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Raman study of the solid-state polymerization of acetylene at high pressure

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The mechanism and kinetics of the pressure-induced polymerization of acetylene were studied by Raman spectroscopy. The polymerization reaction occurred in the orthorhombic phase at room temperature and pressures above 3.5 GPa. Dominant formation of *trans*-polyacetylene suggested that the monomer underwent *trans* opening of the triple bond and polymerized along the diagonal of the *bc* plane of the unit cell. The reaction was described as an idealized one-step and one-dimensional growth process by an Avrami equation with an exponent 1.34.

INTRODUCTION

High-pressure behavior of unsaturated organic compounds is of fundamental interest for the understanding of the nature of chemical bonds. Molecules weakly bonded with van der Waals forces approach each other rapidly on compression. At a threshold value of the intermolecular distance, chemical reactions are expected to occur between the adjacent molecules. Thus, the molecules convert into larger molecules including chain and network polymers. These chemical reactions driven under pressure have been studied for a variety of unsaturated molecules, for instance, alkenes with C=C double bonds¹ and alkynes with C≡C triple bonds.² Most of the high-pressure experiments have been devoted to addition reactions in liquid phases, where molecules exhibit random motions and orientations. There have been few studies for solid-state polymerizations in crystalline phases consisting of regularly arranged molecules.

Developments of the diamond anvil techniques³ have enabled us to investigate the chemical reactions of simple molecular solids at very high pressure by spectroscopic measurements. As a prototype of diatomic molecules having multibonds, the structural transformation of N₂ has been studied intensively from both theoretical⁴ and experimental interests.^{5,6} Raman measurements showed that N₂ molecules still remained up to 150 GPa contrary to the theoretical prediction of the transformation below 100 GPa. Pressure-induced polymerizations have been observed for molecular crystalline CS₂⁷ and C₂N₂.⁸ The chemical reactions observed in CS₂ under static pressure were discussed in relation to those observed under shock loading. The study of C₂N₂ was probably the first experiment on the reaction kinetics of solid-state polymerization induced under pressure. The irreversible conversion from a linear chain of C₂N₂ dimers into a ladder polymer was described as a two-step and one-dimensional reaction process. A similar crosslinking reaction of unsaturated chain molecules has been found in polyacetylene.⁹ The transformation into a transparent phase above 8.0 GPa was interpreted as the formation of saturated network polymers.

Recently, we have found a solid-state polymerization of acetylene under pressure.¹⁰ The reaction occurred in the molecular-crystalline orthorhombic phase at room temperature and pressures above 3.5 GPa, accompanying a color change from colorless transparent to deep red. Raman measurements revealed that the reaction product was *trans*-

polyacetylene, which also has been prepared by polymerization of the monomer gas with Ziegler-Natta-type catalysis.¹¹ The theoretical study, made by LeSar¹² previous to our high-pressure experiments, has predicted a very crosslinked product rather than a linear polymer by solid-state polymerization. He calculated the crystal structure of the orthorhombic phase at 0 K over the pressure range 0–10 GPa and explored possible reaction paths in the *ab* plane of the unit cell. However, a high-pressure path leading to a well-ordered linear polymer was not found in the plane. This disagreement between the experimental and theoretical results suggests that the polymerization reaction is induced in planes other than the *ab* plane.

In this paper, we present the mechanism and kinetics of the solid-state polymerization of acetylene induced under pressure. Possible reaction paths in the orthorhombic crystal are examined using the structural features of recovered products investigated by the resonance Raman technique. The high-pressure reaction, followed by Raman and transmission measurements, is analyzed with Avrami's crystalline growth model.¹³ The reaction process is characterized as an idealized one-step and one-dimensional growth process.

