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Kyoto University

EFFECTS OF PRESSURE ON THE ELECTRICAL PROPERTIES

OF ORGANIC SEMICONDUCTORS

Pyrolyzed Polyacrylonitrile and α, α-Diphenyl-β-Picrylhydrazyl

By KIMIHIKO HARA

The electrical resistivity of PAN obtained at various pyrolysis temperatures and applied pressures and of DPPH obtained by the crystallization from various solvents were measured under high pressures up to 70 kbar by using a compact cubic anvil apparatus. Its temperature dependence which follows the usual exponential law was also measured to obtain the activation energy for conduction. From these values the carrier mobility under high pressure was estimated. The conduction mechanism was also investigated. The contribution of lone-pair electrons must be taken into account for these substances under consideration in addition to the mobile free π electrons.

Introduction

Under very high pressure of more than 20 kbar it is interesting to investigate how organic solids are compressed. In this pressure range there is little data even in the direct measurements of compressibility. Among the ways of measuring the physical properties under compression, the measurement of electrical resistance is an early developed way and the method is used widely in the calibration of pressure by means of the electrical transition points of metals.

The measurement for high resisting organic semiconductors has been also carried out[1]. The change of the electrical resistance of organic solids or polymer materials with pressure gives us information concerning the mechanism of the electrical conduction. such as the mobility of carriers.

In the present work the pyrolyzed products of polyacrylonitrile were chosen as a typical polymer semiconductor which could be obtained by various types of solid state reactions. As the pyrolyzed polyacrylonitrile is stable chemically, thermally and mechanically, and the samples which have different properties depending on pyrolysis temperature are obtainable. this is a material that has been investigated rather widely in the measurements of electrical conduction, thermoelectric power, ESR and so on.

The electrical conductivity of polyacrylonitrile increases with the increase in pyrolysis temperature. The cause of this fact has been considered due to the increase of the conjugated carbon and nitrogen bonds formed by the polymerization of cyanide groups, but at high pyrolysis temperature the

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

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production of lone-pair electrons has been observed and their effect to the conduction must be taken into consideration. The result of the investigation under atmospheric pressure shows that the electrical conduction in organic solids increases exponentially with the reciprocal of absolute temperature, which is mostly due to the mobile free π-electrons.   Therefore, most of these substances are treated as intrinsic semiconductors.   But in order to get appreciable conductivity, it is necessary to form a structure of aromatic polycondensed ring or a long chain structure with conjugated double bonds. On the other hand, little information has been obtained about the contribution of free radicals to the conduction[2].

The stable organic solid free radical α, α-dipheyl-β-picrylhydrazyl (DPPH) behaves as a semiconductor with a considerably low activation energy of 0.13 eV[3]. The values of recent measurements for single crystals are 0.75~0.8 eV by Inokuchi et al.[4] and 0.6 eV by Masuda et al.[5]. However, this substance has rather different properties depending upon the crystal structure.

In this paper the effect of pressure on the electrical properties of pyrolyzed PAN was investigated and the carrier mobility under high pressure was estimated. The comparison was made with the results of DPPH[6][7].

Experimental

Materials

The sample used in this investigation was polyacrylonitrile (PAN) synthesized by emulsion polymerization[8] ($\overline{Mn}=3.8\times10^5$, $[\eta]=4.53$ at 35°C). Elementary analysis: Observed, C: 68.4%, H: 5.87%, N: 26.15%. Calculated, C: 67.94%, H: 5.60%, N: 26.4%.

The DPPH used was prepared by the crystallization of different solvents. DPPH-I is the sample obtained by the crystallization from benzene solution. DPPH-II is the sample obtained by heating the DPPH-I and removing benzene. DPPH-III is the sample obtained by the crystallization from carbon disulfide solution. The crystal structure and some other properties of these samples have been reported previously[7].

