

Diamond and Diamond-Like Carbon from a Preceramic Polymer

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Abstract: The synthesis of poly(hydridocarbyne), one of a class of carbon-based random network polymers and a structural isomer of polyacetylene, is reported. The network backbone of this polymer is primarily composed of tetrahedrally hybridized carbon atoms, each bearing one hydride substituent and linked via three carbon-carbon single bonds into a three-dimensional random network of fused rings. This atomic-level carbon network backbone confers unusual properties on the polymer, including facile thermal decomposition to form diamond or diamond-like carbon high-quality films at atmospheric pressure, by direct deposition or by chemical vapor deposition (CVD), without the use of hydrogen or any other reagent.

Introduction

A multitude of ways of fabricating diamond films by vapor deposition are known. All require a source of reactive hydrogen atoms, provided by hot filament, plasma, or microwave-assisted deposition. A drawback of these methods is that chemical vapor deposition (CVD) diamond films are not smooth or homogeneous enough to use in electronics or in coating for biomechanical devices such as MEMS; films must be machine-polished to attain the necessary smoothness. If highly sp^3 diamond-like carbon (tetrahedral amorphous carbon) is deposited, to exploit these films' smoothness and lubricity, their lack of purity limits their use; about 88% sp^3 carbon is the greatest percentage reported for such materials. CVD is therefore not commercially feasible for many uses, especially for large-area projects.

The preceramic polymer route to diamond films addresses these problems. Soluble polymer precursors may be cast, spun, or molded from the liquid phase, unlike any current diamond precursors, to form smooth films or conformal coatings. Pyrolysis or photolysis then converts the polymer film to a ceramic, the chemical formula of which is determined by the stoichiometry of the polymer backbone and side chains.

An efficient preceramic polymer to diamond must be high in sp^3 carbon, must contain hydrogen substituents to prevent conversion to sp^2 , and must have a high theoretical ceramic yield to obtain defect-free films. It was proposed when the

synthesis and structure of polycarbynes were first reported,¹ and has been confirmed by further research,¹⁻¹² that it is the unique sp^3 -hybridized, tetrahedrally bound carbon network backbone of this class of polymers that is responsible for their facile thermal and photolytic conversion to highly sp^3 carbon ceramics at low pressures. The composition of the polymers has, however, been problematic: the polymer most easily synthesized and studied as a precursor to sp^3 carbon is poly(phenylcarbyne), in which the phenyl groups substituted on the carbon network backbone give the polymer a 7:1 ratio of sp^2/sp^3 carbon. Thus, pyrolysis and photolysis carbon products of this polymer are composed of a high percentage of sp^2 carbon.^{1,3-12} The optimum stoichiometry for a preceramic polymer to diamond is $[CH]_n$, in which the sp^3 network backbone is functionalized only with

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hydrogen atoms; this “poly(hydridocarbyne)” would thus be a structural isomer of polyacetylene. We report here a synthetic procedure that leads to such a tractable, soluble, poly(hydridocarbyne) polymer product, and that, by thermolysis, this preceramic polymer converts to diamond and sp^3 carbon in very high yields.

Experimental Section

General Procedures. All the reactions were carried out under a nitrogen or argon atmosphere, by means of standard Schlenk manipulations or inside a glovebox. Anhydrous pentane, dimethoxyethane, and tetrahydrofuran were purchased from Aldrich and were dried over sodium metal and benzophenone and distilled prior to their use. Bromoform (99%) was purchased from VWR and used as received. Methylolithium (1.4 M in diethyl ether) was purchased from Aldrich and used as received and later titrated to correct the concentration. Liquid 1:1 mole ratio NaK alloy was prepared in a glovebox by adding solid potassium to an equimolar amount of molten sodium. *Caution! NaK alloy is pyrophoric and can be explosively reactive, especially with water and halocarbons. Handle with all necessary precautions and in inert atmospheres only.*

Elemental analyses were performed at the Microanalysis Laboratory, University of Massachusetts, Amherst, using V_2O_5 as a combustion aid. 1H NMR (200.1 MHz) spectra were recorded on a Bruker AC200, and ^{13}C NMR (75.5 MHz) spectra were recorded on an Avance DSX300 instrument. FTIR transmission spectra were obtained using a Midac M12-SP3 spectrometer, operating at 4 cm^{-1} resolution. Electronic spectra were measured using a Shimadzu UV-260 spectrometer. Raman spectroscopy was performed on a Bruker FRA-106 with a Nd:YAG laser at 1064 cm^{-1} and a JY Horiba LabRam HR800 micro Raman spectrograph operating at 785 nm. Microfocus visible Raman spectra were acquired on Kaiser Hololab 5000R Raman spectrometer utilizing a coherent continuous wave Ar ion laser operating at 514 nm. UV Raman spectra at 257 nm were collected with a single stage of a model 1400 SPEX spectrometer equipped with a Princeton Instruments model 1340-PB backthinned charge-coupled device (CCD) detector. A Coherent FRED frequency-doubled argon ion laser was used for excitation at 257 nm. After passing through a Pellin-Broca prism and spatial filter, the laser light was focused at an angle of 35° onto the sample with a spot size of approximately $10\ \mu\text{m}$. The scattered light was collected with a Coherent Ealing 0.5 NA 15 reflecting objective. The Rayleigh scattered light was rejected by a pair of Omega Optical dielectric edge filters. UV Raman spectra at 244 nm were acquired on a Spectra-Physics BeamLok 2060-7s argon ion laser whose 488 nm emission was frequency-doubled to 244 nm by the Spectra-Physic Wavetrain which uses a BBO crystal for SHG, with 0.8 mW power and an acquisition time of 30 s. UV Raman spectra at 229 nm were collected using two Renishaw microRaman 1000 spectrometers on a $40\times$ objective, with a UV-enhanced CCD camera, with 0.3 mW of power. The carbon films were treated immediately prior to the acquisition of Raman spectra by exposure to oxygen plasma (19 mW, 5 min, room temperature) to remove surface layers of adventitious C–H material, which is readily adsorbed by the films, and to avoid spurious signals in the spectra.¹³ Dynamic light scattering was performed at room temperature on an ALV instrument with an ALV5000e correlator and an argon ion laser (514 nm). Size exclusion chromatography was run at $120\text{ }^\circ\text{C}$ in DMSO on a Polymer Laboratories (Amherst, MA) PL220 GPC system with RI detector and a Wyatt (Santa Barbara, CA) high-temperature miniDAWN light scattering detector. ESR spectra were recorded on an ESP-300 electron spin resonance spectrometer (IBM Instruments Inc.). Pyrolysis studies were performed using a Thermolyne 12110 tube furnace, with samples placed in a ceramic boat. Polymer films were

spun using a Headway Research, Inc. Photo Resist spinner model 1-EC101DT-435, from a 0.2 g/mL polymer/THF solution. Film thickness and roughness measurements were obtained using a Tencor Instruments Alpha Step 500 surface profiler. Field emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDS) were carried out a JEOL JSM-6320 FXV field emission scanning electron micrograph. The XRD patterns were recorded on a Siemens D-500 diffractometer in transmission geometry with Ni-filtered $\text{Cu K}\alpha$ radiation. Atomic force microscopy was performed on a NanoScope IIIa scanning probe microscope (Digital Instruments). A JEOL 100CX scanning transmission electron microscope, equipped with an IMIX-XE PGT detector digital spectrometer (Princeton Gamma-Tech), was used for transmission electron microscopy and energy dispersive spectroscopy. X-ray photoelectron spectroscopy was performed on an ESCA 8502A, version 2.0 C instrument (Perkin-Elmer Physical Electronics Division).

