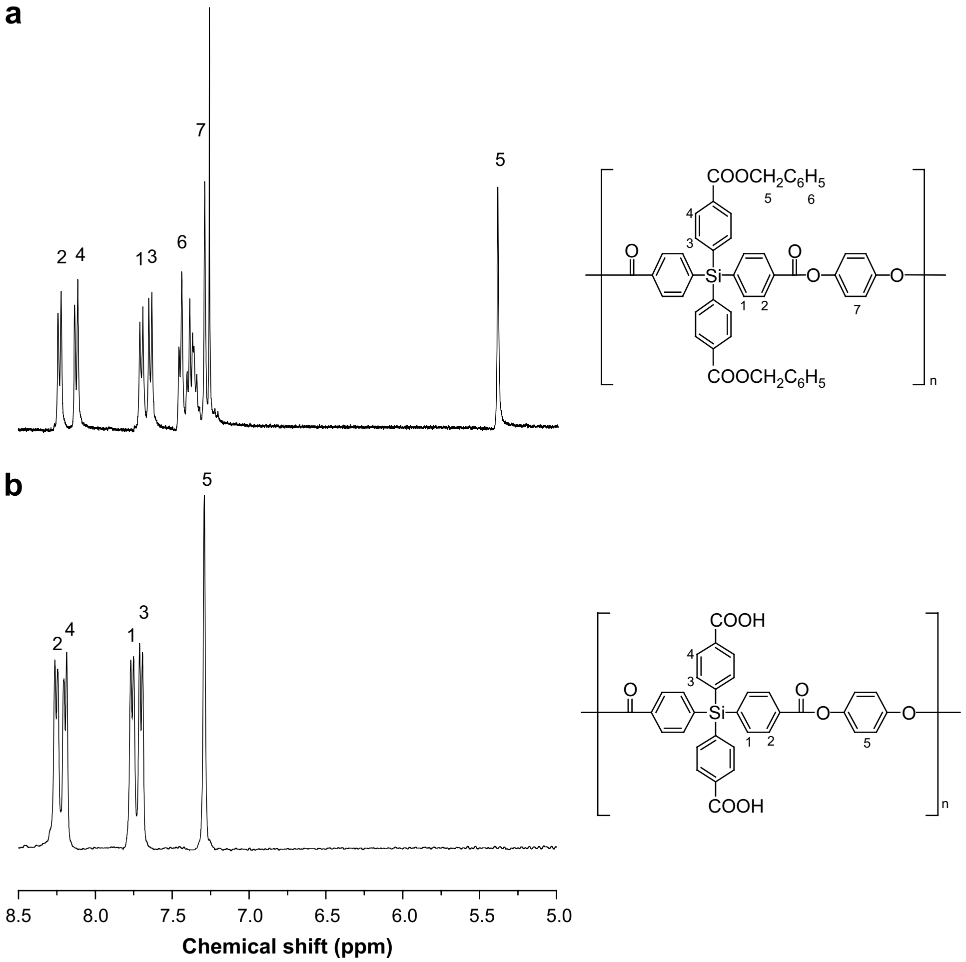


Fig. 5. ^{1}H NMR spectra and the assignments of two polyarylates. (a) PARB; (b) PARB-C.

