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Facile Synthesis of Poly(hydridocarbyne): A Precursor to Diamond and Diamond-like Ceramics

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Polycarbynes have previously been shown to be polymeric precursors to diamond and diamond-like carbon. Here, we report an incredibly simple method for producing one of these polymers, poly(hydridocarbyne). The method simply requires chloroform, electricity, a solvent and an electrolyte. Since the polymer is soluble, the production of diamond objects of any shape is feasible. It is hoped that the ease of the synthesis will make these types of polymers accessible to scientists from all disciplines and that the potential applications for this material, which range from electrical to biomedical, are finally realized.

Keywords: pre-ceramic polymer; diamond; electroinitiated polymerization

1 Introduction

The interface between polymers and ceramics is one of the most important in materials science (1). One aspect of this association is seen in pre-ceramic polymers. These are an important class of polymer which produce ceramic materials upon heating. Generally, the most sought after of these types of polymers are ones which form tough, hard-wearing ceramic materials with high thermal stabilities. Examples of this are polymers which form silicon carbide (2), silicon nitride (3) and boron nitride (4) ceramics on pyrolysis. Perhaps the most highly prized pre-ceramic polymer is one which can be thermolytically converted to diamond or diamond like carbon. Here, we report the synthesis of one such polymer that can be made simply, using electricity (5).

Diamond is one of mankind's most cherished elements, being treasured as a gemstone and used for its hardness for many millennia. More recently, because of diamond's physical and chemical properties, scientists are interested in using the material in a variety of devices and applications, ranging from electrical (6) to biomedical (7). However, the problem is that diamond is an inherently difficult material to work with, especially if a particular shape or film is required. Chemical vapor deposition (CVD) is a partial

solution to this problem, and there are many examples of diamond films being produced in this manner. Unfortunately, the process is relatively expensive and the films do not exhibit the desired smoothness and continuity (8) for many of the envisioned applications, including microelectromechanical systems (MEMS) (9).

These, and other, problems can be overcome if a move is made to a polymeric system that upon moderate heating produces diamond or diamond like material. Using such a methodology, if the polymer is soluble, films, fibers and coatings of any size or shape could be produced easily and quickly. Thanks to the pioneering work of Bianconi and co-workers, such polymers do exist and they have been named polycarbynes (10, 11). Shortly after the publication of their initial work, a slightly simpler method for synthesizing one of these polymers, poly(phenylcarbyne), was reported by Rieke and Chen (12) and Sun and co-workers carried out a variety of studies converting this polymer to diamond/diamond-like ceramics (13–21). Most recently, Bianconi et al. reported the synthesis of a new polymer in this class, poly(hydridocarbyne) (22). Poly(hydridocarbyne) is the most sought after of the polycarbynes due to its high ceramic yield and the superior quality of diamond and diamond-like material that is produced from it. The synthesis of this polymer, however, involves liquid sodium potassium alloy (NaK), which is explosive and pyrophoric, high intensity ultrasound and sometimes further refluxing with methyl lithium, all of which is carried out in highly flammable organic solvents. Such a synthetic procedure would be almost impossible to scale up commercially and is also

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difficult for many scientists who might like to produce this polymer for their own research studies.

In this communication, we report that poly(hydridocarbyne) can be made by a much simpler and quicker method, that is the electrochemical polymerization of chloroform (CHCl_3). A general schematic representation of the synthesis is shown in Scheme 1.

2 Experimental

2.1 Materials

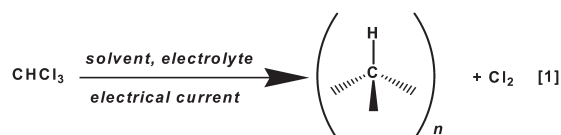
Chloroform (CHCl_3) (Merck), acetonitrile (AN) (Merck), Tetrahydrofuran (THF) (Merck), tetrabutylammonium tetrafluoroborate (Aldrich), LiAlH_4 (Merck), 430 stainless steel.

