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Solid state polymerization of cyanoacetylene into conjugated linear chains under pressure

K. Aoki, Y. Kakudate, M. Yoshida, S. Usuba, and S. Fujiwara

National Chemical Laboratory for Industry, Tuskuba, Ibaraki 305, Japan

Cyanoacetylene underwent polymerization reaction in a solid phase at pressures above 1.5 GPa. The Raman study of the reaction product showed that the polymer had a conjugated linear backbone with CN pendant groups. The Raman spectra for this substituted polyacetylene demonstrated a resonance behavior similar to that reported for *trans*-polyacetylene. The optical gap associated with the π–π^* transition in the conjugated system was smaller than that of *trans*-polyacetylene, probably due to the resonance interactions between the CN triple bonds and the conjugated double bonds.

INTRODUCTION

Studies of physical and chemical properties of conducting polymers have attracted much interest in fundamental and applied research. Among a variety of conducting polymers, the simplest polymer is polyacetylene having a conjugated linear backbone with hydrogen. As a prototype of one-dimensional organic conductors, the structural and electronic properties of polyacetylene have been extensively studied by experimental and theoretical approaches.[1] Peierls instability, the dependence of the band gap on the conjugation length, the mechanism of soliton formation, and the chemical doping effects, etc. are the features all characteristic of polyacetylene. In particular, the chemical doping constitutes an important part of the technology converting the nearly insulating polymer to a conducting material.[2]

Replacement of hydrogen atoms by other elements or groups is another approach by which to alter the electronic state of polyacetylene. The band gap, for instance, may be changed over a wide range by substitution of various kinds of pendant groups. In contrast to the chemical doping effect, which creates midgap states such as soliton and polaron in the forbidden energy states in the band,[3] substituent effects will modify the fundamental band structure. Preparation and characterization of substituted polyacetylene are, therefore, important in facilitating both basic and application studies associated with polyacetylene and its family polymers. However, there have been few studies carried out on substituted polyacetylene to date, probably due to the difficulties involved in the preparation of substituted polymers by the conventional catalytic methods.

Solid state polymerization of acetylene derivatives is a promising way to synthesize substituted polyacetylene. Pressure induced polymerization reactions have been observed for simple molecules such as CS_2,[4] $(CN)_2$,[5] and C_2H_2.[6,7] These substances, existing as gas and liquid phases at atmospheric pressure and room temperature, immediately transform into solid phases on application of pressure, and undergo polymerization reactions on further compression. Among these reactions the direct formation of polyacetylene is particularly interesting. Polyacetylene, which has been prepared exclusively by the catalytic polymerization of the monomer gas, was formed by the solid state reaction induced at pressures above 3.5 GPa. This result suggests the possibility that solid state polymerization of acetylene derivatives leads to formation of the corresponding substituted polymers.

We have made Raman scattering measurements on cyanoacetylene, H–C≡C–C≡N, to examine the chemical reactions that are expected to be induced in the crystalline phase under pressure. The choice of cyanoacetylene was based on the following two reasons. First, its linear molecular shape is convenient for solid state reactions. On compression, the molecules can approach, without steric hindrance, each other close enough to initiate chemical reactions. Second, the substitution of CN group might cause change in the electronic state of the parent conjugated system through electronic interactions between the CN triple and conjugated double bonds. Raman measurements revealed that polymerization reactions occurred in the crystalline phase pressurized above 1.5 GPa, accompanied by a gradual change in color. In this paper, the polymer structure and the reaction mechanism will be discussed on the basis of the observed Raman and transmission spectra.

EXPERIMENTAL

A diamond anvil cell (DAC) was employed for high pressure transmission and Raman measurements. Cyanoacetylene of 97% purity, obtained commercially from Nakarai Kagaku Co., Ltd., was used for the measurements without further purification. The liquid sample was so volatile that it was frozen first and then loaded in the cell. The DAC was maintained below the sample's melting temperature of 278 K by immersion in liquid nitrogen. After the frozen sample was enclosed in the hole of a metal gasket (Inconel-X750), the DAC was warmed up to room temperature for high pressure optical measurements. The initial diameter and depth of the gasket hole were 0.5 and 0.25 mm, respectively. The pressure was determined by the ruby fluorescence technique.[8] A detailed description of the DAC and the sample loading procedure has been reported elsewhere.[9]

The solid state reaction that occurred at pressures above 1.5 GPa was monitored through transmission and Raman

spectra. A Spex double monochromator (Model 1403) was used for these optical measurements. Transmission spectra were recorded in the range 28 000–11 000 cm^{-1} with a xenon light source. Raman spectra were excited with the 647.1 nm line of a krypton ion laser. The excitation laser light was operated at a low power level of 10 mW and focused to a 0.5 mm area on the sample surface. The measured spectral range was 2000–2300 cm^{-1} within which the Raman peaks due to the C≡C and C≡N stretching vibrations were observed. The transmission and Raman spectra were recorded at a time interval of 1 h.

