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Author(s)	Osugi, Jiro; Hara, Kimihiko
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EFFECT OF PRESSURE ON THE ELECTRICAL CONDUCTIVITY OF ORGANIC SUBSTANCES

I Pyrolyzed Polyacrylonitrile

BY JIRO OSUGI AND KIMIHIKO HARA

The electrical conductivity of pyrolyzed polyacrylonitrile has been measured at 15°~100°C, and at pressures up to 50 kb, by the use of a compact cubic anvil apparatus. The conductivity increases markedly with increasing pressure at constant temperature and with increasing temperature at constant pressure. It seems to be closely associated with the amount of π-electron overlap between adjacent molecules. The conductivity under pressure follows the usual exponential law; $\sigma = \sigma_0 \exp(-E/kT)$. The mechanism of pyrolysis has been also investigated.

Introduction

Recently the effects of high pressure on the electrical conductivity of various organic compounds such as polycyclic aromatic hydrocarbons[1] have been investigated. Generally the observed conductivity increases with increasing pressure. This behavior seems to be closely associated with the increase in the amount of π-electron overlap between adjacent molecules. However, the mechanism of electron conduction in most organic compounds is not yet clear.

It has been observed that appreciable conductivity can be generated in polyacrylonitrile by pyrolysis in the temperature range 500°~900°C[2]. After pyrolysis, the material behaves like a semiconductor, exhibiting a thermally activated conductivity. For these reasons this material is quite interesting even though its chemical nature and structure after pyrolysis are not known with any accuracy.

The present work describes the results of resistivity measurements as a function of pressure on pyrolyzed polyacrylonitrile. The temperature dependence of conductivity was also measured in order to obtain the effect of pressure on the activation energy for conduction. The mechanism of pyrolytic reaction is discussed from the measurement of infrared spectrum.

Experimental

Material : The sample examined in this investigation was polyacrylonitrile synthesized by emulsion

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1) G. A. Samara and H. G. Drickamer, *J. Chem. Phys.*, **37**, 474 (1962)

Y. Harada, Y. Maruyama, I. Shirotani, and H. Inokuchi, *Bull. Chem. Soc. Japan*, **37**, 1378 (1964)

2) A. V. Topchiev, M. A. Geiderikh, B. E. Davydov, V. A. Kargin, B. A. Krentzel, I. M. Kystanovich, and L. S. Polack, *Dokl. Akad. Nauk SSSR*, **128**, 312 (1959)

polymerization[3] ($\overline{M}_n$: 38×10^4, $[\eta]=4.53$ at 35°C). After heating at different temperatures for 3 hrs in vacuo, the mechanism of pyrolysis was investigated from the measurement of the infrared spectrum. The spectrometer used was Hitachi EPI S2. This is exothermic reaction and fast enough to reach the state of equilibrium at each temperature in 3 hrs. Heating in inactive gas, argon, gave the same results as in the case of heating merely in vacuo. The pyrolysis of polyacrylonitrile up to 500°C generates considerably high electrical conductivity. The sample used for the measurement of pressure dependence on conductivity is the substance obtained from heating in vacuo at 500°C for 3 hrs. It was washed with dimethylformamide and acetone in order to remove the possible decomposed materials of low molecular weight. The resistivity at room temperature under atmospheric pressure was $1.5 \times 10^7 \Omega \cdot$cm. It is a nearly black material, insoluble and infusible, like many other organic semiconductors.

