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Synthesis and characterization of multiple phenylethynylbenzenes via cross-coupling with activated palladium catalyst

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Several compounds containing multiple phenylethynyl substituents were prepared and polymerized to thermosets through the acetylenic units. Pyrolysis of the polymers afforded high carbon yields. The acetylenic-based compounds were synthesized from the palladium-catalysed coupling reaction of phenylacetylene with multiple-brominated benzenes. Inconsistencies were observed in the reaction yields with time, which were attributed to poisoning of the palladium. A procedure was developed for the activation of palladium using magnesium. The activated palladium gave consistent high yield of cross-coupled products.

(Keywords: cross-coupling; phenylethynyl; activated palladium)

INTRODUCTION

Considerable interest has been shown in the use of polyfunctional arylacetylenes in the preparation of thermally stable polymers[1-5] and recently as precursors to carbon[6-8]. In spite of the importance of carbon–carbon composites, very little work has been carried out on the design of a resin matrix that has a low viscosity, to enable easy impregnation of the carbon fibres, and a high char yield under atmospheric conditions. We are engaged in a project aimed at the synthesis of high-carbon-containing acetylenic compounds that have low melting points, have a broad processing window which is defined as the temperature difference between the melting point and the exothermic polymerization reaction, can be easily polymerized through the acetylenic units to thermosets, and lose little weight during curing and pyrolysis to carbon under atmospheric conditions. Our strategy for the synthesis of these materials involves the preparation of multiple-substituted benzenes bearing phenylethynyl groups. Di-substituted acetylenes have been shown to be less reactive or exothermic at a higher temperature relative to mono-substituted acetylenes. Moreover, some mono-substituted acetylenes have been reported to react explosively[9]. We are interested in the synthesis of compounds containing three or more phenylethynyl groups substituted on the benzene ring.

Several compounds containing multiple phenylethynyl substituents were prepared for our studies. These compounds were synthesized from commercially available brominated aromatic compounds. Aryl bromides and iodides are known to react with mono-substituted acetylenes to afford the corresponding cross-coupled product[10,11]. Higher yields occur from aryl iodides and the reaction conditions are milder. The applicability of the palladium-catalysed coupling reaction of phenylacetylene with multiple-brominated benzenes in which at least three bromo groups were substituted on the benzene ring were investigated. Palladium-catalysed coupling reactions have been mainly developed for monohaloaromatic and dihaloaromatic compounds. The simplicity of the synthetic procedure and the mildness of the reaction conditions enhance the importance of the coupling reaction for the preparation of secondary acetylenes in laboratory quantities.

EXPERIMENTAL

Thermal analyses were performed with a DuPont 2100 thermal analyser equipped with a thermogravimetric analyser (t.g.a., heating rate 10°C min^{-1}) and a differential scanning calorimeter (d.s.c., heating rate 10°C min^{-1}) at a flow rate of 50 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. Thermal and oxidative analyses were conducted in nitrogen and air, respectively. Infra-red spectral studies were carried out with a Perkin–Elmer 1800 FTIR spectrophotometer purged with nitrogen gas. Fourier transform infra-red (*FT*i.r.) spectra of the phenylethynylbenzenes were obtained from thin films solvent-cast on NaCl plates. *FT*i.r. spectra of cured or pyrolysed samples were acquired via KBr pellets.

Synthesis of 1,3,5-tris(phenylethynyl)benzene 3a

Phenylacetylene (1.9431 g, 19.02 mmol), 1,3,5-tribromobenzene (1.6636 g, 5.2843 mmol), triethylamine (22.1 ml, 16.1 g, 158 mmol), pyridine (14.6 ml, 14.3 g, 181 mmol) and a magnetic stirring bar were added to a 250 ml round-bottomed flask. The flask was fitted with a septum and then chilled in an isopropanol/dry ice bath. After the flask had cooled, the mixture was degassed several times by the alternate application of partial vacuum and argon.

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To the flask was quickly added palladium catalyst, which consisted of $Pd(PPh_3)_2Cl_2$ (0.1113 g, 0.1585 mmol), CuI (0.1005 g, 0.5279 mmol) and PPh_3 (0.2218 g, 0.8455 mmol). The septum was refitted and the flask was again degassed. The flask was warmed to room temperature, then placed in an oil bath preheated to 75°C, and stirred overnight. A copious amount of a white precipitate, the amine salt by-product, formed. The reaction product was poured into water, resulting in the formation of a precipitate. The product was collected by suction filtration and purified by recrystallization from toluene and isopropanol to afford the desired product **3a** in 87% yield, m.p. 144–145°C.