Apparatus and procedures

Hydrostatic pressures were generated in a compact cubic anvil device, whose calibration method and other experimental techniques were previously reported in detail[9]. Only a schematic view of the

2) D. D. Eley and M. R. Willis. "Symposium on Electrical Conductivity in Organic Solids", p.257, ed. by H. Kallmann and M. Silver, Interscience Publishers, New York (1961)

3) D. D. Eley and G. D. Parfitt, Trans. Faraday Soc., 51, 1529 (1955)

4) H. Inokuchi, Y. Harada and Y. Maruyama, Bull. Chem. Soc. Japan, 35, 1559 (1962)

5) K. Masuda and J. Yamaguchi, J. Phys. Soc. Japan, 20, 359 (1965)

6) J. Osugi and K. Hara, This Journal, 36, 81 (1966)

7) J. Osugi and K. Hara. Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.), 90, 873 (1969)

8) Y. Fujisaki, Kobunshi Kagaku, 18, 581 (1961)

9) J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, This Journal, 34, 1 (1964)

Fig. 1 Schematic view of a pyrophyllite
sample cube for resistance measure-
ment

1: Thermocouple
2: Pyrophyllite
3: Electrode
4: Teflon or AgCl sleeve
5: Carbon heater

internal structure of the pyrophyllite cube for resistivity measurement is shown in Fig. 1. Two carbon rods serve as a heat source by passing high electrical current through them from anvil to anvil. They are sufficient to produce a well-defined stable temperature up to 250°C. Temperature was monitored by means of a chromel-alumel thermocouple, whose junction was in contact with an electrode in the cell, and whose lead wires could be brought out between the gaps of anvils.

In order to prevent the deformation of the sample and the electrodes, they are wrapped with a sleeve made of teflon or AgCl. Resistivity was measured by means of a VTVM (Toa, PM–8) electrometer.

Results and Discussion

The structural change of PAN with pyrolysis has been considered as follows :

Condensed Aromatic
Naphtyridine Rings

[1]   [2]   [3]

The resistivity of pyrolyzed PAN obtained at various pyrolysis temperatures was measured under atmospheric pressure by Ohigashi[10].

In Fig. 2 the room temperature resistivity is plotted as a function of the inverse pyrolysis temperature. From this plot it is evident that the room temperature resistivity is a thermally activated function of the pyrolysis temperature. The two straight lines whose slopes change at about 390°C are considered to show the difference of the reaction mechanism between the lower and the higher temperatures. The activation energy for the lower temperature process and that for the higher tempera-ture process are *ca.* 0.5 eV and 3 eV, respectively.

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10)   K. Ohigashi. *Kogyo Zairyo*, 13, 19 (1965)