2.2 Equipments

The polymerization reaction was monitored using an HP8453A UV/visible spectrometer. Gel Permeation Chromatography (GPC) was performed using a Polymer Laboratories PL-GPC 220 system using THF as the solvent and calibrated using poly(styrene) standards. ^1H Nuclear Magnetic Resonance (NMR) spectra were obtained using a Bruker-Spectrospin Avance DPX 400 Ultra-Shield (400 MHz, CDCl_3 solvent). Fourier Transform Infra Red (FTIR) spectra (THF solution) were collected using a Nicolet 510 FTIR spectrometer. Raman spectroscopy was carried out using a Jobin Yvon-Horiba spectrograph fitted with a He-Ne laser (wavelength 632.83 nm) and equipped with a Peltier cooled CCD detector. Elemental analysis was performed at the METU Central Laboratory. Heat treatment of the polymer was carried out in an alumina ceramic boat using a Thermolyne tube furnace fitted with an alumina tube under a constant flow of Argon. X-ray Powder patterns (XRD) were taken with a Rigaku Miniflex Diffractometer and $\text{Cu K}\alpha$ (30 kV, 15 mA, $\lambda = 1.54051 \text{ \AA}$) radiation. Scanning was done between $20^\circ < 2\theta < 140^\circ$. All measurements were made with 0.05 degree steps and a 0.5 degree/minute rate. The divergence slit was variable, and the scattering and receiving slits were 4.2 degrees and 0.3 mm, respectively.

2.3 Synthesis of Poly(hydridocarbyne)

Note: results indicate that chlorine gas is produced in the formation of poly(hydridocarbyne) so this synthesis should be carried out using suitable precautions and ventilation.



Sch. 1. Schematic representation of the electrochemical synthesis of poly(hydridocarbyne).

A 1.2 M chloroform (CHCl_3) solution (in acetonitrile (AN)) was electrolyzed in the presence of 0.1 M tetrabutylammonium tetrafluoroborate (AN solution). 150 mL of the electrolyte-solvent couple was placed in a cell equipped with a 430 stainless steel cathode ($10 \text{ cm} \times 8 \text{ cm} \times 0.5 \text{ mm}$) and anode ($10 \text{ cm} \times 8 \text{ cm} \times 0.5 \text{ mm}$). Electrolysis was run at -6.0 V for 4 h, at room temperature, under a N_2 atmosphere. After electrolysis, the insoluble material (presumed to be a higher molecular weight polymer) is filtered from the solution and discarded. AN was then evaporated from the filtered solution and a brown powder was obtained, NMR and elemental analysis shows this material to contain both supporting electrolyte and chlorine, as well as the expected carbon and hydrogen of the polymer.

Tetrahydrofuran (THF) (which had been dried over sodium and benzophenone) was then used to dissolve the brown powder and the solution was reacted (12 h reflux) with LiAlH_4 , which was used to remove any remaining halogen from the polymer. A solid material (supporting electrolyte) precipitates from the solution and is removed. Evaporation of the THF from the solution again yields a brown powder in which analysis still indicates the presence of a small amount of starting electrolyte. The material was then redissolved in dichloromethane and hexane added drop-wise to precipitate a brown powder which our characterization data shows to be pure poly(hydridocarbyne) with no presence of $\text{C}=\text{C}$, $\text{C}-\text{O}$, $\text{C}=\text{O}$, $\text{C}-\text{Cl}$, etc. The polymer is formed in 30–40% yields. It should be noted that although we report here the synthesis of poly(hydridocarbyne), initial data from recent experiments have shown that this method can be used to synthesize other polycarbynes, such as poly(methylcarbyne) and poly(phenylcarbyne), which have also been shown to be precursors to diamond and diamond-like carbon.

2.4 Pyrolysis of Poly(hydridocarbyne)

The polymer was heated to 1000°C in a Thermolyne tube furnace under a constant flow of Argon, at a ramp rate of $10^\circ\text{C}/\text{min}$, held for 24 h and then cooled to room temperature.

3 Results and Discussion

3.1 Synthesis and characterization of poly(hydridocarbyne)

Poly(hydridocarbyne) has a unique network structure of tetrahedrally bound carbon atoms, with each carbon atom having a single “pendant” hydrogen group. This distinctive structure gives rise to a particular electronic spectrum; which consists of broad intense absorptions starting in the ultraviolet (UV) region (at $\sim 200 \text{ nm}$) that tails down to the visible region. It was by using *in situ* UV/visible spectroscopy that we chose to monitor the formation of poly(hydridocarbyne). The UV/

visible spectrum (Fig. 1) shows the progression of this reaction over a one hour period.

Before the reaction is started, the electronic spectrum is featureless, however within as little as 4 min after a voltage is applied, the distinctive spectrum of the polycarbynes in general, and poly(hydridocarbyne) in particular, is observed (10–12, 22). Chlorine gas is emitted during electrolysis, which was detected by pH paper turning red in color when held above the reaction cell. The exact mechanism of formation is as yet undetermined; Rieke and Chen (12) in their work with poly(phenylcarbyne) and Vermeulen and co-workers (23) in work with related silicon network polymers (the polysilynes) have suggested a free radical mechanism, no mechanism has been proposed in Bianconi et al's synthesis of poly(hydridocarbyne).