*Synthesis of 1,2,4-tris(phenylethynyl)benzene **3b**, using activated palladium*

Phenylacetylene (4.858 g, 47.56 mmol), 1,2,4-tribromobenzene (4.159 g, 13.21 mmol), CuI (0.0278 g, 0.146 mmol) and a stirring bar were added to a 100 ml round-bottomed flask (flask 1). Activated palladium catalyst was prepared by the following method. Into a 100 ml round-bottomed flask (flask 2) was added $Pd(PPh_3)_2Cl_2$ (0.0278 g, 0.0396 mmol), PPh_3 (0.0556 g, 0.2122 mmol), Mg (0.0963 g, 3.963 mmol) and diisopropylamine (55.6 ml, 40.10 g, 396.3 mmol). The mixture was thoroughly mixed by stirring. The flask was fitted with a septum, chilled in a dry ice/isopropanol bath, and degassed several times by the alternate application of vacuum and argon gas. The flask was then placed in a hot water bath at 80°C and stirred for 5 min. Upon cooling, the solution was decanted into flask 1. Pyridine (16.0 ml, 15.67 g, 198.2 mmol) was then added to flask 2 and the septum was refitted. The flask was chilled and degassed. This flask was then placed with stirring into a hot water bath at 80°C for 5 min. After cooling this solution was also decanted into flask 1. The reaction mixture in flask 1 was fitted with a septum, chilled in a dry ice/isopropanol bath and degassed several times by the alternate application of vacuum and argon. This flask was then placed in an oil bath and heated overnight at 77°C. A copious amount of a white precipitate, the amine salt by-product, formed during the reaction. The reaction mixture was then poured into a beaker containing water and the product was collected by suction filtration. The solid was recrystallized from methylene chloride and isopropanol to afford 3.19 g (64%) of the desired product **3b**, m.p. found 105–109°C.

*Synthesis of 1,2,4,5-tetrakis(phenylethynyl)benzene **3c***

Phenylacetylene (4.697 g, 45.98 mmol), 1,2,4,5-tetrabromobenzene (4.113 g, 10.45 mmol), triethylamine (29.1 ml, 209 mmol), pyridine (16.9 ml, 209 mmol) and a magnetic stirring bar were added to a 250 ml round-bottomed flask. The flask was fitted with a septum and then chilled in an isopropanol/dry ice bath. After the flask had cooled, the mixture was degassed several times by the alternate application of partial vacuum and argon. To the flask was added palladium catalyst, which consisted of $Pd(PPh_3)Cl_2$ (0.147 g, 0.209 mmol), CuI (0.139 g, 0.731 mmol) and PPh_3 (0.294 g, 1.120 mmol). The septum was refitted and the flask was again degassed. The flask was warmed up to room temperature, then placed in an oil bath at 80°C and stirred overnight, resulting in the formation of a copious amount of a white precipitate. The product mixture was poured into 200 ml of water. The product was collected by suction filtration, washed several times with water, and dried. Recrystallization from methylene chloride and ethanol afforded 1,2,4,5-tetrakis(phenylethynyl)benzene **3c** in 84% yield; m.p. found 194–196°C, lit.[12] 193–194°C.

*Polymerization of 1,3,5-tri(phenylethynyl)benzene **3a***

The monomer **3a** (0.5 g) was weighed into an aluminium planchet and polymerized by heating in air at 200°C for 1 h, at 275°C for 1 h and at 300°C for 3 h. The black polymer was somewhat brittle. An infra-red spectrum showed the absence of an absorption centred at 2212 cm^{-1} attributed to an acetylenic carbon–carbon triple bond.

*Polymerization of 1,3,5-tri(phenylethynyl)benzene **3a** and conversion into carbon*

The monomer **3a** (11.4 mg) was weighed into a t.g.a. boat and cured by heating at 100°C min^{-1} under a nitrogen atmosphere from 30 to 400°C and holding at 400°C for 1 h and at 450°C for 1 h. The sample was then cooled to room temperature. A t.g.a. thermogram in nitrogen showed a char yield of 83% at 900°C.

