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# Direct conversion of highly aromatic phthalonitrile thermosetting resins into carbon nanotube containing solids

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## Abstract

A method for the *in situ* synthesis of multi-walled carbon nanotubes in a bulk solid composition from the pyrolysis of a mixture formulated from $Co_2(CO)_8$ and various high temperature phthalonitrile resins is presented. Carbon nanotube containing compositions in various forms (solid, fiber, and film) can be readily fabricated by this method utilizing slight modifications to the standard resin processing techniques. The formation of carbon nanotubes occurs during the carbonization process at ambient pressure. X-ray diffraction, scanning electron microscopy, and transmission electron microscopy studies show the presence of a copious amount of multi-walled carbon nanotubes in the carbonaceous composition.
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*Keywords:* Phthalonitrile; Carbon nanotube; Curing

## 1. Introduction

The use of high temperature polymers such as the phthalonitrile resins as a carbon source for the formation of carbon nanotubes (CNTs) in the solid phase is an intriguing idea. Phthalonitrile resins containing aryl ether linkages have extremely good thermal properties and high char yields upon thermal treatment to elevated temperatures making them an attractive source of carbon [1]. The phthalonitriles can be melted and readily processed into shaped forms in the presence of a curing additive yielding high temperature thermosetting polymers. The phthalonitriles are being currently evaluated for numerous aerospace, marine, and electronic applications. Upon being exposed to temperatures above 400 °C, the phthalonitriles show superior structural integrity (no $T_g$) relative to other high temperature polymers. Phthalonitriles have been previously shown to readily convert into carbon when heated to temperatures up to 1000 °C [1]. When cured in the presence of a metal salt such as $Co_2(CO)_8$, degradation of the salt occurs above 400 °C to initially produce metal atoms and clusters resulting in the formation of *fcc* Co nanoparticles embedded in the network polymeric system. When the Co nanoparticle-containing phthalonitrile polymer is heated above 500 °C in an inert atmosphere, carbonization to a carbonaceous solid occurs in high yield. Due to the presence of the Co nanoparticles, multi-walled carbon nanotubes (MWNTs) are formed in the carbon during the carbonization process. Besides carbon and hydrogen, the phthalonitrile resins contain nitrogen and oxygen, which is a method for the incorporation of heteroatom dopants [2,3] within the CNT network. These dopants introduced in the solid phase could allow for variations in the electronic structure and properties of the resulting nanotube containing solid compositions.

It has been previously shown by Keller et al. that the mixing of a cobalt complex with 1,2,4,5-tetrakis(phenylethynyl)-benzene followed by carbonization yields CNTs in high yield [4]. Organometallic compounds such as dicobaltoctacarbonyl, $Co_2(CO)_8$, decompose at fairly low temperatures, well before the carbonization process, to initially produce metal

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atoms and clusters. Our previous work has shown that only a catalytic amount of a metal source is needed for the formation of MWNTs in a solid composition [4]. The interaction of the metal atoms early in the carbonization process with the precursor carbon source appears to be crucial in the formation of the MWNTs. The isolation of the metal atoms by the dense carbon matrix allows for control over the size of the particles and results in the effective formation of MWNTs.

The method that we are using for the formation of carbon nanotubes is different and in contrast to previous reports that show the formation of MWNTs [5]. These MWNTs were formed by deposition on the walls of the reaction vessel from volatiles being produced during the pyrolysis of an organometallic aromatic-containing compound. By our method, polycondensed ring structures are formed during the thermal degradation of precursor aromatic compound, which results in the formation of carbon nanoparticles from pairing of free radicals [6,7]. The developing polycondensed ring structures and/or carbon nanoparticles react with the metal species to initiate the CNT growth process [8,9]. Utilizing our approach, the size and concentration of the metal nanoparticles can be easily controlled by variations in the concentration of the organometallic compound to the carbon precursor compound. Applying the same principle to highly aromatic polymers such as phthalonitrile resins results in the inexpensive synthesis of MWNTs in bulk quantities. The CNTs formed in a solid carbonaceous domain can be left in the solid composition or broken up using sonication to isolate the CNTs in small carbonaceous particles for use in various applications. Additionally, the availability of oxygen and nitrogen atoms in the char of phthalonitrile resin systems would permit the incorporation of heteroatoms or dopants into the CNTs [9].

