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# Bis-*ortho*-diynylarene polymerization as a route to solid and hollow carbon fibers

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**Abstract** The preparation, fabrication, and carbonization of bis-*ortho*-diynylarene (BODA)-derived polymers are described. BODA monomers undergo thermal step-growth polymerization to reactive and processable branched polyarylene intermediates. Well-defined intermediates with controlled conversion, molecular weight and viscosity, along with solution or melt processing allow for control in ultimate carbon structure. Fabrication followed by thermal cure and carbonization results in solid or hollow carbon fiber prototypes with interesting thermal and electrical properties. The BODA polymerization and fiber formation were investigated by differential scanning calorimetry, and gel permeation chromatography. The thermal behavior and stability of fibers was measured by thermogravimetric analysis. The surface crystallinity of fibers was studied by Raman spectroscopy. The conductivity of fibers was measured by a multimeter. The surface morphology and dimensions of the fibers were examined by scanning electron microscopy.

## Introduction

Bis-*ortho*-diynylarene (BODA)-derived fibers may be new promising carbon material to be used for microelectronic devices. Their thermal and environmental stability, combined with their light weight, can make these fibers attractive for a number of applications, ranging from electronic devices to biotechnological products [1]. Also, the BODA-derived fibers can be developed for a new class of applications, such as implanted hollow fiber membranes [2] and microdialysis.

A variety of techniques have been developed for the production of hollow fibers [3]. Nearly all commercial carbon fibers are produced by first converting a carbonaceous precursor into fiber form. The precursor fiber is then cross-linked in order to render it infusible and stable to subsequent pyrolysis. Finally, the cross-linked precursor fiber is heated at temperatures from 1,200 to ca. 3,000 °C in an inert atmosphere, converting the precursor to a carbon fiber [4]. We hereby report BODA-derived solid fibers and hollow fibers using melt processing [4, 5] and wet processing [4, 6].

Enediynes were first studied by Bergman to undergo thermal intramolecular cyclization to reactive aryl 1,4-diradical intermediates [7]. A variety of enediyne-containing compounds have since been pursued for their potential biological activity as antitumor drugs [8]. More recently, the Bergman cyclization was used to prepare linear polyarylenes by chemical vapor deposition [9], in addition to thermal step-growth polymerization of diynylarenes in solution and bulk (Fig. 1) [10].

Due to the fabrication limits to which rigid linear polyarylenes are presently confined, the Bergman cyclopolymerization methodology has been expanded

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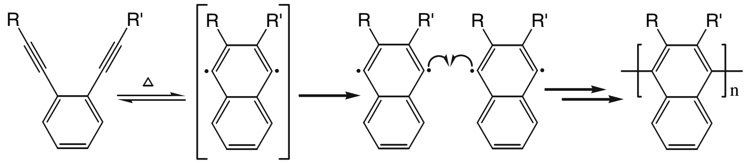

**Fig. 1** Linear Bergman cyclopolymerization of *o*-aryldiynes

to include the controlled polymerization of a tetrayne, or bis-*ortho*-diynylarene (BODA) monomers [11, 12]. The BODA monomers can be prepared from bisphenols in three steps. Monomer intermediates were prepared by selective *ortho*-bromination followed by trifluoromethanesulfonate (triflate) esterification of the corresponding bisphenols and gave aryldibromide ditriflate intermediates. Finally, a Sonogashira-type palladium coupling [13] with phenylacetylene produced tetraynes, or bis-*ortho*-diynylarene (BODA) monomers in quantitative yields (Fig. 2). When heated, BODA monomers give hyper-branched, and thus solution and melt processable-reactive precursors to polynaphthalene networks. A variety of potential applications for these materials have been reported, such as high-temperature thin film dielectrics [11], optoelectronic materials [12], matrix composite resins and precursors of glassy carbon microstructures [14]. Here we investigate and report bis-*ortho*-diynylarene as precursors to solid and hollow carbon fibers.

