Solid State Polymerization of Acetylene at High Pressure and Low Temperature

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Solid state polymerization has the potential to afford topochemical control over reaction pathways. High-pressure solid state polymerization at low temperature may permit a single lowest energy reaction pathway to be favored and also allow reactants to approach more closely before reaction begins, both factors that may favor topochemical reaction. Acetylene begins to polymerize in the solid state at a pressure of 12.5 GPa at 77 K. Further reaction occurs upon release of pressure to 2.5 GPa, suggesting the presence of unsatisfied reactive sites at high pressure. A topochemical polymerization did not result, but Raman spectroscopy indicates the formation of some polymer, which exhibits a spectrum characteristic of *cis*-polyacetylene. This polymer isomerized to the trans form upon warming to 298 K.

Introduction

Carbon exhibits a rich structural chemistry because it can bond in linear, trigonal, and tetrahedral coordination. In the elemental state, it appears in a variety of forms such as chemical vapor deposited (CVD) diamond, diamond-like carbon, fullerenes, polymeric fullerenes, nanotubes, cubic diamond, Lonsdalite, and graphite.[10,15,19,23,25] Theoreticians have had a long-standing interest in the stability of non-diamond and non-graphitic carbon or carbon-based structures, and many have been proposed.[6,7,9,13,14,18] New synthesis strategies have produced molecules that have a large amount of unsaturation, a very high carbon-to-hydrogen ratio, and spectacular topologies.[12] These compounds could serve as building blocks for the synthesis of carbon-rich networks, which could exhibit unprecedented properties or structural features. A key issue is how to link these unsaturated molecules into networks.

Pressure favors the linkage of molecules and solids containing unsaturated bonds into more saturated networks. Saturated networks contain more intramolecular bonding and, therefore, have a smaller volume, which is favored under pressure. Polymerization of unsaturated networks of carbon at high pressure was first accomplished in the late 1920s.[8] All organic compounds are in the solid state under sufficient pressure, leading to the possibility of topochemical reactions. Once more is understood regarding kinetics, reaction mechanisms, and the effect of variables such as nonhydrostatic stress, pressure could offer a “gentler” and more controlled means to induce reactions in the solid state than traditional methods, such as irradiation by γ-rays.

There has been considerable theoretical and experimental interest in the topochemical polymerization of acetylene at high pressure because of its simplicity and the observation that diacetylenes polymerize topochemically. Topochemical polymerization of crystalline molecular acetylene could produce single crystals of polyacetylene, which have never been observed. Experimentally, it has been observed that polymerization of acetylene begins at 3.5 GPa in an orthorhombic molecular phase at room temperature. Topochemical polymerization was not observed, but some conjugated polymers were formed, together with substantial amounts of more saturated products and short conjugated oligomers.[1−4,24]

Here we report the effect of low temperature (77 K) on the polymerization of acetylene at high pressure. Little is known about the effect of low temperatures on the kinetics and mechanism of solid state reactions at high pressure. At ambient pressure, low temperatures inhibit many polymerization reactions because the kinetics may become too slow. Reactions kinetics are also affected by pressure, which can provide a large driving force for reaction. Therefore, low-temperature polymerization reactions that do not proceed at ambient pressure may proceed at high pressures. Furthermore, low temperatures may slow down the reaction kinetics of a solid state reaction at high pressure (when compared with reaction at ambient temperature), potentially favoring a single lowest energy reaction pathway that could be topochemical. Low temperatures can also increase the pressure required to induce reaction, allowing molecules to approach more closely before polymerization begins, also potentially facilitating a topochemical reaction if the initial intermolecular distances in a crystal are too large. Sterically inhibited diacetylenes that do not polymerize at ambient pressure, for example, can be induced to polymerize under high pressure once the distance between carbon atoms is brought below a critical distance of 4 Å.[20]

Experimental Section

Acetylene of 99.8% purity (Specialty Gas) was used after acetone was removed with a charcoal filter. Acetylene was loaded into a Mao-Bell diamond anvil cell (DAC)[16] by condensing it at liquid nitrogen temperatures. A T301 stainless steel gasket, indented to a thickness of 40 μm, was used. A few chips of ruby were placed in the sample chamber for pressure measurements.[5,22] The acetylene was trapped in the sample chamber, which was 150 μm in diameter. Then the DAC was warmed to room temperature to check the purity of the fluid molecular acetylene by means of Raman spectroscopy.