More recently, there has been a concerted effort for the development of a viable and cost-effective method for the formation of CNT-containing fibers, which hold the promise of extremely high tensile strength and flexibility [10]. Various research groups have used aerogels [11] and fuming sulfuric acid [12] to utilize the CNTs grown from the vapor phase in the formation of CNT-containing fibers. By using a thermosetting resin, which can be spun into a fiber, cured, and then carbonized, a different approach to the formation of CNT fibers can be exploited.

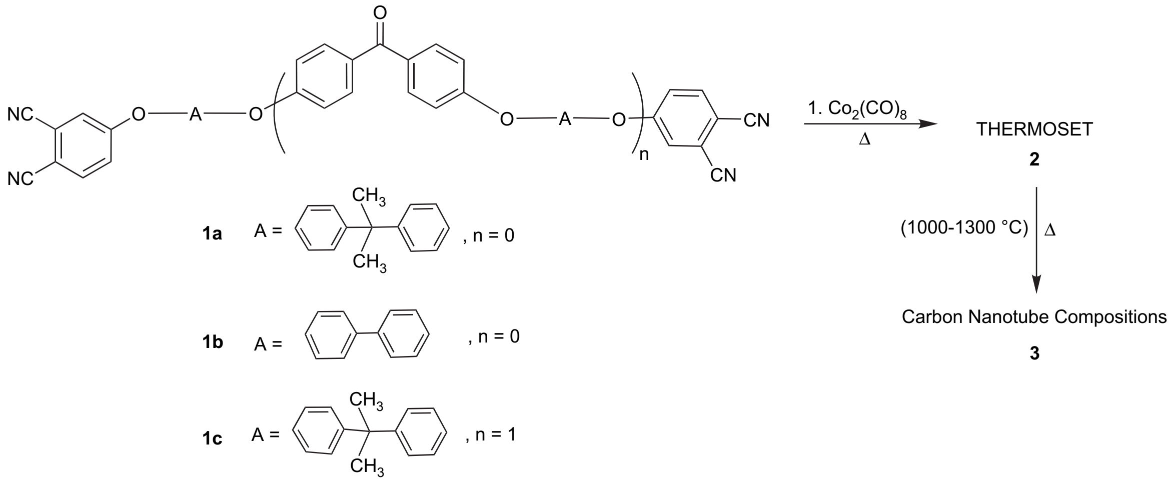
In this paper, we describe a new method for the *in situ* synthesis of MWNTs in a bulk solid composition from the pyrolysis of a mixture formulated from $Co_2(CO)_8$ and various high temperature phthalonitrile resins. Carbon nanotube containing compositions in various forms (solid, fiber, and film) may be readily fabricated by our novel method. This allows for the formation of CNT compositions from any high temperature thermosetting resin utilizing slight modifications to the standard resin processing techniques. We will also describe our effort to formulate fibers from the phthalonitrile resin in the melt phase, followed by conversion to CNT-containing fibers during carbonization.

## 2. Experimental section

The phthalonitrile resins **1a** [13], **1b** [14], **1c** [15–17] described in this paper were synthesized according to previously published procedures (Scheme 1). Thermogravimetric analyses (TGA) were performed on a TA SDT 2960 Simultaneous DTA–TGA module equipped with a TA 3100 thermal analyzer. All thermal analyses were performed using heating rates of 10 °C $min^{-1}$ under a pure nitrogen atmosphere with flow rates of 100 $cm^3\ min^{-1}$. X-ray analyses were performed using a Rigaku 18 kW X-ray generator and a high-resolution powder diffractometer. X-ray diffraction scans of the samples were measured using Cu K$\alpha$ radiation from a rotating anode X-ray source. Scanning electron microscopy (SEM) was performed on a Zeiss Model Supra 55 electron microscope. Transmission electron microscopy (TEM) was performed on a Hitachi H-8100 electron microscope at 200 kV.