Another sample of **3a** (10.4 mg) was weighed into a t.g.a. boat, cured, and carbonized by heating in nitrogen from 30 to 90°C at 10°C min^{-1}, resulting in a char yield of 73%. The monomer lost 13% of its weight between 275 and 375°C. Between 375 and 500°C, little weight loss occurred. From 500 to 600°C, another 10% weight loss occurred. Only a small weight loss occurred between 600 and 900°C, resulting in carbonization.

*Polymerization of 1,2,4-tris(phenylethynyl)benzene **3b***

The monomer **3b** (1.0 g) was weighed into an aluminium planchet and cured by heating either in air or under an inert atmosphere at 200°C for 1 h, at 275°C for 1 h and at 350°C for 2 h. The resulting thermosetting polymer was removed from the planchet. During the heat treatment, the sample lost about 8% of its weight. Infra-red studies showed the disappearance of characteristic absorptions attributed to the acetylenic units.

*Polymerization and carbonization of 1,2,4-tris(phenylethynyl)benzene **3b***

The monomer **3b** (13.3 mg) was weighed into a t.g.a. boat and cured by heating at 200°C for 4 h and at 250°C for 4 h under a nitrogen atmosphere. During the heat treatment, the sample lost approximately 6% weight. The polymer was then cooled. A thermogram was then determined on the polymer between 30 and 900°C in a flow of nitrogen at 50 cm^3 min^{-1}. Between 450 and 600°C, the sample lost another 10% weight attributed to breakage of bonds, reorganization and ultimate carbonization. The carbonized sample had a char yield of 82%.

*Polymerization of 1,2,4,5-tetrakis(phenylethynyl)benzene **3c***

The monomer (0.26 g) was weighed into an aluminium planchet and cured by heating in air at 200°C for 1 h, at 225°C for 2 h and at 275°C for 1 h, resulting in solidification. Almost immediately after melting, the monomer started to darken. Within 45 min, the melt had become fairly viscous. After heating at 275°C, the polymer had not lost any weight. The polymer was removed from the planchet and used for characterization studies. An infra-red spectrum showed the absence of an absorption centred at 2212 cm^{-1} attributed to an acetylenic carbon–carbon triple bond.

Polymerization and carbonization of 1,2,4,5-tetrakis(phenylethynyl)benzene 3c

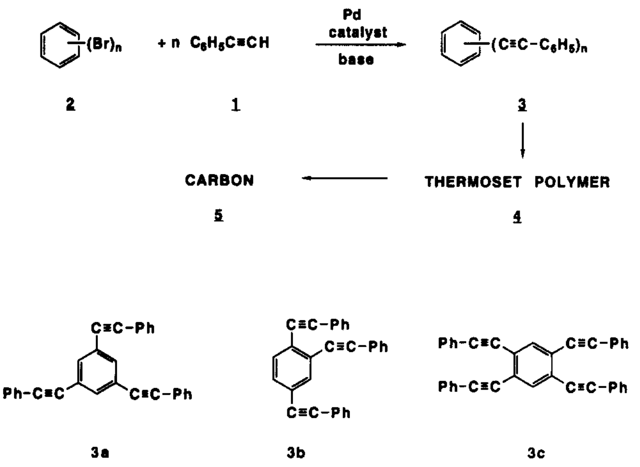
The monomer **3c** (15.1 mg) was weighed into a t.g.a. boat and cured by heating under a nitrogen atmosphere at 225°C for 2 h, at 300°C for 2 h and at 400°C for 2 h, resulting in the formation of a solid thermosetting polymeric material. During the heat treatment, the sample lost 1.1% weight. Upon cooling, a t.g.a. thermogram was taken between 30 and 900°C, resulting in a char yield of 85%.

