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Electrochemical polymerizatıon of hexachloroethane to form poly(hydridocarbyne): a pre-ceramic polymer for diamond production

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Abstract Due to its structural similarity with diamond, poly(hydridocarbyne) (PHC), which is sp^3-hybridized, is a unique polymer that can be easily converted to diamond and diamond-like-carbon ceramics upon heating. PHC can be easily synthesized via the electrochemical polymerization of chloroform as previously reported. Here, we report the electrosynthesis of PHC from hexachloroethane. Since hexachloroethane has six chlorine atoms in its structure, polymerization takes place through the carbons simultaneously. Thus, the polymer is bigger in chain length than PHC obtained from the polymerization of chloroform. UV-vis, FTIR, and NMR spectroscopy were utilized to determine the polymer structure. Conversion of the polymer to diamond was accomplished by heating at 1000 °C under a nitrogen atmosphere as confirmed by Optical Microscopy and Raman analysis. XRD studies showed that the product is an assortment of diamond forms.

Introduction

Diamond is widely used as an industrial material since it has special properties, such as hardness, chemical inertness, and low frictional co-efficient [1, 2]. Due to these properties, it is used as a cutting tool and widely in devices and applications ranging from electrical to biomedical [3–6]. Although diamond is a very useful material, manufacturing it is very difficult and complicated. In addition, diamond is known as a very hard material to work with, especially if a desired shape or diamond film are needed [7]. To circumvent some of these problems, several methods are commonly used, such as chemical vapor deposition (CVD) [8], combustion methods [9], and shock synthesis [10]. Organic precursors such as CH_4 and C_2Cl_6 are used in these methods to produce diamond on the surface directly, instead of a well-known method which produces powder and polycrystalline diamond from graphite at high temperature and pressure [11–13]. CVD runs under low pressure, however, it cannot be used in large scale applications. Since film formed on a surface is not uniform and smooth, CVD is commonly modified with radio frequency plasma and hot filament [14]. Combustion method runs at ambient atmosphere and has relatively high growth rate of diamond film but crystals obtained are large [15, 16] .

Indeed diamond film technology is often hampered by the inability to produce a quality layer of the material. In their recent thorough review on the subject, Das and Singh [17] discuss in detail the problems associated with this, particularly with respect to low-temperature synthesis of diamond films by CVD. One area where scientists would very much like to use diamond film technology is in Micro-Electro-Mechanical Systems (MEMS) applications [18], but again CVD and other synthetic methods cannot produce coatings of the desired quality.

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All methods used in diamond manufacturing technology require complicated equipment operating under controlled pressure and temperature, limiting its production and application. These methods are relatively expensive and the films produced do not exhibit the desired smoothness and continuity [4–19].

One solution to these problems is to synthesize specific polymers, named polycarbynes [20], that produce diamond or diamond-like carbon upon heating. Several of these polymers have been synthesized; poly(methylcarbyne) [20], poly(hydridocarbyne) [21], and poly(phenylcarbyne) [22]. The polymer can be easily coated on any surface and substrate in any thickness and shape due to their solubility in common organic solvents, such as chloroform, tetrahydrofuran, etc. The most promising of these polymers, poly(hydridocarbyne), was originally, ultrasonically, synthesized by Bianconi et al. [21]. Their poly(hydridocarbyne) (PHC) was synthesized using high intensity ultrasound and liquid sodium potassium alloy (NaK) (which is explosive and pyrophoric) and also further refluxed with methyl lithium. Such a synthetic procedure would be almost impossible to scale up commercially and is also difficult for many scientists who might like to produce this polymer for their own research studies.

Here, we report a new synthesis of PHC by a simple and quick method from hexachloroethane (C_2Cl_6). The method can also potentially be used by industry and by scientists with access to fairly rudimentary lab-scale equipment.

Experimental section

Materials

Hexachloroethane (C_2Cl_6) and tetrabutylammonium tetrafluoroborate (TBAFB) were purchased from Aldrich and used as received. Acetonitrile (AN) was also obtained from Aldrich and distilled before use. Tetrahydrofuran (THF) was bought from Merck and purified over sodium metal. Lithium aluminumhydride was purchased from Merck and used as received. A 430 stainless steel was used as the electrode.