The purified isolated brown material was shown to be a polymer by GPC (GPC of purified poly(hydridocarbyne): $M_n = 5644$, $M_w = 6144$, $PD = 1.089$). The molecular weights obtained are lower than in the only other reported synthesis of poly(hydridocarbyne) (22); exact reasons for this are unknown at this present moment in time, but it is perhaps due to the extensive purification of the polymer we undertake.

The $^1\text{H-NMR}$ of purified poly(hydridocarbyne) is shown in Fig. 2.

Figure 2 shows the broad NMR resonances which are expected of these types of polymer (10–12, 22). The very broad, very strong resonance between 0.5–2.1 ppm corresponds to the aliphatic hydrogens of the network polymer. There is also a weaker broad peak at 0.3 which we attribute to aliphatic hydrogens from cyclopropane type structures in the network (24). To the best of our knowledge, it is the first time that these three-membered type rings have been seen in the polycarbynes and we believe this might be due

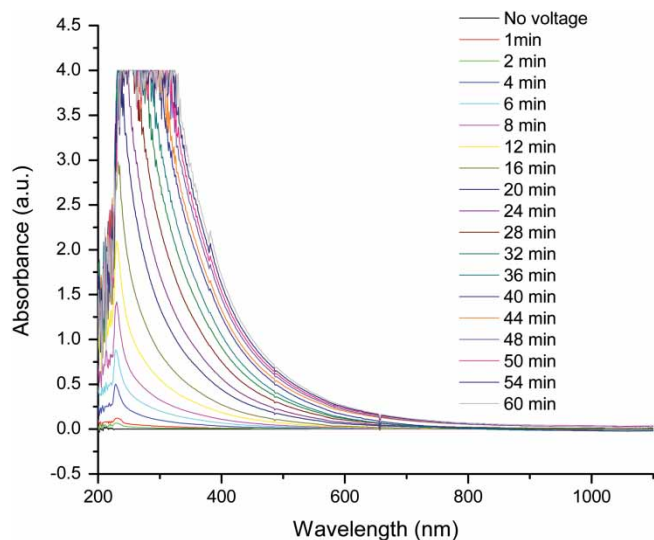


Fig. 1. UV/visible spectrum obtained during the electro-polymerization of CHCl_3 over a one hour period.

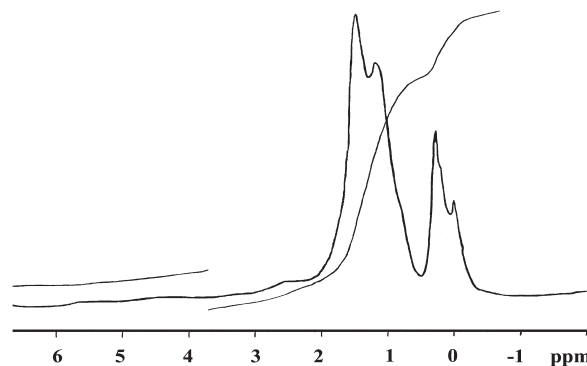


Fig. 2. $^1\text{H-NMR}$ of purified poly(hydridocarbyne).

to the decrease in size of the pendant group (hydrogen) which decreases steric effects between adjacent carbon atoms. There is no evidence of any major amounts of vinylic hydrogens, hydrogens in close proximity of chlorine or oxygen, or any supporting electrolyte in the spectrum. It should be noted that the $^1\text{H-NMR}$ spectrum shown here is more consistent with a pure network $[\text{CH}]_n$ type structure than in the only previous synthesis of poly(hydridocarbyne) (22), in which the spectrum showed three distinct sharp resonances centered at 1.59, 1.25 and one just below 1.0, rather than the broad resonances expected with these types of polymer.

The FTIR spectrum of purified poly(hydridocarbyne) is shown in Fig. 3.

The transmission IR spectrum is consistent with a primarily network backbone structure of the formula $(\text{CH})_n$; there is no evidence of $\text{C}=\text{C}$ being present or C-O or C-Cl . The C-H stretches at 2976 and 2869 cm^{-1} indicate that the hydrogens are present on aliphatic, sp^3 , carbon atoms and the strong band at 1083 cm^{-1} arises from C-C stretching. The spectrum is an exact match for the only other reported IR spectrum of poly(hydridocarbyne) (22).