### 2.1. Preparation of solid CNT samples for characterization studies

Milligram quantities of a 1:20 molar ratio of $Co_2(CO)_8$ to **1** were weighed onto a TGA pan and heated under argon at 270 °C for 12 h, 300 °C for 3 h, 350 °C for 6 h, and 375 °C



Scheme 1. Formation of carbon nanotube compositions **3** from highly aromatic phthalonitrile resins.

for 4 h to form the thermoset polymer **2**. Further heating of **2** at 10 °C min$^{-1}$ to 1000 and 1300 °C (isotherm for 60 min) and then quickly cooling (∼20 °C min$^{-1}$) to ambient condition afforded the CNT-containing compositions **3**. The solid samples were used for the various characterization studies.

### 2.2. Preparation of CNT samples for TEM studies

A 1:20 molar ratio of $Co_2(CO)_8$ to **1** was dissolved in a minimal amount of $CH_2Cl_2$ and dropped onto a clean silicon wafer before heating to 1000 °C at 10 °C min$^{-1}$. The sample was cooled and the solid present on the surface was suspended in ethanol and dropped onto holey carbon grids for examination. For the thicker sample, a small chip (∼20 mg) of the representative sample was ground in a mortar and pestle. The powder was transferred to a beaker and 5 mL of acetone was added. The mixture was sonicated in an ultrasonic processor (Sonics and Materials, 40% amplitude) for 1 h at ambient temperature. The solution was deposited onto a holey carbon grid (200 mesh copper Holey Carbon) for the TEM studies.

### 2.3. Preparation of samples for SEM studies

A 1:20 molar ratio of $Co_2(CO)_8$ to **1** was deposited on a silicon wafer, melted to a film, heated to 1000 °C and held for 1 h yielding a CNT carbonaceous thick film. To formulate a thin film, a 1:20 molar ratio of $Co_2(CO)_8$ to **1** was dissolved in $CH_2Cl_2$ and deposited on the silicon wafer. Heat treatment of the film at 1000 °C afforded a CNT-containing thin film **3**.

## 3. Results and discussion

For the synthesis of CNTs in a bulk solid, precursor compositions with various molar concentrations of $Co_2(CO)_8$ to phthalonitrile resin **1** are formulated, melted and thermally converted into shaped CNT compositions at elevated temperatures (Scheme 1). A 1:20 molar amount of $Co_2(CO)_8$ and **1** was combined in a round bottom flask and suspended in a 50:50 hexane/$CH_2Cl_2$ solvent mixture. The reaction mixture was allowed to stir for 3 h before the solvent was removed under reduced pressure. The solid brown product mixture was used in the studies as isolated. Shaped solid samples were prepared in a circular aluminum planchet. Typically, the 1:20 molar mixture of $Co_2(CO)_8$ and **1** was placed in the planchet, which had been treated with a high temperature mold release agent, and heated on a hot plate preset at about 225 °C inside a vacuum desiccator. The melted mixture was degassed for 2 h to remove any volatile components. Following the cure procedure to a thermoset **2**, void-free carbonaceous compositions containing CNTs were easily fabricated by thermal treatment above 500 °C under inert conditions.

The formation of CNTs from the bulk phthalonitrile composition (shaped solid, fiber, or film) begins with the decomposition of $Co_2(CO)_8$ yielding initially cobalt atoms, which react with the developing aromatic fused rings, and the ultimate formation of cobalt nanoparticles [18,19]. As the phthalonitrile resin proceeds through the carbonization process (>500 °C), decomposition occurs to form a reactive carbon−cobalt nanocomposition in the developing solid carbonaceous matrix, which is the precursor to the CNT formation. As a consequence of the resin structure, oxygen and nitrogen atoms are also present in the complex mixture. As this mixture is further heated to temperatures about 800 °C, the carbon−cobalt nanocomposition converts into MWNTs and cobalt nanoparticles. Although the exact reaction mechanism remains unclear from our studies, the CNTs appear to form in high yield based upon the char yield and XRD data, especially at long reaction times and higher temperatures. Moreover, current studies are underway to determine if the oxygen and/or nitrogen atoms have been incorporated into the tubular nanostructures.