## Experimental

### Materials

The BODA-6F monomer was prepared from *i*-propylidene diphenol in three steps, the details and purification of which is described previously [11–15]. Tetrahydrofuran, 99.9% anhydrous (THF), and all other reagents were purchased from Aldrich Chem. Co. and was used as received.

### Polymerization of BODA monomer and processing of BODA-derived carbon fibers

BODA-6F monomer (100 mg) was added to a 5 mL vial, which was placed in an oil bath. The temperature of the oil bath was adjusted to 210 °C and maintained during the polymerization. The top of the vial was covered with a rubber septum and the thermal polymerization was carried out under $N_2$ with a magnetic stirrer for 4 h to obtain the processable intermediate

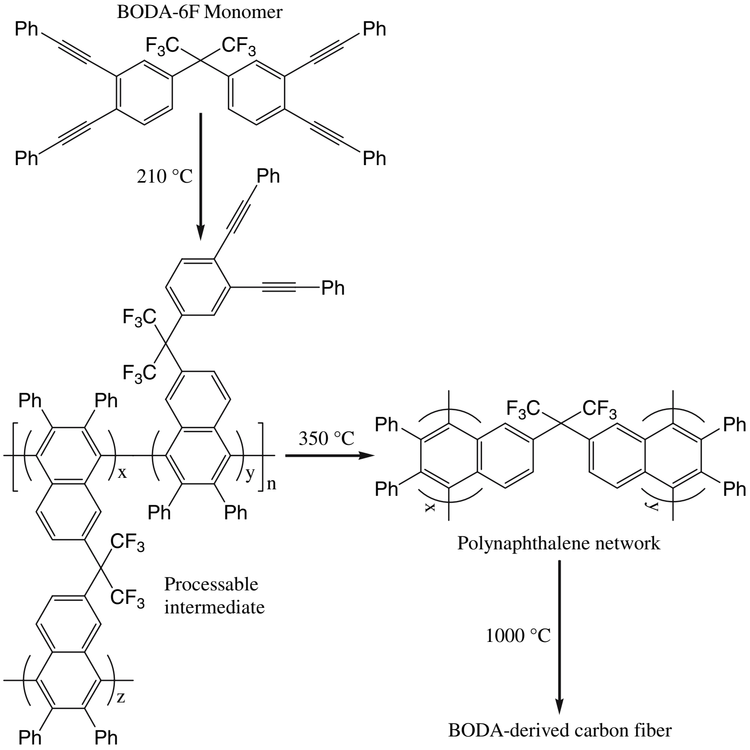

**Fig. 2** Polymerization of BODA-6F monomer and conversion to BODA-derived carbon fiber

(Fig. 2). The product was cooled to room temperature for the solid BODA-derived fibers; this processable intermediate product was grounded and filled into a quartz capillary tube (internal diameter ca. 600–1,000 μm). The bottom of the capillary tube was sealed with aluminum foil and the capillary tube was placed vertically in a vacuum oven. Further polymerization and ultimate gelation was carried out by adjusting the oven temperature to 150 °C for 4 h, to 210 °C for 8 h, and 300 °C for 12 h, respectively. The polymerization was completed and the fiber was cured at 350 °C for 48 h under vacuum. The cured fiber was then removed from the capillary and carbonized in a TGA at 1,000 °C under $N_2$. In the BODA-derived hollow fiber processing, the processable intermediate polymer (40 mg) was dissolved in tetrahydrofuran (THF) (0.5 mL) and the polymer solution was added to the capillary tube. The rest of the process was followed as described above. As a result, the melt process gave a solid fiber, while the wet process gave a hollow BODA-derived carbon fiber. Wet process utilizes solvents which may facilitate physical interactions between solvents and polymer molecules. Thus hollow fiber formation may be affected by resulting polymer concentrations. As solvent evaporates from within the capillaries, the polymer molecules can adhere better to the inner walls of the capillaries, thus resulting in the formation of hollow BODA-derived carbon fibers. The hollow nature of these fibers was examined and confirmed by SEM.