EXPERIMENTAL

Acetylene gas of purity 99.9999%, commercially obtained from Koatsu-Gas Kogyo Ltd. Osaka, was used as a starting material without further purification. Acetylene was loaded in a wedge-driven diamond cell¹⁴ cooled by immersion in liquid nitrogen. The diamond anvils had 0.7 mm diameter faces. A metal gasket of Inconel X-750, prepressed to a thickness of 0.15 mm, was bored with a drill to form a hole of 0.3 mm diameter in it. After solidified acetylene was enclosed together with a ruby chip as a pressure calibrant in the gasket hole, the cell was warmed to room temperature for Raman measurements. The detailed descriptions on the diamond cell and the sample loading technique have been reported elsewhere.¹⁴ A krypton ion-laser (Spectra Physics 171) was used as a excitation light source in Raman measurements. Scattered light, gathered by the 180° backscattering configuration, was analyzed with a double monochromator (Spex 1403) and detected with a cooled photomultiplier tube in a photon counting method. Pressures were determined from the peak shifts of ruby *R* lines of 7.53 cm⁻¹/GPa.¹⁵

Reaction products for structural studies were prepared

by polymerization of the monomer phase at room temperature and pressures above 3.5 GPa. The color change arising from the polymerization reaction appeared to begin uniformly in the sample, indicating that the reaction was not catalyzed by the gasket material or the ruby. The pressure was held for a few days at room temperature. Raman spectra of the reaction products recovered at atmospheric pressure were measured at 77 K for several excitation wavelengths in the infrared and visible regions. The incident excitation light, attenuated in power down to a few milliwatts, was focused to a diameter of about 0.3 mm on the sample face. Radiation effects of the excitation light on the sample were checked by comparison of two spectra successively recorded with the same laser line. No spectral change was observed for the excitation lights with long wavelengths such as the 676.4 and 647.1 nm lines. For the 476.2 nm line a slight increase in the background intensity was observed. This might be related to photochemical structural changes induced by the laser radiation.

We followed the polymerization process by monitoring Raman and transmission spectra of the reacting sample. The reaction was initiated by a jump in pressure beyond a reaction pressure of 3.5 GPa from 3.3 GPa at which the molecular phase remained stable for two days. Raman spectra were measured with the 647.1 nm line. The incident light at an attenuated power of 1 mW was defocused to about 0.4 mm in diameter, a little larger than the sample diameter in order to avoid acceleration of the reaction due to the heating effect of laser radiation. The measured spectral regions were those of 1940–1980 cm^{-1} for the $\text{C}\equiv\text{C}$ stretching of the monomer and 1400–1700 cm^{-1} for the $\text{C}=\text{C}$ stretching of the *trans* polymer. Each spectrum region was scanned five times for 20 min, i.e., 40 min were taken for the two spectral regions. Transmission spectra were also measured for the reacting sample in the region of 28 000–11 000 cm^{-1} with a xenon light. Each spectrum, which was taken by scanning over the region for 15 min subsequently after the Raman measurements, was divided by the reference spectrum previously taken for the monomer phase at 3.3 GPa. One serial measurement of Raman and transmission spectra was made during 1 h. The reaction time was taken when the Raman measurement was completed. The pressure decreased by 0.3 GPa from the initial value of 3.8 GPa by the end of the kinetics run. This pressure drop was probably due to the volume reduction associated with polymer formation.

RESULTS

The Raman spectra of the recovered product taken for various laser lines are shown in Fig. 1. For the 676.4 nm line, two strong peaks at 1480 and 1070 cm^{-1} and two weak ones at 1300 and 1010 cm^{-1} were observed. They could be related to the internal vibrations of *trans*-polyacetylene, assigned as ν_4 (C–H deformation out-of-plane), ν_3 (C–C stretching coupled to C–H deformation in-plane), ν_2 (C–C stretching), and ν_1 (C=C stretching) in the order of frequency.¹⁶ The ν_1 and ν_3 peaks shifted to higher frequency with band broadening as the excitation wavelength decreased, i.e., the excitation photon energy increased. This resonance behavior of *trans*-polyacetylene, having been studied in detail for po-