Equipment

The polymerization reaction was monitored using an HP8453A UV/visible spectrometer. Gel Permeation Chromatography (GPC) was performed on a Perkin–Elmer Series 200 apparatus with a refractive index (RI) detector using TSKgel AM GPC Gel column with *N*,*N*-dimethylformamide eluent at a flow rate of 1.0 mL/min and calibrated using poly(styrene) standards. ^{1}H 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 with a Jobin Yvon–Horiba spectrograph fitted with a He–Ne laser (wavelength 632.83 nm) and equipped with a Peltier cooled CCD detector. 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 nitrogen. X-ray Powder patterns (XRD) were taken with a Rigaku Miniflex Diffractometer (Cu $K\alpha$ 30 kV, 15 mA, $\lambda = 1.54051$ Å) radiation. Scanning was done between $20^\circ < 2\theta < 140^\circ$. All measurements were made with 0.05° steps and $0.5^\circ \mathrm{min}^{-1}$ rate. The divergence slit was variable, and the scattering and receiving slits were 4.2° and 0.3 mm, respectively.

Synthesis of poly(hydridocarbyne)

The electrochemical synthesis of PHC was carried out in a 100 mL undivided cell. The cell was filled with 1.2 M C_2Cl_6 and 0.1 M TBAFB in 50 mL acetonitrile (AN) solution. Stainless steel (430) cathode (10 cm × 8 cm × 0.5 mm) and anode (10 cm × 8 cm × 0.5 mm) were connected to a galvanostat and electrolysis was run at −6.0 V for 4 h, at room temperature under a N_2 atmosphere. After electrolysis, the electrodes were removed from the dark brown solution, and the solution was filtered to discard the brown residue. Both the brown residue and the polymer in solution are expected to be poly(hydridocarbyne). A brown powder was obtained after AN was evaporated from the filtered solution and then dissolved in THF. $LiAlH_4$ was added to the solution and refluxed for 12 h to remove any remaining halogen from the polymer. Remaining supporting electrolyte was also precipitated from the solution and removed. A brown powder was obtained after the evaporation of THF. The polymer was formed in 60% yield.

It should be noted that chlorine gas is generated during the course of the reaction so suitable precautions/ventilation should be employed.

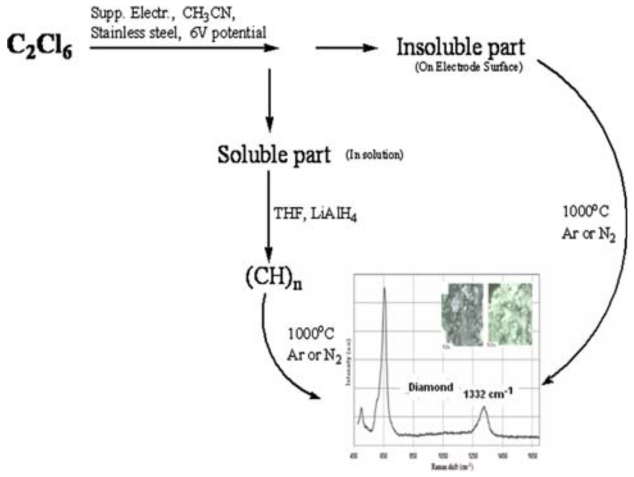
^{1}H NMR ($CDCl_3$) of PHC untreated with $LiAlH_4$: $\delta = \sim 2.1$ ppm (*s*, due to $(CCl)_n$)and $\delta = \sim 1.5$ ppm (broad,due to supporting electrolyte).

^{1}H NMR ($CDCl_3$) of PHC treated with $LiAlH_4$: $\delta =$ between 0.6 and 3 ppm (very broad and sharp, due to hydrogen on the polymer backbone), $\delta = 0.3$ ppm (due to hydrogen cyclopropane).

FTIR: 1080 cm^{-1}, ~981 cm^{-1}, 2980 cm^{-1}, 2879 cm^{-1} (no presence of C=C, C–O, C=O, C–Cl).

Pyrolysis of poly(hydridocarbyne)

A thermolyne tube furnace was used to heat the PHC up to 1000 °C under a constant flow of Argon, at a ramp rate of 10 °C/min. It was held for 24 h and cooled to room



Scheme 1 Schematic representation of the electrochemical synthesis of poly(hydridocarbyne) and pyrolytic convertion of the polymer to diamond

temperature. The electrochemical synthesis of poly(hydridocarbyne) and pyrolytic convertion of PHC to diamond is represented in Scheme 1.