### Measurements, characterizations and instrumentations

The carbonized BODA-derived fiber density was estimated by using Floating Equilibrium method [16]. Dichloromethane and chloroform were used as solvents in this study. The carbonized solid fiber was suspended in a dichloromethane:chloroform mixture at 7:1 volume ratio.

The thermogravimetric analysis (TGA) measurements were performed on a Mettler-Toledo TGA/SDTA851 instrument and a Mettler-Toledo DSC820, equipped with liquid nitrogen cooling accessories was used for conventional DSC scans. Temperature and enthalpy calibrations were performed using indium on this system. About 6 mg of samples were used for each experiment. The samples were sealed in aluminum hermatic pans with a pinhole, and nitrogen was used as the purge gas.

The conductivity of BODA-derived carbon fiber was measured using a Hewlett Packard 34401A Multimeter. The Raman spectra were excited with a filtered 514.5 nm line from a Coherent Innova Model 200 Ar ion laser at three operating power levels of 9.5, 25 and 95 mV. They were scanned at 20 $cm^{-1}$/min with a slit width corresponding to 100 μm.

The surfaces and dimensions of BODA-derived solid and hollow fiber were examined by scanning electron microscopy (SEM). In SEM analysis, the cured and carbonized fiber samples were attached to the carbon tape for surface morphology, and copper tape for cross-section analyses. These samples were then placed onto a aluminum stub and then used without a gold coating for the measurements. The micrographs were taken at an acceleration voltage of 15 kV in a Hitachi S-4700 Field Emission Scanning Electron Microscope.

## Results and discussion

The BODA monomers can undergo thermal cyclopolymerization by a step growth mechanism giving solution or melt processable intermediates (Fig. 2). The processable BODA-derived polymers have molecular weights up to $M_w = 25{,}000$ and a polydispersity index of about 11 (GPC versus PS). The solution processed BODA-derived hollow fibers or melt fabricated BODA-derived solid fibers are typically cured to network polynaphthalenes at 350 °C for stabilization.

Upon pyrolysis at a temperature of 1,000 °C in an inert atmosphere (in $N_2$), BODA-derived polynaphthalenes are converted to electrically conductive carbon fibers in high carbon yield (>75%). The carbonization efficiency coupled with the excellent processability exhibited by the precursor resins suggested that these materials may be suitable candidates for production of fibers, and hollow fibers for electronic and biological applications [1–3].

Figure 3 shows the DSC scans of the BODA monomer; fibers prepared at 210 °C; and fibers cured at 350 °C from 50 to 500 °C at a heating rate of 10 °C/min. It can be observed that the monomer is polymorphic, showing at least two crystalline forms. Upon melting, the $\alpha$ form immediately recrystallizes to the more stable $\beta$ form. The cure onset temperatures of BODA monomer and fibers prepared at 210 °C, measured as the point of intersection of the extrapolated baseline and the initial steep portion of the curve, are 227 and 241 °C, respectively, and the corresponding peak exotherm temperatures are 299 and 302 °C (Table 1).

The heat of polymerization values of BODA monomer and fibers prepared at 210 °C, were found to be 26.5 and 11.6 kcal/mol alkyne, respectively. No

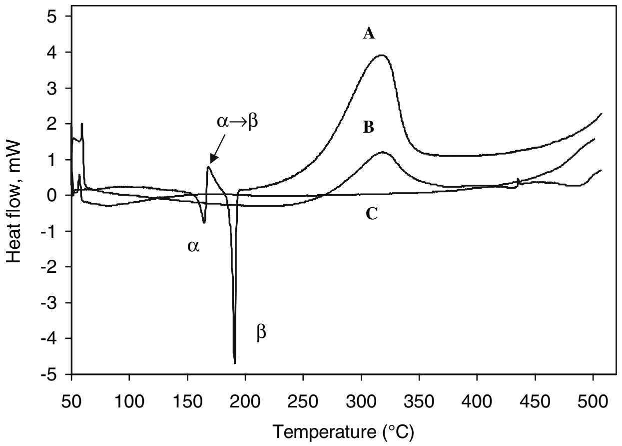

**Fig. 3** DSC plots of (**a**) BODA-6F monomer; (**b**) BODA-derived fiber prepared at 210 °C; and (**c**) BODA derived fiber cured at 350 °C

melting peaks were observed for the fibers prepared at 210 °C. Neither an exotherm, nor an endotherm was observed and therefore, no enthalpy of fusion was detected for the fibers cured at 350 °C.