DISCUSSION

The synthesis of multiple phenylethynylbenzenes is shown in *Scheme 1*. A slight molar excess of phenylacetylene **1** relative to multiple-brominated benzene **2** in the presence of either triethylamine or diisopropylamine, pyridine and a catalytic amount of $Pd(PPh_3)_2Cl_2$ is mixed initially at −78°C. The reaction mixture is then degassed, warmed to room temperature, and then heated at 80°C. 1,3,5-Tris(phenylethynyl)benzene **3a**, 1,2,4-tris(phenylethynyl)-benzene **3b** and 1,2,4,5-tetrakis(phenylethynyl)benzene **3c** were prepared from the reaction of the appropriate brominated benzene **2** and the palladium catalyst in yields of 87, 64 and 95%, respectively. The lower yield observed for **3b** was attributed to the difficulty involved in its purification by recrystallization. The synthesis of **3a** has previously been reported[13] from the reaction of 1,3,5-tribromobenzene and phenylacetylene in the presence of a palladium catalyst and in the presence of copper bronze and potassium carbonate in 42% yield. The melting point and the yield from the palladium-catalysed reaction were not reported. Heck and coworkers[12] reported the synthesis of **3c** from 1,2,4,5-tetraiodobenzene and phenylacetylene using a palladium catalyst in 63% yield.

The cross-coupling reactions, which were carried out with fresh $Pd(PPh_3)_2Cl_2$, initially proceeded to afford **3a**, **3b** and **3c** in good yield. The reaction mixtures were distinguished by the formation of a white amine salt precipitate and a slightly yellow to orange-red solution. When these reactions were repeated several months later, it was noted that the reaction mixtures were turning green, then black during the course of the reaction. Moreover, the reactions failed to proceed except in low conversion. The changing of the argon tank and redistillation of the amine and pyridine did not improve the yields. The possibility that the catalyst had become inactive was considered. The limited shelf life of palladium catalysts has been observed previously by Negishi and coworkers[14].

A procedure, which has been developed for the activation of nickel[15–17], was modified for palladium. Activated palladium was achieved from a mixture of $Pd(PPh_3)Cl_2$, PPh_3 and an excess amount of magnesium (Mg) in pyridine. After cooling in a dry ice/acetone bath, the mixture was degassed several times by the alternate application of vacuum and oxygen-free argon. The palladium was then activated by heating the mixture at 80°C for a short time (times of 5 to 60 min were equally effective). The palladium compounds were found to be more soluble in pyridine than in diisopropylamine. While being heated, the solution changes from light yellow to light yellowish-green. This solution is then transferred to another flask containing the brominated benzene, phenylacetylene, cuprous iodide and diisopropylamine. Our investigation has revealed rapid reaction rates as evidenced by the fast and copious formation of amine salt, which is the side-product of the coupling reaction. This method for the activation of palladium allowed the routine use of 0.001–0.0001 equivalent of palladium catalyst in the coupling of brominated benzenes with phenylacetylene. Typically, coupling reactions are carried out using 0.01–0.05 equivalent of palladium catalyst[14].



Scheme 1

A clear demonstration of the activation of the palladium catalyst is shown by efforts to synthesize 1,2,4,5-tetrakis(phenylethynyl)benzene **3c**. Initial attempts at the synthesis of **3c** starting with 1,2,4,5-tetrabromobenzene and phenylacetylene in the presence of fresh palladium catalyst were highly successful. Further attempts at scale-up several months later resulted in the reaction mixture becoming very dark. Only 1,2,4,5-tetrabromobenzene was recovered from the reaction vessel. It was only after activation of the palladium catalyst that **3c** was again isolated in high yields. Heck and coworkers[12] reported the synthesis of 1,2,3,4,5,6-hexakis(phenylethynyl)-benzene in 53% yield from hexaiodobenzene and phenylacetylene in the presence of palladium. Vollhardt and coworkers[18] reported the synthesis of 1,2,3,4,5,6-hexakis-(1-trimethylsilylethynyl)benzene in 27% yield from trimethylsilylacetylene and hexabromobenzene. Neenan and Whitesides[9] reported the synthesis of 1,2,3,4,5,6-hexakis(1-trimethylsilylethynyl)benzene after prolonged refluxing of the reaction mixture in 1% yield starting from trimethylsilylacetylene and hexaiodobenzene. The inconsistencies in the above reaction yields could be attributed to the activity of the palladium catalyst and to the poisoning of the palladium with time. When the palladium catalyst is activated as described with Mg, our studies indicate that consistent results are obtained from the cross-coupling of brominated benzenes with phenylacetylene.

