

CARBONIZATION STUDIES OF GLASSY CARBON DERIVED FROM BIS-*ORTHO*-DIYNYLARENES (BODA)

Scott T. Iacono¹, Mark W. Perpall¹, Wesley P. Hoffman²,
Phillip G. Wapner³, and Dennis W. Smith, Jr.*¹

¹Department of Chemistry, Advanced Materials Research Laboratories,
Clemson University, Clemson, SC 29634

²Air Force Research Laboratory, Propulsion Directorate
10 East Saturn Blvd, Edwards Air Force Base, CA 93524

³ERC Inc., 10 East Saturn Blvd,
Edwards Air Force Base, CA 93524

*corresponding author e-mail: dwsmith@clemson.edu

Introduction

We have demonstrated bis-*ortho*-diynylarene (BODA) monomers undergo Bergman cyclopolymerizations to form hyper-branched, rigid naphthalene networks that can be further carbonized at 1000 °C to form glassy carbon in high yield (>80 %) (**Figure 1**).¹ It was shown by Bergman that 1,2-aromatic diacetylenes undergo concerted thermal annulations via a 1,4-diradical intermediate to form functionalized aromatic systems.² Tour has further demonstrated enediyne can undergo thermally induced cyclopolymerizations forming linear and branched poly(phenylenes).³ Such linear polyarylenes have been shown to be inherently difficult to process into carbon-based structures due to their low molecular weight and insolubility. On the other hand, glassy carbon materials are ideal for microstructure fabrication because good thermal stability, electrical conductivity, gas impermeability, and low coefficient of thermal expansion.⁴ More so, BODA-derived glassy carbon has shown utility as thin film dielectrics,¹ photonic materials,⁵ precursors for carbon fibers,⁶ and microstructures formed by micromolding in capillaries (MIMIC).⁷ The unique ability to melt or solution process the cured intermediate as shown in **Figure 1** is a key feature to producing such materials. The spacer (X) and terminus (R) can be functionalized in order to tune the range of processing temperatures and wetting capabilities. In our ongoing effort to fabricate carbon-based microstructures⁹ via MIMICs, BODA-derived glassy carbon demonstrates excellent shape retention and high carbon yield for the production of near net-shaped components.

Cure cycles of BODA-derived intermediates have been previously investigated using a differential scanning calorimeter (DSC).¹⁰ However, studies on high temperature heat treatments (HTTs) to form glassy carbon are the focus of this investigation. Herein, we show the coefficient of thermal expansion (CTE) studies of several BODA-derived glassy carbon and study their carbonization cycles.

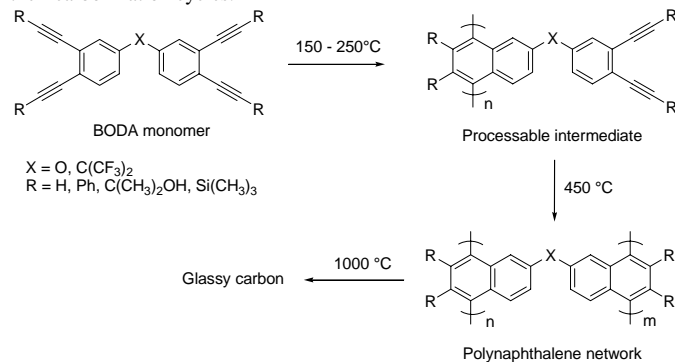


Figure 1. Thermal Bergman cyclopolymerization of bis-*ortho*-diynylarene (BODA) monomers.

Experimental

Materials. Synthesis and characterization of BODA monomers **1–3** (**Figure 2**) were reported elsewhere.¹ Monomer **4** was donated by Dow Chemical. Co-monomers were prepared by mixing with a mortar and pestle a

1:4 weight ratio of **2** and **3** (denoted co-monomer **A**) as well as **2** and **4** (denoted co-monomer **B**).

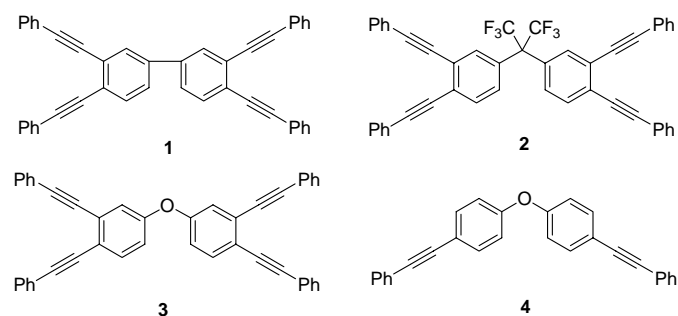


Figure 2. BODA monomers as precursors for high yield glassy carbon.