The thermal properties of phthalonitrile thermoset **2a−c** were determined by thermogravimetric (TGA)-differential thermal (DTA) analyses by heating the samples under nitrogen at 10 °C min$^{-1}$ up to 1000 °C. Samples of **2a**, **2b** and **2c** afforded char yields of 74, 71 and 69%, respectively, at 1000 °C (Fig. 1). Fig. 2 shows the DTA thermograms, which measure the thermal transitions, for samples of **2a**, **2b** and **2c**. All samples exhibited exothermic transitions peaking between 500−530 °C and 700−730 °C, which were attributed to the degradation of the phthalonitrile resin [1,14−17] and reaction of the cobalt species (atoms, clusters, and/or nanoparticles) with the developing carbonaceous matrix and to the formation of the CNTs, respectively.

X-ray diffraction (XRD) scans of the samples **3** were obtained using Cu Kα radiation from a rotating X-ray source (Fig. 3). Following CNT formation by heating **2** to 1000 °C at 10 °C min$^{-1}$ under nitrogen, the shaped solid carbonaceous samples **3** were mounted in the X-ray diffractometer. All the diffraction peaks were identified and indexed based on MWNTs and Co nanoparticles. The peaks at 25.88 (002), 43.01 (100), 53.34 (004), and 78.80 (110) degrees resulted from the structure of MWNTs [20,21] and the peaks at 44.10 (111), 51.66 (200), and 75.78 (220) degrees were

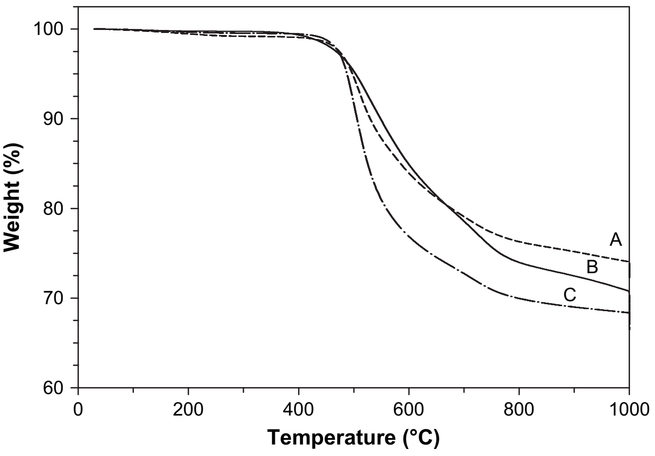


Fig. 1. TGA thermograms for samples of **2** heated to 1000 °C: (A) BPh (**3a**); (B) BAPh (**3b**) and (C) oligomeric phthalonitrile (**3c**).

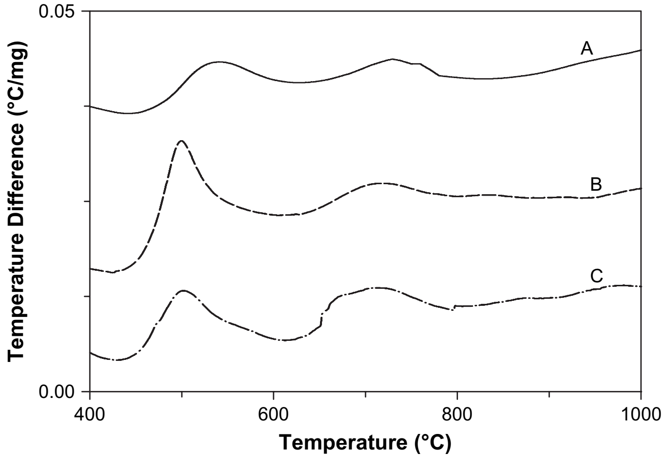


Fig. 2. DTA thermograms for samples of **2a–c** heated to 1000 °C to form **3a–c**: (A) BPh (**3a**); (B) BAPh (**3b**) and (C) oligomeric phthalonitrile (**3c**).