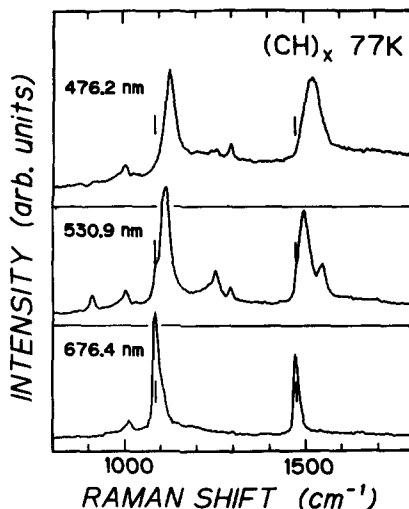


FIG. 1. Raman spectra of the recovered product measured at 77 K for three different laser lines. The four peaks in the bottom spectrum observed for 676.4 nm excitation were attributed to the vibrations of *trans*-polyacetylene. The two strong peaks at 1090 and 1480 cm^{-1} shifted to higher frequency with decrease in excitation wavelength, i.e., increase in excitation photon energy as seen in the spectra from the bottom to top. The fiducial lines give the positions of the two peaks for 676.4 nm excitation. Three peaks additionally observed in the middle spectrum were attributed to the vibrations of *cis*-polyacetylene.

lyacetylene films prepared by the catalytic reaction, was interpreted in terms of a distribution model for the conjugated chain length;¹⁷ the vibrations of the chain segments which have optical energy gaps comparable to an excitation photon energy are resonantly enhanced in scattering intensity.¹⁸ The observed resonance behavior indicated that the recovered product consisted of *trans*-polymer segments having a variety of chain lengths in a manner similar to that prepared by the catalytic reaction.

The spectrum taken for the 530.9 nm line shows evidence of *cis*-polyacetylene. Three peaks, attributed to the internal vibrations of the *cis* polymer,¹⁹ were observed at 1560, 1260, and 810 cm^{-1} in addition to the peaks of the *trans* polymer. The *cis* polymer has been known to show a resonance behavior different from that of the *trans* polymer: the scattering intensity is strongly enhanced for excitation wavelengths near 600 nm without peak shifts and broadening.¹⁹ This resonance behavior also was observed for the *cis*-polymer synthesized by the solid-state reaction. For the 530.9 nm line, close to the resonance wavelength, the peaks of the *cis* polymer were evidently observed owing to the resonance effect. These peaks disappeared in the top and bottom spectra, which were taken for the excitation wavelengths far from the resonance condition.

The *cis* polymer was unstable relative to the *trans* polymer. Figure 2 shows the Raman spectra of the product taken with the 568.2 nm line under various conditions. At high pressure a small amount of the *cis* polymer was prepared simultaneously with the *trans* polymer [Fig. 2(a)]. Both isomers were recovered when the pressure was released to atmospheric pressure [Fig. 2(b)]. The Raman peaks of *cis* polymer became evident because of the peak shifts of the *trans* polymer and the reduction of the background intensi-

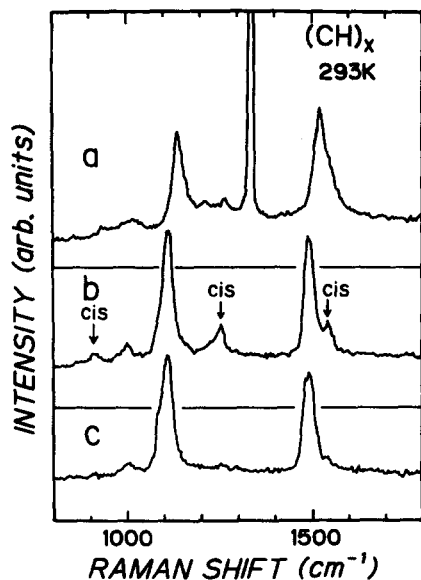


FIG. 2. Raman spectra of the polymer product measured at 293 K for 530.9 nm excitation. (a) The spectrum measured at 3.7 GPa showed that the *cis* polymer was prepared together with the *trans* polymer by the pressure-induced polymerization reaction. A sharp peak at 1333 cm^{-1} was the Raman peak of diamond. (b) The Raman peaks of the *cis* polymer were clearly observed in the spectrum taken for the recovered product out of the diamond cell. (c) The peaks of the *cis* polymer were quenched by heat treatment of the sample at $80\text{ }^{\circ}\text{C}$ for 2 h.

ty. Figure 2(c) shows the spectrum taken for the recovered sample annealed at $80\text{ }^{\circ}\text{C}$ for 2 h in xenon gas. The marked reduction in the peak height suggested that the *cis* polymer isomerized into *trans* polymer by the heat treatment. This result is consistent with that obtained by the phase stability experiment on the polymer prepared by the catalytic reaction. The *cis* polymer partly contained in an as-prepared film converts into the *trans* polymer by heat treatment at temperatures above the preparation temperature.²⁰