The lack of a Raman spectrum is characteristic of the polycarbynes (10, 11, 22), which always give strong luminescence regardless of excitation wavelengths. Elemental analysis (Found C: low and variable, H: 6.9%. Calcd. for (CH) , C: 92.31%, H: 7.69%) of the polymer shows that hydrogen is present in approximately the correct percentage. However,

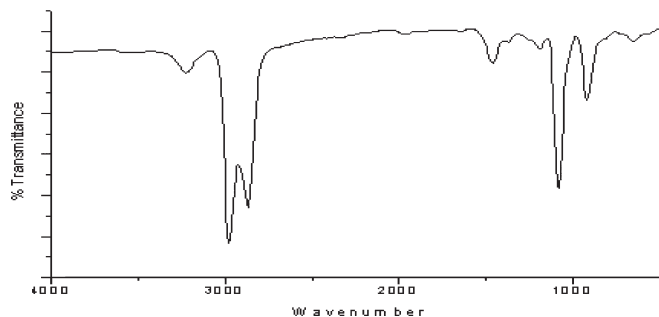


Fig. 3. FTIR spectrum of purified poly(hydridocarbyne).

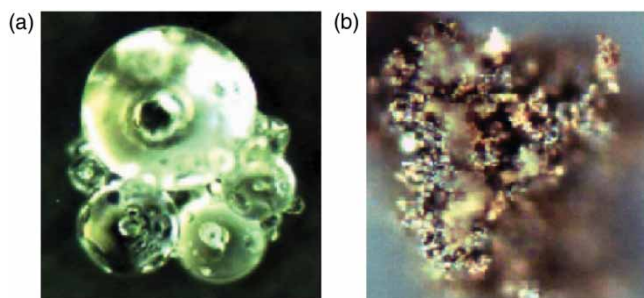


Fig. 4. Pictures obtained from the pyrolytic conversion of poly(hydridarbyne) using an optical microscope of a) (magnification 100 \times) the transparent material and, b) (magnification 200 \times) the darker colored material.

carbon analyses are always low, extremely variable and non-repeatable. That the exact percentage of the element in the backbone is not easily determined is not an unusual phenomenon in these types of polymers (2), and is indicative of rapid conversion of the polymer to a ceramic. Such results are also seen in the combustion analyses of other ceramic precursors which show low values as well (25, 26). There is no evidence of any chlorine remaining on the polymer backbone.

All of the characterization data we have is consistent with the product being poly(hydridarbyne), $[(CH)_n]$ (22).

3.2 Pyrolysis of Poly(hydridarbyne)

Heat treatment of the polymer produces a hard crystalline substance in high yield; typically in the range of 10–40%, but it is highly dependent on processing conditions, molecular weight of the polymer, etc. These ceramic yields are comparable to those obtained from poly(phenylcarbyne) of 40–45% (10), we are unable to find any exact numbers for

Table 1. Selected powder diffraction data of the material produced from the pyrolysis of poly(hydridarbyne) compared to lonsdaleite (PDF file 19-0268)

Sample d-spacings (\AA)	I/I ₀ (based on most intense assignable peak)	Lonsdaleite 19-0268 d-spacings (\AA)	I/I ₀
2.19	85	2.19	100
2.06	15	2.06	100
		1.92	50
1.48	100	1.50	25
		1.26	75
1.15	24	1.17	50
1.10	33	1.075	50
1.04	32	1.055	25
0.87	22	0.855	25
0.84	27	0.82	25

poly(hydridarbyne) (22). Both to the naked eye and under an optical microscope small, transparent particles, which refract light like gem quality diamond are clearly seen along with a greater proportion of darker colored material (Fig. 4).

The X-ray powder pattern (Fig. 5) of this mixture shows it to consist of lonsdaleite, a hexagonal form of diamond first reported in 1967 (27). For clarity, only the region above $2\theta = 40^\circ$ is shown. Analysis of the reflections, which match lonsdaleite, are presented in Tables 1 and 2.

The hexagonal a and c unit cell parameters were calculated using PDF file 19-0268 and are shown in Table 2.

It has been suggested that there may possibly be a small amount of the more common cubic diamond A peak at $d = 2.06$ which is observed in our x-ray pattern is also seen in the powder diffraction files (PDF files - The International