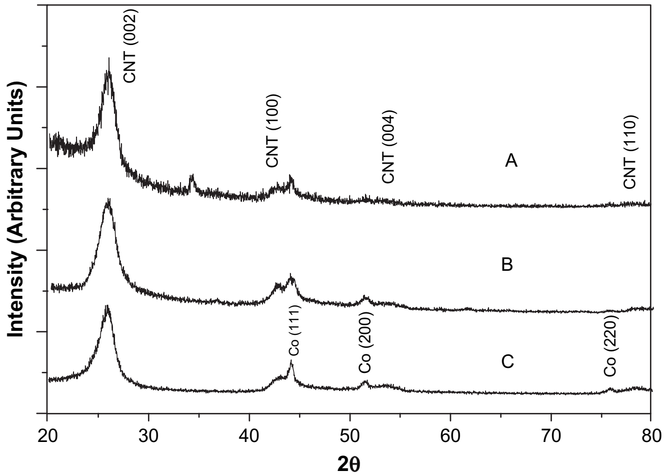


Fig. 3. XRD data for samples of **3**: (A) BPh (**3a**); (B) BAPh (**3b**) and (C) oligomeric phthalonitrile (**3c**).

attributed to the *fcc* cobalt nanoparticle phase. The interplanar spacing for the CNT (002) peak was calculated to be 3.40 Å [22,23]. There appears to be little unordered or amorphous carbon present in all of the samples studied, which indicates that the reaction to produce the highly crystalline phase typically observed for MWNTs proceeds to high yield.

Scanning electron microscopy (SEM) images were obtained on a CNT carbonaceous film **3** that was formed on a silicon wafer by heating a 1:20 molar concentration of $Co_2(CO)_8$ and **1** to 1000 °C. Fig. 4A shows an abundant amount of small bundles of CNTs and long individual CNT strands in a random arrangement. Many of the tubes are more than 100 μm long. With an enhancement in the resolution (Fig. 4B), it appears that the tubes are quite uniform and are around 20–50 nm in diameter. From these images, we can conclude that the reaction of the cobalt nanoparticles with the phthalonitrile resin at high temperatures results in the efficient formation of MWNTs.

Transmission electron microscopy (TEM) studies were performed on turbostratic carbonaceous compositions obtained from pyrolysis of 1:20 molar samples of $Co_2(CO)_8$ to **1** heated to 1000 °C (Fig. 5). A TEM of a thin sample grown on a silicon wafer shows MWNTs existing in abundance throughout the carbonaceous domain (Fig. 5A). A thick solid sample also showed the existence of a copious amount of tube-shaped carbon nanostructures. The carbonaceous material (Fig. 5B) was visible as a tangled mass of randomly oriented MWNTs with Co nanoparticles and a small amount of amorphous carbon scattered throughout the sample. Within these images, the graphitic-like spacing of the MWNTs is clearly discernible (Fig. 5C) and shows the underlying texture typically observed for MWNT walls. The distance between the graphitic layers was measured to be 0.34 nm, which was consistent with the *d*-spacing found from XRD analysis. While the interlayer spacing within the graphitic patterns appears fairly uniform, MWNTs of varying tube diameter and graphitic layers are found throughout the carbonaceous composition.

In an effort to develop a method for the fabrication of CNT-containing fibers, experiments were conducted whereby fibers were drawn from the melt of $Co_2(CO)_8$ and **1**. There is currently an intense effort throughout the scientific community to efficiently disperse MWNTs into polymeric fibers to take advantage of the exceptional mechanical properties of carbon nanotubes [24–26]. Similarly, carbon nanofibers have been