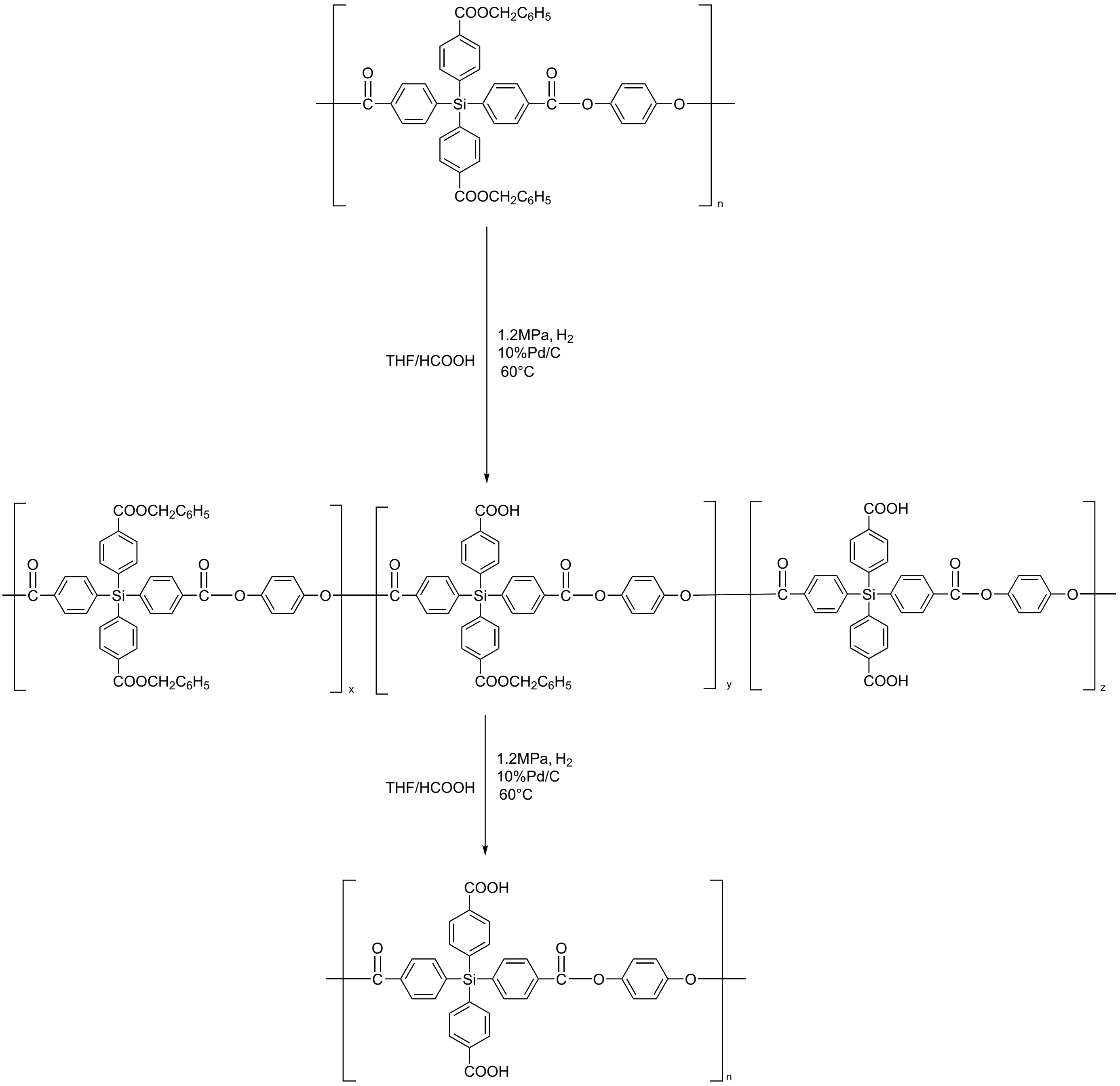
associated with their easy hydrolyzability, which causes difficulties in their synthesis and storage. Here, the polyarylate PARB was prepared by direct polycondensation of the diacid BBCS with p-dihydroxybenzene in pyridine solution, using dimethylformamide as the activator and p-tosyl chloride as the condensing agent (Scheme 2). It was previously reported that, during the addition of diacid, an insoluble intermediate product would precipitate in pyridine unless the system temperature was heated to above 120 °C [37–39]. However, in our case, the polymerization solution was always clear through the whole polymerization reaction even at room temperature. This phenomenon could be attributed to the kinked polymer structure due to the existence of pendant bulky benzyl ester groups, which improved the solubility properties. Therefore, the polycondensation reaction could be conducted under more mild condition (below 80 °C). The polyarylate was reprecipitated in methanol from a chloroform solution, washed with methanol, and dried in a vacuum oven at 100 °C to obtain white product. Yield was typically greater than 90%.