The DAC was loaded into a specially designed vertical helium flow cryostat (type SP152-P, Cryo Industries of America, Inc. Atkison, NH), in which the pressure could be varied in situ. The temperature of the sample was then lowered to 77 K. Raman spectra were collected by means of a Dilor XY spectrometer

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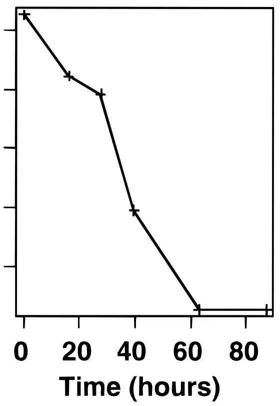

Figure 1. Intensity of the acetylene carbon−carbon stretch mode as a function of time at 12.5 GPa and 77 K.

equipped with a Princeton Instruments CCD camera and 514.5 nm excitation. Ruby fluorescence pressure measurements were corrected for the effect of low temperature.

Results and Discussion

Reaction of crystalline, orthorhombic molecular acetylene began upon increasing the pressure to 12.5 GPa at 77 K. In contrast, at ambient temperature polymerization began at a much lower pressure, 3−3.5 GPa.[4,3] The progress of the reaction was monitored by observing intensity of the peak in the Raman spectrum due to acetylene carbon−carbon triple bond stretching near 1960 cm^{-1}, which slowly decreased over a period of 63 h (Figure 1). After this time, the intensity remained at a constant value much lower than the initial peak intensity, indicating that reaction had gone substantially to completion. The pressure also decreased slightly due to a decrease in sample volume associated with reaction. This may be why small amounts of unreacted monomer remain. The intensity of the background fluorescence gradually increased with time, mirroring the decrease in the intensity of the peak due to acetylene triple bond stretching. As the reaction progressed, the sample changed from colorless to a yellow color, suggesting the formation of structures containing some conjugation.

Raman spectra collected on the reaction product at 12.15 GPa and 77 K exhibit peaks at 1964, 661.6, 638, 385.6, and 253.6 cm^{-1} due to small amounts of remaining acetylene monomer (Figure 2). There are peaks at 1644.1 and 1623.8 cm^{-1} located in a region where C=C vibrations of short polyenes are typically found.[21,17] These two peaks are superimposed on a broader feature around 1600 cm^{-1}, which we assign to the cis configuration of (CH)$_x$, which is just beginning to form at this pressure. Peaks at 900.9 and 1265.4 cm^{-1} are due to the C−C stretch in the cis configuration of polymerized (CH)$_x$. Several other weak peaks superimposed upon a broad fluorescence background are assumed to be due to either short polyenes or somewhat higher molecular weight (CH)$_x$.

When the pressure was slowly released while the temperature was held at 77 K, the color of the sample slowly changed from a light yellow to a deeper, less transparent orange-red, suggesting increasing amounts of conjugation. At 2.45 GPa the sample turned to a dark red color. When acetylene is polymerized at high pressure at ambient temperature, a similar dark red color is observed upon increasing the pressure to approximately 3.5 GPa.[2,4,3] Thus, surprisingly, at low temperature additional reaction is observed to occur upon *release* of pressure.

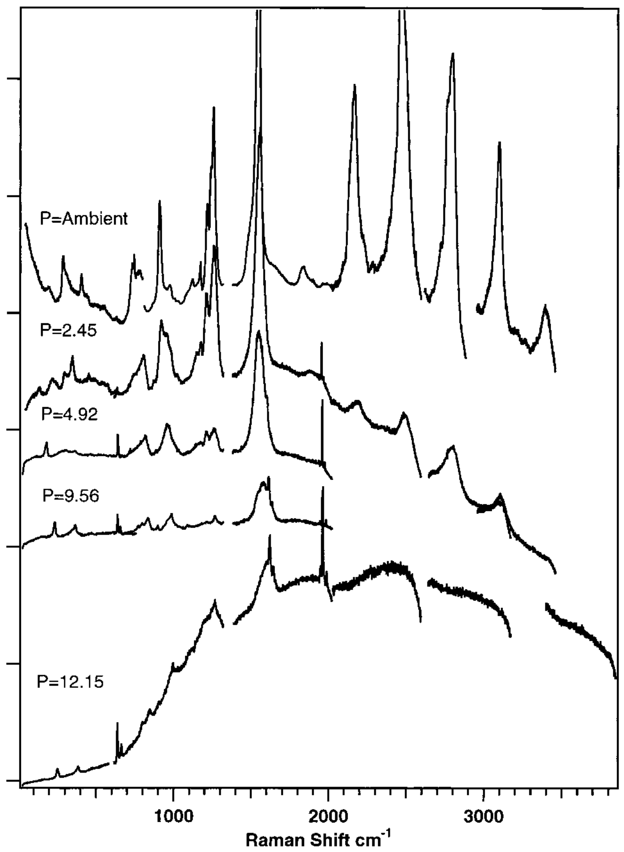

Figure 2. Raman spectra collected during decompression of reacted acetylene sample at 77 K. Many separate spectra at each pressure have been joined together.

