New Route to Graphite Flakes and Films: Pyrolysis of Aromatic and Heteroaromatic Compounds under Dehydrogenation Conditions

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Highly conducting carbon flakes and films are prepared in high yield from the pyrolysis of benzene, biphenyl, naphthalene, and pyrazine, by heating the parent compound in a vapor stream in the presence of a dehydrogenating agent at 800–900 °C. Pyrolysis at these temperatures normally produces carbons in powder form, but the simple addition of halogen vapor easily provides flakes of thicknesses up to 20 μm and lengths up to 1 cm on a side. If chlorinated or brominated benzenes are used, films and flakes are obtained even in the absence of any added halogen vapor. Quartz substrates and walls can also be coated with thin or thick films in this manner. The flakes and films are metallike in appearance and have a conductivity of about 200–300 S cm^{-1} at room temperature. By heat treatment to 2600 °C, graphitic order is improved and the conductivity rises to ≈10 000–15 000 S cm^{-1}.

Introduction

There are an enormous body of work on the pyrolysis of organic compounds to form carbon and a general understanding of the reaction mechanisms involved.[1] In the case of pyrolysis of unsubstituted aromatic compounds, even at temperatures as low as 300 °C, there is evidence for direct ring condensation forming di- and triarenes via free-radical intermediates. As such materials are heated to higher and higher temperatures, graphitic domains are formed of various sizes and degrees of ordering. Although essentially all organics will carbonize, the formation of carbons in a manner that will ultimately result in a controlled morphology is not so easy. The formation of graphitic fibers, films, and flakes that can be utilized in materials applications has required the development of specialized starting materials and/or specialized processing conditions. In the area of carbon fiber formation, for example, heating precursor fibers such as poly(acrylonitrile) or fibers formed by extruding mesophase pitch are successful commercial routes to high-conductivity, high-strength materials.[2]

Several techniques have been developed for the preparation of thin carbon films via evaporative techniques. In the more recent work, aromatic precursors have been examined that would lead to condensed aromatic structures. One such approach has utilized aromatic carboxylic dianhydrides that by elimination of CO and CO_2 lead to a polyconjugated structure. For example, polyperinaphthalene (PPN) was found to deposit on both the inner wall of a quartz tube and onto inserted substrates when the chemical pyrolysis of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) was conducted at 700–900 °C in a vacuum.[3] The thickness of the PPN films varied from several hundred angstroms to approximately 1 μm. Formation of PPN fibers and ribbonlike PPN was reported by several groups.[4–7] Thin films of pristine PPN and $NbCl_5$-doped PPN were deposited on quartz substrates by heating PTCDA at 530–600 °C in a vacuum in the absence or presence of the salt.[8] The conductivity of these films was an order of magnitude lower than that of PPN whiskers prepared by Murakami.[7]

Another approach to a polyconjugated system is to utilize a radio-frequency (rf) discharge. Rf plasma decomposition of benzene vapor in the range 400–1000 °C has been reported to form thin carbon films on quartz substrates.[9] Oligomer decomposition can also lead to thin carbon films. For example, the pyrolysis of quinoline oligomers in a sealed quartz tube at 900–1200 °C generated shiny black films on the inner wall of the reaction tube.[10] The films had a conductivity higher than 400 S cm^{-1} at room temperature and thickness in the range 80 nm to 30 μm.

Highly conductive graphitic films can also be obtained by heat treatment of aromatic polymers at very high temperature. Three kinds of poly(*p*-phenylenevinylene) films at different stretching ratios can be pyrolyzed up to 3000 °C to yield highly conductive pyropolymer.[11] Cast films of polyoxadiazole can decompose to carbon films with a bright metallic luster by heat treatment above 2800 °C[12,13] to give conductivities greater than 10^4 S cm^{-1}. Intercalation compounds of these films showed conductivities above 10^5 S cm^{-1} comparable to those of highly oriented pyrolytic graphite (HOPG).[11,12]