Apparatus and Procedure : Hydrostatic pressures up to 60 kb were generated in a compact cubic anvil device. The pressure calibration techniques have been reported in detail earlier[4]. The vertical cross section of the apparatus is shown in Fig. 1. Six anvils advance to compress solid pressure transmitting
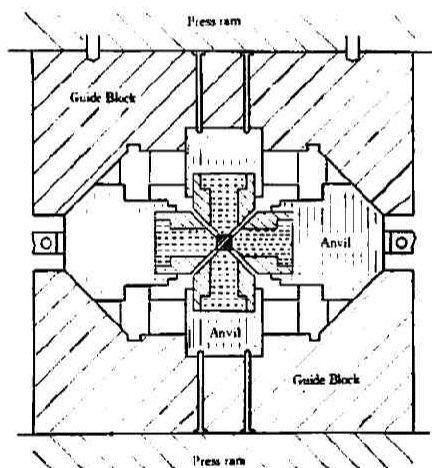

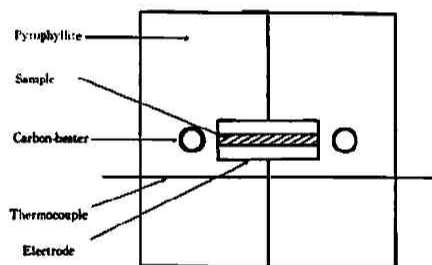Fig. 1 Vertical cross section of compact cubic anvil apparatus

Fig. 2 Cross section of a sample cubic used for resistance measurements

medium, a cubic block of pyrophyllite ($Al_4[Si_5O_{20}](OH)_4$), in which the sample was held. Schematic view of the internal structure of the sample cube for resistivity measurement is shown in Fig. 2. The two cylindrical carbons serve as a heat source due to the passage of high alternating current at low voltage from the two opposing anvils. They are sufficient to produce a well-defined stable temperature. Temperature was measured with chromel-alumel thermocouple, whose lead wires could be brought out between the anvils. The temperature range of this work was 15°C~100°C. The wires for the resistivity measurement are lead from other two opposing anvils.

3) Y. Fujisaki, *Kobunshi Kagaku*, 18, 581 (1961)
4) J. Osugi, K. Shimizu, K. Inoue, and. M. Yasunami, *This Journal*, 34, 1 (1964)

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    The sample was consisted of a thin wafer of 4 mm diameter and the thickness after compression of
about 1 mm. The sample resistivity, ρ was calculated by using the equation, $\rho = RS/l$, where R is the
measured resistance, S is the cross-sectional area, and l is the final thickness of the sample. These contact
resistances would be eliminated under the first few kilobars, as was proved for several organic materials
by Eley and Parfitt[5].

                                            Results

    The plot of resistivity versus pressure at room temperature is shown in Fig. 3. The resistivity at 10
kb is $9.5 \times 10^6 \Omega \cdot cm$, and $6.5 \times 10^3 \Omega \cdot cm$ at 60 kb. The change is of the order of about three powers of
ten in the pressure range. This is the result of the ascending pressure, but a hysteresis arises largely
from the friction in the sample holder. The all results are the average values of several runs. No chemi-
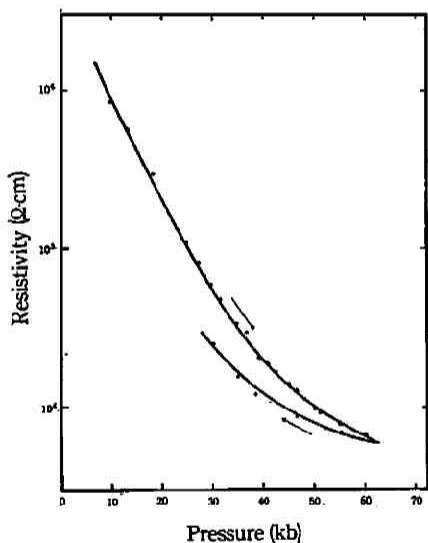cal change occurred in the pressure range of this work.

Fig. 3   Resistivity *vs* pressure at room
         temperature

    Fig. 4 contains the results of pressure dependence of resistivity at different tmperatures. $\log \sigma$ versus
$1/T$ plots shown in Fig. 5 were obtained from 15° to 100°C at various pressures and resulted in single
straight lines, the slope of which gave the activation energies for conduction.