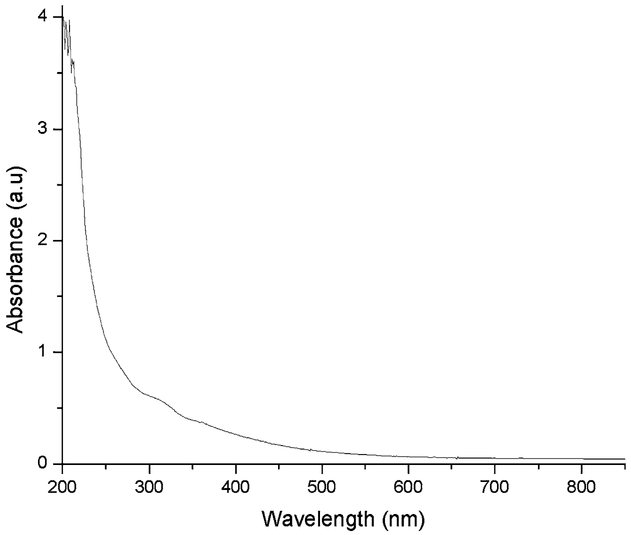


Fig. 1 UV/visible spectrum of PHC

Results and discussion

Characterization of poly(hydridocarbyne)

Polycarbynes can be easily converted to diamond and diamond-like carbon (DLC) unless they contain functional groups like double bonds which give an absorbtion band in the visible region. Hence, UV/vis spectroscopy was performed to monitor whether the polymer has a functional group on its backbone or not. The results showed that spectrum has only characteristic broad intense absorption starting in the ultraviolet (UV) region at 200 nm and continues to the visible region (Fig. 1). This proves that the polymer is PHC and can be readily converted to diamond and DLC [1, 2, 20–22].

The FTIR spectrum of PHC showed C–C stretching at ~1080 cm^{-1} and ~981 cm^{-1} [1, 2, 8–10]. Peaks at 2980 cm^{-1} and 2879 cm^{-1} can be attributed to aliphatic C–H stretching due to cyclopropane end groups. It is important to note that there is no evidence of C–Cl, C=C, and C=O and any other functional groups. This is also consistent with UV/vis spectrum.

^{1}H NMR of untreated (Fig. 2a) and treated (Fig. 2b) PHC with $LiAlH_4$ are shown in Fig. 2. ^{1}H NMR of PHC given in Fig. 2b is also consistent with the first reported synthesized PHC in literature [1, 2, 11–13]. Figure 2a reveals that the sample contains both $(CCl)_n$ and the supporting electrolyte. The sharp peak at ~2.1 ppm is due to $(CCl)_n$ and broad peak at ~1.5 ppm is due to supporting electrolyte. Figure 2b showed that sample contains mostly PHC, $(CH)_n$. The very broad and characteristic peak between 0.6 and 2 ppm is due to C–H resonance, and the weak peak at 0.3 ppm can be assigned to aliphatic hydrogens of cyclopropane end group. The NMR spectrum hence, differs from the one obtained by Bianconi et al. which has methyl end groups.

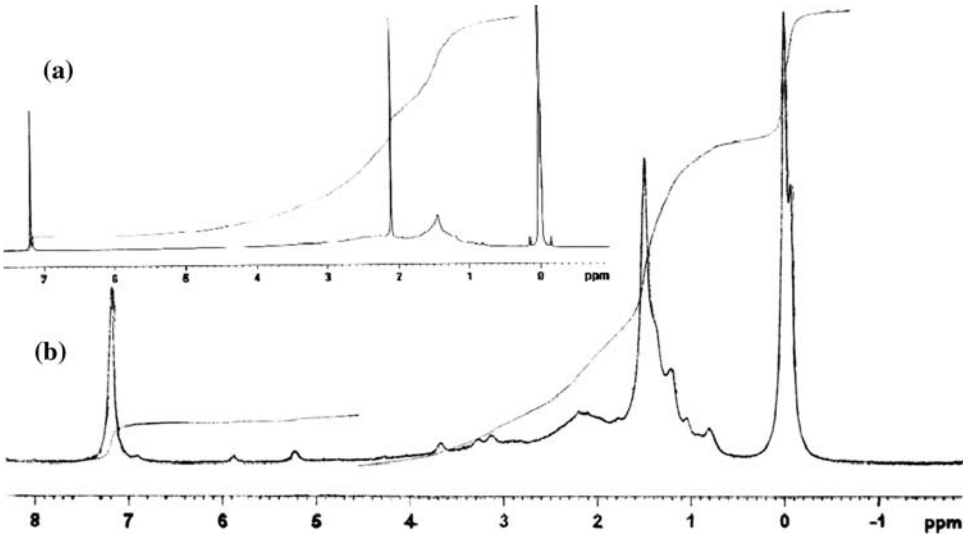
Number (M_n) and weight (M_w) average molecular weights of PHC were determined by GPC. Since PHC has a highly branched network structure, the true molecular weight of the polymer should be higher than the one determined [23]. Thus, the molecular weight determined by GPC for PHC must be several times higher than molecular weight obtained as reported earlier. The molecular weight maxima was found to be between ~10000 and ~52000 daltons with polydispersity of 1.09, where M_n and M_w were 21700 and 23800 daltons respectively. The molecular weights obtained are aproximately four times higher than that of PHC synthesized electrochemically from $CHCl_3$ [1, 2] .