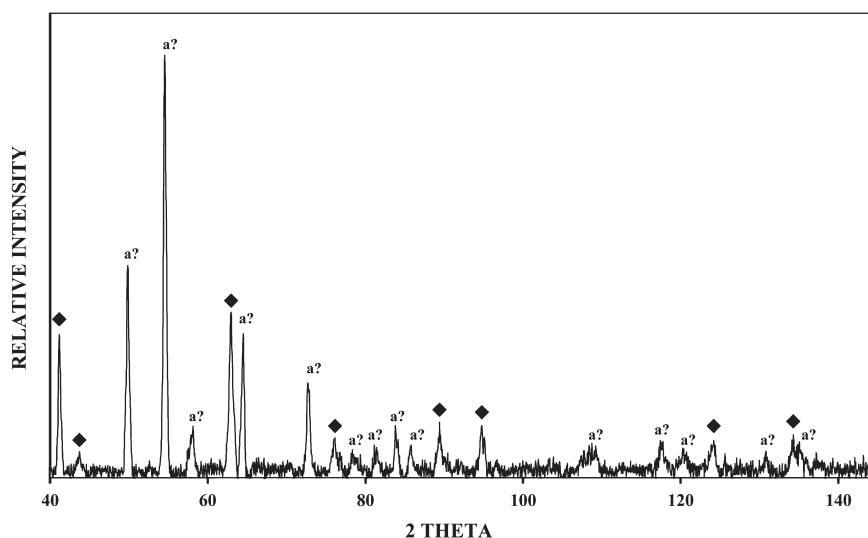


Fig. 5. X-ray pattern of the pyrolysis products of poly(hydridarbyne), ◆ denotes lonsdaleite (PDF file 19-0268), a? denotes possible alumina (Al_2O_3) reflections (various PDF files).

Table 2. Unit cell parameters of the lonsdaleite material produced from the pyrolysis of poly(hydridocarbyne) compared to lonsdaleite (PDF file 19-0268)

Unit cell parameters (Å)	Sample	Lonsdaleite 19-0268
a	2.53	2.52
c	4.12	4.12

Center for Diffraction Data[®] (ICDD[®])) of almost all cubic diamond phases present, but the lack of other expected reflections and the overlap of some of these reflections with lonsdaleite, would make this claim tenuous, at best. No evidence of graphite or other forms of carbon are seen. These results are again consistent with the only other report of the heat treatment of poly(hydridocarbyne) (22). It is noteworthy that the X-ray pattern of the crystalline lonsdaleite material produced in this study is superior to the only previous study; this is probably due to the fact that an alumina tube is used as opposed to a quartz one and also due to pyrolysis being undertaken on a poly(hydridocarbyne) polymer powder rather than a film cast on a substrate; the only other study of the ceramic derived from this polymer was carried out on a silicon chip and the resulting X-ray pattern was dominated by c-Si reflections. Further analysis of the ceramic material is precluded due to lack of suitable electron microscopy and access to multi-wavelength Raman facilities which are necessary for a detailed study of the ceramic material produced from this polymer (22).

There are also some peaks in Fig. 5 which cannot be assigned to lonsdaleite or any other diamond phase. Pyrolysis of the sample is carried out in an alumina crucible and an alumina tube and we believe that these peaks arise from Al₂O₃ contamination. Every peak except one can be possibly identified by, between three and thirty-eight recorded, reflections of a variety of alumina: 26-0031, 31-0026, 37-1462, 46-1212, 71-1123, 71-1124, 71-1125, 71-1126, 71-1127, 71-1128, 71-1683, 71-1684, 73-152, 73-2294, 74-0323, 74-1081, 75-0782, 75-0783, 75-0784, 75-0785, 75-0786, 75-0787, 75-0788, 75-1862, 75-1863, 76-0144, 78-2426, 78-2427, 80-0786, 81-1667, 81-2266, 81-2267, 82-1399, 82-1467, 83-2080, 83-2081, 85-1337, 86-1410, 88-0107, 88-0826. The other peak at $\sim 2\theta = 25^\circ$ (not shown in Fig. 5) matches only one possible reflection from one of these PDF files.

As a demonstration of ultimately how simple this synthesis could become, we set up an experiment with the most rudimentary sources of both electricity and an electrolyte that we could find; namely a series of four 1.5 volt batteries and common table salt (10 mg). Using acetonitrile (3 mL) as the solvent, stainless steel electrodes and 0.5 mL of water we polymerized chloroform (2 μ L). The reaction was again followed by UV/visible spectroscopy. The resulting spectrum and the brown color of the material produced confirm the formation of poly(hydridocarbyne). The facile



Fig. 6. A simple reaction set-up for electro-polymerization of CHCl₃.

experimental set-up (Fig. 6.) indicates that this polymer could be produced by almost anyone.

4 Conclusion

The results of this work demonstrate a cheap and simple method for producing poly(hydridocarbyne) which produces diamond/diamond-like carbon upon heating. As the polymer is soluble the production of diamond objects of any shape is feasible. The straightforwardness and ease of the synthesis we have developed will open up the production of this polymer, both on a commercial scale and in the laboratory, to scientists of all disciplines. Consequently, the myriad of potential applications that are envisaged for this material might finally be realized.

5 Acknowledgements

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