The entropy of polymerization for monomer and fiber samples may readily be determined from the enthalpy of polymerization as below Eq. 1:

$$\Delta S_{\text{polym}} = \frac{\Delta H_{\text{polym}}}{T_{\text{f}}} \tag{1}$$

where $T_{\text{f}}$ is the cure onset temperature.

The enthalpy and the entropy decreased dramatically from monomer to fiber prepared at 210 °C. Since no enthalpy of fusion was observed for the fiber cured at 350 °C, the heat of polymerization value approaches zero. Therefore, the entropy of the fiber cured at 350 °C approaches zero. The calculated results are summarized in Table 1.

The thermal stability as a function of conversion and carbonization is illustrated in Fig. 4 for each step of fiber processing. Thermogravimetric analysis (TGA) was used to determine the weight loss versus temperature, at a heating rate of 10 °C/min, in nitrogen. The % TGA weight loss data obtained between 50 and 1,000 °C. The onset of the decomposition for thermograms A and B was about 400 °C, and 500 °C for thermogram C and the weight losses are shown in their respective thermograms (Fig. 4). Most of the weight losses occurred between 500 and 650 °C. Thermograms of the fibers carbonized at 1,000 °C indicated that no changes, thus no weight loss. It can be seen that treatment of fibers at high temperature increases the thermal stability of fibers. Thus, these fibers have thermal and environmental stability after high temperature treatments.

Surface morphology and cross section of BODA-derived fibers were characterized by scanning electron microscopy (SEM). The micrographs for the cured and carbonized solid fibers revealed a smooth outer texture, and the diameters of the cured and carbonized solid fiber were measured to be 987.5 and 604.6 μm, respectively (Fig. 5). Also, the micrographs for the cured and carbonized hollow fibers revealed a smooth outer texture. The external diameter (ED), internal diameter (ID), and the wall thickness of the cured hollow fiber were 675 μm, 412.5 μm, and 131.3 μm, respectively. The external diameter, internal diameter, and the wall thickness of the carbonized hollow fiber were 612.5 μm, 375 μm, and 118.8 μm, respectively (Fig. 6). The calculated total results from micrographs are summarized in Table 2.

Figure 7 shows the Raman spectrum of the carbonized BODA-derived fiber. Two intense peaks at about 1,336 and 1,603 $\text{cm}^{-1}$ were observed. The peak at 1,336 $\text{cm}^{-1}$ may represent the D line of the BODA-derived fiber. This peak is present in poorly graphitized fibers with a tendency to disappear at higher graphitization temperatures. This peak is not present in single graphite crystals [17, 18] and is attributed to the breakdown of the lattice symmetry of the graphite cell and assigned to the $A_{1g}$ vibrational mode of the graphite plane, introduced by small crystal size and structural disorder. The peak at 1,603 $\text{cm}^{-1}$ may represent the D′ line of the BODA-derived fiber. This peak is present in non-graphitized fibers, strong in low annealing temperatures and was detected as a shoulder

**Table 1** DSC calculation results of BODA-6F monomer and BODA-derived fibers

| S | $T_{\text{Melting}}$ (°C) | $T_{\text{Cure onset}}$ (°C) | $T_{\text{Cure max}}$ (°C) | $\Delta H_{\text{polym.}}$ (kcal/mol) | $\Delta S_{\text{polym.}}$ (kcal/mol °C) | Density (g/mL) | Conductivity (S $\text{cm}^{-1}$) |
|---|---|---|---|---|---|---|---|
| M | $\alpha$ = 163<br>$\beta$ = 190 | 227 | 299 | 26.5 | 0.117 | | |
| $\text{F}^1$ | None | 241 | 302 | 11.2 | 0.046 | | |
| $\text{F}^2$ | None | None | None | 0 | 0 | | |
| $\text{F}^3$ | – | – | – | – | – | 1.346 | 42.52 ± 0.15 |

