The Electrochemical Synthesis of Poly(methylcarbyne) for Diamond Film Coatings

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ABSTRACT: The polycarbynes are polymeric precursors that can be used in the synthesis of both diamond films and powders. They are soluble in common organic solvents; therefore, they can be coated on any surface in various thicknesses and then converted to diamond via sintering. Polycarbynes can be synthesized in a simple undivided electrochemical cell so their synthesis are both cheap and easy. Here, we report the electrochemical synthesis of poly(methylcarbyne). The poly(methylcarbyne) was characterized using UV/visible spectroscopy, Gel Permeation Chromatography and ATR FTIR, ^1H NMR, ^{13}C NMR spectroscopies. The polymer was converted to diamond via sintering and characterized by Optical microscopy and Raman and X-ray spectroscopies. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3626–3632, 2012

Key words: coatings; diamond; electrochemistry; polycarbynes; sintering

INTRODUCTION

Scientists have carried out research on the synthesis and applications of diamond for decades due to its well-known chemical and physical properties; like hardness, chemical inertness, and low friction coefficient.[1,2] Due to these properties, diamond finds use in many high technology applications ranging from electrical[3] to biomedical.[4] They are useful materials for MMEs,[5] inkjets for corrosive liquids,[6] and as a stable platform for chemical and DNA sensing.[7] However, diamond is a difficult material to work with, especially if you want to prepare a diamond film on a surface. Thus, several methods are used to overcome the difficulties, some of which are combustion flame,[8] chemical vapor deposition (CVD),[9] physical vapor deposition (PVD),[10] and the use of polymeric precursors.[11–14] In the first method, diamond crystals are nucleated by combustion flame on tungsten. CVD and PVD are well-established ways to produce diamond/DLC films on a surface. However, these techniques do not have wide commercial application since they require complex and expensive instrumentation.[13–16] The use of polymeric precursors to diamond, known as polycarbynes, have aroused interest among researchers owing to the facile synthesis of polymers, the solubility of polymers in common solvents, and the ability to control the polymer film thickness on the surface. The polymers can be converted to diamond via sintering under inert and ambient atmospheres.[15]

Poly(methylcarbyne) (PMC), poly(phenylcarbyne) (PPC), and poly(hydridocarbyne) (PHC) are the previously synthesized polymeric precursors that can be used for diamond production. These precursors can be produced via sonochemistry,[15] Grignard reagents,[16] or electrochemistry.[11] The Electrochemical method is a patented method by Toppare and Pitcher[17] to produce these polymeric precursors.[17] This method is much easier and cheaper than others and it is possible to scale up commercial production of those polymers, potentially being used by both industry and by scientists with access to fairly rudimentary laboratory equipment.

EXPERIMENTAL

Materials

1,1,1-Trichloro ethane (CH_3CCl_3) (Merck), acetonitrile (AN) (Merck), tetrahydrofuran (THF) (Merck), tetrabutylammonium tetrafluoroborate (Aldrich),

Lithium Aluminumhydride ($LiAlH_4$) (Merck), 430-stainless steel. All reagents were used as received.

Equipments

The polymerization reaction was monitored using an HP8453A UV/visible spectrometer (UV/Vis). Gel Permeation Chromatography (GPC) was performed on a PerkinElmer Series 200 apparatus with a refractive index (RI) detector using TSK gel AM GPC Gel column with N,N-dimethylformamide eluent at a flow rate of 1.0 mL/min and calibrated via polystyrene standards. ATR-Fourier Transform Infra Red (ATR-FTIR) spectra were collected using Bruker Alpha-T brand 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. Elemental analysis was performed with LECO, CHNS-932 brand instrument 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 nitrogen. JEOL JSM-6400 model SEM was used for looking at the diamond film formed on surfaces. X-ray Powder patterns (XRD) were taken with a Rigaku Miniflex Diffractometer and Cu Kα (30 kV, 15 mA, λ = 1.54051 Å) radiation. Scanning was done between $5° < 2\theta < 140°$. All measurements were made with $0.05°$ steps and a $0.5°$/min rate. The divergence slit was variable, and the scattering and receiving slits were $4.2°$ and 0.3 mm, respectively.