Synthesis of Poly(hydridocarbyne) (1). An oven-dried 600-mL beaker was placed in a nitrogen atmosphere drybox equipped with a high-intensity (475 W, 20 kHz, 1/2 in. tip) ultrasonic immersion horn and was charged with THF (200 mL), anhydrous dimethoxyethane (10 mL), and sodium potassium alloy (NaK, 2.33 g, 37.5 mmol). The ultrasonic horn was immersed in the reaction mixture to a depth of 1 in. above the bottom of the beaker, and the solvents and NaK were irradiated at 17% power output for 5 min, producing a blue emulsion. Bromoform (6.32 g, 25 mmol) was diluted with 40 mL of THF and was added to the NaK emulsion dropwise over approximately 12 min, while being sonicated as before. During the addition, the reaction mixture heated to reflux; care was taken to control the vigor of the reaction by controlling the rate of addition of the remaining bromoform. The emulsion became dark brown upon addition of the bromoform and turned black by the end of the addition. After the addition was complete, sonication was continued for approximately 18 min. The black reaction mixture was allowed to cool and was then transferred to a shielded fume hood under ambient atmosphere. Water (5 mL) was added to the reaction mixture to quench any unreacted NaK. The solution was then decanted from white salts that had precipitated upon the addition of water, and the solvents were evaporated under vacuum. A dark brown waxy solid, combined with a white band of salts, remained. Dichloromethane (10 mL) was added, forming a dark solution with a white salt precipitate. The solution was decanted from the salts and was reduced in volume by half; hexanes (approximately 15 mL) were gradually added until a fine tan to brown precipitate of poly(hydridocarbyne), **1**, formed, which was gravity-filtered and air-dried. The polymer was typically obtained as a fine brown powder in yields of 0.15–0.28 g (46–85%). Additional polymer could be recovered by evaporating the filtrate solution to dryness, redissolving the solids in minimum dichloromethane, and precipitating with hexanes as before. 1H NMR (CDCl_3): δ 1.0–3.0 (weak, CH), 1.59, 1.25 (C–CH₃). ^{13}C CPMA NMR: δ 15 (CCH₃), 30.08 (aliphatic CH), 50–100 (broad, CBr), 114.8 (vinylic CH, cis), 138 (vinylic CH, trans). IR (THF solution, cm^{-1}) 2975 (s), 2874 (s), 2858 (s), 1458 (m), 1365 (w), 1180 (w), 1068 (vs), 911 (s), 657 (w). Anal. Calcd for (CH): C, 92.31; H, 7.69. Found: C, 65.34–70.42; H, 7.71–8.21; Br, <0.1; Li, <0.1; Na, <0.1; K, <0.1.

If the polymer product is soluble in water after the reaction is quenched as above, more bromine may need to be removed from the polymer backbone during the synthetic procedure. To accomplish this, methylolithium (5.0 mL, 0.6 M in diethyl ether) can be added to the reaction mixture after the addition and sonication of the bromoform is completed. The reaction mixture is then further sonicated for 20 min after the methylolithium addition is complete and quenched with water as above. The now water-insoluble polymer can be purified and collected as before.

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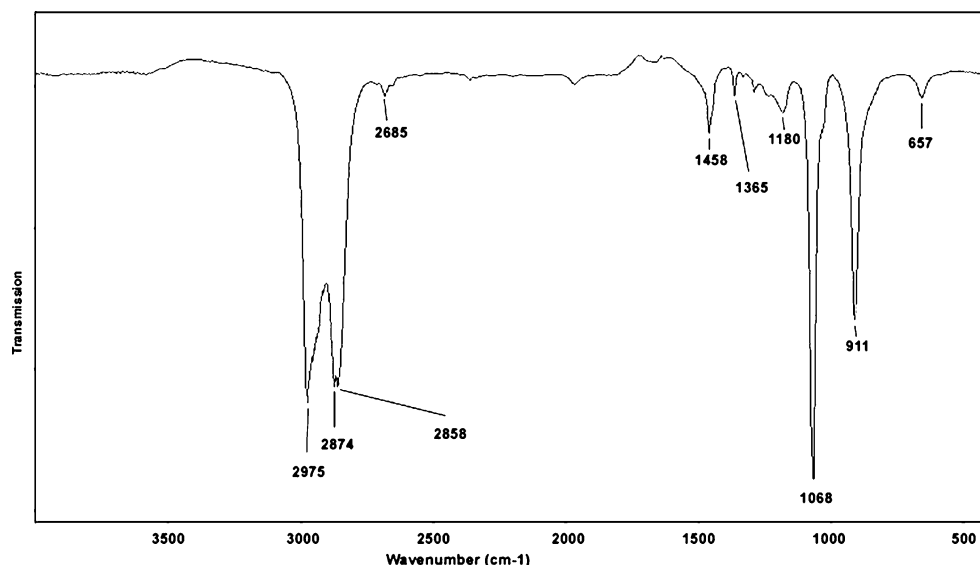
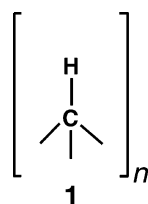
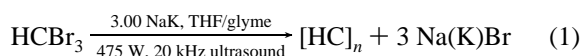


Figure 1. Transmission IR spectrum (THF solution) of **1**.

Results and Discussion

Synthesis of Poly(hydridocarbyne). Poly(hydridocarbyne) (**1**) was synthesized by the method shown in eq 1.



Successful synthesis of this polycarbyne requires some significant variation in procedures from those previously reported for carbon network backbone polymers.^{1,2} Lower ultrasound power is used, which allows a high degree of polymerization with less shearing of large polymer species, but still produces a fine enough NaK/solvent emulsion to reduce the monomer quickly and to avoid a high degree of formation of sp^2 bonds. Optimized solvent manipulation is required to achieve the best polymer product. The solvent mixture's degree of polarity determines the characteristics of the NaK/solvent emulsion and thus determines the product's molecular weight, purity, and other physical properties. Considering that the reaction conditions stated heat the solvent mixture to slight reflux, resulting in some loss of the lower-boiling solvent, the starting ratio of solvents in the reaction mixture must be carefully chosen.

Once insoluble in water (by optimized synthesis or by endcapping; see Experimental Section), poly(hydridocarbyne) is then separated from salts and from oily or oligomeric products by precipitation with hexane from a methylene chloride solution. Poly(hydridocarbyne) **1** is isolated as a dark brown air-stable solid, which is very soluble in polar organic solvents such as THF. The solutions are dark black in color and clear, with no apparent viscosity or turbidity. With optimized synthetic procedures, no high molecular weight insoluble products are formed.

Characterization of Poly(hydridocarbyne). Chemical analysis of **1** reveals that bromine and alkali metals are essentially completely removed from the CHBr_3/NaK starting materials. The percentage of hydrogen found in **1** is consistent with the presumed formula $[\text{CH}]_n$ (the hydrogen content should be somewhat higher than calculated for endcapped, methylated polymers; see Experimental Section). The very low carbon percentage is consistent with carbon analyses obtained on other high char yield preceramic network backbone polymers² and is known to be a consequence of the network backbone structure. When the polymer is heated for conversion to CO_2 during combustion analysis, some conversion to diamond and diamond-like carbon occurs, and these species are not amenable to oxidation. The conversion of the polymer to CO_2 is therefore not quantitative, and thus, the carbon analysis appears to be low. However, the low carbon analysis found for **1** is indicative that linear polyacetylene-like sp^2 bonding is not the primary structural feature of the polymer, since polyacetylene is easily analyzed to give correct carbon percentages.²² Analysis therefore is consistent with an empirical formula of $[\text{CH}]_n$ for **1**, with a predominantly network backbone, polycarbyne, structure.

The transmission IR spectrum of **1** is shown in Figure 1. The spectrum is dominated by the strong band at 1068 cm^{-1} , which arises from C–C stretching. No absorption characteristic of cis-carbon–carbon double bonds (ca. 1600 cm^{-1}) is seen. Carbon–hydrogen bond stretches in the IR spectrum of **1** appear at 2975 and 2874 cm^{-1} , indicating that the hydrogens are present on aliphatic (sp^3) carbons. The 911 cm^{-1} absorption seen in the IR spectrum of **1** could arise from a variety of C–H vibrations. No C–Br stretches are seen; methyl groups (added as polymer-capping groups during the synthesis), evidenced by absorptions at 1458 and 1365 cm^{-1} , are the only identifiable chemical functionalities. IR spectra, therefore, also indicate a primarily network backbone structure for **1** of $[\text{CH}]_n$ formula.