The pressure was decreased to atmospheric pressure, after being held at the reaction pressure for three days. Detailed Raman measurements were carried out for the reaction product taken out from the DAC. The spectra were taken with several excitation lines of the krypton laser. The wide-range spectrum in 20–2400 cm^{-1} was measured with the 647.1 nm line. For the range of 1000–1800 cm^{-1}, several excitation lines from blue to red were employed. In this frequency region, three Raman peaks due to the stretching vibrations of the polymer backbone were observed. The incident laser power was reduced to 2 mW from 10 mW to avoid photochemically induced structural changes. For each excitation line, fifty repeated measurements were required to obtain an integrated spectrum of a good quality. No spectral change was detected during repeated measurements at such a reduced laser power.

RESULTS

Cyanoacetylene showed a liquid–solid transition at 70 MPa. A small single crystal in a parallelepiped shape was obtained in the DAC by a careful control of pressure at the solidification pressure. With a slight increase in pressure, the crystal first grew along one crystal axis until the growing face reached the inside wall of the gasket hole, and then grew in the perpendicular direction. From the Raman spectrum taken for the crystal, the high pressure phase was immediately identified with the low temperature phase appearing below 278 K at atmospheric pressure.[10] The unit cell determined by an x-ray diffraction[11] is a monoclinic lattice that belongs to the space group P21/m containing two molecules aligned antiparallel with each other.

The chemical reaction induced at 1.5 GPa was accompanied by a gradual change in color from colorless transparent into black. Transmission spectra taken for the reaction process are shown in Fig. 1. The absorption edge rapidly shifted to a longer wavelength with time, soon leaving the measurement limit of 11 000 cm^{-1}. The absorption in this visible region is associated with the π–π* transition in the conjugated double bond. It has been shown that the band gap of the conjugated system decreases monotonically with an increase in the chain length.[12] The resulting absorption edge shift toward a lower energy can be understood in terms of a gradual growth of the conjugation chain length with time. A similar edge shift has been observed in the polymerization process of acetylene.[6] In the case of acetylene, the absorption edge remained in the near-infrared region around 12 000 cm^{-1} even after the completion of the reaction.
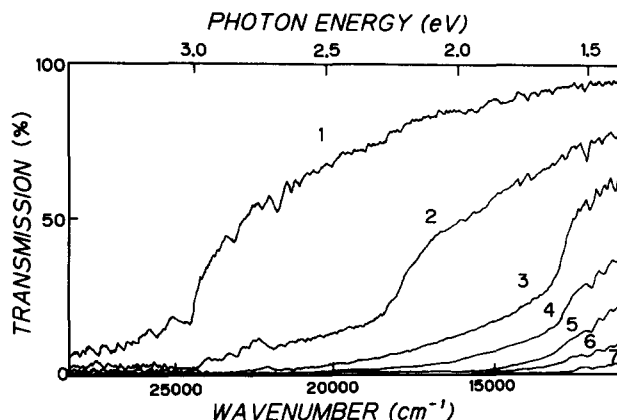

FIG. 1. Transmission spectra taken at 1 h time intervals for the reaction process of cyanoacetylene.

The Raman spectra measured for the C≡C and C≡N stretching region are shown in Fig. 2. As the polymerization reaction proceeded, two peaks showed a rapid decrease in the scattering intensity with the ratio of the peak heights almost constant. Disappearance of both the C≡C and C≡N stretching peaks does not mean that the two triple bonds equally took part in the polymerization reaction. As shown in the spectrum measured for the recovered product (see Fig. 3), the Raman peak due to the C≡N stretching vibration is still observed at 2215 cm^{-1}, lower by 55 cm^{-1} from the original position of 2270 cm^{-1}. The fundamental frequency of the C≡N stretching vibration merely shifts as a result of the formation of the conjugated polymers.