Synthesis of poly(methylcarbyne)

The synthesis of poly(methylcarbyne) was carried out using a similar method as reported previously.[11] A 1.2M 1,1,1-trichloro ethane (CH_3CCl_3) solution (in acetonitrile (AN)) was electrolyzed in the presence of 0.1M tetrabutylammonium tetrafluoroborate (AN solution). Electrolyte–solvent couple (150 mL) was placed in a undivided cell equipped with a 430 stainless steel cathode (10 cm × 8 cm × 0.5 mm) and anode (10 cm × 8 cm × 0.5 mm). Electrolysis was run at −6.0 V for 4 h, at room temperature in a fume hood. After electrolysis, the insoluble material (presumed to be a higher molecular weight polymer) is filtered from the solution and AN was then evaporated and a reddish brown powder was obtained. This powder was washed with brine. NMR and elemental analysis shows this material to contain PMC and both supporting electrolyte and chlorine.

After the powder was washed with brine and dried under vacuum, tetrahydrofuran (THF) dried over sodium and benzophenone was used to dissolve the reddish 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 (containing supporting electrolyte) precipitates from the solution and is removed. Evaporation of the THF from the solution again yields a reddish brown powder (6–10%) in which our characterization data shows to be pure poly(methylcarbyne) with no presence of C=C, C—O, C=O, C—Cl, etc.

^{1}H NMR ($CDCl_3$), δ (ppm from **1**): 2.01 and δ (ppm from **1** due to cyclopropane end group): 0.5 to 0.3.

^{1}H NMR ($CDCl_3$), δ (ppm from **2** due to CH): 1.5 and 1.2 δ (ppm from **2** due to cyclopropane end group): 0.5 to 0.3.

^{13}C NMR ($CDCl_3$), δ (ppm from **2** due to quaternary C and H of methyl group): 48, 44, 37, and 28.

Elemental analysis: calculated for **2**: C, 88.9; H, 11.1%. Found: H and C: low and variable.[18]

Conversion of poly(methylcarbyne) to diamond

The polymer was heated in a Thermolyne tube furnace at atmospheric pressure under a constant flow of nitrogen and then cooled to room temperature. The polymer was drop casted on a ceramic plate (5 cm × 5 cm × 1 cm). Typical sintering conditions are a dynamic nitrogen atmosphere, $10°C$/min ramp rate, from room temperature to $1000°C$ and 24 h at that temperature.

RESULTS AND DISCUSSION

Synthesis of poly(methylcarbyne)

Although polycarbynes have been succesfully synthesized via both sonication and Grignard reagents as reported before by Bianconi et al.[18] and by Rieke et al.,[13] respectively, our electrochemical synthesis of the polymers is easier, cheaper, and more convenient to for both large scale industrial synthesis and in the lab. The synthesis of poly(methylcarbyne) is presented in Scheme 1.
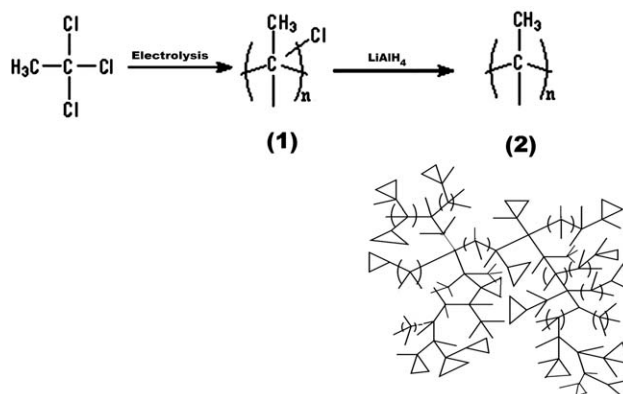
Scheme 1 Electrochemical production of poly (methylcarbyne).
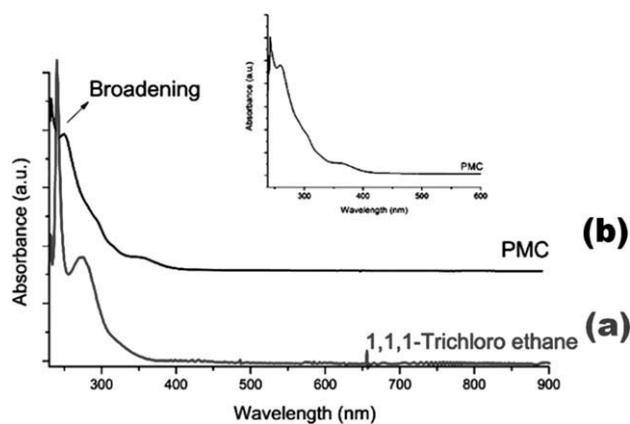
Figure 1 UV/Vis spectrum of (a) 1,1,1-Trichloro ethane and (b) PMC.