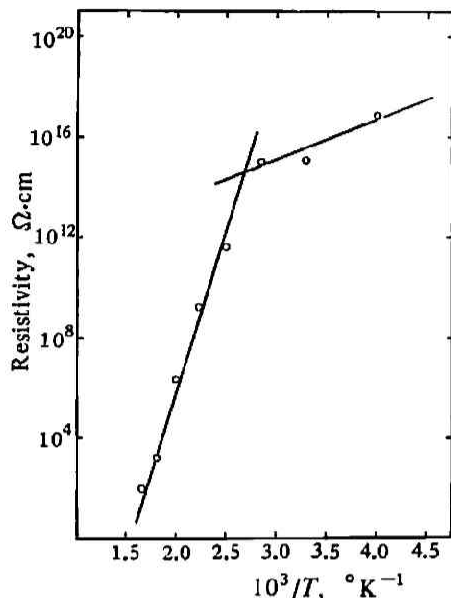96   K. Hara

Fig. 2 Relation between the room temperature resistivity and the reciprocal of reaction temperature at normal pressure[10]
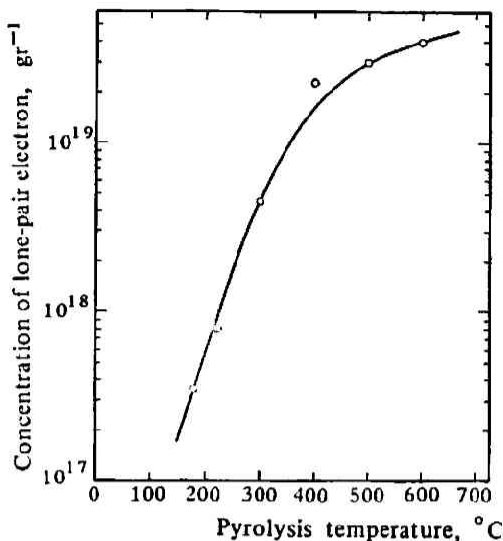
Fig. 3 Relation between the concentration of lone-pair electrons and the reaction temperature[11]

On the other hand, the dependence of the concentration of lone-pair electrons on pyrolysis temperature has been obtained by the measurement of ESR by Hasegawa and Shimizu[11]. As is shown in Fig. 3, the concentration of lone-pair electrons increases with the increase in pyrolysis temperature. The cause of this fact seems to be the occurrence and the gradual increase in the elimination of hydrogen atoms or the scission of the polymer chain. However, the formation of [3] with the increase in pyrolysis temperature retards the rate of the increase of the concentration of lone-pair electrons.

The above results indicate that only the reaction [1] $\longrightarrow$ [2] proceeds up to ca. 250°C, while at the temperature higher than ca. 400°C lone-pair electrons are formed and the reaction [2] $\longrightarrow$ [3] occurs because of the elimination of hydrogen atoms or the scission of the polymer chain.

On the other hand, the change of the electrical resistance with pyrolysis temperature was followed under high pressure. One of the results at 30 kbar is shown in Fig. 4. The temperature at which the abrupt change of resistance occurs corresponds exactly to the temperature at which the concentration of lone-pair electrons abruptly increases (cf. Fig. 2). The dependence of this temperature upon the applied pressure is shown in Fig. 5. These facts agree well with the results of elementary analysis which are shown in the preceding paper[12].

Therefore, the experimental value for the activation energy of pyrolysis obtained from Fig. 2, 0.5 eV for the lower temperature process seems to correspond to the energy required to break a

11)   S. Hasegawa and T. Shimizu, *Oyo Butsuri*, **37**, 669 (1968)

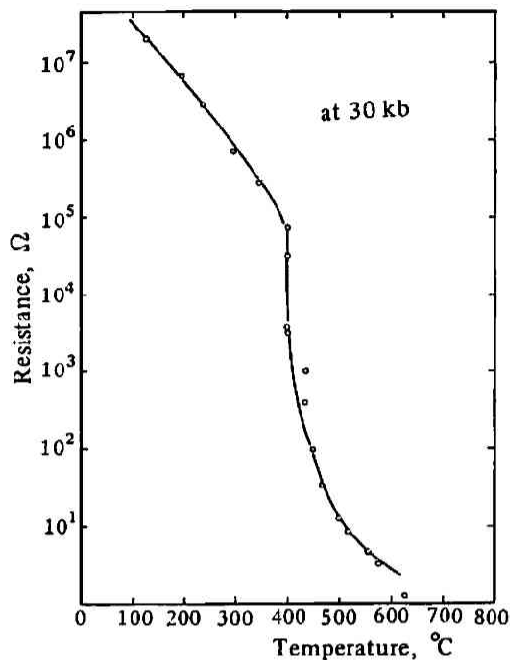12)   K. Hara, *This Journal*, **40**, 73 (1970)