Figure 3 shows the transmission and Raman spectra recorded at several times during polymerization at 3.8 GPa and room temperature. The optical absorption edge, associated with interband transitions in the conjugated chain, showed nearly parallel shift to lower energy [Fig. 3(a)]. Theoretical study has shown that the interband energy gap decreases with increase in the chain length, converging into 2.3 eV for the infinite chain in correspondence with an experimental value.²¹ Hence, the observed edge shift can be attributed to gradual growth of the conjugated chains. The process of the polymer formation was clearly observed in the Raman spectra. The $\text{C}\equiv\text{C}$ stretching peak of the monomer decreased steadily after the initiation of the reaction [Fig. 3(b)], while the $\text{C}=\text{C}$ stretching peak of the *trans* polymer contrarily grew with time [Fig. 3(c)]. The number of conjugated bonds can be estimated from the dependence of the resonance wavelength on the chain length.²² About 50 was given for the chain segments resonating to the excitation wavelength of 647.1 nm. The measured Raman spectra, thus, indicated that the chain segments a few tens of nanometers long had already grown at early stages of the reactions.

For numerical analysis of the reaction process, relative

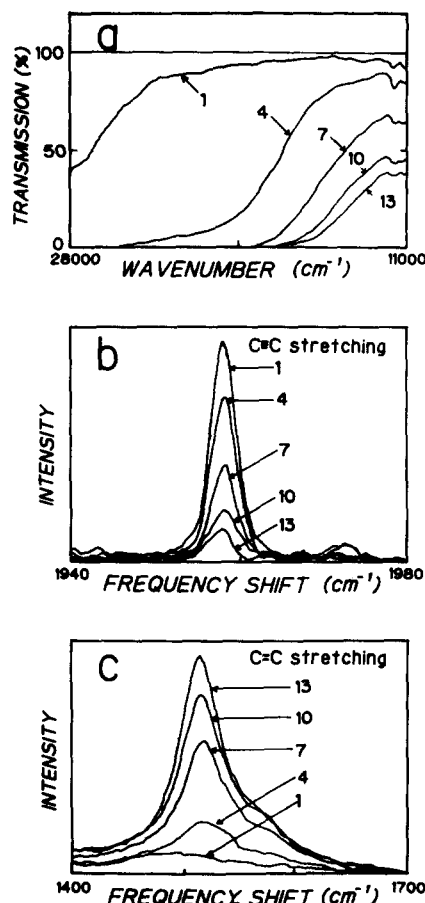


FIG. 3. Typical transmission and Raman spectra taken for the reacting sample at 293 K and 3.8 GPa: (a) transmission spectra; (b) Raman spectra in the region of the $\text{C}\equiv\text{C}$ stretching vibration of the monomer; and (c) Raman spectra in the region of the $\text{C}=\text{C}$ stretching vibration of *trans*-polyacetylene. The Raman spectra were excited with the 647.1 nm line. A number given to each spectrum indicates time t in hours after the initiation of the polymerization reaction.

Raman intensities were calculated from the spectra recorded time dependently. The measured integrated peak intensities $A(t)$ were corrected for absorption of the incident and scattered lights due to polymer products using the transmission spectra measured simultaneously in the kinetic run. Relative intensities $X(t)$ were defined as $X_m(t) = A_m(t)/A_m(0)$ for the $\text{C}\equiv\text{C}$ stretching vibration of the monomer, and $X_p(t) = A_p(t)/A_p(\infty)$ for the $\text{C}=\text{C}$ stretching vibration of the polymer, where the integrated intensity obtained after 24 h from the initiation of the reaction was employed as $A_p(\infty)$ for a practical reason. The relative Raman intensities thus obtained are plotted as a function of the reaction time t in Fig. 4.