Instrumentation. A vertical Linseis dilatometer L75 with single push rod was used to study carbonization and measure CTE. STM measurements were performed by a Digital Instruments Nanoscope III. X-ray powder diffraction was performed using a Scintag XDS 2000 with a voltage of 24 kV.

Sample Preparation. Sample dilatometer discs were prepared by placing monomer or co-monomer powder (ca. 100 mg) in machined single bore extrusion mullite molds (Vesuvius McDaniel, 6.35 mm O.D. and 4.75 mm I.D.). The monomer or co-monomer was then heated in a Lindbergh furnace from ambient temperature to 350 °C at a ramp of 10 °C/min under a constant flow of nitrogen. The samples were then further cured at 350 °C for 48 hours. The solid disks were removed by machining away the mullite mold and were used without further cleaning. The prepared cured solid disks tested for CTE had a nominal diameter and thickness of 6.35 mm in 2.34 mm, respectively.

Cured sample disks were then heated in argon from ambient to 1000 °C or 1500 °C at 10 °C/min. The carbonized samples were cooled to room temperature under argon. Carbonized samples were then reheated from ambient to 1000 °C or 1500 °C at 10 °C/min to determine their CTE. The CTE (α) was determined by linear graphical regression using the equation $\alpha = (1/L_0)(\Delta L/\Delta T)$, where L_0 is the initial sample length, ΔL is the change in length from ambient to elevated temperature, and ΔT is the change in temperature from ambient. Measurements were taken in triplicate for each sample.

Results and Discussion

Co-monomers **A** and **B** were the focus of this investigation because they demonstrate accelerated cure times at lower temperatures compared with monomer precursors **1–3**.⁹ A representative carbonization cycle of cured BODA co-monomer **A** is shown in **Figure 3**. It shows the onset of carbonization temperature (T_{onset}), as determined graphically by the initial dimensional change in sample length.

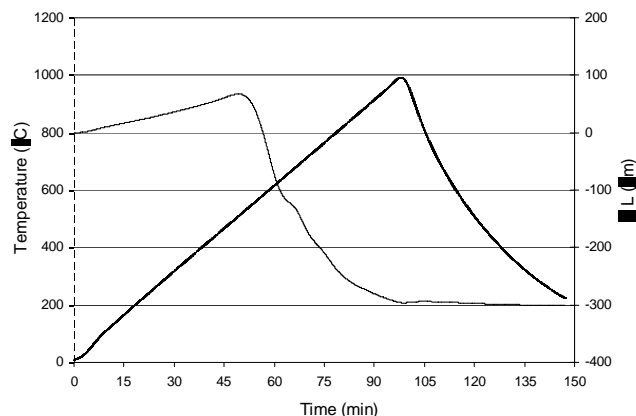


Figure 3. Carbonization cycle of BODA co-monomer **A**.

A dimensional loss of 9.7 % and 13.5 % was observed for co-monomer **A** in length and diameter, respectively. The thermal removal of volatile organic groups affords such dimensional dilation at 550 °C. Upon further heating to 1000 °C, the carbon yield was 81 %. Carbonization cycles at 1000 °C for 24 hours produced no further dimensional change within the dilatometer's detectable limits. Monomer **1** and co-monomer **B** show similar geometry dilation compared to co-monomer **A**. Carbon yields were determined as 83 % and 81 % for monomer **1** and co-monomer **B**, respectively. These carbon yields are similar to BODA-derived carbonized structures reported elsewhere.¹

The CTEs of the carbonized BODA samples were measured over a range of programmed temperatures as shown in **Figure 4**. Non-linear regions were observed for temperature ranges 20–300 °C. This behavior is due the signal instability of the dilatometer over low temperature ranges. Linear CTE plots have been interpolated to include this range because the regression error analysis is minimal ($r^2 > 0.80$).