Raman spectroscopy of **1**, at visible and even at IR excitation wavelengths (514 , 785 , and 1064 nm) gives only strong luminescence; no Raman spectrum can be seen (Figure 2a). This luminescence behavior is seen in all other polycarbyne network polymers^{1,2} and demonstrates that **1** is not primarily of the polyacetylene structure, since Raman spectra of polyacetylene,

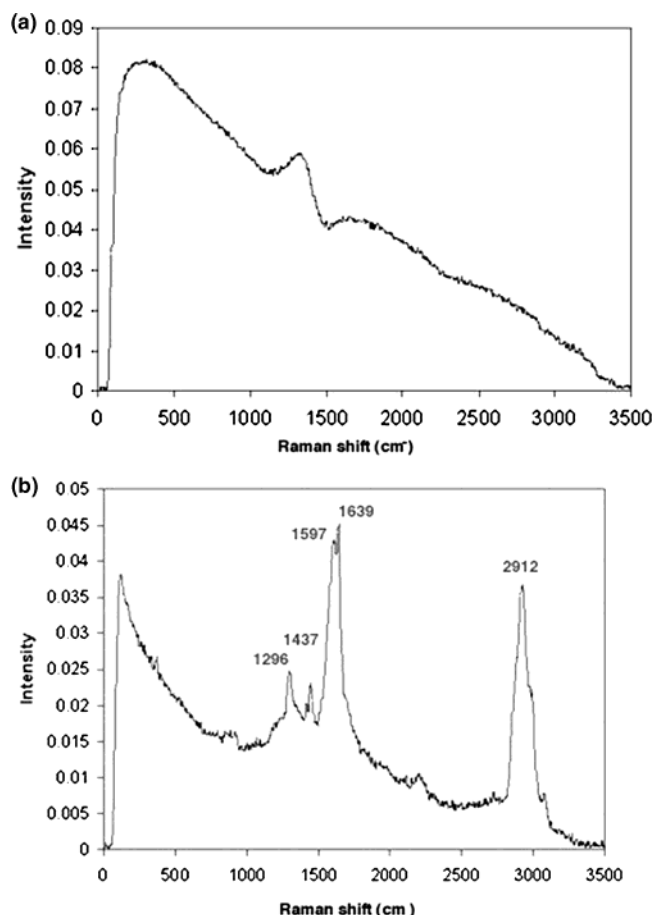


Figure 2. Raman spectra of **1**. (a) Raman spectrum of **1** at excitation wavelength of 1064 nm. (b) Raman spectrum of poor-quality **1** at excitation wavelength of 1064 nm.

not masked by luminescence, can easily be acquired using visible excitation wavelengths.¹⁴ The polycarbyne luminescence arises from the network structure of the backbone: Raman of the oily solids that result from nonoptimized syntheses of **1** gives spectra with bands at 1597 and 1639 cm^{-1} , showing incorporation of $\text{C}=\text{C}$ functionalities into the polymer backbone (Figure 2b).

At room temperature, poly(hydridocarbyne) exhibits an ESR signal indicative of a carbon-centered radical ($g = 2.0042$, peak-to-peak line width 8.5 G; Figure S2). The peak-to-peak width of the ESR signal of polyacetylene (0.95 G for trans, 7.2 G for cis, $g = 2.00263$)¹⁵ is associated with the freedom of movement of the solitons on the polymer backbones. The larger peak-to-peak width of the signal of **1** may indicate limited electron mobility, as do larger peak-to-peak line widths in polyacetylene.

In consequence of these unpaired spins, ^1H NMR spectra of **1** (Figure S3a) show only a very weak and broad baseline resonance in the 1–3 ppm region (often not detectable) that arises from the hydrogens directly bound to the paramagnetic, rigid, network backbone. This is in contrast to proton spectra of polyacetylene, which are readily detectable¹⁶ Sharp peaks in the 1 to 2 ppm region that may arise from methyl edge groups. Carbon CPMAS (Figure S3b) spectra of **1** show as the primary

feature an intense, broad, resonance centered at approximately 30 ppm (Figure S3) that arises from the C–H groups of the aliphatic network backbone.¹⁷ A peak at 15 ppm may indicate the presence of methyl edge groups. A broad resonance between 50 and 100 ppm arises from residual C–Br sites. The resonance of trans-polyacetylene structure appears at its reported chemical shift of 138 ppm, and cis-polyacetylene structure is assigned to the resonance at 114 ppm (this peak may appear at higher field than the reported value of 126 ppm due to lack of conjugation). Sideband suppression solid-state carbon NMR (Figure S3c) reveals the three major peaks more clearly, with lessened signal intensity due to paramagnetic relaxation. The resonance at 180 ppm (masked by a sideband in the CPMAS spectrum) may arise from carbonyl groups that form by reaction of ambient oxygen and water with carbon backbone radicals.

Spectroscopy and analysis of **1** indicate a formal stoichiometry of $[\text{CH}]_n$ predominantly bonded in an sp^3 overconstrained network of fused rings, similar to other reported polycarbynes. Poly(hydridocarbyne) is therefore a geometric isomer of the linear, sp^2 -bonded polymer of the same empirical formula: polyacetylene. Although the empirical formulas of these two polymers are identical, the predominant sp^3 versus sp^2 hybridizations of their backbones result in very different chemical and physical properties. Poly(hydridocarbyne) shows much more resemblance to the extended networks of saturated carbon–carbon bonds, known as “compressed benzene” or “polymeric amorphous hydrogenated carbon”, which are produced by pressurizing benzene or by chemical vapor deposition using benzene.^{18–24} These materials have high hydrogen contents^{20,21} and show efficient room-temperature photoluminescence¹⁸ that prevents the acquisition of Raman spectra using visible wavelengths.^{18,21,22} Some are reported to be yellow-orange to brown in color,²¹ and their electronic²³ and IR spectra^{18,21–24} are nearly identical to those of poly(hydridocarbyne), with one exception. The IR spectra of these cross-linked polymeric materials are dominated by the aliphatic C–H stretching bands between 2850 and 2920 cm^{-1} ,²¹ while the IR spectrum of **1** also shows the very intense band at 1068 cm^{-1} , indicative of a much greater degree of sp^3 C–C bonding. The very extensive carbon–carbon-bonded network backbone of **1**, versus the more limited cross-linking formed by the compression or vapor deposition of benzene, accounts for this difference.

Poly(hydridocarbyne) was determined to be a macromolecular species by size exclusion chromatography and dynamic light scattering. The (lower-molecular weight) portion of the DMSO colloidal suspension of **1** that can pass through a 0.25 μm frit was examined by size exclusion chromatography at 120 $^\circ\text{C}$. Absolute M_w maxima between 200,000 and 2.6 million daltons, with polydispersities between 1.0 and 2.0, were found. Dynamic light scattering in THF solution at room temperature shows two