S = Sample; M = Monomer; $\text{F}^1$ = BODA-derived fiber prepared at 210 °C; $\text{F}^2$ = BODA-derived fiber prepared at 350 °C; $\text{F}^3$ = BODA-derived fiber carbonized at 1,000 °C

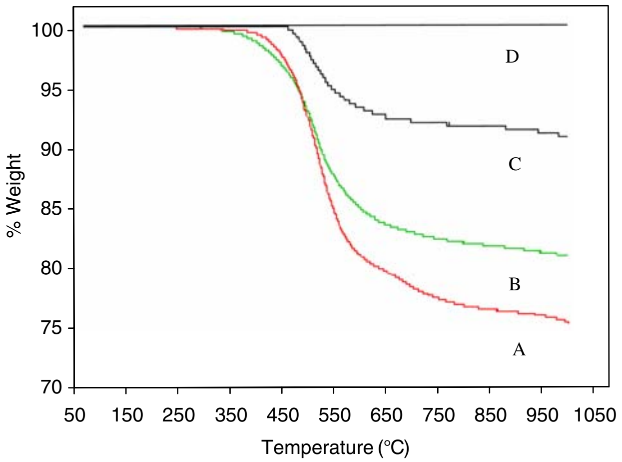

**Fig. 4** Thermogravimetric curves of (**a**) BODA-6F monomer; (**b**) BODA-derived fiber prepared at 210 °C; (**c**) BODA-derived fiber cured at 350 °C; and (**d**) BODA-derived fiber carbonized at 1,000 °C

of the G-line in higher ultimate firing temperature (UFT). This peak attributed to the disorder and small crystallite size. It becomes attenuated when two-dimensional ordering is established and disappears at well-graphitized fibers. The major Raman lines of carbon fibers were reported in detail [17–20].

The density of carbonized solid fiber $d_{\text{BODA}}$ was calculated to be 1.346 g/mL by the Floating Equilibrium method [16], using Eq. 2:

$$d_{\text{BODA}} = d_{\text{mix}} = \frac{d_1 V_1 + d_2 V_2}{V_{\text{tot}}} \tag{2}$$

where $d_1$ and $d_2$ density and $V_1$ and $V_2$ volume of the dichloromethane and chloroform, respectively. $d_{\text{BODA}}$ is density of BODA-derived fiber, and $V_{\text{tot}}$ is the total volume.