We wish to report finding conditions under which simple aromatic hydrocarbons and aromatic heterocycles can be efficiently converted to highly conducting films and flakes. In this paper, preparation of pyrolytic films and flakes from the decomposition of benzene (PB), biphenyl (PBP), naphthalene (PNA), and pyrazine (PPZ) as well as chloro- (PClB) and bromobenzene (PBrB) is described. These flakes and films have a metallic luster, high electrical conductivity, and are chemically inert and thermally stable. The starting materials are simple and inexpensive, and the yields of graphitic material are relatively high. As opposed

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[1] See, for example: Fitzer, E.; Mueller, K.; Schaefer, W. *Chemistry and Physics of Carbons*; Walker, P. L., Jr., Ed.; Marcel Dekker: New York, 1971; Vol. 7, p 238.

[2] See: Donnet, J.-B.; Bansal, R. C. *Carbon Fibers*; Marcel Dekker: New York, 1984.

[3] Kaplan, M. L.; Schmidt, P. H.; Chen, C.; Walsh, W. M., Jr. *Appl. Phys. Lett.* **1980**, *36*, 867–869.

[4] Murakami, M.; Yoshimura, S. *J. Chem. Soc., Chem. Commun.* **1984**, 1649–1650.

[5] Murakami, M.; Yoshimura, S. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 95–102.

[6] Iqbal, A.; Ivory, D. M.; Marti, J.; Bredas, J. L.; Baughman, R. H. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 103–110.

[7] Murakami, M. *Synth. Met.* **1987**, *18*, 531–536.

[8] Iqbal, Z.; Maleysson, C.; Baughman, R. H. *Synth. Met.* **1986**, *15*, 161–167.

[9] Onuma, Y.; Kao, Y.; Nakao, M.; Matsushima, H. *Jpn. J. Appl. Phys.* **1983**, *22*, 888–889.

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[11] Ohnishi, T.; Murase, I.; Noguchi, T.; Hirooka, M. *Synth. Met.* **1987**, *18*, 497–502.

[12] Murakami, M.; Yoshimura, S. *Synth. Met.* **1987**, *18*, 509–514.

[13] Yoshimura, S.; Murakami, M.; Yasujima, H.; Mizogami, S. *Synth. Met.* **1987**, *18*, 473–478.

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to previous approaches, it is relatively easy to produce thick films and free-standing flakes by this approach.

Experimental Section

Benzene, biphenyl, naphthalene, pyrazine, and chloro- and bromobenzene were 99+% grades from Aldrich and were used as received without purification. The pyrolysis reaction was carried out in a quartz tube heated by a clam-shell furnace or a Lindberg furnace. Either argon or nitrogen could be used as a carrier gas and was purged through the system prior to each synthesis. The flow rate of carrier gas was kept at 10–20 cm^3 min^{-1} and passed through or over the heated hydrocarbon. Bromine vapor was injected into the system by bubbling inert gas into the bromine liquid at a flow rate of 10–20 cm^3 min^{-1}. Cl_2 gas (cylinder pressure 85.3 psig) was diluted by the carrier gas at the same flow rate. The organic vapor (except for the halogenated benzene) was mixed with either chlorine or bromine vapor before entering the hot zone. The halogenated benzenes were simply passed in a vapor stream into the hot zone. After the reaction was completed, shiny mirrorlike coatings consisting of film and flake were found to deposit on the surface of the tube, and unreacted hydrocarbon was recovered from an exit cold trap. The contents of the cold trap were largely unreacted benzene as well as a complex mixture of higher molecular weight condensation products such as biphenyl, etc., and hydrogen halide. The thickness of the films varied in the range 2–20 μm as measured by scanning electron microscopy. Heat treatment to 2600 °C was performed in a Thermal Technology Group 1000 furnace that was fitted with a graphite hearth. The samples were placed in a graphite crucible and heated in a helium atmosphere for periods of 1–4 h at the required temperature.