The structure of the tetraphenylsilane-containing polyarylate was confirmed by FTIR and ^{1}H NMR methods. The FTIR spectrum of PARB (Fig. 4a) displayed characteristic carbonyl absorptions at 1739 and 1722 cm^{-1}, which were attributed to ester bonds in the main chain and protective groups of benzyl ester, respectively. The band for C–H stretching of the –CH$_2$– group was observed at 2925 cm^{-1}. A strong band around 1500 cm^{-1} was observed for the benzene ring. Peaks at 754 and 696 cm^{-1} correspond to δ_{CH2} deformation vibration in pendant benzyl group. Absorption bands at 1455 and 1017 cm^{-1} are characteristic of C–Si bond. In the ^{1}H NMR spectra (Fig. 5a), the main peaks marked with numbers could be assigned to the corresponding hydrogen atoms of PARB.

GPC measurement was performed to determine the molecular weight and molecular weight distribution of the polyarylate precursor. As a result, high molecular weight of M_w 79.7 kg/mol with the polydispersity index (PDI) of 2.10 was obtained for PARB. Tough, transparent, and flexible film could be cast from the chloroform solution of polyarylate.

3.3. *Synthesis of polyarylate with carboxyl groups on the tetraphenylsilane unit*

In this study, catalytic hydrogenolysis over Pd/C (10 wt%) was adopted to eliminate the benzyl ester protective groups to achieve the desired polyarylate with well-defined carboxyl groups on the tetraphenylsilane unit, and meanwhile to avoid the break of other ester linkages in the main chain of polyarylate precursor (Scheme 3). The catalytic activity of Pd/C in the reaction system depends on a variety of factors, including the concentration of the polymer solution, reaction solvent, molecular weight of polymer, pressure of hydrogen and system temperature, etc. In our study, a number of solvents, including ethyl acetate, acetone, tetrahydrofuran, dioxane, dimethylformamide (DMF) and their mixture with methanol, were



Scheme 3. The synthetic route for PARB-C by catalytic hydrogenolysis.

examined as the reaction medium. However, most of them were ineffective. Fortunately, we found that the mixed solvents of tetrahydrofuran and formic acid was available, and the debenzylation reaction was smoothly performed under 1.2 MPa H_2 atmosphere at 60 °C.

The hydrogenolysis process was monitored by FTIR spectroscopy. As shown in Fig. 4b and Fig. 4c, after 72 h, the intensity of absorption peak at 1722 cm^{-1} corresponding to the carbonyl of benzyl ester group decreased greatly, and a new peak at 1690 cm^{-1} emerged, which was attributed to the carbonyl of carboxyl group. Furthermore, after a 120-h reaction time, almost all benzyl ester groups were removed, as evidenced by the disappearance of the δ_{CH} vibrations of benzyl group (754 and 696 cm^{-1}) and the $\nu_{C=O}$ stretching vibration of benzyl ester group (1722 cm^{-1}). Besides the $\nu_{C=O}$ absorption at 1690 cm^{-1}, the stretching bands between 2500–3400 cm^{-1} was strengthened tremendously after hydrogenolysis due to the formation of pendant COOH groups.

In addition, in the ^{1}H NMR spectrum (Fig. 5b), the disappearances of the peaks at 5.4 ppm (–CH_2–Ar) and 7.3–7.4 ppm (–Ar–*H*)

Table 1
Solubilities of tetraphenylsilane-containing polyarylates.

Polymer	DMF	NMP	DMSO	THF	$CHCl_3$	Acetone	Methanol
PARB	+	+	+	+	+	+	−
PARB-C	+	+	+	−	−	−	−

+: Soluble at room temperature; −: insoluble.