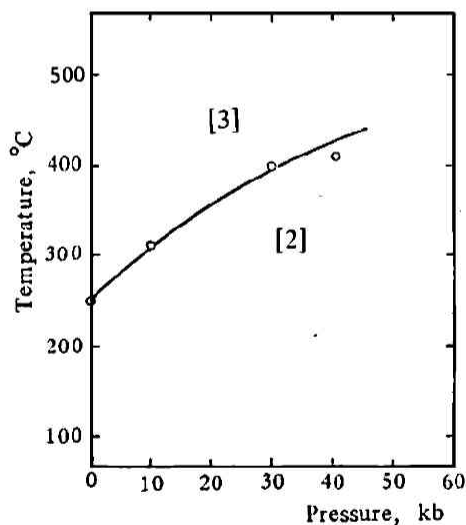Fig. 4   Change of resistance with pyrolysis temperature at 30 kbar

Fig. 5   Pressure dependence of the temperature at which the reaction [2] $\longrightarrow$ [3] occurs

triple bond and form a conjugated structure. This value, however, is thought to be somewhat small even if the stabilization of cyanide groups by strong dipole-dipole interactions is taken into account.

On the other hand, 3 eV obtained for the higher temperature process corresponds to the energy

13)   W. D. Brennan, J. J. Brophy and H. Schonhorn, "Organic Semiconductors, p. 159, ed. by J. J. Brophy and W. Buttry, Macmillan Co., New York (1962)

K. Hara
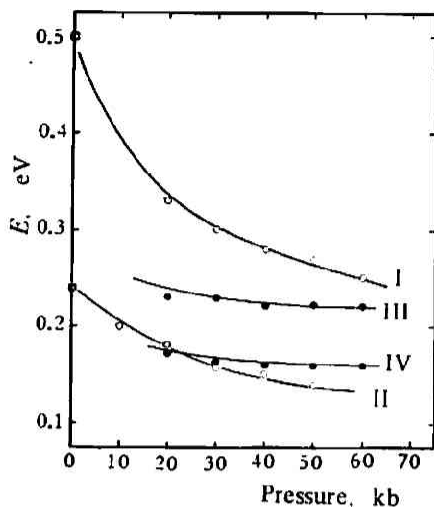
Fig. 6 Relations between E and pressure for PAN obtained under various pyrolysis conditions

    I: 1 bar, 400°C
    II: 1 bar, 500°C
    III: 30 kbar, 350°C
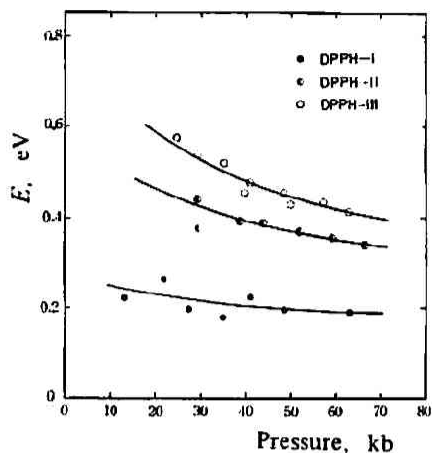   IV: 30 kbar, 400°C

Fig. 7 Relations between E and pressure for DPPH-I, II, III
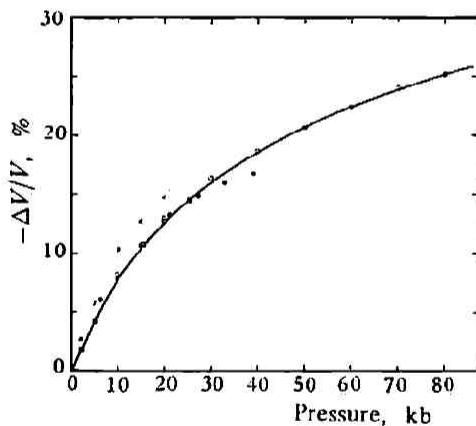
●: DPPH-I
◗: DPPH-II
○: DPPH-III

Fig. 8 Change in volume of molecular crystals with pressure

●: DPPH
×: Naphthalene
□: Anthracene
○: Sulfur

to break a C–H bond or a C–C bond and to form free radicals. Brennan, Brophy and Schonhorn[13] have reported that the reaction [1] ⟶ [2] proceeds up to 700°C, but it seems probable that under atmospheric pressure the reaction proceeds up to 400°C at the highest from the results of Figs. 2, 3 and 5.