Raman spectroscopy utilizing the microprobe technique allowed for characterization of the degree of graphitic order of the pyrolytic films. Conductivity was measured by the standard four-probe technique, attaching four gold or silver wires to the film on a thin insulating substrate with silver paint (Du Pont 4922) or conducting adhesive (Amicon CT5047-2). Thermogravimetric analysis (TGA) was used to determine the thermal stability of the films. Elemental analysis was carried out by Huffman and Galbraith Laboratories. X-ray powder diffraction data were obtained on a Rigaku D/Max 2 instrument at the University of Pennsylvania.

The weight loss of the pyrolytic films was recordered by using a Perkin-Elmer TGS-2 thermogravimetric analyzer. Only 4.54% weight loss was observed for benzene (PB) film up to 995 °C. Pyrazine (PPZ) film had ~14% weight loss in the same temperature range. Both these films showed thermal stability superior to those reported for PPN films.[5]

Other hydrocarbons and heterocycles were examined that gave very poor yields under these conditions. Pyridine, for example, did not give good yield. Kouvetakis et al.[14] had reported preparing a nitrogen-containing carbon from a pyridine–chlorine mixture but gave no indication of the yield of this product. Pyrene, triazine, and cyanuric chloride gave only traces of carbonaceous powdery products.

Results and Discussion

Reaction temperatures lower than 800 °C resulted in low yield. The yield increased appreciably in the presence of either chlorine or bromine vapor, with no discernible difference between them. In the case of benzene, after correction for the amount of total hydrocarbon recovered from the exit stream, the yield of graphite flakes was ~ 75%. All the flakes were made at 800–900 °C and then heated to a different heat treatment temperature (HTT) under He gas for an hour or more in the high-temperature furnace.

Table I. Elemental Analyses and Composition of the Pyrolytic Products at Various Temperatures

compd (HTT, °C)	C, %	H, %	N, %	compn
PPZ (850)	81.18	1.98	15.35	$C_{6.15}H_{1.8}N$
PPZ (1400)	98.3		1.7	$C_{68}N$
PB (850)	98.93	0.76		$C_{10.8}H$
PB (1700)	100.07			C
PNA (850)	98.46	0.78		$C_{10.5}H$
PBP (900)	99.43	0.40		$C_{20.7}H$

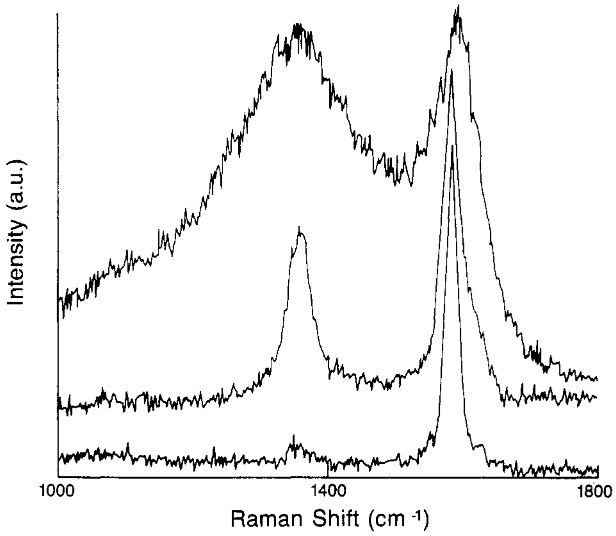

Figure 1. Raman spectra of carbon films prepared from benzene at 850 °C (top) and heat treated for 1 h at 2000 (middle) and 2600 °C (bottom).

The flakes were typically 5–20 mm on a side and tend to be somewhat rectangular. In some cases, much larger pieces of films were formed, the largest achieved thus far being approximately 10 cm long by 1.5 cm wide. Their surfaces were highly reflective and silvery or silvery black in appearance. Attempts to deposit the flakes on other catalytic surfaces such as Pt and Ni have been carried out by placing the metal plates in the quartz tube in or near the hot zone. Instead of forming smooth, shiny flakes, some powderlike deposits were obtained on the metal plates. All the films are insoluble in common organic solvents and concentrated inorganic acids such as HCl, HNO_3, and H_2SO_4.