After the electrochemical synthesis of poly(methyl-carbyne), the reddish brown powder should be washed with brine to remove salts that may occur during electrolysis before LiAlH$_4$ treatment.

Characterization of poly(methylcarbyne)

Poly(methylcarbyne) has a unique network structure with tetrahedrally bonded carbon atoms having a single "pendant" methyl group as seen in Scheme 1. All polycarbynes due to their distinctive structure have a particular electronic UV/Vis spectrum; which consists of broad intense absorption starting in the ultraviolet (UV) region (at $\sim$ 200 nm) that tails down to the visible region.[11–16] UV/Vis spectroscopy was used to monitor the formation of **2** (Fig. 1). This broadening can be seen in Figure 1(b) indicating network structure formation.

The ATR-FTIR spectrum of **2** is consistent with a primarily network backbone structure of the formula (CH$_3$C)$_n$ (Fig. 2). There is no evidence of C=C, C—O, or C—Cl. The spectrum is dominated by the strong bands at υ_{max}/cm^{-1}: 2965, 1471, 1381, and

885 which arise from vibrations of C—H stretching, scissoring, deformation, and oscillation, respectively. The peak at 1037 cm^{-1} is due to cyclopropane C—C vibration, and the peaks at 799 and 737 cm^{-1} are due to C—C skeleton vibrations (rocking).[11–16]

Figure 3 shows the broad NMR resonances which are expected for such polymers.[11–18] The very broad and strong resonances between 0.5 and 2.1 ppm (δ_h: CH and CH$_3$) correspond to the aliphatic hydrogens of the network polymer. This occurs since rigid the network backbone causes unexpected paramagnetic field hindering to differentiate hydrogens of methyl groups.[11–16] There is also a weaker broad peak at 0.3 ppm which is attributed to aliphatic hydrogens from cyclopropane structure in the network.[11,12,19] Figure 3(a) represents ^{1}H NMR spectrum of **1**. Resonance at 2.1 ppm is due to Cl atoms on the polymer backbone which could not be removed during electrolysis. ^{1}H NMR spectrum of **2** [Fig. 3(b)] shows three broad resonances at $\sim$ 0.8, 1.2, and 1.4 ppm which are due to H on (C—H) and (CH$_3$). C—H resonance is due to dechloronation of polymer backbone by adding LiAlH$_4$, resulting in hydrogenation. Figure 3(c) shows ^{13}C NMR spectrum of **2**. Three broad but very weak peaks between 40 and 50 ppm are due to quarternary C—C resonances, and the very weak resonance being between 30 and 40 ppm is due to primary CH$_3$—C— bonds.