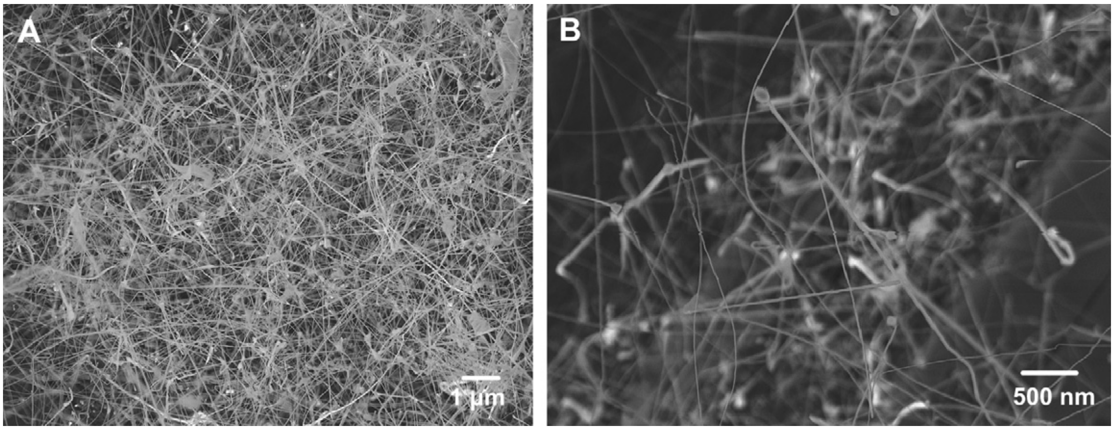


Fig. 4. SEM of film of a 1:20 molar sample of $Co_2(CO)_8$ to **1** heated to 1000 °C on a silicon wafer showing (A) CNT bundles and long horizontal strands and (B) higher magnification of CNT bundles and strands.

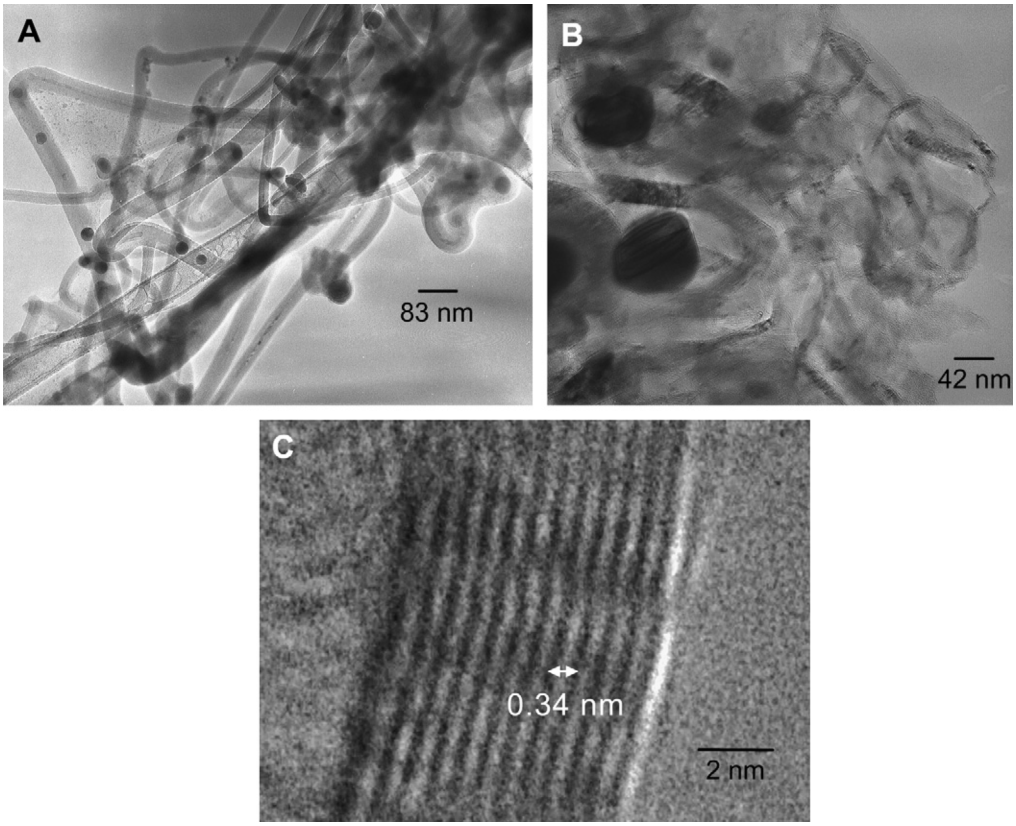


Fig. 5. TEM images of 1:20 molar samples of $Co_2(CO)_8$ to **1** heated to 1000 °C yielding **3**: (A) sample heated on silicon wafer; (B) sonicated sample from thick solid piece; and (C) high-resolution image showing interlayer spacing.