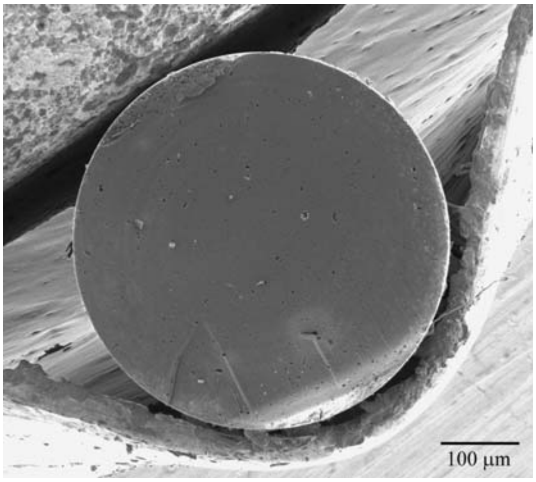

**Fig. 5** SEM of cross-section of BODA-derived solid fiber carbonized at 1,000 °C

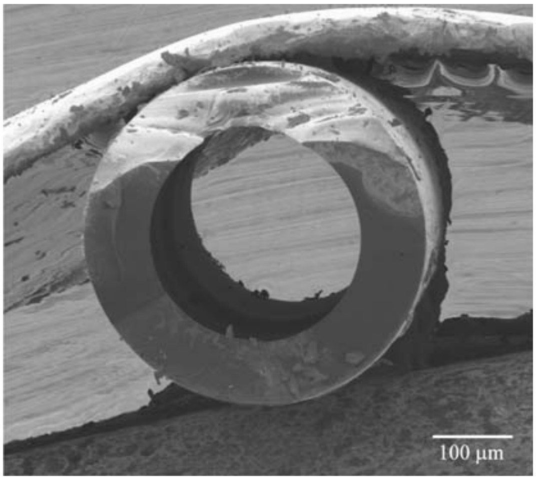

**Fig. 6** SEM of cross-section of BODA-derived hollow fiber carbonized at 1,000 °C

The resistivity of carbonized BODA-derived fiber was measured to be 0.02352 Ω cm and the conductivity was measured to be 42.52 ± 0.15 S $\text{cm}^{-1}$.

## Conclusions

In summary, the object of the present investigation was to illustrate that proper ratio of diameter-to-wall thickness of BODA-derived fibers can be obtained for desired applications. Also, to describe the technical possibilities available, which may open up profitable areas of research and development.

Polymerization of BODA monomers were controlled to obtain intermediate processable precursor and the production of BODA-derived fibers (solid and hollow) were successfully accomplished by melt process and wet process. The DSC results indicated the polymerization enthalpy and entropy of the fibers dramatically decreased. The TGA results showed that the high temperature treated BODA-derived fibers are thermally and dimensionally stable. The Raman spectrum of the carbonized BODA-derived fiber showed that these fibers are disordered glassy carbon fibers. The micrographs for the fibers revealed a smooth outer texture and highly condensed material.

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**Table 2** Calculated dimensional results from SEM of BODA-derived fibers

| Type | ED (µm)[1] | ID (µm)[a] | WT (µm)[a] | ED (µm)[b] | ID (µm)[b] | WT (µm)[b] |
|---|---|---|---|---|---|---|
| Hollow | 675 ± 12.5 | 412.5 ± 6.25 | 131.3 ± 3.13 | 612.5 ± 12.5 | 375 ± 6.25 | 118.8 ± 3.13 |
| Solid | 987.5 ± 12.5 | – | – | 604.6 ± 4.6 | – | – |
|  | $\Delta L^{ED}$ (µm) | $\Delta L^{ED}$ (%) | $\Delta L^{ID}$ (µm) | $\Delta L^{ID}$ (%) | WT′ (µm) | WT′ (%) |
| Hollow | 62.5 | 9.26 | 37.5 | 9.09 | 12.5 | 9.52 |
| Solid | 382.9 ± 7.9 | 38.78 ± 0.8 | – | – | – | – |

ED = External diameter; ID = Internal diameter; WT = Wall thickness of the hollow fiber; $\Delta L^{ED}$ = Shrinkage according to external diameter; $\Delta L^{ED}$(%) = Percentage shrinkage according to external diameter; $\Delta L^{ID}$ = Shrinkage according to internal diameter; $\Delta L^{ID}$(%) = Percentage shrinkage according to internal diameter; WT′ = Wall thickness shrinkage; WT′ (%) = Percentage wall thickness shrinkage

[a] Cured sample at 350 °C

[b] Carbonized sample 1,000 °C

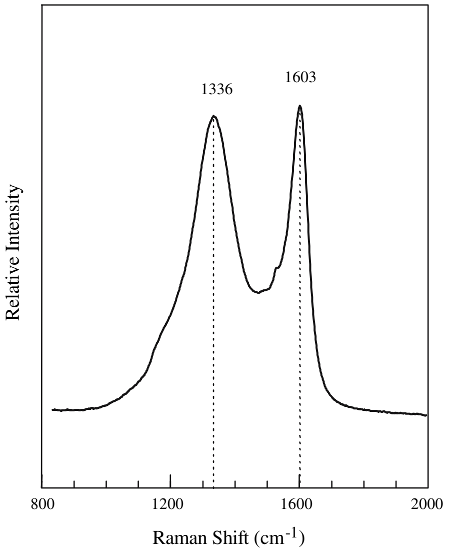

**Fig. 7** Raman spectrum of the carbonized BODA-derived carbon fiber

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