The electron-withdrawing effect of the acetylenic substituents and their position on the benzene ring affect the position of characteristic *FT*i.r. absorptions. The absorption peaks of interest for **3a**, **3b** and **3c** were the aromatic (=CH and C=C) and acetylenic (C≡C) groups. These compounds in sequence show =CH absorptions at 3053, 3052 and 3048 cm^{-1}. The characteristic C=C absorptions were at 1596 and 1581, 1597 and 1572, and 1596 and 1571 cm^{-1}, respectively. Another characteristic absorption associated with the aromatic nucleus was centred at 1489, 1501, and 1502 and 1496 (doublet) cm^{-1}. Each compound had an absorption at 1442 cm^{-1}. The acetylenic absorptions were at 2209 (singlet), 2216 (shoulder) and 2210, and a doublet centred at 2224 and 2204 cm^{-1} (see *Figure 1*). The sharp peak (2209 cm^{-1}) associated with the acetylenic absorption of **3a** indicates the non-interaction of the acetylene groups relative to the other two compounds. In the case of **3b** and **3c**, the observation of two distinctive acetylenic absorptions, which is more pronounced for **3c**, perhaps shows the substituent effects (*ortho*, *meta* and *para*) in regard to the changing electronic environment.

Figure 2 shows the d.s.c. thermograms of **3a**–**c**. Compounds **3a**, **3b** and **3c** had endothermic transitions (melting point) peaking at 147, 109 and 195°C, and exothermic transitions (polymerization reaction) peaking at approximately 330, 310 and 290°C, respectively. The observed difference in the melting points and the position of the polymerization reactions are probably attributed to the arrangement of the phenylethynyl groups on the benzene rings. In **3a**, the acetylenic units are substituted symmetrically about the benzene ring. The non-symmetrical substitution of the three acetylenic moieties for **3b** is probably responsible for the lower melting point relative to **3a**. Compound **3c** has four symmetrically substituted acetylenic groups, which explain the higher melting point. Moreover, the greater ease of polymerization observed for **3b** relative to **3a** is attributed to two of the acetylenic groups being *ortho* to each other and thus being able to interact more easily during polymerization. The two groups of *ortho*-substituted acetylenic groups on **3c** probably explain its greater ease of polymerization as determined by a lower temperature for the exothermic transition relative to both **3a** and **3b**. These results indicate that the processing window becomes narrower from symmetrical substitution and as the number of acetylenic substituents on the benzene ring increases.

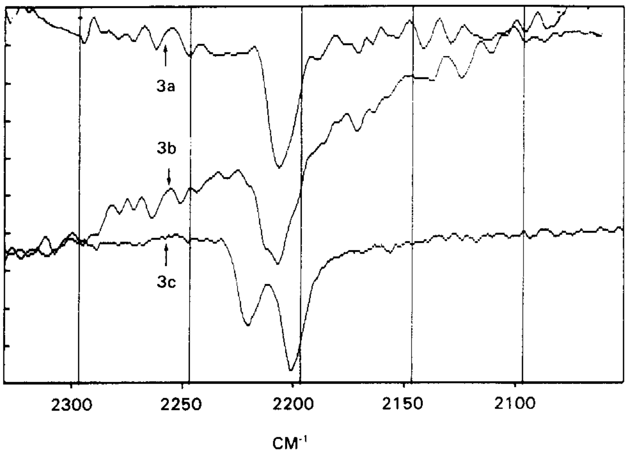


Figure 1 *FT*i.r. absorptions for acetylenic group of **3a**, **3b** and **3c**

The thermal stability of the polymers **4a**–**c** was determined by t.g.a. *Figure 3* shows the weight loss that occurs when **3a**–**c** are heated from 50 to 900°C at 10°C min^{-1} under nitrogen. During the heat treatment, the acetylenic compounds **3a**–**c** are initially converted into dark brown thermoset polymers **4**, which behave as precursor polymers for further conversion into carbon **5**. Compounds **3a** and **3b** upon heating lost weight between 250 and 360°C and between 260 and 330°C, respectively. Attempts at reducing or eliminating this initial weight loss were unsuccessful under atmospheric curing conditions. Only small improvements in the weight retention were obtained by conversion of **3** to polymer **4** by isothermal heat treatment at various temperatures up to 400°C before pyrolysis to 900°C and formation of **5**. This initial weight loss, which occurred more readily for **3a**,