recently produced from the pyrolysis of electrospun nanofibers from PAN [27] and from pitch [28]. Therefore, since our method for the formation of CNTs occurs directly from a mixture of $Co_2(CO)_8$ and phthalonitrile **1** in a shaped composition, we thought it to be an ideal candidate to spin polymeric fibers that could be directly converted into MWNT-containing carbon fibers during the carbonization process. As a demonstration of the versatility of our method, fibers have been drawn from the melt of a 1:20 molar mixture of $Co_2(CO)_8$ to **1b**. A sample of the mixture was heated in an aluminum pan to around 325 °C. When the mixture had become viscous (~5–10 min.), a glass rod was inserted into the sample and fibers drawn upward. Depending on the rate at which the fibers were drawn from the melt, the diameter can be controlled. Fig. 6 shows a photograph of fibers with different diameters drawn from the resin melt. The small diameter fiber (top) was obtained by faster drawing relative to the larger diameter fiber (bottom). Once drawn, the fibers were cured at 270 °C for 12 h (overnight), 300 °C for 3 h, 350 °C for 6 h, and 375 °C for 4 h to form thermoset polymeric fibers **2**, which were carbonized by heating at 1 °C $min^{-1}$ to 1000 °C. Drawing the fibers at 325 °C permitted the retention of shape during the curing process, which was initiated at a lower temperature (270 °C). Upon cure and carbonization, XRD and TEM studies confirmed the presence of copious amounts of MWNTs in the carbonized fibers.

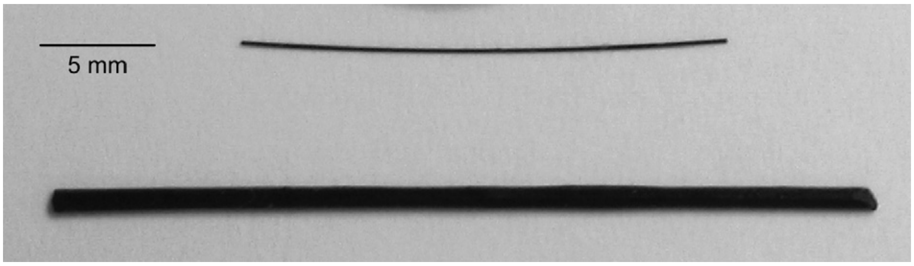


Fig. 6. Image of carbonized samples of **3b** after drawing from the melt of **2b** and heating to 1000 °C; (top) small diameter fiber (~0.2 mm); (bottom) large diameter fiber (~1 mm).

## 4. Conclusion

The conversion of highly aromatic phthalonitrile thermosetting resins into MWNTs is a significant milestone in the development of a potentially inexpensive route to CNTs. The MWNTs are not produced in the vapor phase using a complex high pressure, high temperature apparatus but in the solid phase during carbonization. As a result, a simple potentially cost-effective method can be realized for their production in large quantities. Moreover, this is the first example of using a high temperature thermosetting resin as a carbon source for the formation of CNTs. The MWNTs formed by this method are currently being evaluated for various applications in the battery, electronic, fuel cell, and structural realms. Since the MWNT-containing carbonaceous solid also contain magnetic Co nanoparticles in a homogeneous array, devices utilizing both the nanotubes and the magnetic Co nanoparticles could be produced. By using standard resin processing techniques, various shaped carbonaceous configurations containing a large percentage of CNTs can be realized. Carbon nanotube-containing fibers can also be easily fabricated by drawing from the melt at elevated temperatures or by conventional spinning techniques followed by carbonization. In future papers, we will explore variations of this approach on other thermosetting resins and polymers, employ resin fiber spinning technology to obtain CNT-containing fibers, and determine their properties.

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