The kinetic data was analyzed with Avrami's equation¹³:

$$V(t) = 1 - \exp(-bt^n),$$

where V is the fractional conversion of a new phase at time t , and b and n are parameters related to the specific rate and topochemistry of the reaction. In the present analysis, we substituted V for $(1 - X_m)$, assuming that $(1 - X_m)$ represented the volume fraction of a new phase, i.e., the polymer

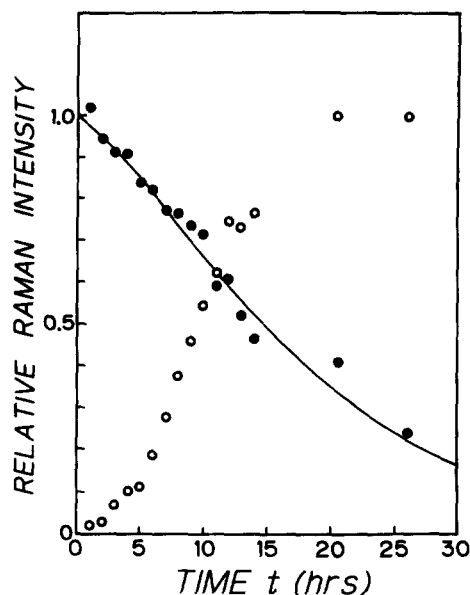


FIG. 4. Kinetic data for the polymerization reaction converted from the Raman peaks measured at 273 K and 3.7 GPa. Solid and open circles indicate the relative Raman intensities of the monomer peak and of the polymer peak, respectively. The solid line is the result of least-square fitting with Avrami's equation (see Fig. 5).

phase. It should be recalled that the relative intensity X_p just represents the partial fraction of the distributed chain segments, whose Raman scattering intensities are resonantly enhanced for the excitation light employed. The parameters b and n were immediately determined by taking double logarithm of the equation. A linear relation is obtained between $\ln[-\ln(x)]$ and $\ln(t)$ as shown in Fig. 5. By a least-square fitting of these experimental data, $n = 1.34$ and $b = 0.018$ were obtained.

DISCUSSION

The mechanism and kinetics of the polymerization reaction in solid acetylene are discussed using the experimental

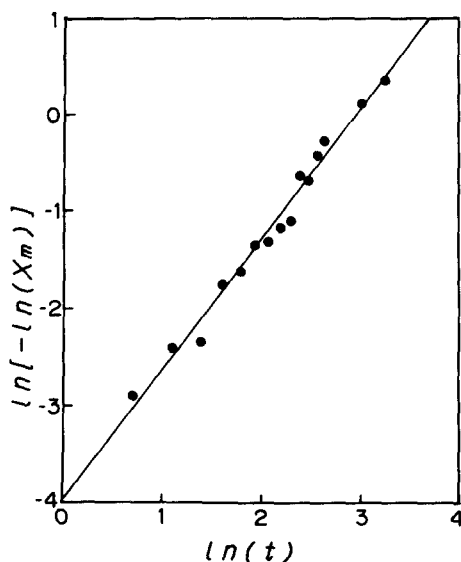


FIG. 5. Double logarithm plotting of the kinetic data for the polymerization reaction. A least-square fitting of the linearized data with Avrami's equation gave 1.34 for exponent n and 0.018 for specific rate constant b .

results obtained by the present Raman measurements. The results are summarized as follows:

- (1) The polymerization reaction was induced in the orthorhombic phase at room temperature and at pressures above 3.5 GPa.
- (2) The reaction product consisted of two kinds of conjugated polymers, *trans*-polyacetylene and *cis*-polyacetylene. The major element was the *trans* polymer.
- (3) The analysis of the reaction process gave $n = 1.34$ as the exponent of Avrami's equation.

We first examine possible reaction paths which lead to the *trans* polymer or *cis* polymer in the orthorhombic crystal. Figure 6 shows the structure of the orthorhombic phase at 0 K and 4.0 GPa. The molecular positions were drawn using the lattice parameters theoretically calculated by LeSar.¹² Acetylene molecules form planar zigzag patterns in the *ab* plane of the unit cell. These molecular planes are stacked along the *c* axis at a $c/2$ interval with offset by $b/2$. A notable feature of the molecular arrangement is that the nearest neighboring $\text{C}\equiv\text{C}$ cores are not situated in the *ab* plane but in the *bc* plane. The intermolecular C-C distance in the *ab* plane contracts from 3.81 Å at atmospheric pressure to 3.45 Å at 4.0 GPa, while that in the *bc* plane contracts from 3.56 to 3.05 Å. In the *ab* plane, closer approach of the neighboring $\text{C}\equiv\text{C}$ cores is prevented by the hydrogen atoms bonded to both ends of the $\text{C}\equiv\text{C}$ core. Hence, the polymerization reactions, which accompany opening of the triple bonds and crosslinking of the monomer molecules, are expected to occur in the *bc* plane rather than the *ab* plane. LeSar also has pointed out in the theoretical study that the