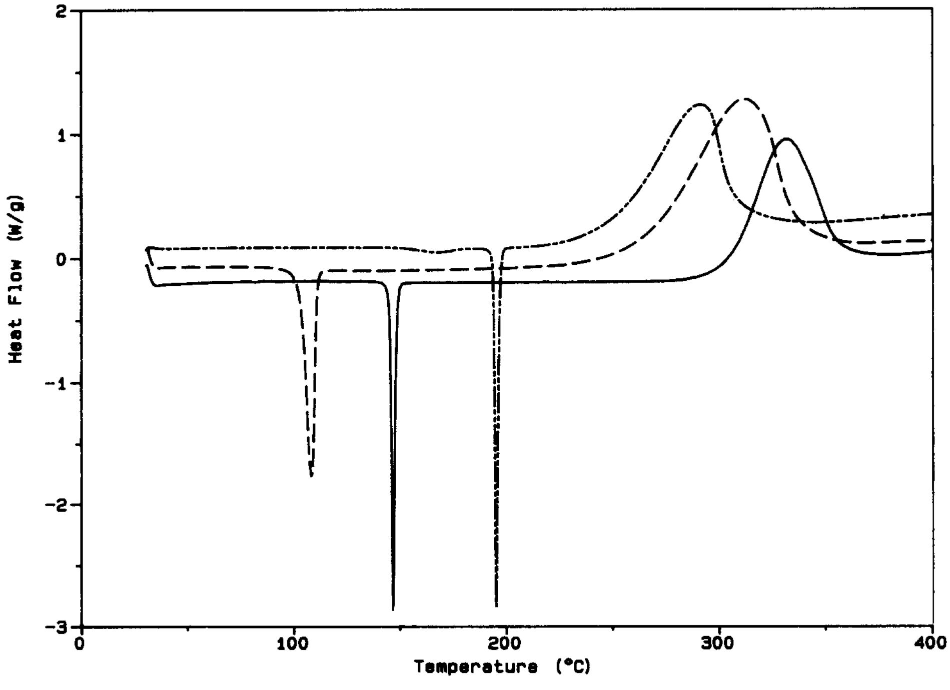


Figure 2 D.s.c. thermograms of **3a** (——), **3b** (– – –) and **3c** (–··–)

is believed due to the intense heat generated during the exothermic polymerization reaction, which causes the volatilization of starting material as the temperature is increased. This initial weight loss did not occur in **3c**. Compound **3c** did not commence to lose weight until approximately 400°C and retained a char yield of 83% at 900°C.

Figure 4 shows the oxidative stability of the carbonaceous mass **5**. The stability was found to be a function of where the acetylenic units were substituted on the benzene ring of **3**. The chars from **3a** and **3c** showed the least and the greatest stability, respectively. Apparently, the char obtained from the *ortho*-substituted acetylenic compounds **3b** and **3c** forms a more dense mass, which reduces the oxidative process relative to **3a**. Moreover, the char of **3a** and to a lesser extent that of **3b** gained weight when heated in air between 300 and 450°C, indicating an easier diffusion of oxygen into the carbon mass relative to **3c**.