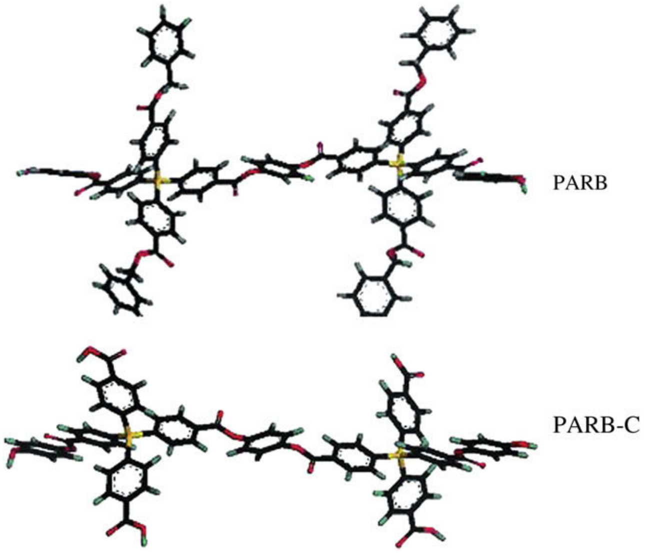


Fig. 6. Models of a fragment of PARB and PARB-C.

also confirmed the complete removal of pendant benzyl groups in the polyarylate.

Table 2
WAXD and thermal analysis results of polyarylates PARB and PARB-C.

Polyarylates	*d*-Spacing (Å)	T_g (°C)	$T_{5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Char yield (%)[a]
PARB1	4.81	172	360.	378	533	52.4
PARB-C	4.08	177	401.	482	–	55.6

[a] Determined at 700 °C in N_2 atmosphere.

3.4. Properties of polyarylates

One of the key elements in the strategy of postpolymerization modification is that the precursor must own good solubility in organic solvents. Although most of wholly aromatic polyesters are insoluble and infusible, the precursor PARB prepared in this study was soluble in most polar aprotic solvents such as dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), Dimethyl sulfoxide (DMSO), and even can dissolve in more common solvents like chloroform, acetone, tetrahydrofuran, and pyridine (Table 1). Relative to its precursor, the solubility of resultant polyarylate PARB-C becomes poor due to the formation of strong intermolecular hydrogen bonding between the carboxyl groups along the backbone of the polyarylate, but is still soluble in polar aprotic solvents such as DMF, DMSO, NMP and dimethylacetamide, which characteristic is very important for its subsequent preparation of polymer with ordered three dimension crosslinking framework as well as other functional modification.

In order to explain the solubility behavior of polyarylates obtained, molecular modelings were carried out for both PARB-C and its precursor PARB. As illustrated in Fig. 6, the energy-minimized segment of PARB contains a tetrahedral structure with a center of silicon atom in each repeat unit, and there are two bulky benzyl ester groups pendant on the benzene rings of tetraphenylsilane. The rigid kinked structure forces the polymer chains to open apart and is advantageous for the solvent molecules to penetrate between polymer chains, and thus leads to polymer excellent solubility. After removal of benzyl group, the existence of high density of tetraphenylsilane moieties along the PARB-C backbone is still effective to inhibit the dense packing of polymer chains, leading to PARB-C good solubility.

The WAXD diffractograms for polyarylates of PARB and PARB-C are illustrated in Fig. 7. PARB and PARB-C displayed amorphous structures and had very similar diffraction patterns. Relative to its precursor PARB, the pattern for PARB-C was obviously broadened. This outstanding change was ascribed to the increased intrachain and interchain interaction in PARB. Furthermore, the diffraction

