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Bis-*o*-diynylarene (BODA) Derived Polynaphthalenes as Precursors to Glassy Carbon Microstructures

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Enediynes were first shown by Bergman to undergo thermal intramolecular cyclization to reactive aryl 1,4-diradical intermediates.[1] A variety of enediyne-containing compounds have since been pursued for their potential biological activity as antitumor drugs.[2] More recently, the Bergman cyclization was used to prepare linear polyarylenes by chemical vapor deposition[3] in addition to thermal step-growth polymerization of diynylarenes in solution and bulk (Figure 1).[4]

Due to the obvious fabrication limits to which rigid linear polyarylenes are presently confined, we have expanded the Bergman cyclopolymerization methodology to include the controlled polymerization of tetrayne, or bis-*o*-diynylarene (BODA) monomers.[5,6] Currently, hundred gram quantities of BODA monomers can be prepared from commercially available bisphenols in three high-yielding steps (Figure 2). When heated, BODA compounds give hyper-branched—and thus solution and melt proccessable—reactive precursors to polynaphthalene networks. We are currently pursuing a variety of potential functions for these materials such as high-temperature thin film dielectrics,[5] optoelectronic materials,[6] matrix composite resins, and, as we report here, precursors to glassy carbon microstructures.

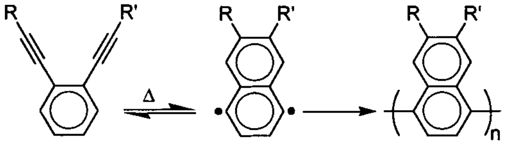

Figure 1. Linear Bergman cyclpolymerization of o-aryldiynes.

Glassy carbon is currently sought for its thermal and dimensional stability, electrical conductivity, low gas permeability, low coefficient of thermal expansion, lower modulus (vs silicon), and low density.[7] The syntheses of high-yield carbon-rich materials for acetylenic precursors, in general, have received much attention.[8] In particular, glassy carbon is an attractive candidate for microelectromechanical systems (MEMS).[9] Although previous approaches have provided excellent routes to high-yield glassy carbon,[7−9] the BODA strategy offers a versatile choice of monomer precursors prepared from inexpensive commodity starting materials. In addition,

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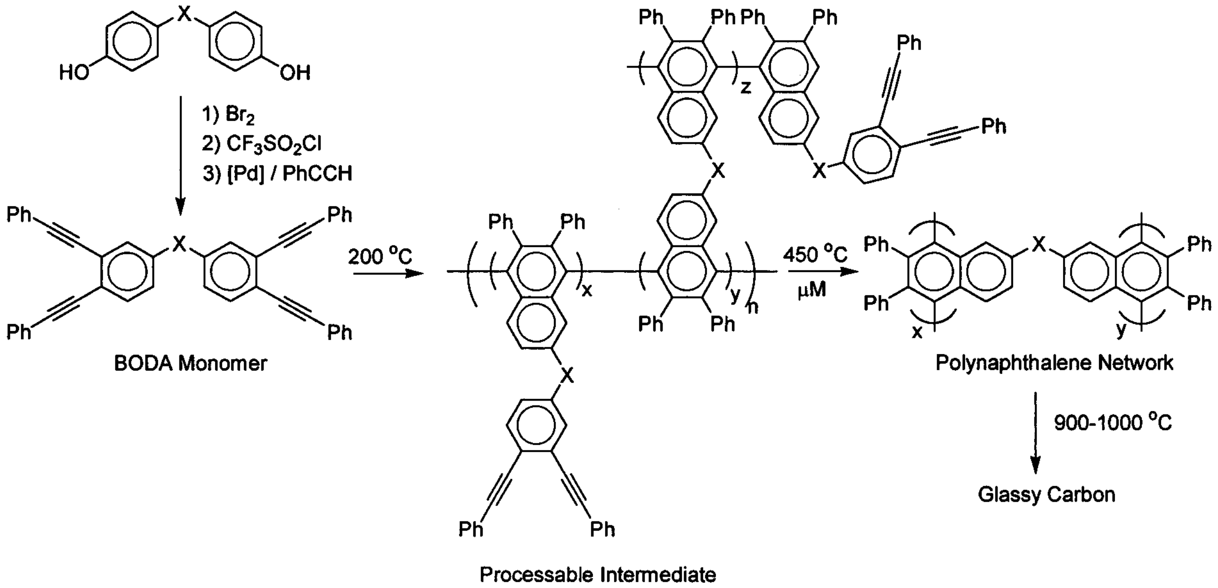

Figure 2. BODA monomer synthesis, polymerization, and conversion to glassy carbon (for X = −O−, −C(CF$_3$)$_2$−, a C−C bond, and 9,9-fluorene).