Characterization of diamond

Diamond is obtained after heat treatment of PHC under inert gas, N_2. The crystal size and yield may depend on processing conditions and the molecular weight of the polymer. The XRD analysis of diamond produced is given in Fig. 3.

Selected powder diffraction data of diamond given in Table 1 shows that the material obtained from pyrolysis of PHC is a mixture of several forms of diamond, and consistent with the previous reports in literature [1, 2, 21, 24–27]. The data represents lonsdaleite, a hexagonal form of diamond and the fit is even better than the one in a previous work [1]. The hexagonal a and c unit cell parameters were calculated using

Fig. 2 ^{1}H NMR of PHC (**a**) before and (**b**) after adding $LiAlH_4$



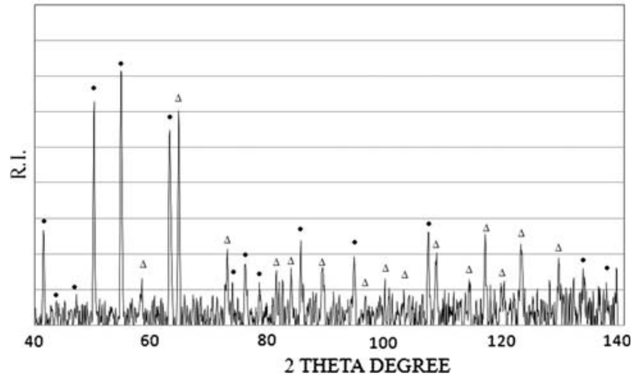


Fig. 3 X-ray pattern of the pyrolysis product of poly(hydridocarbyne): (●) denotes diamond crystals reflections (PDF Files: 19-0268, 26-1078, 26-1082, and 43-11040); (Δ) denotes possible alumina (Al_2O_3) reflections

PDF file 19-0268. The data suggests that there may possibly be a small amount of the more common cubic diamond. A peak at *d* 2.06 which is observed in the X-ray pattern is also seen in the powder diffraction files of almost all cubic diamond phases present, but the lack of other expected reflections and the overlap of some of these reflections with lonsdaleite, makes this identication difficult. Also no evidence of graphite or other forms of carbon are seen.

Raman analysis of the diamond produced is given in Fig. 4. The Raman spectrum of diamond obtained from the soluble PHC is shown in Fig. 4a. The spectrum consists of a broad band at about 1332 cm^{-1}, which is the characteristic peak of diamond [10–18]. Figure 4b shows the spectrum of diamond produced from insoluble PHC, which probably has a higher degree of crosslinking and molecular

Table 1 Selected powder diffraction data of sample produced from the pyrolysis of poly(hydridocarbyne) compared to other types of diamond

Sample d(Å)	Lonsdaleite 2H Diamond 19-0268 d(Å)^{a,b}	8H Diamond 26-1078 d(Å)^{b}	12H Diamond 26-1082 d(Å)^{b}	20H Diamond 26-1082 d(Å)^{b}	*n*-Diamond 43-11040 d(Å)^{b}
2.17	2.09	2.184/2.165	2.15	2.18/2.14	
2.06	2.06	2.059	2.06	2.06	2.06
1.94	1.93		1.93	1.93	
1.82		1.821			1.78
1.67			1.64	1.63	
1.47	1.50				
1.32		1.316			
1.29					
1.24	1.26	1.235	1.26	1.26	1.26
1.10	1.092/1.075/1.17				
1.05	1.055/1.075	1.056			1.07
0.95		0.9618			
0.85	0.855				0.898
0.82	0.82	0.8273			0.813

