

SYNTHESIS OF HIGHLY OXIDATIVE STABLE CARBON MATERIALS FROM BORON CONTAINING POLYDYNE PRECURSOR

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INTRODUCTION

Carbon, including carbon fiber and carbon/carbon composites, is known to exhibit unique properties for many applications. However, one major drawback of carbon is its susceptibility to oxidation¹ above 500 °C. Most research approaches to minimize the oxidation of carbon have been based on the method of oxidative protection with a ceramic coating layer², such as SiO₂, SiC and B₂O₃. However, in high temperature the tensile stresses develop in the coating which will cause it to crack, due to difference in the thermal expansions. Some attempts to incorporate boron into graphite-like structure, by simple addition of boron reagents³, showed poor acceptance of boron in graphite lattice, which may be due to the stable boron clusters, high melting point of boron and the difficulty in forming chemical bond between boron and precursor during pyrolysis. It is clear that there is a fundamental need, both scientifically challenge and technological importance, to develop a new method to prepare carbon material with high oxidative stability.

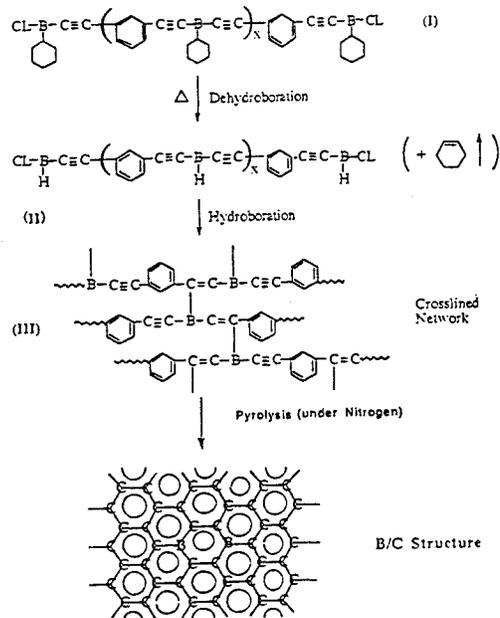
Our approach has been focusing on the new boron-containing precursors which can be converted to B/C materials with high yield and homogeneous distribution of boron elements in carbon structures. In this paper, a new boron containing polydyne precursor will be discussed.

EXPERIMENTAL

In a typical reaction of polydyne, a stoichiometrically equivalent amount of 0.225 M solution of cyclohexyl dichloroborane was added to a suspension of 1 g of dilithio phenylene diacetylide. The reaction was maintained at 0 °C under an inert atmosphere, over a period of 12 hours with stirring. On the addition of the reagent, the reaction mixture developed a muddy brown coloration. The reaction was then warmed to room temperature and allowed an additional 12 hours before the solvents employed were distilled off under high vacuum, leaving behind a reddish polydyne material. The ¹¹B NMR of this material exhibited two distinguish peaks, assignable to the boron species at the chain ends, and in the polymer backbone.

RESULTS AND DISCUSSION

One of polydynes (I) is illustrated in Equation 1.



Pyrolysis Studies The stabilization reaction was carried out under nitrogen by heating compound (III) to 550 °C. Figure 1 shows the TGA results from step-wise and isothermal heating processes.

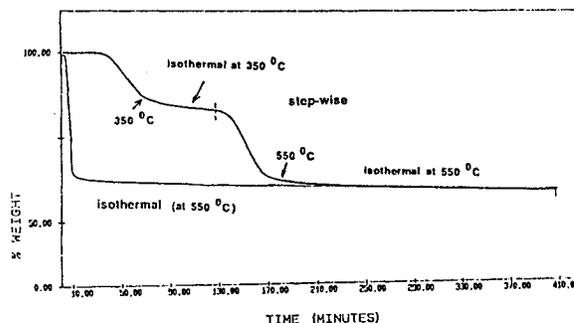


Figure 1, TGA curves of compound (I) with step-wise (a) and isothermal (b) heating processes.

In both processes, the total weight loss is about 40 weight % at 550 °C. The dehydroboration and hydroboration in Equation 1 must be responsible for

the results, the 40 % weight loss is due to the by-product of cyclohexene. In compound (II), the subsequent hydroboration reaction of alkynyl species takes place rapidly, even at room temperature, to produce highly conjugated structure (III). In fact, the product (III) is deep black and is insoluble in organic solvents, and shows no visible change after exposing to air. All results indicate a crosslinked product with high conjugation around boron moieties. The following carbonization reaction was carried out at higher temperature under nitrogen. Both step-wise and isothermal processes show very low % of weight losses. In fact, even up to 1200 °C, more than 94 weight % was retained. The product was hard and shiny black particles. It is interesting to note that X-ray diffraction evinced no crystalline order in this material. However, a sharp morphological transition was observed at about 1800 °C with a well-defined X-ray diffraction and an interlayer 002 spacing of 3.36 Å ($2\theta = 26.465^\circ$) in Figure 2 (a).



Figure 2, X-ray diffractions of B/C materials prepared at 1800 °C (a), 2100 °C (b) and 2300 °C (c).

In addition, the signals at $2\theta \sim 43^\circ$, corresponding to 100 and 101 planes, are clearly observed. All peaks become sharper as the pyrolysis temperature increase. At 2300 °C (Figure 2,c), the interlayer spacing (002) decreases to 3.35 Å ($2\theta = 26.614^\circ$) accepted for the graphitic structure, and two distinctive peaks at 42.48° and 44.52° , corresponding to 100 and 101 planes, respectively.

Oxidative Stability The oxidative stability of two

carbonized products prepared from thermal treatments at 800 and 1200 °C respectively, was studied by TGA technique (Figure 3). Both samples were heated up to 800 °C under pure O₂ conditions.

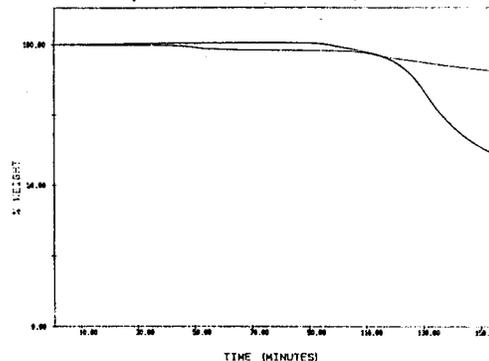


Figure 3, TGA curves in pure O₂ conditions for two B/C materials prepared at 1200 (a) and 800 °C (b).

A significant higher oxidative stability (curve a) shows in sample with 1200 °C thermal treatment. Only less than 10 % weight loss at 800 °C was observed, which is significantly lower than 45 % weight loss (curve b) in sample with 800 °C thermal treatment. The higher carbonization temperature may produce more complete carbonization product and better crystal structure. Obviously, more research is needed to find the relationship among B/C structure, oxidative stability and carbonization temperature.

CONCLUSION

The new boron containing polydyne is a valuable precursor to prepare B/C materials with uniform composition. In pyrolysis, the boron containing polydyne precursor behaves very differently from the traditional carbon precursors. The carbonization reaction not only follows a well-controlled reaction pathways but also lowers the graphitization temperature. The resulting B/C materials show a significant improvement in their oxidative stability.

ACKNOWLEDGEMENT

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