Studies by gas chromatography/mass spectroscopy

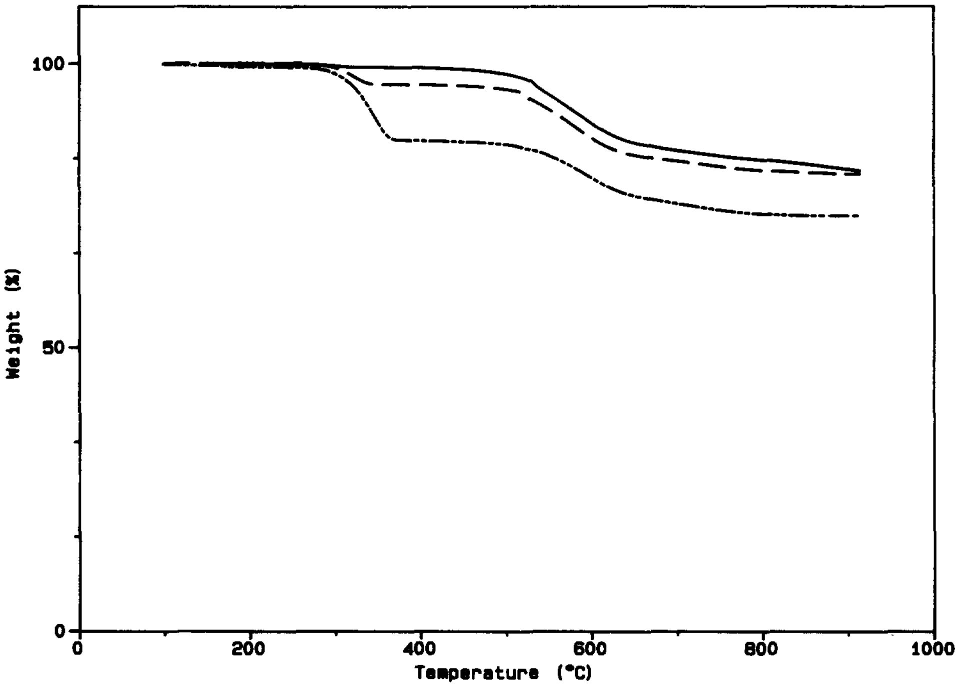


Figure 3 Thermal conversion of **3a** (–··–), **3b** (– – –) and **3c** (——) into carbon **5**

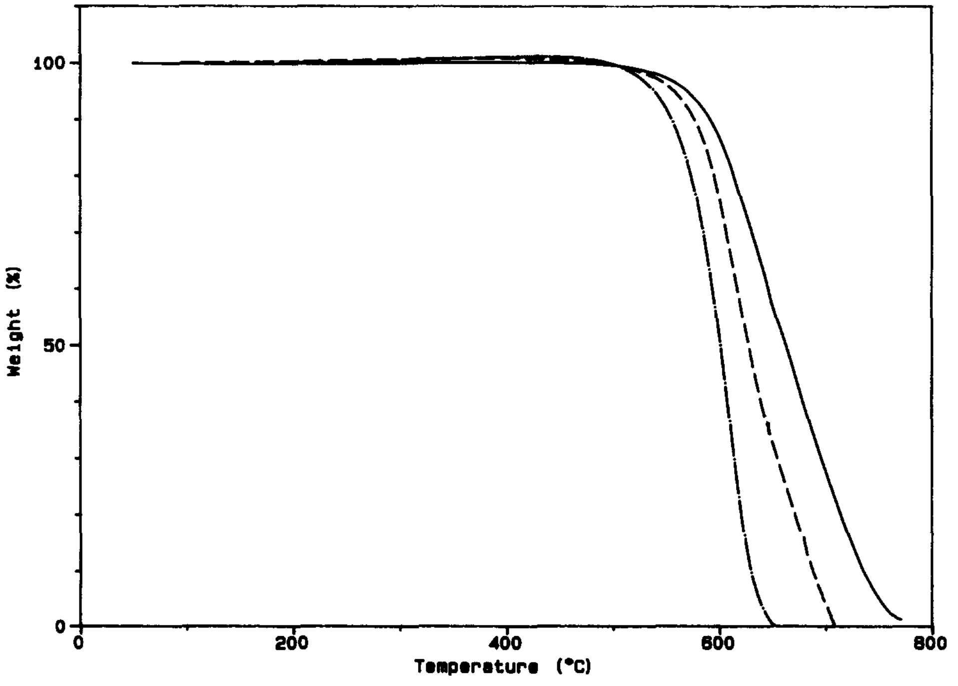


Figure 4 Oxidative stability of char **5** from **3a** (–·–), **3b** (– – –) and **3c** (——)

using a pyroprobe attachment[18,19] were performed on polymers **4** in an attempt to more fully understand the mechanism of thermal degradation between 500 and 700°C. The analysis was not clear cut. Any possible fragment that could be produced was identified in the volatiles which were generated. Upon heating to 900°C, compounds **3a–c** lost about the same amount of volatiles in the sampling region.

SUMMARY

A method has been developed for activating palladium such that minute quantities can be used in the synthesis of acetylenic-based aromatic compounds. Multiple phenylethynylbenzenes have been synthesized as potential carbon matrices from the appropriate brominated benzenes and phenylacetylene in the presence of a catalytic amount of palladium. These low molecular weight secondary acetylenic compounds were converted into highly crosslinked thermosets and then further pyrolysed under atmospheric conditions at elevated temperatures to carbon. High carbon yields were observed for the three compounds studied. A key feature of these compounds is their one-step synthesis from brominated benzenes and phenylacetylene, which are readily available materials. Furthermore, the melting points are sufficiently below the polymerization temperature such that a good processing window exists for their conversion into high temperature polymers and carbon. An added bonus of using a pure compound as a carbon precursor material is the uniformity of properties such as the melting point and the viscosity of the melt.

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