The purified isolated reddish brown material was shown to be a polymer by GPC (GPC of **2**: M_n = 9252; M_w = 16,773; PD = 1.8). The molecular weight obtained is relatively low; however, it should be noted that the GPC is calibrated with linear polystyrene; polystyrene is structurally very different from the three-dimensional polycarbyne network structure, so may not be a true measure of the molecular weight.[11,12,14,15,18]
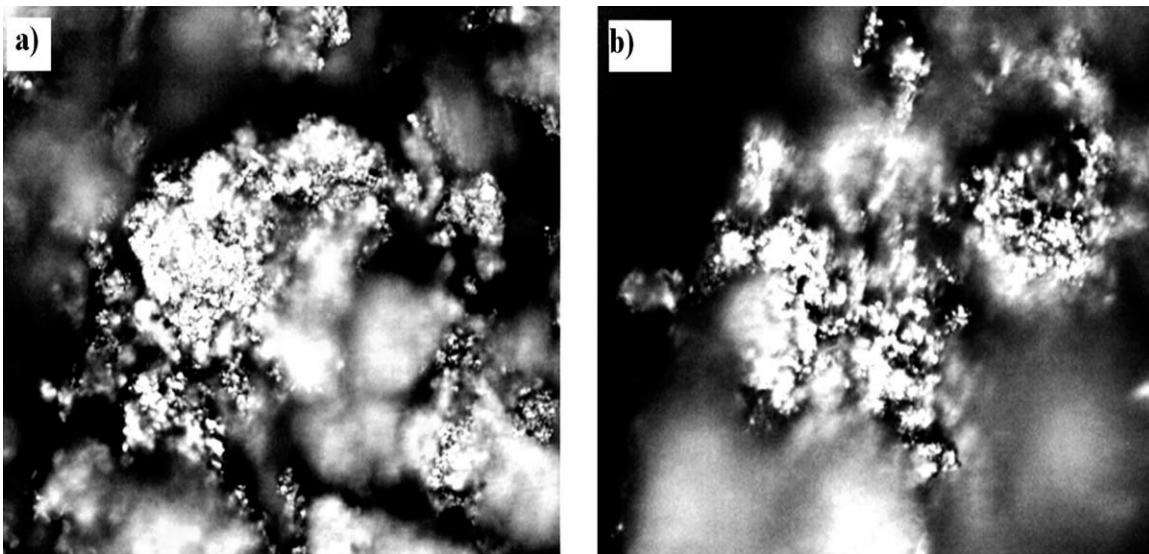
Elemental analysis results (Found: H and C: low and variable, Calc. for **2**: C, 88.9; H, 11.1%) are not
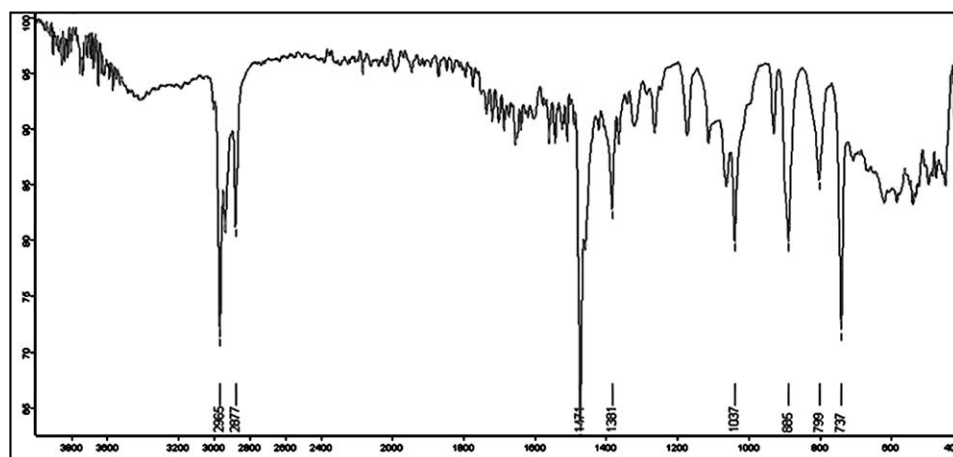
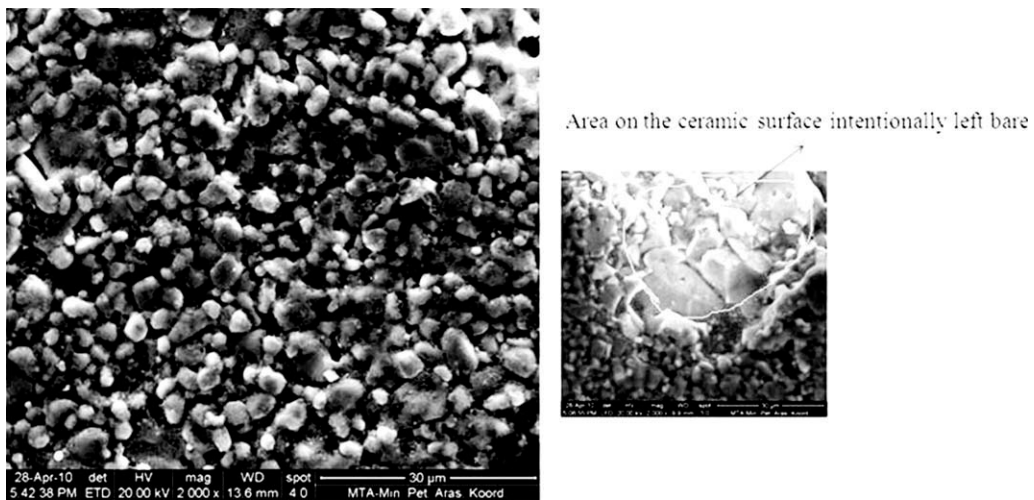**Figure 2** ATR-FTIR spectrum of PMC.
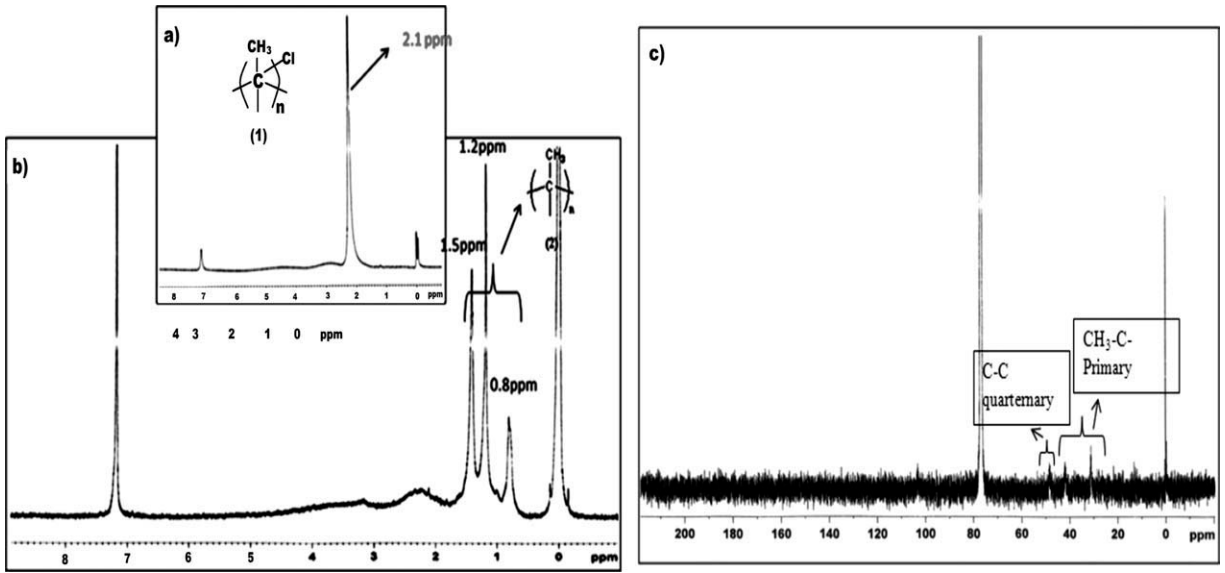
Figure 3 ^{1}H NMR of (a) Before treatment with LiAlH$_4$ (1), (b) After treatment with LiAlH$_4$ (2), and (c) ^{13}C NMR of PMC (2).