The Raman spectrum taken for the reaction product in the wide frequency range is shown in Fig. 3. Three strong peaks are observed in the region of 1000–1500 cm^{-1}. In the low frequency region below 1000 cm^{-1}, several weak peaks are observed. The spectral profile in the C≡C and C≡N stretching vibrational region, i.e., 2000–2300 cm^{-1}, is particularly important for an investigation of the reaction mechanism and the polymer structure. In this region, one weak peak is observed at 2200 cm^{-1}. This peak is assigned to the C≡N stretching one on the basis of a characteristic fre-
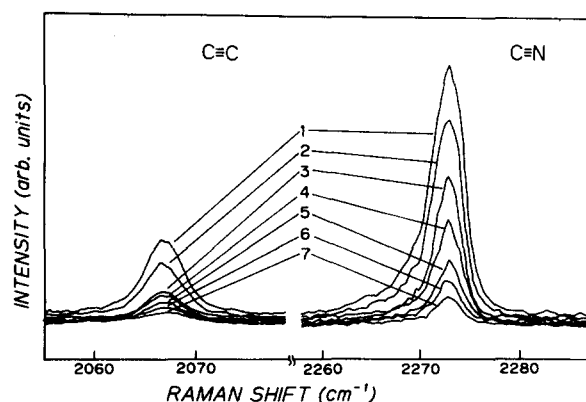

FIG. 2. Raman spectra taken at 1 h time intervals for the reaction process of cyanoacetylene. The peaks at 2068 and 2275 cm^{-1} are due to the C≡C and C≡N stretching vibrations of the molecule, respectively.
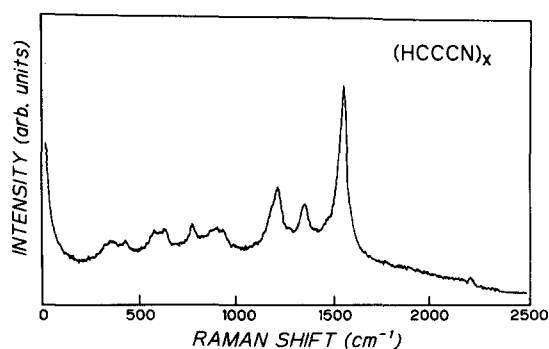
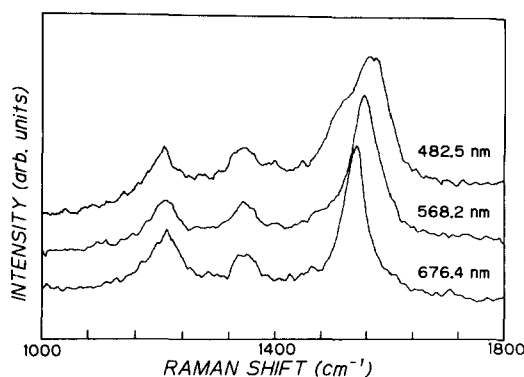FIG. 3. A typical Raman spectrum of the reaction product measured for the 647.1 nm line.

FIG. 4. Typical Raman spectra of the reaction product measured for the 482.5, 568.2, and 676.4 lines. The strong peak observed around 1600 cm^{-1} shifts to a higher frequency with a decrease in the laser wavelength.

quency analysis. In contrast, the C≡C stretching peak was not observed in the spectrum. The measured peak frequencies are listed in Table I together with those of cyanopropene[13] for comparison.

Raman spectra in the 1000–1800 cm^{-1} region taken with several excitation wavelengths are shown in Fig. 4. A strong peak observed around 1600 cm^{-1} shows a large shift to a higher frequency with a decrease in the laser wavelength, i.e., an increase in the laser photon energy. The band width of the strong peak broadens as the peak shifts. In addition, a shoulder peak newly appeared on the low frequency side of the dominant peak as seen in the top spectrum measured for the excitation laser wavelength of 482.5 nm. Other two peaks at 1208 and 1345 cm^{-1} show no change either in profile or frequency. The observed resonance behavior is quite similar to that reported for *trans*-polyacetylene.[14] The Raman peak due to the C=C stretching vibration in *trans*-polyacetylene shifts to a higher frequency with band broadening.

DISCUSSION

We first discuss the structure of the reaction product using the observed Raman and absorption spectra. Cyanoacetylene molecule has two reactive sites, the C≡C and C≡N triple bonds, which are capable of participating in the polymerization reactions. The C≡C stretching Raman peak disappeared after the reaction, while the C≡N stretching peak still remained. The disappearance of the C≡C stretching peak indicates that the C≡C triple bonds took part in the chemical reaction. The most likely structure for the reaction product is a conjugated linear polymer having the same backbones as polyacetylene. As discussed in the ensuing paragraphs, the conjugated polymer of cyanoacetylene, namely, poly-cyanoacetylene, can be formed by crosslinking the neighboring molecules with C–C single bonds. The transmission spectra provide further evidence for the formation of conjugated polymers. The reaction product absorbed light in the entire visible region, showing graphite-like luster. This can be explained in terms of the π–π* transitions in the conjugated system.