[a] Ref. [1] and [2]

[b] Ref. [12]

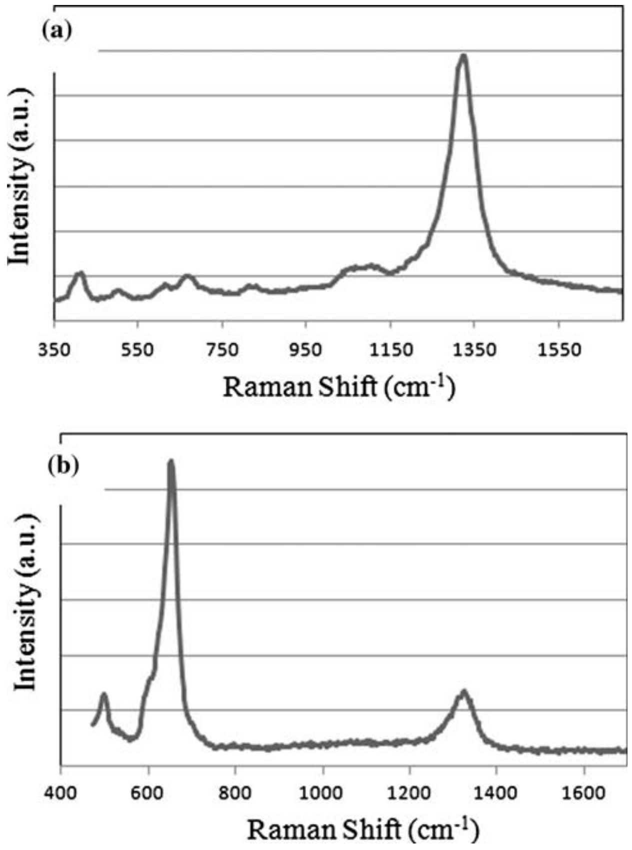


Fig. 4 Raman spectra of diamond obtained from the pyrolytic conversion of (**a**) soluble poly(hydridocarbyne); (**b**) insoluble poly(hydridocarbyne)

weight. The spectrum contains two significant peaks. One of them is a very broad peak at about 1332 cm^{-1}, the another is a broad and sharp peak at about 650 cm^{-1}. The latter is due to nanosize diamond crystals [14–17], thus it can be concluded that the size of crystals lies between nano and micrometers.

Under an optical microscope small, transparent particles, which refract light-like gem quality diamond are clearly seen (Fig. 5).

Conclusion

This work has shown that PHC can be synthesized from hexachloroethane and used as a polymer precursor in diamond production. The Raman analysis shows that crystal form may depend on molecular weight of the polymer. Ongoing research deals with the relation between the crystal form, the diamond and the molecular weight of the precursor polymer. Diamond obtained from the soluble PHC has Raman spectra contains only a single peak at 1332 cm^{-1}.

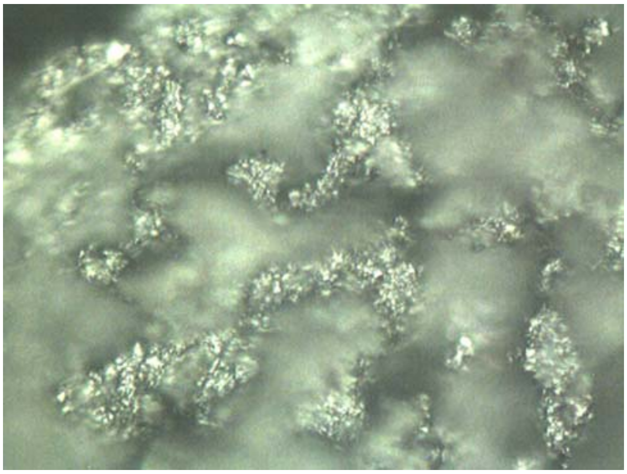


Fig. 5 Micrograph obtained by the pyrolytic conversion of poly (hydridocarbyne) using an optical microscope of magnification 50×

XRD results seems to indicate that the diamond is not a single diamond phase, but a mixture of several types of diamond.

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