the Bergman cyclopolymerization mechanism allows for a wide range of processable reactive oligomers and controlled network structures prior to carbonization.[5]

The fabrication of carbon MEMS is desired since presumably less expensive high carbon yielding organic polymers may serve as precursors in a rapid prototyping scheme.[9] A variety of techniques have been developed for the microfabrication of organic polymers, including microcontact printing (μCP),[10] micromolding in capillaries (MIMIC),[11] and microtranfer molding (μTM).[12]

Thermal cyclopolymerization of BODA monomers (Figure 2) proceeds by a step growth mechanism giving solution or melt processable intermediates of variable molecular weight up to M_w = 25 000 and M_w/M_n = 11 (GPC vs PS). Solution spin coated thin films or melt fabricated solids are typically cured to network polynaphthalenes at 450 °C. Glass transition temperatures have not been observed for these materials below 400 °C, and their thermal stability at 450 °C is typically <1.5%/h weight loss.[5]

Upon pyrolysis at temperatures above 900 °C in an inert atmosphere, BODA-derived polynaphthalenes are converted to electrically conductive glassy carbon in high yield (>75% in most cases). The carbonization efficiency coupled with the excellent processability exhibited by the precursor resins suggested that these materials might be suitable candidates for micromolding of glassy carbon for applications such as MEMS.

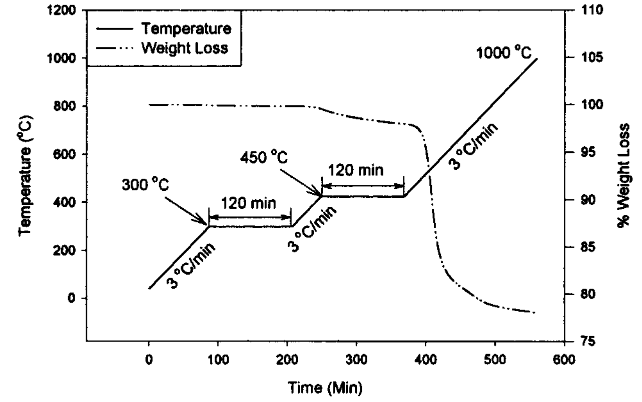

Figure 3. Carbonization schedule and TGA data for conversion of BODA-DPO oligomers to glassy carbon.

For initial micromolding studies, we chose the BODA−DPO monomer (Figure 2, X = O) which contains >90% carbon present before carbonization. BODA−DPO monomer exhibits a melting temperature and onset of polymerization at 108 and 205 °C, respectively (DSC at 10 °C/min). The precursor resin used for micromolding studies was prepared by heating the neat monomer in an inert atmosphere for 1 h at 250 °C which gave a soluble monomer/oligomer mixture with M_n = 2500 (GPC) and melting point of ca. 80 °C. Figure 3 depicts the TGA curve and the cure schedule used for carbonization of the precursor resin. Upon complete cure near 400 °C, the polymer exhibits slow degradation (ca. 1%/h) after which a rapid weight loss ensues as the sample is heated to 1000 °C giving an overall weight loss of ca. 25% prior to carbonization. The glassy carbon structures exhibit essentially zero weight loss upon further heating at 1000 °C.

Carbon microstructures previously prepared from phenol−formaldehyde or furfuryl alcohol−phenol resins containing 50% carbon present before/after carbonization exhibit obvious problems due to the dramatic

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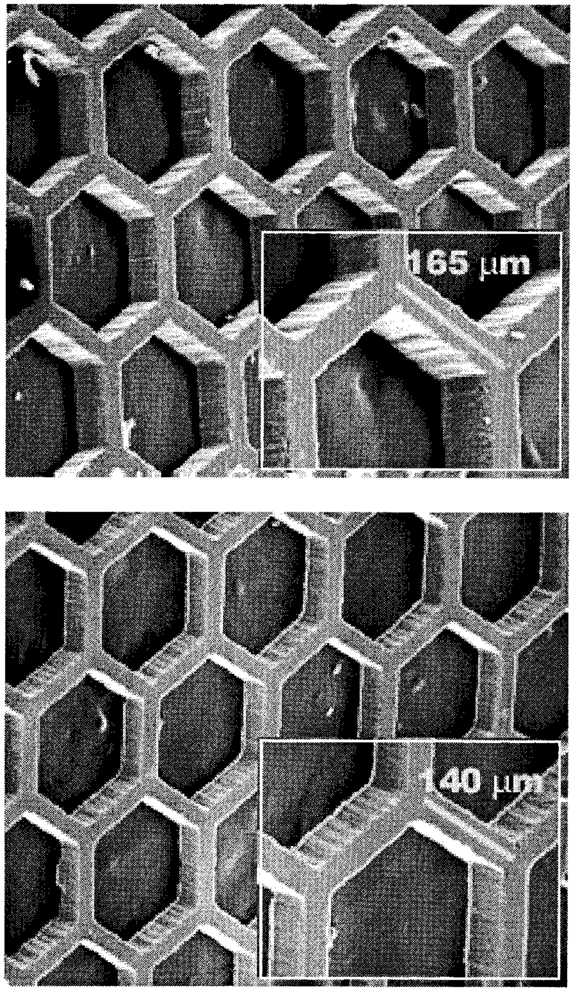