The structure of poly-cyanoacetylene is examined more precisely by comparison of the observed Raman frequencies with those of cyanopropene.[13] Cyanopropene, CH_3–C(CN)=CH$_2$, is the simplest molecule having a conjugated double bond with a CN pendant group. It shows the frequencies of 1631 and 1270 cm^{-1} for the C=C and C–C stretching vibrations, respectively. The corresponding frequencies obtained for poly-cyanoacetylene are 1542 and 1208 cm^{-1}. A strong peak at 1345 cm^{-1} may be related to the C–H bending vibration by analogy with the 1295 cm^{-1} peak of *trans*-polyacetylene. Assignment of other peaks observed below 1000 cm^{-1} are also made by frequency comparison: a sharp peak at 770 cm^{-1} is assigned to the C–CN stretching vibration and two doublet peaks around 600 and 400 cm^{-1} to the bending vibrations of C–C–CN (or C=C–CN) and C=C–C backbones, respectively. Thus, the correspondence in Raman frequencies indicates that poly-cyanoacetylene is a conjugated linear polymer having a repeating unit of [–CH=C(CN)–].

The polymerization paths leading to the formation of polycyanoacetylene are examined in the molecular crystal.

TABLE I. Summary of Raman frequencies (cm^{-1}) of polycyanoacetylene and cyanopropene.

Polycyanoacetylene	Cyanopropene[a]	Approximate description
	3117	CH$_2$ asymmetrical stretch
	3040	CH$_2$ symmetrical stretch
	2999	CH$_3$ asymmetrical stretch
	2943	CH$_3$ symmetrical stretch
2215	2227	C≡N stretch
1545	1631	C=C stretch
	1468	CH$_3$ asymmetrical deformation
	1405	CH$_2$ deformation
	1382	CH$_3$ symmetrical deformation
1345		
1218	1270	C–CH$_2$ stretch
	1016	CH$_3$ rock
	955	CH$_2$ rock
903		
771	750	C–CN stretch
629, 569	582	H$_2$C–C=C bend
428, 359	378	CH$_3$–C=C bend
	202	C–C≡N bend

[a] Reference 13.

Since the molecular arrangement in the monoclinic crystal is very simple and highly anisotropic, some structural considerations based on stereochemistry enable us to find the possible crosslinking reaction paths. Figure 5 shows the crystal structure of cyanoacetylene[11] projected along the *b* axis. The linear molecules, joined by hydrogen bonding between C–H and N≡C, form infinite chains along the *a* axis, which are nearly close-packed. Each chain is surrounded by two parallel nearest neighbors in the same molecular plane and four antiparallel ones in the upper and lower molecular planes. The reaction sites of C≡C triple bonds are located most close in the *ac* plane, where each molecule has just two nearest neighbors on both sides. Hence, the possible reaction path is uniquely determined to be a crosslinking path propagating in the C≡C array along the *c* axis.

A schematic polymerization process is also illustrated in Fig. 5. The reaction process involves opening of the triple bonds and formation of the crosslinking single bonds. These reactions are accompanied by a change in the bonding state from the C≡C triple bonding to the sp^2 hybrid state. Cyanoacetylene molecules, in turns, bend at the central carbon atom to attack the neighboring molecules. The polymerization reaction thus propagates along the *c* axis to form an isotactic zig-zag polymer. The intermolecular C···C distance in the crystal is 0.38 nm at 248 K and atmospheric pressure. Assuming that poly-cyanoacetylene has the same polymer backbone as that of *trans*-polyacetylene,[15] the value of 0.25 nm was obtained for the corresponding C···C distance in the polymer. The neighboring molecules in the crystal seem to be located too far away to form crosslinking bonds between them. Here, it should be recalled that the value of 0.38 nm is the distance at atmospheric pressure and the reaction occurs at high pressures above 1.5 GPa. The molecules will approach each other very rapidly on compression, since they are joined with weak intermolecular forces such as van der Waals forces. At the reaction pressure the molecules are thought to be close enough to initiate the chemical reaction.

Polycyanoacetylene exhibits two interesting features related to the vibrational and electronic properties; the resonance Raman effect and the small band gap.