Figs. 6 and 7 show the dependence of activation energy for conduction E on pressure for PAN obtained at various pyrolysis temperatures and applied pressures.

The rate of decrease in volume with pressure has been measured for several molecular crystals and there is not so large a difference among them, as is shown in Fig. 8. By using these data, the change of resistivity and activation energy for conduction are replotted against $\Delta V/V$. The results
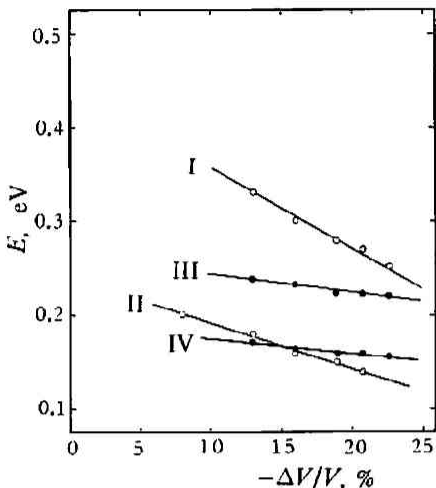
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Fig. 9 E vs $-\Delta V/V$ for PAN

I: 1 bar, 400°C
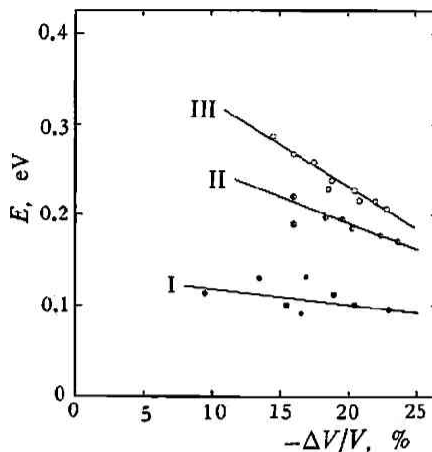II: 1 bar, 500°C
III: 30 kbar, 350°C
IV: 30 kbar, 400°C

Fig. 10 E vs $-\Delta V/V$ for DPPH

●: DPPH-I
◗: DPPH-II
○: DPPH-III

for the latter are shown in Fig. 9 for PAN and Fig. 10 for DPPH. All exhibit linear relations.

Both samples can be treated as intrinsic semiconductors without any contradiction.

The electrical resistivity ρ which is the reciprocal of electrical conductivity σ is given by

$$\rho = \frac{1}{\sigma} = \frac{1}{e\mu n}, \tag{1}$$

where n is the carrier concentration and μ is their mobility. If the exponential temperature dependence is assumed to originate solely from n, then equation (1) is written by

$$\rho = \frac{1}{e\mu n_0} \exp(E/kT). \tag{2}$$

where E is the thermal activation energy for conduction and n_0 the effective density of states in the conducting level of the crystal. If $\ln \rho$ is differentiated by $\Delta V/V$. then from equation (2),

$$\frac{\partial \ln \rho}{\partial (\Delta V/V)} = -\frac{\partial \ln \mu}{\partial (\Delta V/V)} - \frac{\partial \ln n_0}{\partial (\Delta V/V)} + \frac{1}{kT}\frac{\partial E}{\partial (\Delta V/V)}. \tag{3}$$

On the other hand.

$$n_0 = 2(2\pi kT/h^2)^{3/2} (m_e m_h)^{3/2}, \tag{4}$$

where m_e and m_h are the effective mass of electron and hall. The change of effective mass with pressure is comparatively small. Thus the change of n_0 with pressure is assumed to be small, i. e. $\partial \ln n_0/\partial (\Delta V/V)=0$, so that from equation (3) the volume dependence of mobility, i.e. $\partial \ln \mu/\partial (\Delta V/V)$ can be estimated by using the values of $\partial \ln \rho/\partial (\Delta V/V)$ and $\partial E/\partial (\Delta V/V)$ from Figs. 9 and 10. These results are listed in Table 1.