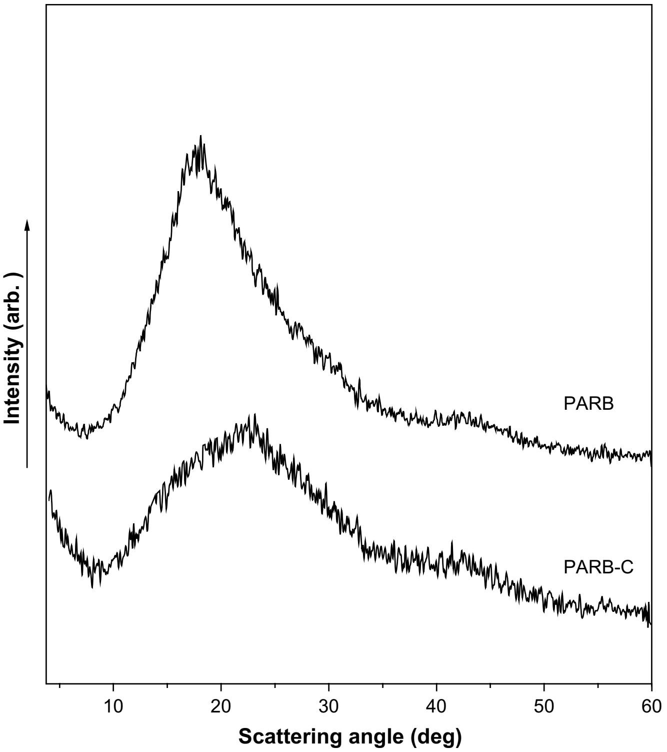


Fig. 7. Wide angle X-ray diffractograms of two polyarylates.

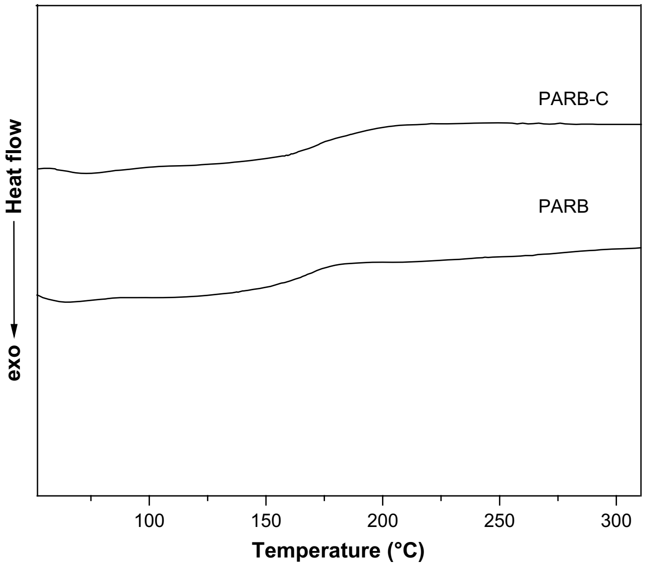


Fig. 8. DSC thermograms of two polyarylates.

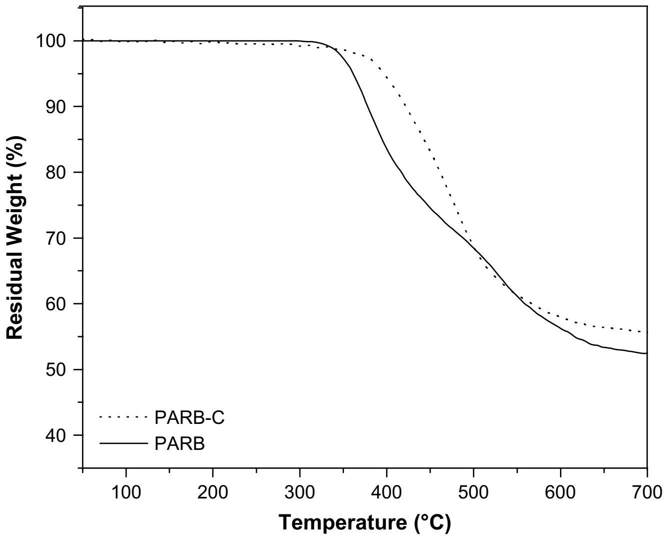


Fig. 9. TGA curves of two polyarylates.

halo of PARB-C shifted toward a larger diffraction angle (2θ). According to the Bragg's equation: $\lambda = 2d\sin\theta$, the interchain distance (d-spacing) could be calculated, and used to indicate the openness of chain packing. The d-spacing results in Table 2 show that the removal of pendant benzyl ester groups and intermolecular hydrogen bonding lead to a apparently reduced interchain distance from PARB of 4.81 Å to PARB-C of 4.08 Å.

The glass-transition temperatures of polyarylates were determined by means of DSC method (Fig. 8). The glass transitions of polyarylates were clearly observed and the T_g values range from 172 to 177 °C. As expected, after removal of the benzyl group from the polymer, the resulting carboxyl-containing polyarylate PARB-C exhibited slightly higher glass-transition temperature ($T_g = 177$ °C) due to the effect of interchain hydrogen-bonds.