TABLE 1: Raman Spectral Lines at 77 K after Releasing Pressure to Ambient[a]

position (cm^{-1})	intensity	assignment
287.5	m	C−C−C deformation, out of plane *cis*-polyacteylene
405.9	w	*n*-alkanes?
770.8 ridge	m	?
909.9	m	C−C stretch *cis*-polyacteylene
975.6	m	C−H deformation out of plane *cis*-polyacteylene
1121.8	w	C−H deformation in plane residual *trans*-polyacteylene
1174.1	w	C−H deformation in plane *cis*-polyacteylene
1217.9	m	?
1245.4	s	C−C stretch *cis*-polyacteylene
1258.8	s	C−C stretch *cis*-polyacteylene
1548.8	vs	C=C stretch *cis*-polyacteylene
1839.9	m	?
2166.6	s	C-=C stretch alkyl acetylene
2468.6	s	C−C stretching
2800.7	s	CH_2 or CH_3 stretch
3099.9	m	CH *cis*-polyacteylene or CH from C=CHR derivatives
3394.2	m	=CH alkyl acetylene

[a] Raman lines characteristic of *cis*-polyacetylene are found, together with lines characteristic of more saturated products. Plausible assignments for some of the more saturated products are indicated.

As the pressure was decreased, several peaks that can be assigned to the cis form of polyacetylene grew in intensity (Figure 2, Table 1). At 2.45 GPa the Raman spectrum shows a large peak at 807.5 cm^{-1}, which can also be seen at somewhat higher frequencies at 4.92 and 9.56 GPa. This peak is also seen in *cis*-polyacetylene prepared at atmospheric pressure, but its

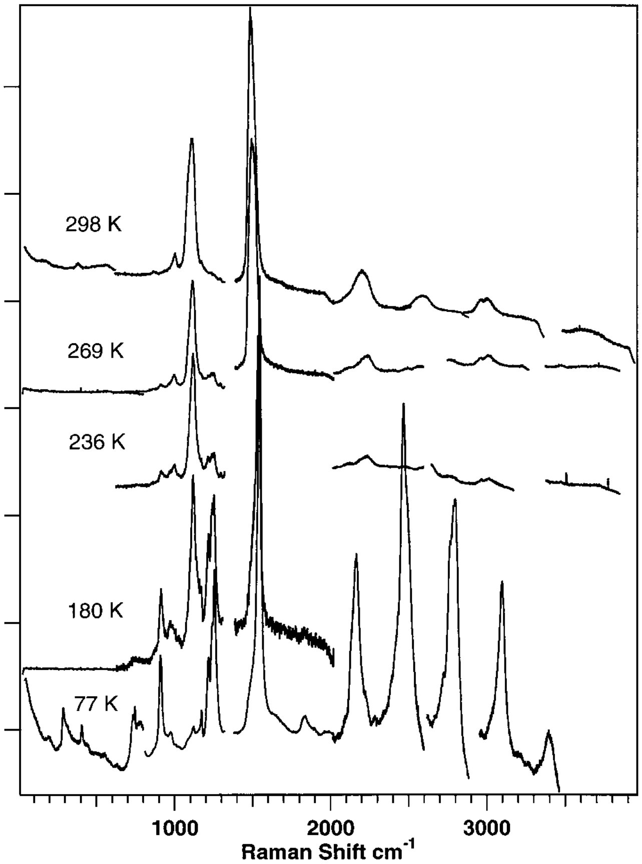

Figure 3. Raman spectra collected during warming of reacted acetylene sample at ambient pressure. Many separate spectra at each pressure have been joined together.

TABLE 2: Raman Spectral Lines after Warming to Ambient Temperature at Ambient Pressure[a]

position (cm^{-1})	intensity	assignment
384.7	w	?
562.0	w	?
866.3	w	*trans*-polyacteylene
1004.7	m	C−H deformation out of plane *trans*-polyacteylene
1113.4	s	C−C stretch *trans*-polyacteylene
1486.9	vs	C═C stretch *trans*-polyacteylene
2202.2	m	?
2592.3	m	?
2965.4	m	═CH_2 stretch
3002.6	m	C−H stretch

[a] Raman lines characteristic of *trans*-polyacetylene are found, together with lines characteristic of more saturated products. Plausible assignments for some of the more saturated products are indicated.

origin remains unidentified.[11] At ambient pressure, it flattened to form a ridge, indicating that there may be many types of cross-linked products. There were three peaks at ambient pressure that were not identified. They are believed to be associated with crossed-linked products. Several other peaks associated with carbon−carbon triple bonds and various carbon hydrogen bonds were found at higher frequencies (Table 1), indicating that there are products other than *cis*-polyacetylene forming upon polymerization at high pressure and low temperature. Because conjugated polymers can exhibit significant resonance enhancement of Raman scattering intensity, further experiments will be necessary to determine the relative proportions of polymer and other more saturated and cross-linked products.