Figure 4 Pictures obtained from the pyrolytic conversion of poly(methylcarbyne) using an optical microscope of (a) 200 magnification and (b) 500 magnification.

Figure 5 SEM images of a coated alumina ceramic surfaces.
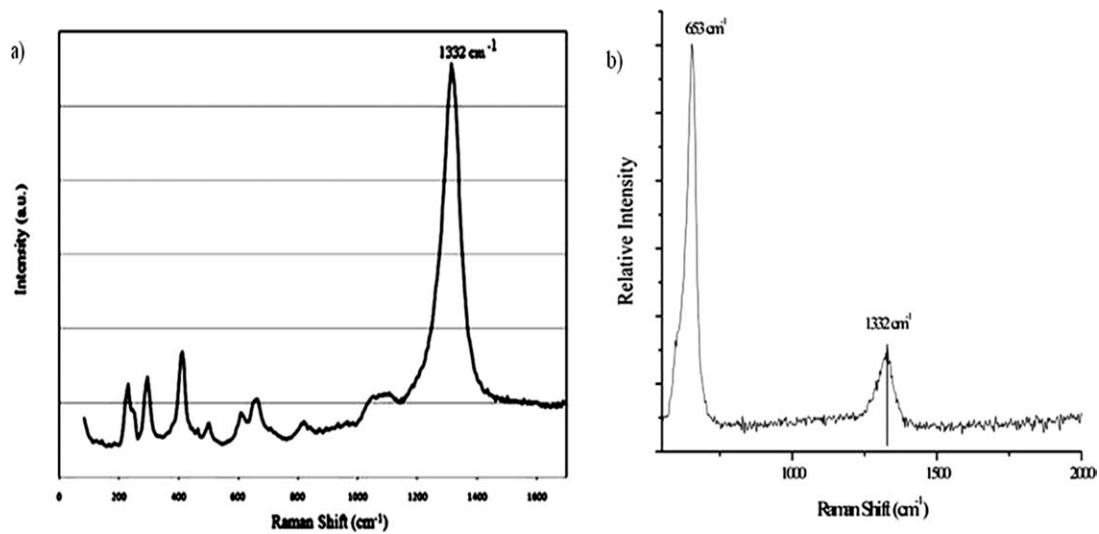
Figure 6 Raman spectra of (a) diamond film formed on an alumina ceramic surface and (b) diamond powder.

