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Electrical and Optical Properties of a Stable Synthetic Metallic Polymer: Polypyrrole

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Absorption and reflection spectra of the polypyrrole films prepared by electrochemical polymerization are shown over the wide wavelength region and the best fit of the calculated reflection spectra is presented to the observed spectra. Electrical conductivity of the film is measured as a function of temperature and a plot of log σ *vs.* $T^{-1/4}$ gives a straight line over the 4.2—300 K region. Furthermore, the thermoelectric-power, S, of the polypyrrole film is shown in the form of S *vs.* T on a linear scale. Based on these results, the conduction mechanism of polypyrrole film is discussed.

In recent years, many polymers such as polysulfur nitride, $(SN)_x$,[1] and AsF_5 doped polyacetylene, $(CH)_x$[2,3] have arrested attention because they exhibited metallic properties. These discoveries have encouraged the search for other polymeric systems with greater chemical stability and plasticity.

Diaz *et al.*[4—7] have synthesized a strongly adhered, durable film; polypyrrole, by electrochemical polymerization of pyrrole on platinum surface. The films have shiny blue-black color and show metallic properties like $(SN)_x$ and doped $(CH)_x$. The room temperature electrical conductivity of the present films is as high as 4.4 Ω^{-1} cm^{-1}. The films are stable in air.

In the present paper, we report the absorption spectra in the 250—4000 cm^{-1} region, the reflection spectra in the 250—33000 cm^{-1} region. The electrical conductivity and the thermoelectric-power of polypyrrole are measured over the wide temperature range and the conduction mechanism of polypyrrole is discussed based on these experimental results.

Experimental

The black films of polypyrrole (*ca.* 0.8 μm thick) were synthesized as described by Diaz *et al.*[4—7] Polypyrrloe was prepared on a platinum surface (1.0×3.0 cm^2) by passing 24 mC/cm^2 of charge in a cell containing 0.54 g (0.1 mol/dm^3) of Et_4NBF_4 and 0.10 g (0.06 mol/dm^3) of pyrrole in 25 cm^3 of 99% aqueous acetonitrile. The films adhere to the electrode surface strongly. The films were washed with distilled water and dried at room temperature in air. Tetraethylammonium tetrafluoroborate (Et_4NBF_4) was prepared by neutralizing 10% aqueous solution of tetraethylammonium hydroxide with 42% aqueous hydrofluoroboric acid.[8] Pyrrole and lithium perchlorate ($LiClO_4$) were products of Nakarai Chemicals Ltd. and they were used as received.

The absorption spectra of the thin polypyrrole film were measured with Hitachi IR 260-50 (250—4000 cm^{-1}), and the reflection spectra of polypyrrole film were measured with Hitachi IR 260-50 and a microscopic spectrophotometer (4000—33000 cm^{-1}) made in our laboratory. It consists of an Olympus microscope, a Carl Zeiss Ultrafluar lens (×10), a Nikon crystal mount, a HTV 928 photomultiplier and a PbS cell, and an Intel 8080 microcomputer for data processing.

The best fit of the calculated reflection spectra of polypyrrole film to the observed spectra were made on a Facom M-200 computer of Nagoya University by using SALS program.

For the thermoelectric-power measurements, a rectangular sample (4×15 mm^2) was mounted lengthwise between two copper blocks using pressure contacts. A temperature difference (ΔT) was established by heating one of the copper blocks, and the voltage generated by the thermal gradient across the sample was measured. The ΔT across the sample was measured with a copper-constantan differential thermocouple.

Results and Discussion

Figure 1 shows the IR absorption and reflection spectra of thin polypyrrole film prepared by using Et_4NBF_4 as supporting electrolyte. The color of the films prepared with Et_4NBF_4 is shiny black and the films prepared by using $LiClO_4$ is brown-black. IR absorption spectra show the bands characteristic of pyrrole confirming the presence of the pyrrole rings in the polymer.[9] For example, the skeletal stretching of the pyrrole ring is found at 1500 cm^{-1} region, the =C–H in-plane deformation is found at 1300 and 1180 cm^{-1}, the =C–H out-of-plane bending at 775 cm^{-1}, and the ring breathing at 920 cm^{-1}. The peak near 1035 cm^{-1} is assigned to the BF_4^- ion since this band is observed in the spectra of Et_4NBF_4 in KBr disk.

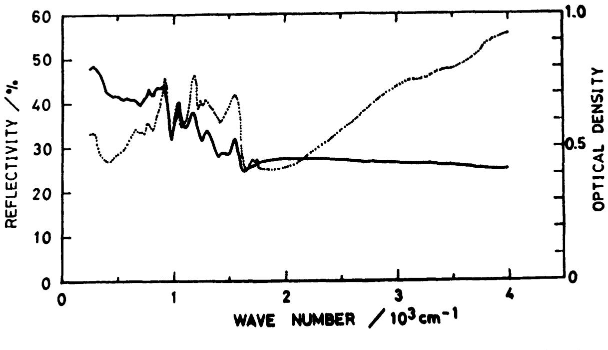

Fig. 1. Comparing between the absorption and the reflection spectra of polypyrrole film prepared by using Et_4NBF_4 in the IR region.
……: Absorption spectrum, ——: reflection spectrum.