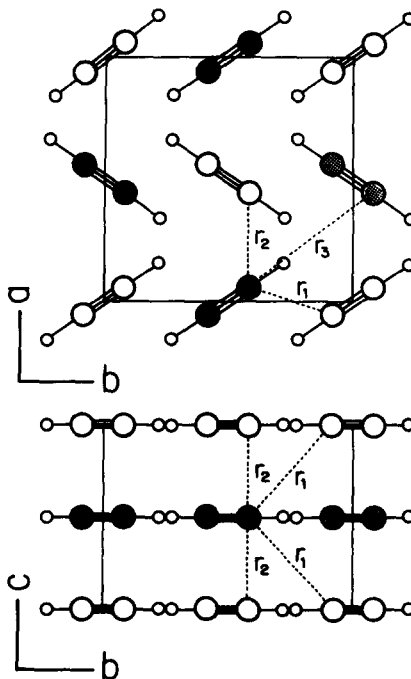


FIG. 6. Crystal structure of the orthorhombic phase of acetylene at 0 K and 4.0 GPa, where the positions of carbon (large circles) and hydrogen atoms (small circles) are drawn using the lattice parameters theoretically calculated by LeSar.¹² The intermolecular C-C distances are 3.05 (r_1), 3.22 (r_2), and 3.45 Å (r_3).

molecular arrangement in the *ab* plane was not favorable for formation of the conjugated linear chains.¹²

There are two possible reaction paths for polymerization in the *bc* plane. One is a linear path running along the diagonal of the *bc* plane (path A). The reaction proceeds by *trans* opening of the triple bonds and crosslinking of the adjacent molecules to form a *trans* polymer. The other is a zig-zag path, leading to a *cis* polymer by *cis* opening of the triple bonds and successive crosslinking reaction of the molecules (path B). These two reaction paths are schematically illustrated in Fig. 7. For the reactive chain end of an oligomer chain, the following reacting molecules are situated at equivalent two positions at the upper and lower molecular planes. Consequently, polymerization reactions seem to occur equivalently along both path A and path B. The dominant formation of a *trans* polymer, however, indicates that other factors such as motions and shapes of the reacting monomer should be taken into consideration.

The polymerization reaction along path A involves less molecular motions than that along path B. The molecules located along path A form a molecular plane inclined somewhat with respect to the *b* axis of the unit cell. The molecular orientation in this plane is very favorable to a topochemical polymerization; a *trans* polymer can be formed simply by crosslinking of the adjacent molecules with C–C single bonds. On the other hand, the reaction along path B involves molecular rotations prior to crosslinking reactions. As can be seen in Figs. 6 and 7, the axes of the molecules at *cis*-geometry sites along path B are not in the same plane, canting slightly with respect to the backbone plane of the *cis* polymer to be formed. Therefore, rotations of the molecules into suitable reactive sites in the *bc* plane are required to form a *cis* polymer. In molecular solids, reactions involving the least changes in molecular positions are favored.²³ This least motion principle suggests that path A is preferable to path B for the solid-state polymerization.

The *trans*-bent shape of excited acetylene molecule is another factor suggesting that the reaction occurs by path A.

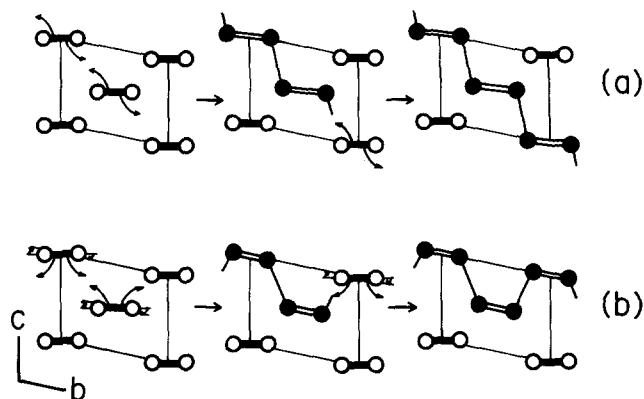


FIG. 7. Two possible paths for the polymerization reaction in the *bc* plane. The C≡C cores of monomer and the backbones of the conjugated *trans* polymer and *cis* polymer are schematically drawn. (a) Path A: *trans* polyacetylene is formed by a one-step process accompanying the *trans* opening of the triple bond. (b) Path B: *cis*-polyacetylene is formed by a two-step process accompanying rotation of the molecules and the *cis* opening of the triple bonds.