Table I shows the element percentage and chemical composition of several of the pyrolytic films. The numbers in parentheses refer to the HTT. No chlorine or bromine was found in these materials, which indicated that the halogens served only as hydrogen scavengers and/or free-radical initiators during the thermal reaction. Less than 2% N was found in the PPZ films after heating up to 1400 °C for 1 h. PB films could be converted into pure carbon at 1700 °C.

Both FT-IR spectra and FT-IR reflectance spectra showed a disappearance of all of the aromatic peaks of the pyrolytic films, consistent with the observations of Chiang et al.[10] Raman spectroscopy proved to be a useful tool to characterize the structures of these substances. From the Raman scattering, two peaks at 1360 and 1580 cm^{-1} were found in all the films. The peak at 1580 cm^{-1} was assigned to an ordered graphitic structure and the peak at 1360 cm^{-1} to disordered carbon.[11,12] No difference was observed in the Raman spectrum of the PB films annealed at 850 °C for a prolonged period of time. Figure 1 presents spectra of PB films treated at different HTT. The intensity of the disorder peak at 1360 cm^{-1} decreased with increasing HTT, while the peak at 1580 cm^{-1} sharpened with increasing HTT. No disorder peak was observed for the PB film heated to 2600 °C, which suggested that a highly ordered graphitic structure could be established at this temperature. PPZ films heated to 2600 °C still exhibited

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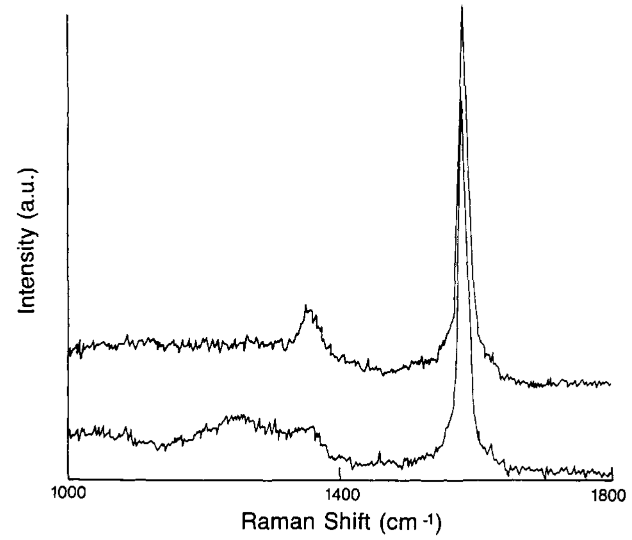

Figure 2. Raman spectra of carbon films derived from pyrazine heat treated at 2600 °C for 1 h (top) and at 2300 °C for 4 h (bottom).

Table II. Intensity Ratio of Three Major Peaks in the X-ray Diffraction Patterns of Graphite Flakes as Compared to Natural Graphite

sample (HTT, °C)	*hkl*	*d*, Å	I/I_0
graphite	002	3.36	100
	004	1.68	80
	006	1.12	20
PB (2000)	002	3.56	100
	004		
	006		
PB (2600)	002	3.37	100
	004	1.68	11
	006	1.21	2
PPZ (2600)	002	3.36	100
	004	1.68	10
	006	1.20	1

a very weak peak at 1360 cm^{-1} (Figure 2, top curve). However, this disorder peak could be completely eliminated by heating PPZ films at 2300 °C for 4 h (Figure 2, bottom curve).

Table II presents X-ray powder diffraction data for samples of PB and PPZ at various HTT and compares them with graphite. Only the (00*l*) peaks are seen, indicating that the graphite layer is essentially parallel to the flat surface of the flake. Samples prepared at 850 °C show no graphite diffraction, and the intensities of the (00*l*) reflections increase with HTT. (004) and (006) reflections are considerably less intense for PB- and PPZ-derived samples than those in natural graphite.

