

SYNTHESIS OF (B/C) MATERIALS FROM BORON-CONTAINING PHENYLACETYLIDES

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Introduction

In our previous paper^{1,2}, we have reported a specifically designed boron-containing precursors, i.e. 9-chloroborafluorene. This precursor can be thermally transformed to boron containing graphitic (B/C) materials with high crystallinity and large crystal size at relatively low temperature (2000 °C). Up to 7 % of boron (similar B concentration in the precursor) was homogeneously substituted in the graphitic structure. The overall results seems to indicate that by carefully taking into account the chemistry of boron and the mechanism of carbonization we can tailor the precursor to produce B/C materials with desirable compositions. It is very interesting to understand the scope and limitations of this new precursor approach, especially the development of new precursors which can be easily synthesized, and the effect of different amounts of boron in the precursor on the graphitization reaction. With this purpose in mind, we have systematically synthesized three boron containing phenyl acetylide precursors which have similar molecular structures and different boron contents. The effects of boron concentration and chemical nature at various temperatures along the graphitization pathway were studied.

Experimental

Three boron containing phenylacetylides, dichloro(phenylacetylide)borane (DPB), bis(phenylacetylide)chloroborane (BCB) and tris(phenylacetylide)borane (TPB), were prepared by the condensation reaction³ of phenylacetyl lithium and BCl₃. The metallation of phenyl acetylene is basically quantitative. The extent of subsequent substitution is governed by the stoichiometric ratio of phenylacetyl lithium and BCl₃. Figure 1 shows the ¹¹B NMR spectra of DPB, BCB and TPB, produced by the stoichiometric ratio of 1/1, 2/3 and 1/3 between phenylacetyl lithium and BCl₃, respectively. Figure 1 (a) shows two chemical shifts, with a peak at 43 ppm and a shoulder around 40 ppm. Some minor di-substitution product (BCB) clearly coexists with the expected DPB material. However, both di- and tri-substitution reactions are quite clean to produce BCB and TPB, with the ¹¹B chemical shifts at 40 and 35 ppm (shown in Figure 1 (b) and (c)), respectively.

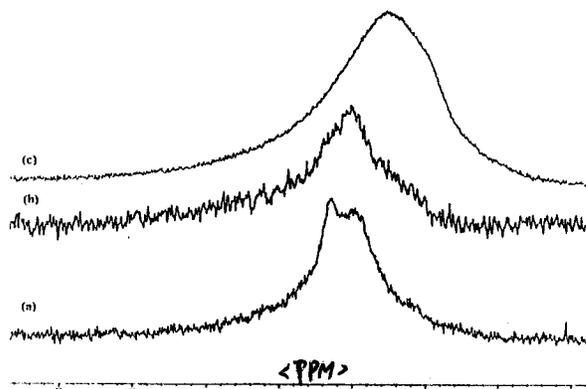


Figure 1, The comparison of ¹¹B NMR spectra of three precursors, (a) TPB, (b) BCB and (c) DPB.

Results and Discussion

We attempted to understand the effect of boron (chemical nature and concentration) on the stabilization and carbonization reactions. The initial concentration of boron (in terms of the C/B ratio) and the number of reactive B-Cl group in the precursor compounds vary from 8/1 to 18/1 and 2 to 0, respectively. The TGA results for each of the three compounds are compared in Figure 2.

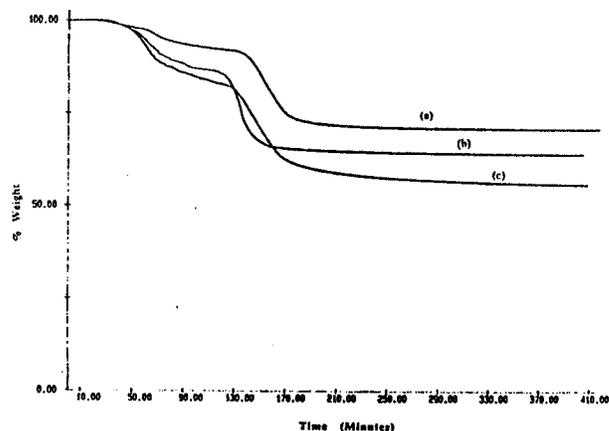


Figure 2. DSC curves of (a) TPB, (b) BCB, (c) DPB.

In general, the weight loss for all three compounds started at about 230 °C with the extent of weight loss dependent on the precursors. It is very desirable to have the stabilization reactions completed below 230 °C, because this increases the molecular weight and prevents precursor

volatilization during the carbonization procedure (> 230 °C). For DPB, the weight loss during the carbonization procedure (up to 550 °C) is theoretically (assuming loss of all hydrogen and halogen atoms) 41.5 percent. However, the weight losses for BCB and TPB are as high as 35.50% and 29.29% respectively, (the theoretical weight losses being 18.31% and 4.77% respectively). It is believed that the primary stabilization reactions are haloboration of the alkynyl group by the boron-halogen bond, and the cyclization (2p + 4p), and (2p + 2p) reactions. The haloboration reactions of alkynyl groups usually occur fairly easily even at subambient temperatures. On the other hand, the normal (2p + 4p) reactions require slightly elevated temperatures of 50-100 °C, while the (2p + 2p) reactions are only facilitated at temperatures in excess of 200 °C. The haloboration reactions are only possible in DPB and BCB. It would be expected that the haloboration reaction of alkynyl species by the boron-chlorine bond would be expected to occur with higher probability in DPB. In the case of TPB, haloboration is not possible, some molecules might be evaporated before any intermolecular reaction, which could be the reason for the significant deviation of weight losses from theoretical expectations.

After having established by TGA that carbonization was effectively completed by 550 °C, the samples were further heated up to the desired graphitization temperature and maintaining that temperature for the desired period of time (generally 30 min.). Relatively small weight loss (< 15%) was observed in each case of the graphitization reactions. The carbonized compounds from DPB, BCB and TPB will henceforth be abbreviated to PDPB, PBCB and PTPB, respectively. The x-ray diffraction patterns of the B/C materials show significant development of the secondary (100) and (101) peaks (at $2\theta \sim 43^\circ$) as the temperature increased from 1800 to 2200 °C. Table 1 summarizes the x-ray crystallite parameters of interlayer d-spacing (i.e. the 002 reflection) and Lc (crystal size) of the different compounds at various processing temperatures. Apparently, only 2200 °C was necessary to obtain x-ray crystallite parameters that typically require much higher temperature (> 3000 °C) to achieve in traditional carbons. Clearly, the concentration of boron (B/C ratios between 1/8 and 1/18) in the precursor are adequate for enhancing the graphitization reaction. It is also immediately apparent that the rate at which the graphitic structure develops in PTPB is fairly different from

those in PDPB and PBCB cases. The initial high layer plane d-spacing and low Lc values for PTPB may arise from the non-coplanar molecular structure during the stabilization and carbonization reactions. As discussed, PTPB was prepared from the precursor only containing boron-alkynyl bonds which can form non-coplanar molecular structure via out-of-plane (2p + 2p) reactions. Thus, these bonds would need to be cleaved and reformed to accommodate the development of graphitic structure. At 2200 °C, the d-spacing of PTPB approaches that of natural graphite (3.35 Å). It is very interesting to note that despite having the lowest concentration of boron in the three cases, PTPB forms a better graphitic structure, with smaller d-spacing and larger Lc.

Conclusion

Three boron containing phenyl acetylide precursors were synthesized and studied for the stabilization, carbonization and graphitization reactions. Despite the significant differences in boron concentration and chemical nature between precursors, all graphitization reactions were very effective and took place at relatively low temperature. Clearly, the in situ boron is catalyzing graphitization to form B/C material in all three cases. By virtue of the precursors, containing both boron and carbon in their molecular structure, the graphitization reactions produce B/C materials with a uniform distribution of substitutional boron in the graphitic structure.

Acknowledgements

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References

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Table 1. A Summary of d-Spacing and Lc in B/C Materials Prepared Under Various Temperatures

Temp (°C)	d spacing (Å)			Lc (Å)		
	PDPB	PBCB	PTPB	PDPB	PBCB	PTPB
1200	3.5495	3.5463	3.6935	20.2076	18.8673	19.4031
1400	3.5401	3.5267	3.6976	22.1331	21.3969	18.4227
1600	3.4938	3.4962	3.4312	24.7134	23.7934	40.3417
1800	3.4919	3.4701	3.4277	35.7821	29.2415	29.9457
2000	3.4387	3.4067	3.4035	35.8107	40.3562	39.1217
2200	3.3898	3.3874	3.3797	177.4037	136.5970	405.9437