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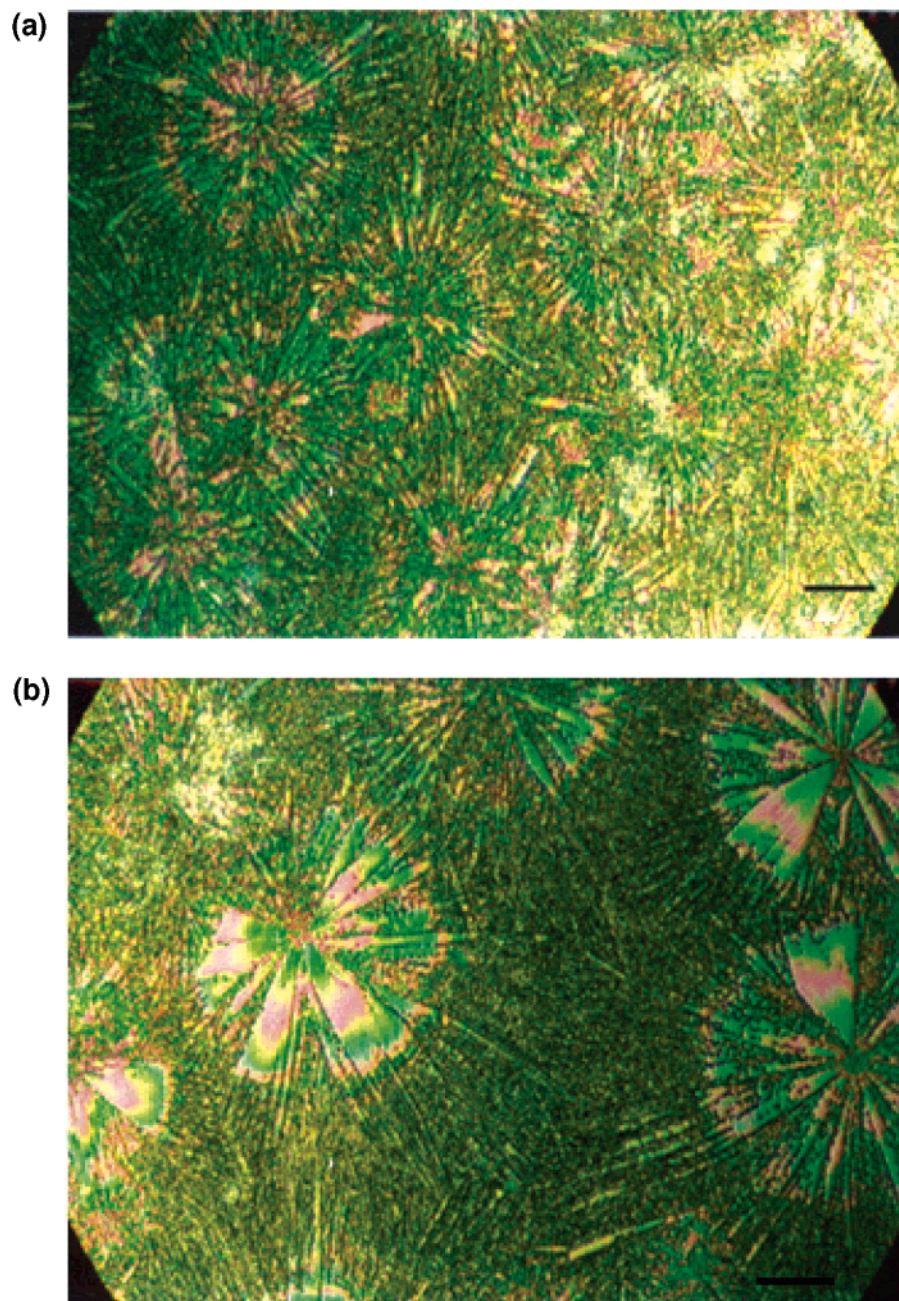


Figure 3. Optical micrographs (under crossed polars) of diamond-like carbon film produced from poly(hydridocarbyne) on a silicon substrate. Processing conditions: polymer film pyrolyzed at 0.2 °C/min from room temperature to 450 °C, held for 9 h, cooled, reheated under hydrogen to 1120 °C, and held for 2 h. (a) Scale bar = 30 μm . (b) Scale bar = 50 μm .

distinct size regimes of colloidal particles, with hydrodynamic radii of 30 nm and 3 to 4 μm , respectively. From these data, the exact M_w , M_n , and other molecular weight and size parameters of poly(hydridocarbyne) cannot be specified with accuracy, but obviously poly(hydridocarbyne) is present in solvents as large, colloidal aggregates or particles.

Conversion of Poly(hydridocarbyne) to Diamond and Diamond-Like Carbon. A typical thermal gravimetric analysis of poly(hydridocarbyne), heated in inert atmosphere at a ramp rate of 10 °C per minute, shows that mass loss begins at 185 °C and that the polymer is heated to a constant weight by 600 °C. These are typical conversion temperatures, but all conversion properties, including decomposition temperatures and conversion yield, are seriously dependent on the pyrolysis processing

conditions, especially the polymer's molecular weight, the physical form of the polymer (powder or film), any pretreatment of the polymer (for example, photo-cross-linking), and ramp rate.

Poly(hydridocarbyne) films of approximately 2 μm thickness (by profilometry) can be spun onto silicon substrates at a speed of 1000 rpm for 5 min from a 0.2 g/mL THF solution. These films were then pyrolyzed under various temperatures and at various ramp rates, all under argon or a selected reactive atmosphere. Typical pyrolysis conditions are a dynamic argon atmosphere, 1 °C/min ramp rate, from room temperature to 800 °C or to 1100 °C. For optimum coverage of the substrate and smoothness of the resulting carbon film, ramp rates of 0.1 °C/min were used.

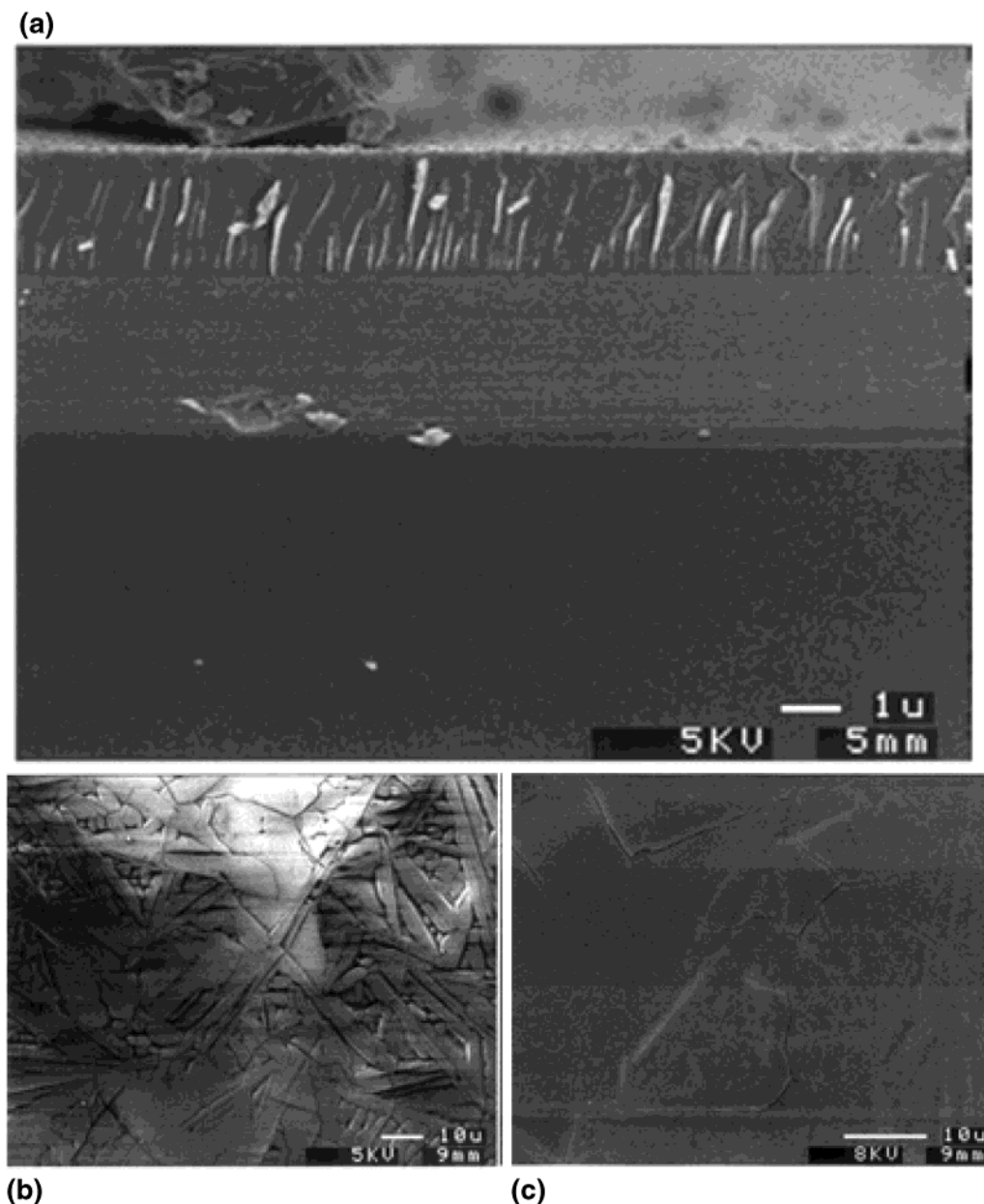


Figure 4. Field emission scanning electron micrographs of diamond-like carbon film on silicon substrate (a) cross-sectional view (gold-sputtered), (b) without gold sputtering, and (c) with gold sputtering. Processing conditions are the same as for Figure 3.

After pyrolysis, both sides of all substrates were found to be coated with carbon films, the characteristics of which (smoothness, thickness, completeness of coverage, and degree of crystallinity) depended strongly upon the characteristics of the polymer precursor and on the conditions of the pyrolytic processing. All the carbon films appear to the eye only as a rainbow sheen on the black silicon substrates; by optical microscopy, the carbon films again appear rainbow-like or transparent.

A pyrolytic carbon film on silicon was examined by optical microscopy under crossed polars and is shown in Figure 3. The film appears continuous, and the polarized light indicates various apparent crystalline regions and apparent topography.

Field-emission scanning electron microscopy of the same sample (Figure 4b) again shows apparent topography, though charging effects, caused by the insulating properties of the film, dominate. When this sample was sputtered with approximately 10 Å of gold, it was seen that the film is in fact featureless

(Figure 4c); what appeared to be topography are different regions of crystallinity, density, or degree of electron charging. The carbon film is extremely smooth: tapping mode AFM done on a $5\ \mu\text{m} \times 5\ \mu\text{m}$ area and on a $40\ \mu\text{m} \times 40\ \mu\text{m}$ area shows that the R_q of the surface is approximately 50 nm (Figure S4). Profilometry of this sample over a distance of 2 mm shows a similar R_q of 525 Å. The carbon film is much smoother than most CVD diamond films, and on the order of smoothness of tetrahedral amorphous carbon films. Both AFM tapping mode height and phase images show no regular features or topography in the film, and no apparent variations of phase. X-ray photoelectron spectroscopy of the film shows only carbon, with oxygen atmospheric contaminants adsorbed on the surface, with the C1s peak at 285.7 eV, indicative of sp^3 carbon.

Infrared spectroscopy confirms that oxygen is present only as an adsorbate on the carbon film's surface (Figure 5). No

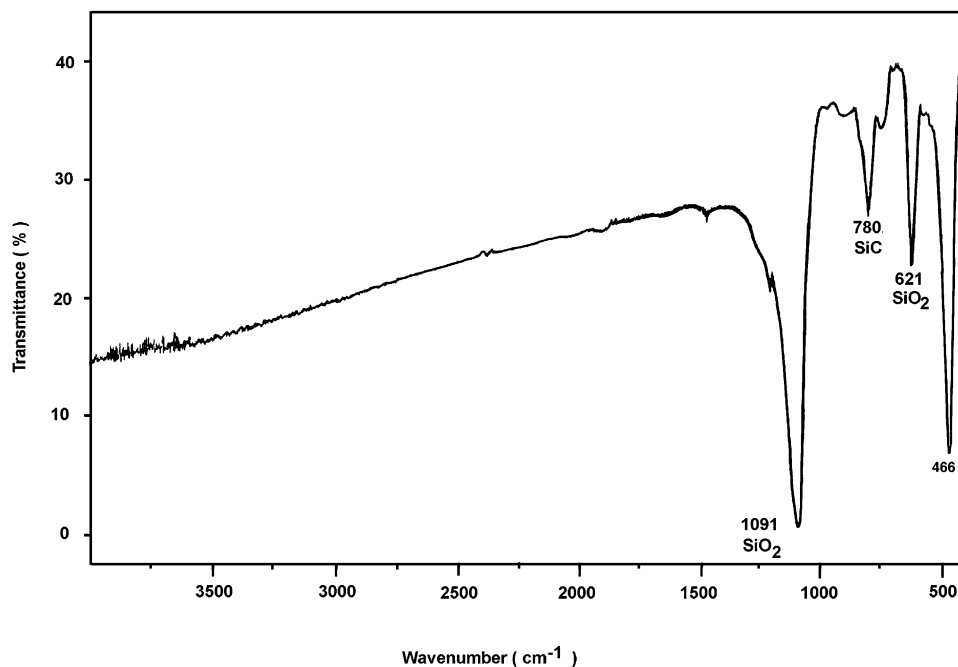


Figure 5. Transmission IR of diamond-like carbon film on silicon substrate. Processing conditions are the same as for Figure 3.



Figure 6. Optical micrograph (under crossed polars) of crystals formed on a diamond-like carbon film produced from poly(hydridocarbyne) on a silicon substrate. Processing conditions: thermolysis under argon to 1000 °C, ramp rate of 0.1 °C/min, held at 1000 °C for 24 h, and cooled to room temperature at 0.1 °C/min. Scale bar = 50 μm.

C–O–C or carbonyl vibrations were detected; oxygen is seen only as silica. A band characteristic of SiC, not seen in blank substrates, appears at 780 cm^{-25} in many samples; no identifiable C–Br stretches are seen. No absorptions in the 1500–1700 wavenumber region, characteristic of cis-C=C bonds, are seen, confirming the lack of sp^2 carbon in this film. Elemental analysis verifies this finding: no carbon or hydrogen is detected in the films by combustion analysis, suggesting that the films are highly sp^3 carbon. By IR spectroscopy, the diamond-like carbon produced from the poly(hydridocarbyne) precursor is

much more pure than that produced from the previously studied poly(phenylcarbyne) precursor, especially in the former's complete lack of bands attributable to OH, CH, C=O, and C=C species.²⁶

A cross section of the fracture edge of a cleaved carbon film on silicon was examined by field-emission scanning electron microscopy (Figure 4a). The carbon films obtained from **1** are between approximately 700 nm and 1.7 μm in thickness, as demonstrated by EDS line analysis (Figure S5). A layer of silicon carbide also appears, located between the carbon film and a layer of silica.