The thermal stabilities of polyarylates were characterized by TGA measurement under a nitrogen atmosphere at a heating rate of 10 °C/min. Fig. 9 shows the thermogravimetric curves and Table 2 summarizes the thermal decomposition temperatures for all the polymers. The PARB was stable up to 320 °C, with 5% decomposition temperatures of 360 °C. The DTG curve (Fig. 10) showed that PARB obviously had two stages of weight loss. The first stage ($T_{max1} = 378$ °C) was due to the thermal cleavage of the pendant benzyl ester groups, and the second stage ($T_{max2} = 533$ °C) was attributed to the decomposition of the main chain of the polymers. Compared to PARB, PARB-C displayed 5% weight loss temperature over 400 °C, which was significantly higher than that value of its precursor PARB, and the DTG curve of PARB-C had only one stage of weight loss ($T_{max1} = 482$ °C). The char yield of PARB-C at 700 °C in N_2 atmosphere was higher that of PARB, which agreed with the content of silicon atom in the main chain of polymer.

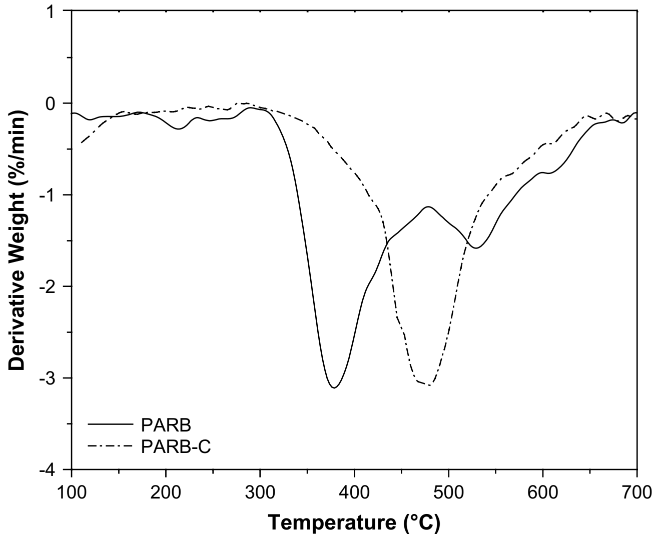


Fig. 10. DTG thermograms of two polyarylates.

4. Conclusions

In this paper, a new difunctional monomer with tetrahedral structure bis[p-(benzyloxycarbonyl)phenyl]-bis(p-carboxyphenyl)-silane (BBCS) was designed and synthesized successfully through a series of synthesis procedures. Then, polyarylate PARB with tetraphenylsilane inserted in the main chain and two benzyl ester protective groups on the phenyls tetraphenylsilane was obtained by direct polycondensation of the BBCS with p-dihydroxybenzene in pyridine solution. Subsequently, the pendant benzyl ester groups of PARB were smoothly converted to carboxyl groups by catalytic hydrogenation, leading to the formation of PARB-C with two carboxyl groups accurately attached to the tetraphenylsilane per repeat unit. To the best of our knowledge, this is the first synthesis of functionalized polyarylate having a well-defined functional groups obtained via postpolymerization modification. The chemical structures of all the monomers and polymers synthesized were characterized through the various methods. Both the precursor and PARB-C were completely amorphous and owned good solubility in most polar aprotic solvents. Although there are large amount of carboxyl groups along the backbone, PARB-C still exhibited good thermal stability and showed less than 5% weight loss up to 400 °C.

Taking advantage of the two carboxyl groups and the tetrahedral tetraphenylsilane in each repeat unit, the further work in our laboratory is being undertaken to prepare the hypercrosslinked covalent organic framework materials with permanent microporous structure and high surface. Moreover, due to the σ–π conjugation of the silicon atom in tetraphenylsilane unit, the introduction of chromophoric groups via reaction with carboxyl groups on the polyarylate would lead to polymer unique optoelectronic properties. This part of work is in progress and will be reported subsequently.

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Appendix 1. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2009.03.016.

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