consistent with the emprical formula $(CH_3C)_n$ and not reproducible due to the rapid conversion of the polymer to a ceramic during the analysis which is common for preceramic materials. Other ceramic precursors like polysilynes show such results in the combustion analyses.[11,20–22]
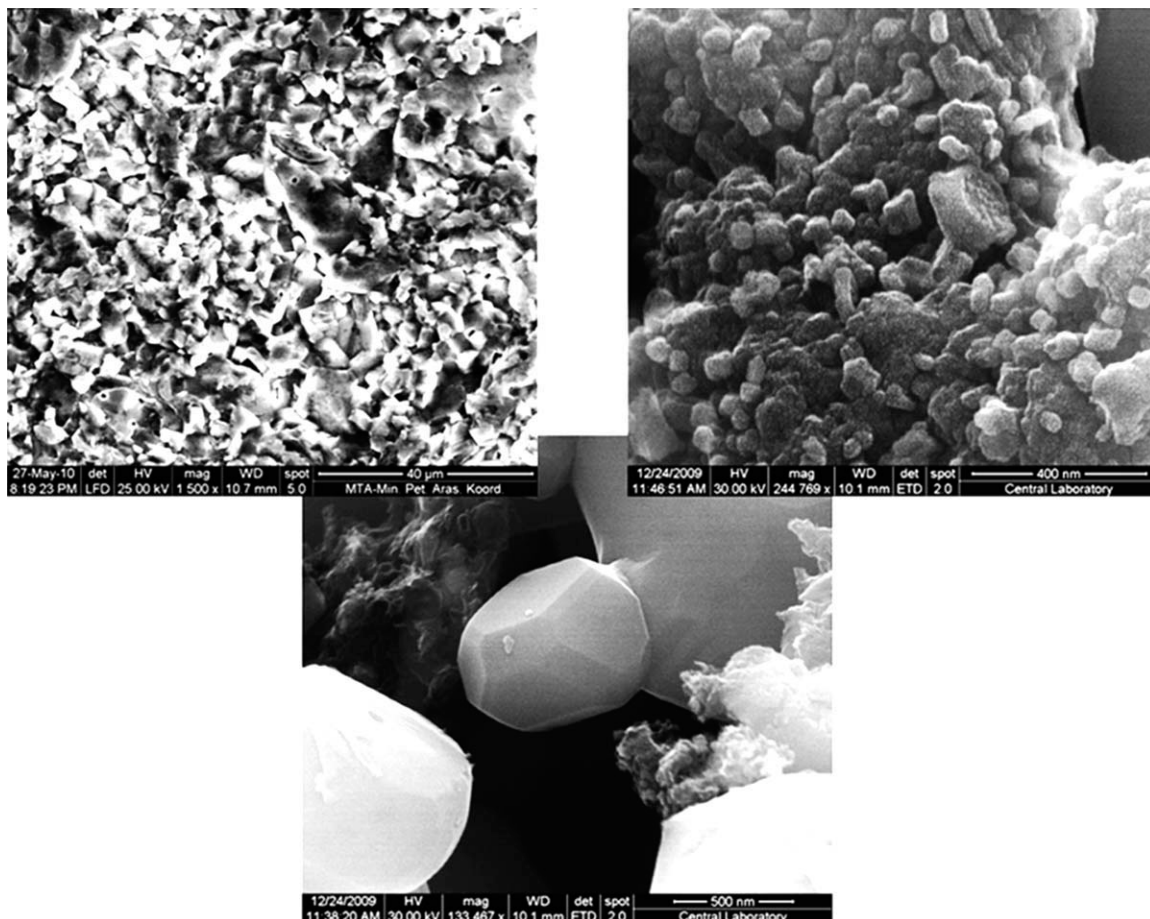

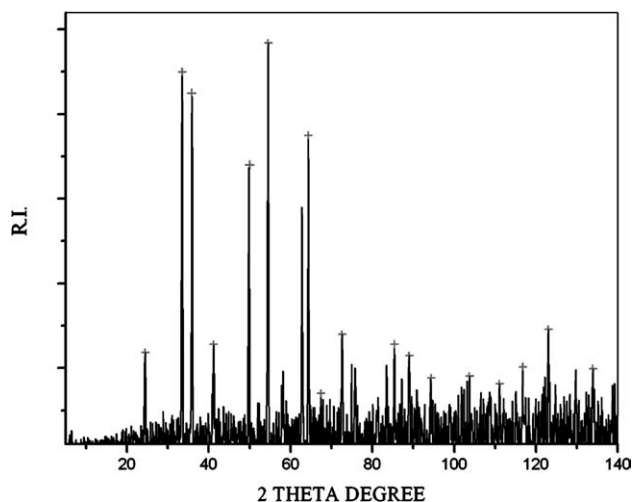**Figure 7** SEM images of diamond powder.

Figure 8 X-ray diffraction spectrum of diamond powder.

Characterization of diamond

All characterization/analysis data showed the pyrolytic conversion of poly(methylcarbyne) has produced diamond. Shiny transparent particles refract light-like gem quality diamond powder and are clearly seen under an optical microscope (Fig. 4).