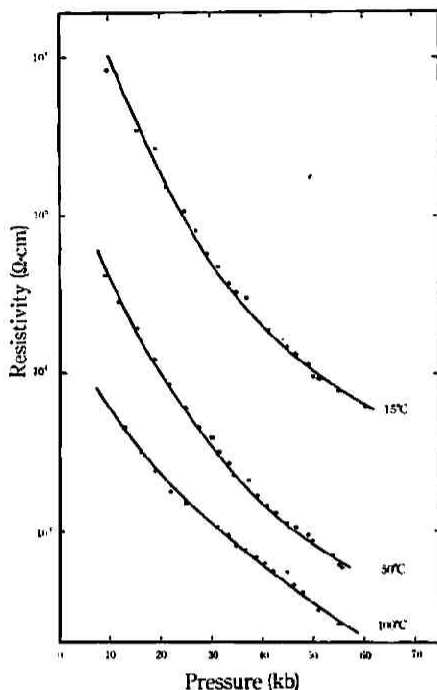   5) D. D. Eley and G. D. Parfitt, *Trans. Faraday Soc.*, **51**, 1529 (1955)
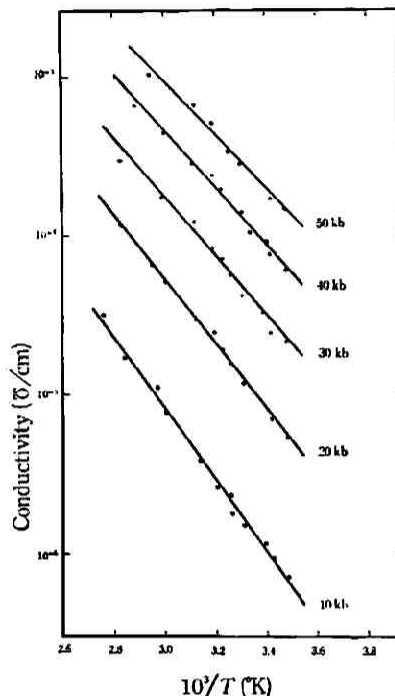
Fig. 4 Resistivity *vs* pressure; 15°C, 50°C, 100°C

Fig. 5 logσ *vs* $1/T$ at various pressures

Consideration

According to the infrared spectrum of pyrolyzed polyacrylonitrile shown in Fig. 6 (a) and (b), the absorption band of C≡N stretching, 2247 cm^{-1} weakens and the band due to —C=N—C=N— appears at 1550∼1700cm^{-1} as the heating temperature increases. It suggests the occurrence of the naphthylidine type polycyclic structure. The gradual shift toward long wave length of this band means the increase of this conjugate system. Besides, the absorption bands of C—H stretching, 2936cm^{-1} and C—H bending, 1456cm^{-1} become weak. On the other hand, Grassie[6] reported that the gradual deepening color also depends on the ring formation which constructs the conjugated double bond system, —C=N—C=N—. Therefore, the main reaction in polyacrylonitrile due to heating seems to be the production of the naphthylidine like structure as shown in Fig. 7. Thus the considerably high conductance comes from the mobile π-electrons in the conjugate system.

The electrical conductivity of many conductive organic substances increases with increasing temperature. In this sense and from the order of the conductivity these are regarded as semiconductors. The relation between conductivity and temperature is given by

$$\sigma = \sigma_0 \exp(-E/kT), \qquad (1)$$

and E is the activation energy for conduction. It is of the order of magnitude of 0.1∼2.0 eV. The