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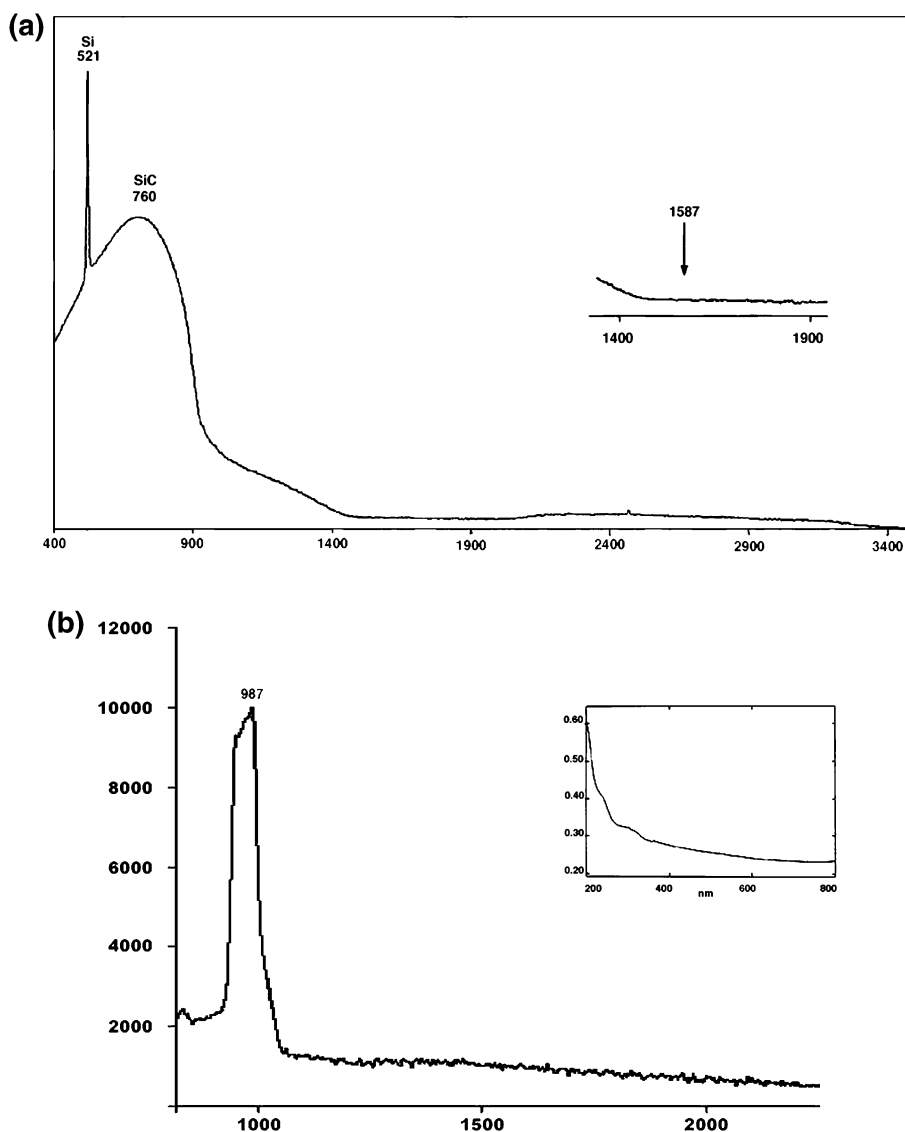


Figure 7. IR and visible Raman spectra of a diamond-like carbon film produced from poly(hydridocarbyne) on a silicon substrate. Processing conditions: 0.2 °C/min to 800 °C, held for 24 h, argon atmosphere. (a) Irradiation wavelength = 1064 nm. (b) Irradiation wavelength = 514 nm. Inset: electronic spectrum of diamond-like carbon produced from poly(hydridocarbyne), quartz substrate.

Known procedures for increasing the crystallinity of deposited films, such as scratching the substrate, addition of diamond or SiC seed crystals to the polymer solution, and ultrasonic or other abrasion of the substrate with seed crystals, all increase the crystallinity of the resulting films, and different processing methods produce other types of film morphologies. Often, if sites for nucleation are provided, large crystals are seen (Figure 6). Before thermolysis, a scratch was made only in the polymer film (not in the substrate) of this sample. That crystals nucleate along this scratch suggests that the scratch in the polymer film is preserved in the carbon ceramic.

Raman spectroscopy of the carbon films produced from **1** reveals that the films consist almost entirely of sp^3 carbon, both crystalline and amorphous. No bands are seen in the 2900–3100 cm^{-1} or the 2100–2300 cm^{-1} regions, indicating the absence of C–H bonds and C–C triple bonds. A Raman spectrum at the IR irradiation wavelength of 1064 nm is shown in Figure 7a. The resonance of the substrate is seen at 521 cm^{-1} ,

and a broad and intense band, characteristic of silicon carbide, appears at 760 cm^{-1} .^{27,28} The broad feature between 900 and 1400 cm^{-1} at this irradiation wavelength is a possible indicator of sp^2 carbon.²⁹ However, both Si and SiC have Raman bands in this region, at 950–1050 cm^{-1} and 973 cm^{-1} , respectively, which contribute to this feature.^{27,28} This Raman irradiation wavelength selectively detects sp^2 structure over sp^3 and can detect even small amounts of amorphous carbon in well-crystallized diamond films.^{29,30} However, the spectrum of the diamond-like carbon film displays no resonances at all between 1500 and 1700 cm^{-1} (the G band region; see inset, Figure 7a), the frequency regions for C=C stretching of graphitic carbon and of isolated carbon–carbon double bonds, respectively.³¹

Raman spectra of carbon films produced from **1** acquired at the visible laser irradiation wavelength of 514 nm (Figure 7b)

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again show no bands in the G or D region, indicating the absence of sp^2 carbon. At this laser irradiation wavelength, sp^2 carbon has such a high cross section that sp^3 components are not visible; hence, Raman spectra acquired at this wavelength monitor the state of sp^2 -bonded materials only.^{29–35} The intensity of the silicon second-order band at 987 cm^{-1} indicates the high transparency at this visible wavelength of the carbon film,^{31–33,36} an indication of a high degree of sp^3 bonding and a low degree of sp^2 clustering.^{31,32} The transparency of the diamond-like carbon produced from **1** is confirmed by electronic spectroscopy, shown in the insert in Figure 7b. This degree of transparency in the visible region appears to be among the highest of those reported for tetrahedral amorphous carbon.^{37,38}

In Raman spectroscopy at ultraviolet irradiation wavelengths, sp^3 and sp^2 carbon vibrational states are equally enhanced, and Raman spectroscopy of carbon materials at these wavelengths provides an evenly weighted probe of sp^2 and sp^3 sites.^{29,31–35,39–41} In Raman spectra of carbon films produced from **1** acquired at the UV irradiation wavelength of 244 nm (Figure 8a), a sharp intense band at 1087 cm^{-1} , characteristic of sp^3 C–C bonding, appears. This “T-band”³⁹ has been observed in the spectra of tetrahedral amorphous carbon films; however, the T-bands of these samples are much sharper and more intense than those reported for other highly sp^3 carbon materials. Again, no well-defined resonance in the G region ($1500–1700\text{ cm}^{-1}$) region is discernible, another departure from the reported UV Raman spectra of highly sp^3 carbon films and another indication of extremely low sp^2 content. In the UV Raman spectra of highly sp^3 carbon materials, the position of the T band has been used to estimate sp^3 content;^{31,34,40,42,43} a T-band at 1087 cm^{-1} was found to be characteristic of approximately 86% of sp^3 carbon.^{31,42} The lack of a G-band, however, and the transparency of the film to this wavelength (as evidenced by the appearance of the silicon carbide band), suggests a much higher sp^3 percentage.

The sharp 1087 cm^{-1} T-band shown in Figure 8a is sometimes superimposed on a broader resonance centered at approximately 1180 cm^{-1} (Figure 8a). This feature is not seen in the visible Raman spectra, nor is it accompanied by a ca. 1450 cm^{-1} band;⁴⁴ it thus may represent the E_{2g} mode of hexagonal diamond^{45–51} (see below).

In the most highly crystalline films produced from **1**, UV Raman spectroscopy reveals the presence of hexagonal diamond.

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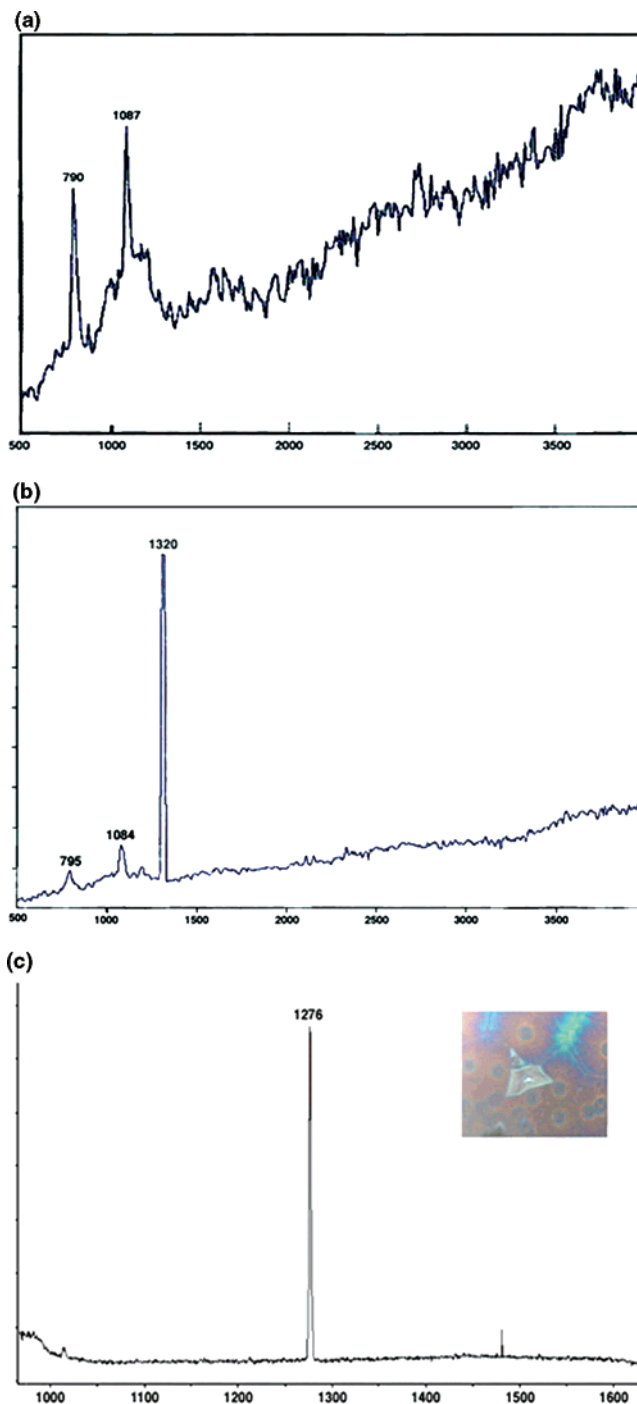


Figure 8. UV and near-IR Raman spectra of diamond and diamond-like carbon films produced from poly(hydridocarbyne) on silicon substrates. (a) UV Raman (244 nm) of a diamond-like carbon film. (b) UV Raman (244 nm) of hexagonal diamond. Processing conditions: argon atmosphere, $1\text{ }^{\circ}\text{C}/\text{min}$ to $1170\text{ }^{\circ}\text{C}$, held for 121 h, heated in air to $1300\text{ }^{\circ}\text{C}$, and held for 24 h. (c) Near-IR Raman (785 nm) of the crystal shown in the insert. Processing conditions are the same as in Figure 7.

The 244-nm Raman spectrum of such a film is shown in Figure 8b. The sharp band observed at 1320 cm^{-1} is characteristic of the A_{1g} mode of hexagonal diamond;^{45–51} this identification was confirmed by X-ray diffraction: weak diffraction features appear, which are absent from films not treated at high

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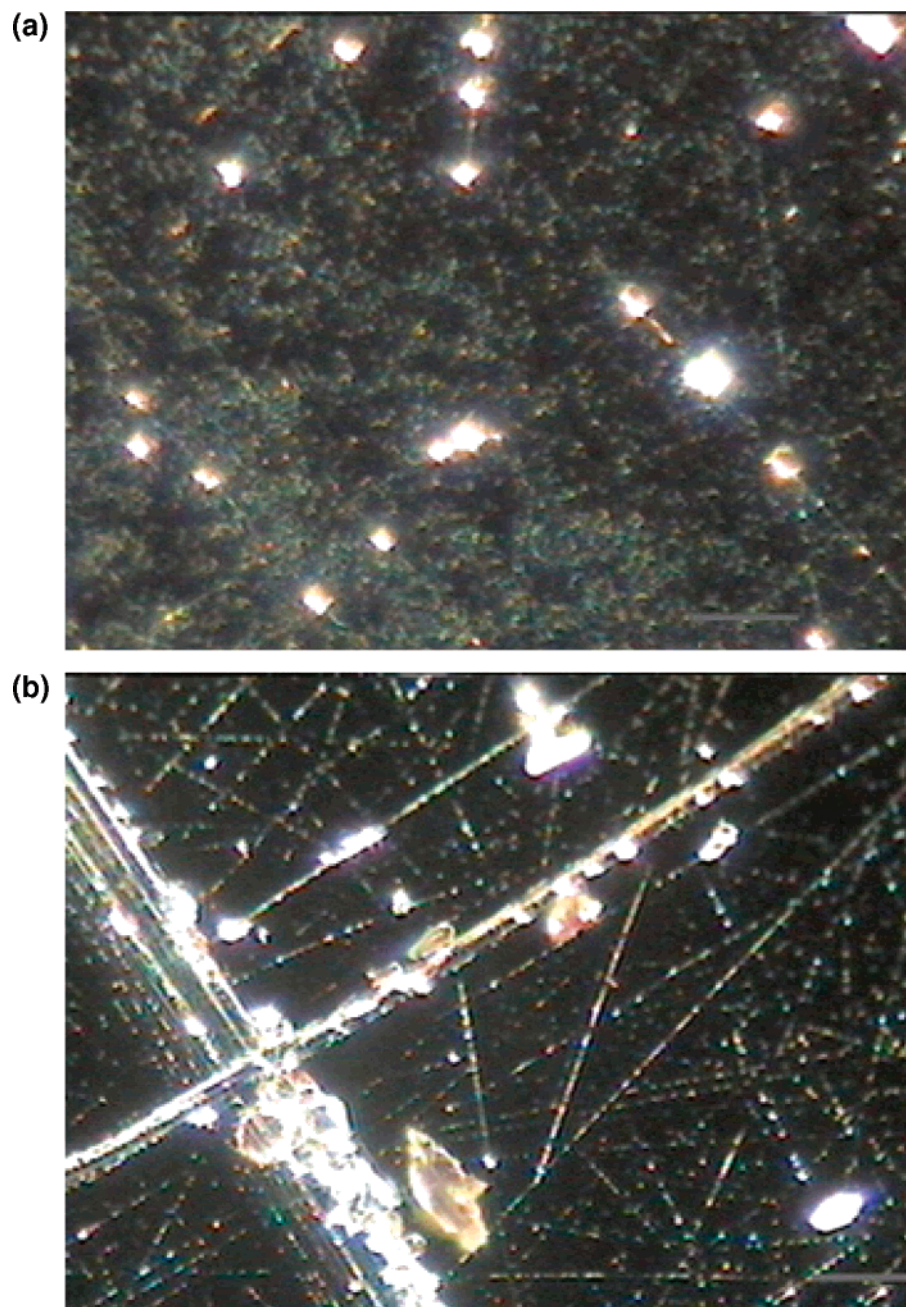


Figure 9. Optical micrographs (under crossed polars) of diamond-like carbon produced from poly(hydridocarbyne) on silicon substrates. (a) Diamond-like carbon film on a silicon substrate produced from a film of poly(hydridocarbyne). (b) Diamond crystals produced by chemical vapor deposition from poly(hydridocarbyne) on a blank silicon substrate. Scale bars = 50 μm .

temperatures, that correspond to one or more known phases of hexagonal diamond (Figures S6–S8).^{48–50,52,53} In UV Raman spectra of the most highly crystalline regions of some films (at irradiation wavelengths of 244 and 257 nm), bands at approximately 1164 cm^{-1} (broad) and 662–667 cm^{-1} (sharp) also appear; these may represent the E_{2g} and E_{1g} bands of the hexagonal diamond.^{45–51}

Multiwavelength Raman spectroscopy therefore indicates that the carbon films produced by pyrolysis of **1** consist of very pure sp^3 carbon and that, with some processing conditions, diamond can be produced. These conclusions are confirmed by

all other characterization techniques employed. The optimization of the polycarbyne structure, shown by the very different carbon products obtained from pyrolysis of poly(hydridocarbyne) and the prototype poly(phenylcarbyne),^{1,3–12} demonstrates that tailoring of a polymer's chemical formula gives designed