Lattice modes for crystalline, orthorhombic acetylene are present at 12.15 GPa, shifting to lower frequencies as the pressure is released. Two modes at 135 and 226 cm^{-1} can be seen at 2.45 GPa, in reasonable agreement (in view of the difference in temperature) with previous observations at ambient temperature. Observation of lattice modes indicates that unreacted acetylene maintains its orthorhombic crystal structure upon releasing the pressure down to at least 2.45 GPa. Thus, the high-pressure reaction to form short polyenes takes place while the molecular acetylene is in a crystalline form, a necessary (but not sufficient) condition for a topochemical reaction. Upon release of pressure below 2.45 GPa, these short polyenes must react to form longer chain polyenes and other cross-linked products because little or no molecular acetylene remains.

The cis conformation of $(CH)_x$ predominated at the low temperatures, but as the temperature was increased the sample rearranged to the trans conformation (Figure 3, Table 2). Similar behavior has been observed in polyacetylene prepared by catalytic means, where cis dominates at low temperature and rearranges to trans at high temperature. When acetylene was polymerized under high pressure at ambient temperature, the trans conformation was formed together with small amounts of cis polymer.[2,4,3] In the present experiment, saturated and unsaturated products remain together with the *cis*-$(CH)_x$ upon warming to room temperature.

The observed behavior, in which substantial additional reaction occurs upon release of pressure to 2.45 GPa, suggests for the polyenes formed from acetylene at 12.5 GPa at low temperatures there is insufficient molecular motion and/or diffusion to permit further reaction. Reactive sites may form that cannot find additional functionality to react with until the magnitude of molecular motion and/or diffusion is increased upon the release of pressure.

Solid state reactions in molecular crystals of unsaturated monomers such as acetylene are governed by the balance between propagation and termination of reactive sites. These two processes are controlled by both the amount of molecular diffusion and the topology of the crystal structure. In topochemical reactions the structure of the final product is controlled by the structure of the monomer. Therefore, in order to find a topochemical pathway, the amount of molecular diffusion/motion cannot be too large. For the room temperature high-pressure polymerization of acetylene, it was observed that carbon−carbon single bonds appeared after a while and then continued to increase in number, while the C═C concentration stayed constant.[24] During this time the Raman modes associated with the monomer triple bond stretch shifted from a position characteristic of the crystalline orthorhombic phase to that of fluid acetylene. This shift indicates the presence of a considerable amount of molecular diffusion and the crystal structure would not be able to influence the reaction pathway.[24]

At low temperature the position of the monomer peaks remained in position characteristic of the orthorhombic molecular phase while the pressure was increased up to 12.5 GPa. During this low-temperature reaction, much less molecular diffusion was possible than at ambient temperature, thus increasing the potential for topochemical structural control over the reaction mechanism. Thus, it is possible (although it has not been demonstrated) that the initial stages of the reaction to form short polyenes are topochemical. Unfortunately, the geometry of the molecular crystal at low temperatures and high pressure must have precluded the topochemical formation of only crystalline polyacetylene;[20] short polyenes were the primary product before the pressure was reduced. These polyenes may have reactive sites that remain until the pressure is decreased because there is insufficient molecular diffusion and/or an unfavorable geometry to satisfy them.

The present results suggest some strategies for the search for topochemical reactions induced by high pressure. At ambient temperature, the crystal structure of the molecular acetylene monomer is not maintained during the polymerization process. Polymerization is likely facilitated by movement/diffusion of acetylene molecules to reactive sites. In contrast, at low temperatures this molecular diffusion is much less. Much higher pressures are required to induce reaction, likely because of an unfavorable solid state reaction geometry. Thus, when searching for candidates for topochemical solid state reactions, low temperature may play a useful role, but solid state molecular geometry is also of critical importance. Low temperatures may allow certain geometric obstacles to reaction to be overcome because reaction can occur at higher pressures where intermolecular distances are smaller. Further progress in this field will be facilitated as more molecular crystal structures are determined at high pressure, both at low temperatures and at ambient temperature.

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