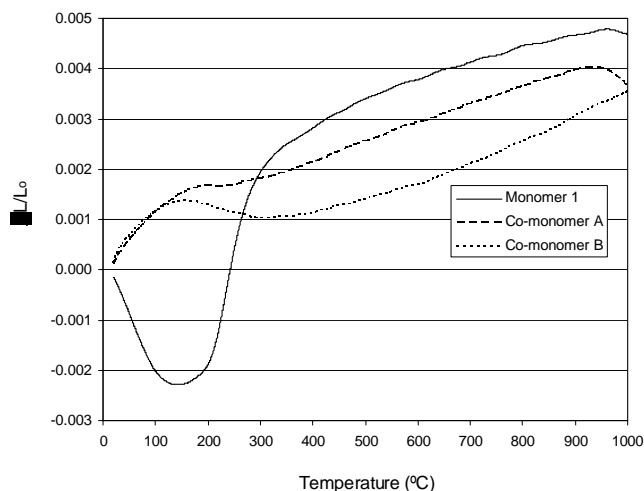


Figure 4. CTE profiles of monomer **1** and co-monomers **A** and **B** over temperature range.

Table 1 illustrates CTE analysis of glassy carbon samples derived from BODA monomer **1** and co-monomers **A** and **B**. Monomer **1** showed a notably higher T_{onset} compared with co-monomers **A** and **B**. The CTE values were observed for samples that were heat treated at 1500 °C than for samples carbonized lower at 1000 °C (compare entry 3 and 4). Carbonizing cured co-monomer **B** to 1500 °C showed repeatable CTE values within 0.08 ($\times 10^{-6} \text{ C}^{-1}$) over the ranges 20–1000 °C and 20–1500 °C (compare entry 4 and 5).

Table 1. CTE Measurements Over A Range Of Heat Treatments For BODA Derived Glassy Carbon

Entry	Compound	T_{onset} (°C)	HTT (°C)	CTE α ($\times 10^{-6} \text{ C}^{-1}$)	Std Dev ($\times 10^{-6} \text{ C}^{-1}$)	Range (°C)
1	1	575	1000	6.92	0.68	20-1000
2	A	545	1000	3.33	0.25	20-1000
3	B	540	1000	3.20	0.50	20-1000
4	B	535	1500	2.85	0.31	20-1000
5	B	535	1500	2.93	0.45	20-1500

Additional weight loss was observed for co-monomer **B** after being carbonized to 1500 °C. This reduced the carbon yield to 65 % compared with 81% when carbonized to 1000 °C. Upon STM analysis of co-monomer **B** heat treated at 1500 °C showed evidence of graphitic regions possessing hexagonal distances of 2.46 Å on the Basal plane. Therefore, the observation of lower CTE values for co-monomer **B** heated to 1500 °C in comparison to samples

heated to 1000 °C are a result of carbon reorientation to form planar graphite sheets inducing stronger π - π stacking interactions producing a more dense material. Furthermore, X-ray powder diffraction shows characteristic peaks of graphite, (002) and (110) planes, become narrower and taller at higher heat treatment temperatures (**Figure 5**).

Density measurements are also consistent with the observation of lowering CTE at higher HTTs. Densities of 1.608–1.651 g/cm^3 were observed for heat treated samples at 1000 °C for monomer **1** and co-monomer **A** and **B**. The density was further lowered to 1.547 g/cm^3 and 1.405 g/cm^3 for co-monomer **B** at HTTs of 1500 °C and 1700 °C, respectively.

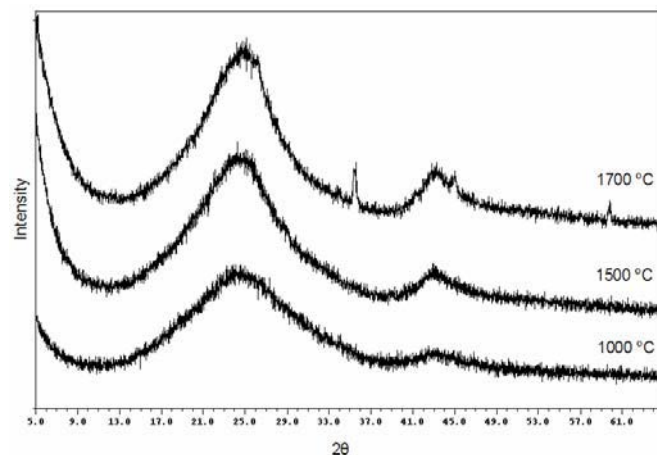


Figure 5. X-ray diffraction patterns for BODA-derived glassy carbon of co-monomer **B** as a function of heat treatment.

Conclusions

Dilatometry has provided insight to the thermal carbonization cycles of BODA polynaphthalenes. The onset of carbonization can be determined for each cured polymer providing a means to optimize thermal cycling. Furthermore, CTEs were determined for various BODA-derived glassy carbon systems to determine compatibility for MIMIC applications. We anticipate the use of these high carbon yield materials as potential use in fiber reinforced composites, microtubes, as well as other microdevices.

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