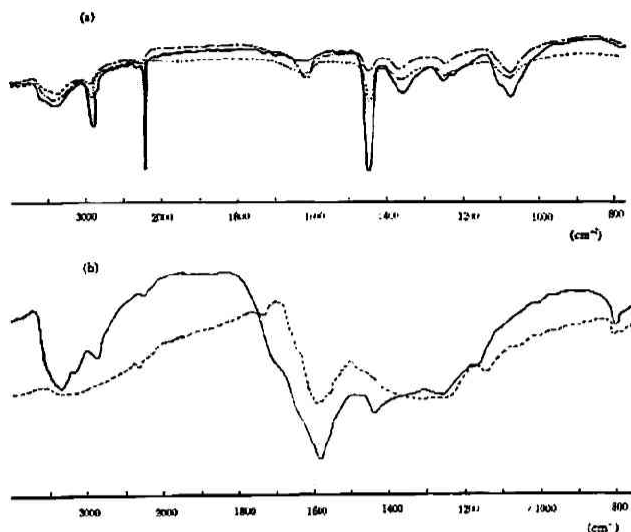6) N. Grassie, *J. Polymer Sci.*, 39, 211 (1959)

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Fig. 6 The infrared absorption of polyacrylonitrile pyrolyzed at
various temperatures
(a) ————, original sample; ------, heated at 100°C
for 3hrs; —— —— — —, at 200°C for 3hrs;
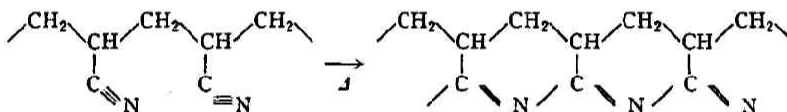(b) ·------, at 400°C for 3hrs; ————, at 500°C for 3hrs

Fig. 7 Pyrolysis of polyacrylonitrile

.emperature dependence of conductivity for the present substance is found to follw Eq. (1) under each
pressure. (cf. Fig. 5.)

In intrinsic semiconductors, the population of carriers, n, obeys the exponential relation,

$$n = n_o \exp(-E_g/2kT), \qquad (2)$$

where E_g is the forbidden energy gap. The conductivity is related to the numbers of carriers and to the
mobility by

$$\sigma = ne\mu. \qquad (3)$$

Extensive experimental studies of the mobilities of electrons and holes in anthracene and naphthalene
show that the mobilities increase with decreasing temperature as $T^{-\alpha}$, with α between 1 and 2. This
weak temperature dependence of the mobilities implies that the major cotribution to the temperature
dependence arises from the temperature dependence of the number of carriers. From Eqs. (1), (2). and
(3), we have

$$\sigma = \sigma_o \exp(-E/kT) = \sigma_o \exp(-E_g/2kT) \qquad (4)$$

$E = E_g/2$, if the band theory is applicable from above assumptions. E under each pressure can be obtained
from the slope of the curve in Fig. 5. As shown in Fig. 8, it decreases with pressure. Inokuchi and
Ohigashi's value[7] at atmospheric pressure is shown for the purpose of comparison.

7) H. Inokuchi and K. Ohigashi, *High Polymers. Japan (Kobunshi)*, 13. 272 (1964)
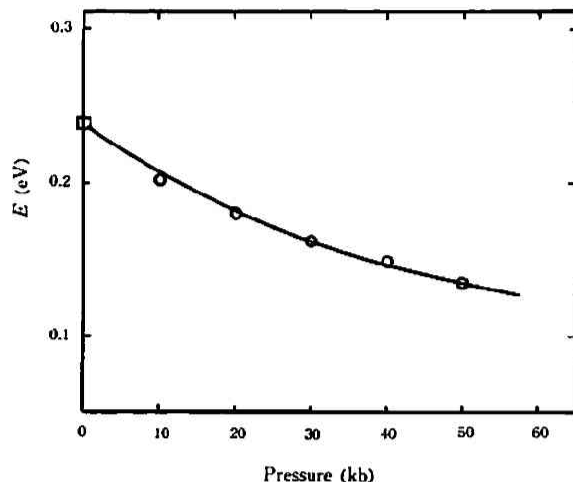
Fig. 8 Variation of the activation energy for conduction, E, with pressure (□: Inokuchi and Ohigashi's value[7])