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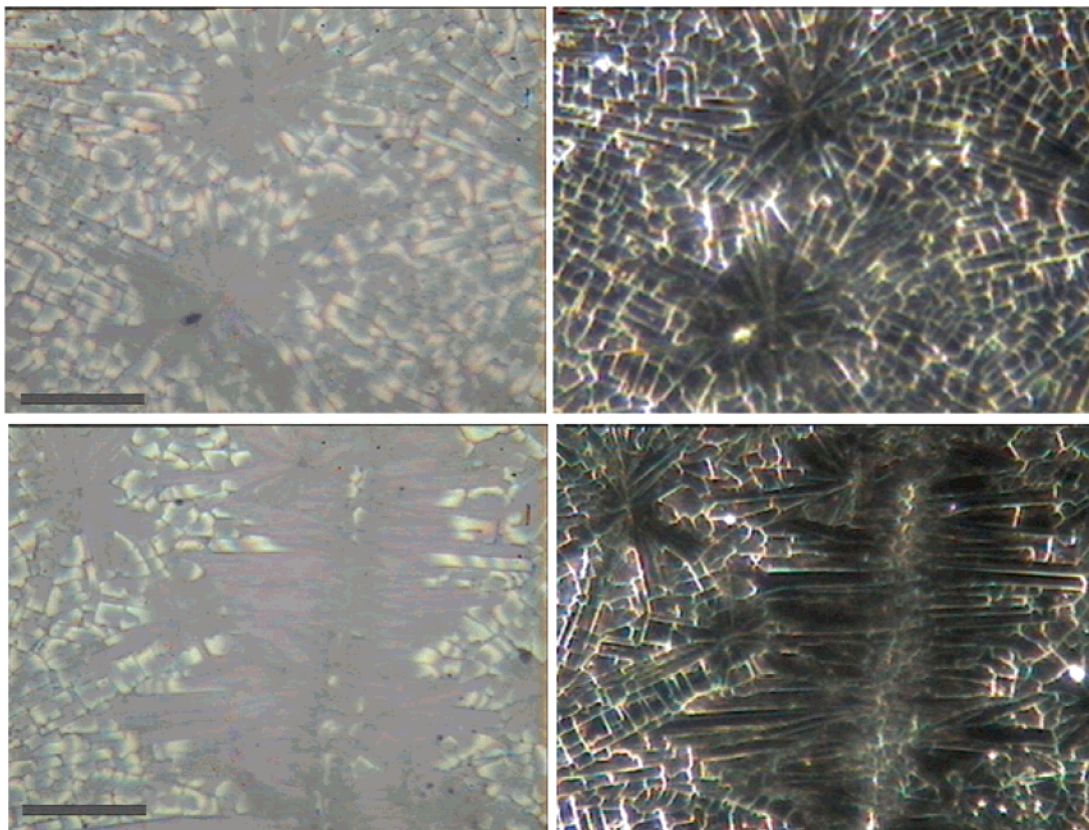


Figure 10. Optical micrographs (left, nonpolarized light; right, under crossed polars) of the hexagonal diamond on silicon produced by chemical vapor deposition using poly(hydridocarbyne) as a precursor. Scale bars = 50 μm .

ceramics; thus, the designed inclusion of other elements into the backbone or side chains of this polymer would produce carbon-based ceramics of designed material properties. Also, these results demonstrate that the nanostructure of a precursor can be manipulated to determine the structure of product, even if that product is thermodynamically metastable.

An unusual feature seen in some of the Raman spectra of carbon films obtained from **1** is a sharp resonance appearing between approximately 1250 and 1270 cm^{-1} . An example is shown in Figure 8c; the insert shows the micrometer-dimension crystal on which the micro-Raman beam was focused for this acquisition. The narrow fwhm of these resonances shows that they arise from crystalline materials. We conclude that this band arises from a form of crystalline carbon, perhaps previously unknown, as this is a previously unreported frequency region for the Raman resonances of diamond-structured carbon. The frequencies of the Raman resonances of diamond are, however, known to be shifted by a variety of causes, such as pressure,⁵⁴ stress,⁴¹ laser damage,⁴⁰ etc.; the shift to the 1250–1270 cm^{-1} region that we observe may also be due to some or all of these factors.

Poly(hydridocarbyne) is also a precursor to CVD diamond by simple heating, without addition of hydrogen or any activation procedure. This was demonstrated by placing a blank, scratched, silicon substrate downstream in a pyrolysis tube from a similar substrate that was coated with a film of poly(hydridocarbyne). The samples were then heated to 800 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$ under dynamic argon and held at that temperature for 24 h. As shown in Figure 9a, the polymer coat on the

substrate converts to a carbon film with some isolated crystals nucleated on the surface. The blank, however (Figure 9b), displays only isolated crystals along the scratches of the substrate, which are the result of the nucleation of vapor-deposited polymer, or polymer fragments. The electron diffraction patterns of these crystals again show reflections characteristic of a phase of hexagonal diamond (Figure S9).

That poly(hydridocarbyne) can be used as an efficient precursor to CVD films was shown by a minor alteration in the polymer processing conditions. Poly(hydridocarbyne) was placed as a powder in a ceramic boat, and the boat and its contents were heated under dynamic argon at 10 $^{\circ}\text{C}/\text{min}$ to 1100 $^{\circ}\text{C}$ and held there for 12 h. A blank, scratched silicon substrate was placed downstream of the ceramic boat. The polymer, under these processing conditions, was completely vaporized; none remained in the ceramic boat. However, both the pyrolysis tube and the silicon substrate were coated with a bright white-colored carbon film.

This material was found to be carbon by XPS, but showed no detectable carbon, hydrogen, or silicon by combustion analysis; this resistance to oxidation demonstrates that the carbon is highly diamond-like. Optical microscopy shows that, along the scratched surfaces of the silicon substrate, large clusters of crystals have formed (Figure 10). Raman spectroscopy at 514 nm and X-ray diffraction analysis (Figure S9) again reveal no resonances for sp^2 carbon and diffraction features characteristic of a phase or phases of hexagonal diamond, respectively. Thus, use of poly(hydridocarbyne) may represent a means of fabricating CVD films, which may in its ease and simplicity rival

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current methods of CVD carbon film production, and may make CVD economically viable.

Conclusions

Poly(hydridocarbyne), a carbon network backbone polymer that is a structural isomer of polyacetylene, has been synthesized and characterized. The predominant structural feature of the polymer's backbone is a network of sp^3 CH units that are linked via three carbon-carbon single bonds into a continuous random network. The polymer exists as nanoparticles or as colloidal aggregates in solution. This synthetic optimization of the side chain functional groups of the network backbone structure of polycarbynes has been shown to allow a designed polymer to be an excellent precursor to smooth, high-quality films of pure sp^3 carbon and to produce diamond. The conversion of this new precursor to carbon ceramic that is reported here is by no means optimized; the usefulness of this method of carbon film production could be greatly enhanced by employing polymer processing techniques more sophisticated than simple pyrolysis, such as conversion of the precursor to ceramic by laser irradiation, flash heating, and many others. That continuous films of highly sp^3 carbon, or even of diamond, can be easily fabricated from a polymer precursor opens up many possibilities for the use of carbon/diamond films in materials science. Application of a diamond or diamond-like carbon film from the liquid phase (or possibly from a supercritical fluid) is currently not possible with any other diamond fabrication technique; it will allow for the conformal coating of previously impossible or inconvenient substrates, such as very large or complex shapes, MEMS and other biomechanics, and electronic

devices. The ease and simplicity of the technique, both direct deposition and CVD, will possibly render both methods cost-effective for a wide variety of applications, even of large or low-cost items. Now that it has been shown that diamond can be both p- and n-doped, its use in electronics will escalate; the simplicity and manipulability of this precursor will allow many fabrication options in new diamond-based electronic devices.

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Supporting Information Available: Electronic, ESR, 1H - and ^{13}C NMR spectra of poly(hydridocarbyne) and AFM, EDS, X-ray, and TEM analysis of carbon films (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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