Figure 4. SEM of BODA-derived microstructures of polymer cured at 250 °C (top) and glassy carbon prepared at 1000 °C (bottom).

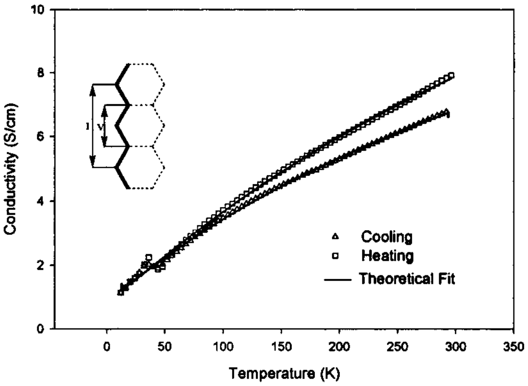

Figure 5. Electrical conductivity of glassy carbon microstructures as a function of temperature with theoretical fit and circuit geometry (inset).

volume reduction imposed by low carbon yield.[10−12] We have found, however, that less dimensional change is observed when high-carbon BODA precursors are used. Microstructures were fabricated using a procedure known as micromolding in capillaries (MIMIC).[11] In this technique, poly(dimethylsiloxane) (PDMS) molds were prepared by casting PDMS on a photolithographically generated silicon master containing microhexagon features. The PDMS mold was then placed on a heated silicon wafer with the micropattern facing the wafer. The mold was filled through a top access channel with neat molten oligomer by application of a moderate vacuum. Further polymerization and network formation was achieved by placing the entire wafer assembly in a N_2-purged oven at 250 °C for 12 h. The microhexagon mold was then removed, and the supported polymeric structure was converted into free-standing glassy carbon in a N_2-purged thermogravimetric analyzer (TGA) using the cure schedule shown in Figure 3.

Figure 4 shows the electron micrographs[13] of the precarbonized polynaphthalene microstructures (top) and the resulting carbon structures obtained after pyrolysis (bottom). The inset hexagon with scale bar shows clearly that little shrinkage has occurred upon carbonization. The glassy carbon structure has been reduced on a linear scale of ca. 15%, which compares well with that predicted from the weight loss measured by TGA.

Finally, the free-standing glassy carbon microstructures could be easily removed from the SEM mount and their electrical conductivity examined for the geometry shown in Figure 5 (inset).[14] The electrical conductivity was found to increase with increasing temperature indicative of semiconductor behavior (Figure 5). The temperature dependence could be fitted by means of a semiempirical relation:[15]

$$\sigma(T) = \sigma_{\mathrm{m}} + \sigma_{\mathrm{h}} \exp(-\alpha T^{-1/4})$$

where the first term, σ_{m}, is attributed to strongly scattering metallic conductivity independent of temperature and the second term, σ_{h}, corresponds to variable range hopping mechanism between localized states. Slight hysteresis is also observed upon cycling the temperature from 4 to 300 K, and the origin of the reproducible transition at ca. 50 K is not clear. The room temperature conductivity along the indicated geometry is about 7 S/cm. The rather low conductivity observed may be due to dimension measurement error, whereas similarly cured bulk samples (ca. 0.25 cm^2) gave a conductivity near 100 S/cm as also found for other precursor-derived glassy carbon.[7,9]

Thus, the polynaphthalene precursor microstructures prepared at 250 °C and carbonized at 1000 °C exhibited low dimensional change due to the highly aromatic network. The fabrication of microstructures with smaller feature sizes and the micromolding of more complex geometries are currently underway to better explore the generality of this approach.

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(13) Scanning electron micrographs (SEM) were obtained using JEOL IC848 SEM. Precarbonized microstructures were sputtered with a light coating of gold to prevent charging. Carbonized structures were scanned without modification.

(14) Data were collected from 4 to 350 K using a conventional four-probe technique on the geometry shown in Figure 5 via gold wire and silver paint contacts.

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