Now we consider the number of charge carriers existing in a molecule. The activation energy may be estimated by applying the approximate free electron theory[8], which gives good results for energy and intensity of optical transitions in polyenes. The difference of boundary conditions gives the following two equations :

$$E_f = \frac{h^2}{4ma^2}\frac{1}{N} \quad \text{or} \quad \frac{h^2}{8ma^2}\frac{N+1}{N^2}, \tag{5}$$

where N is the number of π–electrons. m is mass, and a is the bond distance. E_g from electrical conduction is considered to be equal to E_f from optical transition. Most data for organic substances were found to lie between the two lines. Table 1 contains the number of N estimated from E_g by using Eq. (5). a is the carbon-nitrogen distance in aromatic compounds, i. e. 1.28Å[9]. which seems to be constant in this pressure range. The value of N increases uniformly and reaches twice at 50 kb. In other words, it implies that the energy gap at 50 kb amounts to the value corresponding to the molecule which contains 88~176 free electrons, while it is still a molecule containig 48~95 electrons at atmospheric pressure.

Table 1 Observed E and estimated N

P (kb)	E (eV)	N
0	0.48	48~ 95
10	0.40	57~114
20	0.36	64~127
30	0.32	71~143
40	0.30	76~153
50	0.27	88~176

8) H. Kuhn, *J. Chem. Phys.*, **17**, 1198 (1949)
9) C. A. Coulson. "Valence" Oxford University Press (1951)

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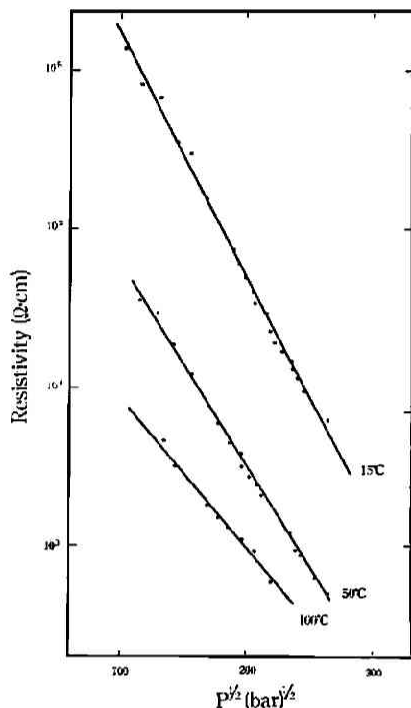
Fig. 9   Resistivity vs $P^{\frac{1}{2}}$; 15°C. 50°C, 100°C

In Fig. 3, the resistivity decreases rapidly in the lower pressure region, and then the rate of decrease becomes slow as pressure increases. This seems to be qualitatively ascribed to higher compressibility in the former and lower compressibility in the latter. Pohl et al.[10] reported that $\log\sigma$ is proportional to the square root of pressure, i. e.

$$\log(\sigma/\sigma_o)=bP^{\frac{1}{2}}, \qquad (6)$$

where σ_o is the conductivity at zero pressure and b is a constant. They confirmed this fact experimentally by PAQR-polymers.[*] It is interesting to note that the replotting of the curves in Fig. 4 against $P^{\frac{1}{2}}$ gives the straight lines. (Fig. 9)

The increase in conductivity as the π-electron clouds of adjacent molecules caused to increasingly overlap is closely associated with the production of carriers and carrier mobility. Both of them were considered in Pohl et al's treatment. But each contribution does not appear explicitly in the last formulation, since it was deduced merely under the assumption that the overlap between molecules is proportional to the square root of pressure. The large decrease of the compresssibility in the lower pressure region and the small decrease in the higher pressure region may be related to the carrier mobility and the production of carriers. Therefore, it is reasonable that the pressure dependence curve of E is also concave to the pressure axis.

These considerations suggest that the pressure dependence of conduction in organic substances can not be explained only by band model or only by hopping model but that both should be considered

10)   H. A. Pohl, A. Rembaum, and A. Henry, J. Am. Chem. Soc., **84**, 2699 (1962)

*)   polyacene quinone radical polymers

together. Further detailed experimentation is necessary to explain fully these interesting pressure effects.

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Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan