Research Article

Poly(hydridocarbyne) as Highly Processable Insulating Polymer Precursor to Micro/Nanostructures and Graphite Conductors

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Carbon-based electronic materials have received much attention since the discovery and elucidation of the properties of the nanotube, fullerene allotropes, and conducting polymers. Amorphous carbon, graphite, graphene, and diamond have also been the topics of intensive research. In accordance with this interest, we herein provide the details of a novel and facile method for synthesis of poly(hydridocarbyne) (PHC), a preceramic carbon polymer reported to undergo a conversion to diamond-like carbon (DLC) upon pyrolysis and also provide electrical characterization after low-temperature processing and pyrolysis of this material. The results indicate that the strongly insulating polymer becomes notably conductive in bulk form upon heating and contains interspersed micro- and nanostructures, which are the subject of ongoing research.

1. Introduction

Poly(hydridocarbyne) (PHC) is an sp³ hybridized random network carbon polymer, comprised of amonomeric unit containing one carbon-hydrogen and three carbon-carbon single bonds not unlike hydrogenated tetrahedral amorphous carbon (ta-C:H). Much interest was generated by the synthesis of this easily processable polymer and the report of its conversion to diamond and DLC by means of pyrolysis [1]. Diamond has been reported to have interesting electrical properties [2, 3] and applications in MEMS [4] and biology [5]. And ta-C:H has also been shown to be relevant to the electrical and biological communities in the form of protective coatings in magnetic disk memories [6] and a haemocompatible material [7], respectively.

2. Experimental

We developed a new method for the synthesis of PHC [8] which enables faster, easier production and makes this interesting material more accessible for research. The method of synthesis involves the electropolymerization of chloroform (CHCl₃) which proceeds as shown in Figure 1. UV/visible data collected during the polymerization are consistent with the production of a polycarbyne, namely PHC [1, 9, 10]. Transmission infrared spectroscopy shows no evidence of carbon-carbon double bonds, only carbon-carbon single bond and carbon-hydrogen stretches.

Pyrolysis of the PHC polymer was performed under constant Ar flow at 1000°C for 24 hours in a Thermolyne tube furnace. A blackened bulk material was produced...
which we electrically analyzed and characterized via Raman spectroscopy. This bulk material was probed (Figure 2) and found to be much more conductive than the annealed polymer despite exhibiting a nonlinear I(V) for |V| > 0.25. This increase in conductivity is rationalized by the formation of sp² hybridized carbon constituents during pyrolysis (see the following).

3. Raman Analysis

A vast body of work has been published on Raman spectroscopy of carbon-based materials and the techniques used to fit Raman spectra using their individual constituent peaks, and this remains an active area of research as certain peak contributions are still debated or are of unknown origin. Nonetheless, a literature review revealed well-developed theory, which enabled us to curve fit our sample to good approximation.

Figure 3 shows the spectrum of our material plotted against that of unknown diamond, the intended product of the pyrolysis. The two broadened features seen in our spectrum occur in the vicinity of the well-known D (disordered) and G (graphite) peaks that occur around 1360 cm⁻¹ and 1560 cm⁻¹, respectively, [11] in graphitic carbon materials and are particularly characteristic of microcrystalline graphite [12].

To elucidate this, we followed the convention of curve fitting the spectrum using a Lorentzian function for the D peak and a Breit-Wigner-Fano (BWF) function for the contribution near the G peak (Figure 4). The motivation for the use of the BWF function lies in its ability to represent the merging of the G and D' peaks, a phenomenon which occurs when the crystalline domains of a graphitic material are sufficiently small [13, 14]. Due to the close fitting of our spectra using this methodology, we find the majority of the pyrolysis product is small-crystalline graphite, which explains the notable increase in conductivity after burning the PHC.

SEM did however reveal micro and nanostructures that were clearly morphologically distinct from the majority
product (Figure 5). We attempted to account for this material by adding an additional Lorentzian to the curve-fitting procedure (Figure 6). The added Lorentzian is relatively small in magnitude is centered at 1513 cm\(^{-1}\), and improves the curve fitting of the sample’s spectrum. Interestingly, an \(\sim 1500\) cm\(^{-1}\) peak in the spectrum of a related polymer precursor, poly(phenylcarbyne) (C\(_{6}\)H\(_{5}\)C)\(_n\), was observed after laser irradiation [15]. It has been suggested that such a peak could arise due to either impurity-carbon amorphous networks or amorphous networks of sp\(^2\) and sp\(^3\) carbon [16]. However, only the latter suggestion is applicable to our method of pyrolysis. Therefore, the micro and nanostructures interspersed throughout the bulk may be comprised of such three- and four-fold coordinated amorphous carbon networks.

4. Conclusion

We have developed a novel and facile method for the synthesis of PHC, an easily processed, insulating polymer. Upon pyrolysis in inert atmosphere, we note a significant increase in conductivity of the product with respect to the precursor for the sample we investigated. The majority of the product analyzed was shown to be consistent with small-crystalline graphite by way of curve fitting the sample’s Raman spectrum. An improved curve fitting was found through incorporation of an additional minority constituent contributing to the spectrum at \(\sim 1500\) cm\(^{-1}\). This contribution may be the result of micro and nanostructures within the bulk observed by SEM.

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