The resonance Raman behavior appeared as a frequency shift of the C≡C stretching peak observed around 1600 cm^{-1}. This peak showed shift to a higher frequency with increasing excitation photon energy at a rate of 40 cm^{-1}/eV. A similar resonance behavior has been observed for *trans*-polyacetylene. In *trans*-polyacetylene, both the C≡C and C–C stretching peaks show shifts at a rate of 60 cm^{-1}/eV.[16] The resonance mechanism in *trans*-polyacetylene has been studied in terms of interactions between the normal vibrations and the electronic state.[16–18] It will be of interest to study the resonance mechanism of poly-cyanoacetylene for further understanding of the strong coupling between the molecular vibrations and the electronic state in the linear conjugated systems.

The small optical gap is the other characteristic feature of poly-cyanoacetylene. Complete absorption in the measured 28 000–11 000 cm^{-1} region indicates that poly-cyanoacetylene has an optical gap less than 1.36 eV (11 000 cm^{-1}). This value is smaller than the optical gap of *trans*-polyacetylene. In the spectrum of *trans*-polyacetylene[19] the absorption rises abruptly at about 1.4 eV to a peak at 1.8–1.9 eV. These optical absorptions are associated with the π–π^* transitions in the conjugated double bond, i.e., the transitions from the valence band to the conduction band. Thus, the substitution of the CN group resulted in a reduction in the band gap energy. This substitution effect contrasts to that reported for the methyl group, CH_3. The visible and UV absorption spectra of poly-methylacetylene showed two peaks, respectively, at 220 nm (5.6 eV) and 290 nm (4.3 eV).[20] The band gap was considerably widened by the substitution of the CH_3 group.

There are two kinds of substitution effects which modify the band gap of the parent polyacetylene: electronic interactions with the conjugated double bond and steric distortions of the backbone conformation. In the case of the CN group, electronic interactions may be dominant. The CN triple bonds resonate with the conjugated double bonds where single and double bonds alternate regularly. The resonance interaction enhances delocalization of π electrons in the conjugated backbone, thus decreasing the tendency of the bond alternation. In the limit of the uniform bond order, the band gap originating from the bond alternation vanishes.[21] Consequently, the decrease in the band gap energy is thought to be attributed to the resonance interactions of the CN group. On the other hand, steric distortions play a dominant role in the CH_3 substitution. The cone-shaped CH_3 group, having no multibonds capable of resonating with the conjugated double bonds, causes steric distortions such as a twisting of the polymer backbone. These distortions reduce the π-orbital overlap and the effective conjugation length, widening the original band gap in the parent polyacetylene.

There has been one report on the preparation of poly-cyanoacetylene. Matsumura *et al.* obtained thin films by effecting polymerization of cyanoacetylene vapor onto a heated substrate.[22] This polymer had an electric conductivity of 7.7×10^{-2} S/cm at room temperature, which is extremely high as compared to that of undoped polyacetylene. The polymer structure proposed on the basis of the measured Raman and IR spectra was the same as that of poly-cyano-
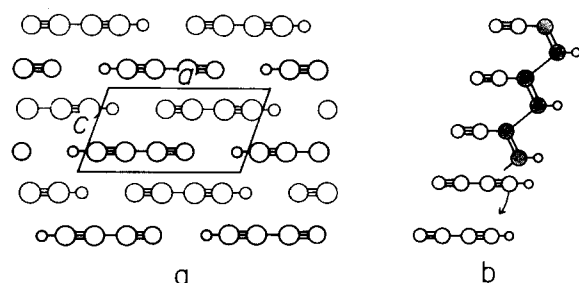

FIG. 5. (a) Crystal structure of the monoclinic phase of cyanoacetylene at 248.5 K. Small, middle, and large circles represent hydrogen, nitrogen, and carbon atoms, respectively. Molecules are joined by C–H···N≡C hydrogen bonds into linear infinite chains parallel to the *a* axis. (b) A possible reaction path for the solid-state polymerization. Crosslinking reactions propagate along the *c* axis, forming a conjugated liner polymer.

acetylene having been discussed in the present paper. However, two strong Raman peaks observed at 1360 and 1580 cm^{-1} suggested thermal decomposition of the monomer into graphite. Besides, there is a possibility of formation of other polymers. Polymerization of molecules randomly oriented on a substrate could lead to formation of some steric isomers. Further comparative studies will, therefore, be necessary for the polymers prepared by the two different methods.

SUMMARY

Cyanoacetylene polymers were prepared by the solid state reaction of monomers at pressures above 1.5 GPa. The Raman spectra indicated that the polymer backbone consisted of conjugated double bonds. The resonance Raman behavior was another experimental evidence supporting the formation of a conjugated polymer. The polymer showed a small optical gap. This is probably due to the resonance interaction between the CN triple bonds and the conjugated double bonds.

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