The typical room-temperature conductivity for the films formed at 800–900 °C is 200–300 S cm^{-1}. Table III summarizes the conductivities of the films at different HTT. The temperature dependence of the resistivity was studied from 80 to 300 K. Figure 3 shows the temperature dependence of resistivity of PB films. The resistivity of the films formed at 800–850 °C increased slightly with decreasing temperature, while the films prepared at higher HTT showed an essentially temperature-independent resistivity.

The mechanism of the graphitization process most likely involves the formation of aromatic and heteroaromatic radicals when halogen extracts hydrogen from the compound. Benzene, for example, might then form biphenyl via radical coupling, and stepwise reactions could lead to a graphitic network. It is frequently the case that compounds containing nitrogen graphitize rather readily, but the precise role of nitrogen in this process remains to be elucidated. Further evidence as to the efficacy of halogen in promoting formation of a radical that can condense to form a carbon network is obtained from the experiments with chloro- and bromobenzene. These substituted aromatics do not require addition of halogen for efficient film and flake formation. Since the energies of the C–Cl and C–Br bonds are both considerably lower than that of the C–H bond, it would be expected that these compounds would cleave more readily to benzene radical than benzene itself. Thus one might surmise that the role of halogen involves promoting the formation of an aromatic radical by lowering the energy barrier for its formation.

Table III. Room-Temperature Conductivity of Pyrolytic Films Produced at Various Temperatures

compd (HTT, °C)	conductivity, S cm^{-1}	compd (HTT, °C)	conductivity, S cm^{-1}
PPZ (850)	200–300	PB (2000)	1200–1500
PPZ (1500)	1000–1200	PB (2600)	12 000–15 000
PPZ (2000)	1000–1200	PNA (850)	200–300
PPZ (2600)	9000–10000	PBP (900)	~300[a]
PB (850)	200–300	PClB (850)	~300[a]
PB (1500)	1200–1500	PBrB (850)	~300[a]

[a] Limited data available on these samples.

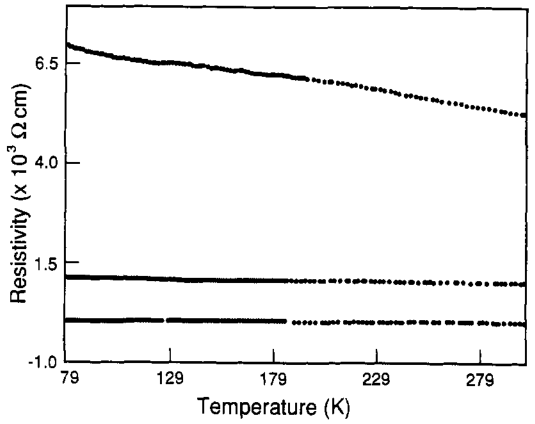

Figure 3. Temperature dependence of the resistivity of carbon films derived from benzene at 850 °C (top) and heat treated for 1 h at 1500 (middle) and 2600 °C (bottom).

Conclusions

It has been discovered that conditions can be found in which benzene, chlorobenzene, bromobenzene, biphenyl, naphthalene, and pyrazine vapors easily form films and flakes of a graphitic nature in high yield. They have a high intrinsic conductivity and are chemically inert and thermally stable. Further heat treatment of the films formed at 800–900 °C can improve their graphitic structure and enhance the electrical conductivity to values of the order of 10^4 S cm^{-1}.

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Registry No. PB, 71-43-2; PBP, 92-52-4; PNA, 91-20-3; PPZ, 290-37-9; C_6H_5Cl, 108-90-7; C_6H_5Br, 108-86-1; Br_2, 7726-95-6; Cl_2, 7782-50-5; graphite, 7782-42-5; quartz, 14808-60-7.