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Table 1   The volume dependence of ρ, E and μ

Substance	$\dfrac{\partial \ln \rho}{\partial(\Delta V/V)}$ ($\Omega \cdot cm$)	$\dfrac{\partial E}{\partial(\Delta V/V)}$ (eV)	$-\dfrac{\partial \ln \mu}{\partial(\Delta V/V)}$ ($cm^2/V \cdot sec$)
PAN–II	4.2×10^1	5.0×10^{-1}	2.2×10^1
PAN–IV	2.8×10^1	1.0×10^{-1}	-1.0
DPPH–I	1.1×10^2	2.0×10^{-1}	9.9×10^1
DPPH–II	1.3×10^2	6.0×10^{-1}	1.1×10^2
DPPH–III	1.1×10^2	9.5×10^{-1}	6.8×10^1

The values of the product $\mu \cdot n_0$ can be calculated from equation (2) by using the experimental values of ρ and E. In the case of free molecules, in which the intermolecular interaction is neglected, the value of n_0 is assumed to be the product of the multiplicity of the first excited electronic level of each molecule, which is roughly equal to the number of π-electron in the molecule, and the concentration of molecules in a crystal. From the above assumption the upper limit of n_0 is estimated to be of the order of 10^{23} in the substances under consideration. Even in crystals with strong binding, such

Table 2   Activation energies and estimated mobilities under various
pressures at room temperature

Substance	Pressure (kbar)	Activation energy (eV)	Estimated mobility ($cm^2/V \cdot sec$)
PAN–II	30	0.16	5.5×10^{-5}
	40	0.15	1.2×10^{-4}
	50	0.14	1.5×10^{-4}
PAN–IV	30	0.17	1.6×10^{-4}
	40	0.16	1.6×10^{-4}
	60	0.16	3.7×10^{-4}
DPPH–I	30	0.11	2.4×10^{-8}
	40	0.10	5.7×10^{-8}
	60	0.09	3.6×10^{-7}
DPPH–II	30	0.21	3.0×10^{-6}
	40	0.20	1.8×10^{-5}
	60	0.18	8.2×10^{-5}
DPPH–III	30	0.26	2.1×10^{-5}
	40	0.24	5.0×10^{-5}
	60	0.21	9.3×10^{-5}
Phthalocyanine	12.5	0.44	1.7×10^{-2}
	50	0.34	3.4×10^{-2}
Cu-Phthalo-cyanine	12.5	0.49	3.7×10^{-3}
	50	0.43	7.4×10^{-3}

as germanium, n_0 is about 10^{20}. As the binding in molecular crystals is weak, the lower limit can be reasonably taken to be of the order of 10^{20}. Thus, Many, Harnik and Gerlich[14] made an attempt to separate the two quantities by assuming the order of magnitude of n_0 as 10^{21}.

Therefore, assuming that n_0 is 10^{21} and independent on pressure, as is stated above, the carrier mobility under various pressures was estimated. Table 2 shows the estimated carrier mobilities. For comparison, those for Phthalocyanine and Cu-Phthalocyanine calculated from the experimental data of Bradley *et al.*[15] are also listed.

The values of the estimated mobilities for PAN and DPPH fall in a similar order, *i.e.* $10^{-4} \sim 10^{-8}$, while those calculated under the same assumption for various organic semiconductors[14] are ranged in the order of $10^{-12} \sim 10^{2}$. This seems to indicate that the carriers of both samples are similar.

Acknowledgments

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14) A. Many, E. Harnik and D. Gerlich, *J. Chem. Phys.*, **23**, 1733 (1955)
15) R. S. Bradley, J. D. Grace and D. C. Munro, *Trans. Faraday Soc.*, **58**, 776 (1962)