The shape of the molecule undergoing polymerization will contribute much for the determination of the possible reaction path. There has been no structural study of acetylene molecule in the excited electronic state in solids. We, therefore, consider the results on the free molecule, molecular shapes of which have been investigated in detail by absorption measurements in the ultraviolet regions.²⁴ This may be of some help for discussion of the polymerization path. The rotational analysis of the ultraviolet bands of the gas phase has indicated that the excited molecule has a *trans*-bent shape with C_{2h} symmetry. The determined C–C–H angle and the C–C distance are 120° and 1.388 Å, respectively. The corresponding values of the ground state molecule are 180° and 1.206 Å. We assume that the molecule thermally excited for polymerization in the crystalline phase adopts the same *trans*-bent shape as the free molecule, although the excited state may be affected by the crystal fields. The *trans*-bent shape thus assumed gives a great advantage to the reaction by path A over that by path B, accounting consistently for the dominant formation of a *trans*-polymer experimentally observed by the high-pressure study.

The reaction process of the solid-state polymerization is described as a one-step and one-dimensional growth process. According to Avrami's kinetics model for phase transitions in solids, topochemical features of crystal growth are characterized by the exponent *n* of the equation.¹³ For diffusionless reaction process, the values of *n* lie between the corresponding limits for the various types of growth;

$$1.0 \leq n \leq 2.0 \text{ for linear growth,}$$

$$2.0 \leq n \leq 3.0 \text{ for plate-like growth,}$$

and

$$3.0 \leq n \leq 4.0 \text{ for polyhedral growth.}$$

For the polymerization reaction of acetylene, $n = 1.34$ was obtained from the experimental data (see Fig. 5). This value clearly shows that the polymerization process is well characterized as a diffusionless linear growth, i.e., one-step and one-dimensional growth.

In general, phase transitions in solids can be represented as combinations of two different types of elementary steps: (a) transport (diffusion) of reactants to reactive sites, and (b) formation of chemical bonds at reactive sites. The value of $n = 1.34$ obtained for the polymerization of acetylene implies that the reaction proceeds by only step (b). Diffusion processes such as reorientation of molecules are not involved in the reaction. Contribution of diffusion steps to the exponent of *n* has been demonstrated in the solid-state polymerization of cyanogen. Yoo and Nicol found the exponent *n* of Avrami's equation to be between 0.53 and 0.58 for the polymerization process of a linear chain of cyanogen dimers into a paracyanogen ladder of fused pyrazine rings.⁸ From these values they proposed a two-step mechanism for the growth of paracyanogen; reorientation of the molecules (the first step) and cycloaddition reaction between adjacent chain-like molecules (the second step). If the reaction along path B was dominant for the case of the polymerization of acetylene, its two-step process might give a value less than unity to the exponent *n*. The experimentally obtained value,

$n = 1.34$, indicates that the actual polymerization reaction proceeds along path A.

One aspect of the previous argument about the reaction paths for polymerization deserves further high-pressure studies. The intermolecular C—C distance between the adjacent molecules in the *bc* plane is 3.05 Å even at pressures as high as 4.0 GPa. This distance is much larger in comparison to the C—C single-bond length 1.43 Å of *trans*-polyacetylene determined by electron diffraction studies.²⁵ The question is whether crosslinking reactions between the molecules separating at such a large distance are possible or not. The structural parameters of the orthorhombic unit cell, which were employed in our discussion on the spatial arrangement of molecules, were calculated ones. There has been no experimental data available for discussion on the reaction mechanism. Structural investigations of the high-pressure orthorhombic phase by x-ray diffraction will be of great help for the further study of the solid-state polymerization in acetylene.

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