An SEM image of the surface is shown in Figure 5. A small area represented in Figure 5 was deliberately not coated to show the difference between the coated and bare surfaces. The SEM image shows that the film is smooth and continuous; a desired property in coating technology.[11–15,18]

Raman analysis is used widely in diamond research due to diamond's specific spectrum. A strong, sharp peak at 1332 ± 26 cm^{-1} in the Raman spectrum is indicative of sp^3 hybridized bond formation and is strong evidence for diamond.[22,23,24] Peaks between 1315 and 1332 cm^{-1} are due to strained diamond or lonsdaleite. Raman analysis of our diamond film formed on the alumina ceramic surface is given in Figure 6(a); the peaks indicate the formation of diamond, diamond 21R, and hexagonal lonsdaleite.[11,12,18,22–27] There is no evidence of graphite in either the Raman spectrum or X-ray pattern (Fig. 8).

In addition, there are several experimental and theorical studies on Raman analysis of diamond where most of them conclude that peaks between

TABLE 1
Comparison of X–ray Diffraction Data of Powder Diamond to PDF-ICDD

Diamond 21R(79-14739) d-spacing	Intensity	hkl	Lonsdaleite (74-1602 & 79-1468) d-spacing	Intensity	hkl	Sample d-spicing	Intensity
14.150	1	003				–	–
7.2075		006				–	–
4.8050	1	009				4.8306	2
3.6037	1	0012				3.6375	32
2.8830	1	0015				2.S868	3
2.4025	1	0018				2.3923	3
2.1814	3	101	2.1824/2.19	100	100	2.1816	29
2.1731	9	012				2.1641	4
2.1409	23	104				2.1469	3
2.1177	29	015					
2.0593	100	107	2.0600	52	002	2.0517	5
2.0593	100	0021					
2.0251	24	01S				2.0255	4
1.9496	11	1010	1.9285	49	101		
1.9093	6	0111				1.8937	2
1.8258	1	1013				1.8225	55
1.6988	1	1016				1.6765	85
1.6572	1	0117					
1.6017	1	0027					
1.5759	1	1019				1.5582	4
1.5366	1	0120					
1.4611	1	1022	1.4980	16	102	1.4586	3
1.4250		0123				1.4248	
1.3561	3	1025					
1.3233	4	0126					
1.2610	36	1028	1.2600	27	110	1.2638	3
1.2610	36	110					
1.2316	6	0129					
1.1757	5	1031	1.1623	24	103		
1.1492	4	0132					
1.0991	2	1034					
1.0907	1	202	1.0912	4	200	1.0931	15

450 and 700 cm^{-1} are due to the formation of diamond nanocrystals Figure 6(b); crystals in that size regime (and the effect on the Raman spectrum) can be clearly seen in our SEM pictures (Fig. 7).[11,12,27–31] The broadening in Raman shifts is attributed to the diversity in the size of the crystals and the formation of crystals smaller than micrometer size; as seen in the SEM images in Figure 7. The variety in the size of crystals is also seen clearly by SEM images in Figure 7. At the moment, we have no significant means to control the crystal size.

Diamond was also produced as a powder from poly(methylcarbyne) to perform powder diffraction on the diamond product. The peaks in X-ray diffraction pattern (Fig. 8) were then compared with the powder diffraction files (The International Center for Diffraction Data (ICDD)) (Table I). With a Raman shift centered at 1332 cm^{-1}, it may be thought that our sample consists of bulk diamond; however, X-ray analysis showed that the material consists of both hexagonal diamond (lonsdaleite) and diamond 21R.

Red colored labeled peaks in Figure 8 are due to Diamond 21R and lonsdaleite; when matched to diffraction data (ICDD) (Table I).

All these data indicate that these polymeric precursors are viable alternatives to CVD in the production of diamond films, and possibly have advantages, one of which being the relatively simplicity of the synthesis route.

Physical and chemical properties of the film are still under investigation and will be reported in future.

CONCLUSIONS

This study demonstrates a cheap and simple method for synthesizing poly(methylcarbyne) which produces both films and powders of diamond/diamond-like carbon upon heating. The investigation and results presented here are consistent with our previous syntheses of other polycarbynes, but for the first time, we have succeeded in producing high quality diamond films. The synthesis of both the polymer and the resulting diamond films is relatively straightforward and simple and it is hoped that this will allow researchers access to this technology who were previously excluded.

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