Figure 2 shows the reflection spectra of polypyrrole films prepared by different supporting electrolytes. The reflectivity in the lower energy region increases and a broad band around 3000—4000 cm^{-1} region is intensified with increasing conductivities. The lower energy

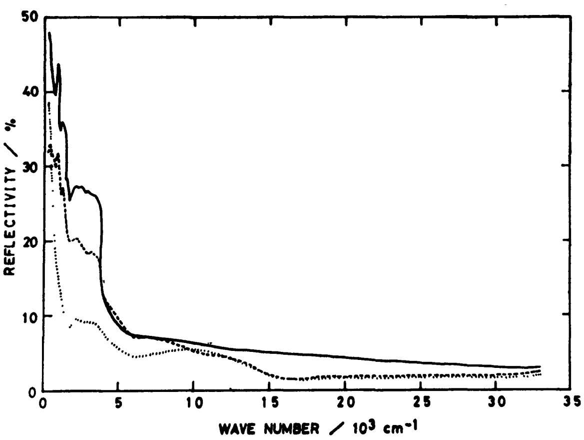

Fig. 2. Reflection spectra of polypyrrole film prepared by using different supporting electrolytes.
——: Et_4NBF_4 ($\sigma_{295K}=4.4\Omega^{-1}\,cm^{-1}$), ------: Et_4NBF_4 ($\sigma_{295K}=0.74\ \Omega^{-1}\,cm^{-1}$), ······: $LiClO_4$ ($\sigma_{295K}=0.016\ \Omega^{-1}\,cm^{-1}$).

transition may be assigned to the zero-band gap transition. The origin of the peak around 3000 cm^{-1} region is not evident, but it may be correlated with the number of carriers because the intensity is enhanced with the conductivity.

Even if the same supporting electrolyte was used, the reflection spectra of the films were not the same from each other due to polymerization conditions. Comparing the reflection spectra of the films prepared with Et_4NBF_4, the film of lower dc conductivity ($\sigma_{295K}=0.74\ \Omega^{-1}\,cm^{-1}$) is shown to have a lower reflectivity throughout whole spectral region than the film of higher d.c. conductivity ($\sigma_{295K}=4.4\ \Omega^{-1}\,cm^{-1}$). The reflectivity at 300 cm^{-1} is 48% for the films of higher conductivity but 38% for the films which has lower d.c. conductivity.

It is noteworthy that the reflectivity is lower for the films prepared by using $LiClO_4$ which has the d.c. conductivity of $\sigma_{295K}=0.016\ \Omega^{-1}\,cm^{-1}$. However, the broad bands are clearly found at 3000 cm^{-1} and at 6000—16000 cm^{-1} region.

The dielectric function of a linear chain of zero-band gap may be expressed by the following equation,[10)]

$$\varepsilon(\omega) = \varepsilon_{\text{core}} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}, \qquad (1)$$

where

$$\omega_p = \left(\frac{4\pi N e^2}{m^*}\right)^{1/2}. \qquad (2)$$

γ is the band width, N is the number density of free carrier, and m^* is the effective electron mass.

The reflectivity R can be expressed by the following equation,[10—12)]

$$R = \frac{1+|\varepsilon| - \sqrt{2(|\varepsilon|+\varepsilon_1)}}{1+|\varepsilon| + \sqrt{2(|\varepsilon|+\varepsilon_1)}}, \qquad (3)$$

and

$$|\varepsilon| = \sqrt{\varepsilon_1^2+\varepsilon_2^2}, \qquad (4)$$

where ε_1 and ε_2 are the real and imaginary parts of the dielectric function. Accordingly, the best fit of Eq. 3 to the observed reflection spectrum except the broad band around 3000—4000 cm^{-1} is obtained by using the following parameters with Eq. 1,

$$\omega_p = 17230\ \text{cm}^{-1},$$

$$\gamma = 39340\ \text{cm}^{-1},$$

and

$$\varepsilon_{\text{core}} = 2.4.$$

By using these values, the relaxation time is calculated as

$$1/\tau = 2\pi c\gamma = 7.41 \times 10^{15}\ \text{s}^{-1},$$

and we obtain

$$\tau = 0.135 \times 10^{-15}\ \text{s}.$$

This value is same magnitude with the value ($\sigma_0=0.277\times10^{-15}$ s) obtained for the $ClSO_3H$ heavily doped polyacetylene.[11)] The calculated reflection spectrum based on these values is in good agreement with the observed curve except the 3000—4000 cm^{-1} region as is shown in Fig. 3.

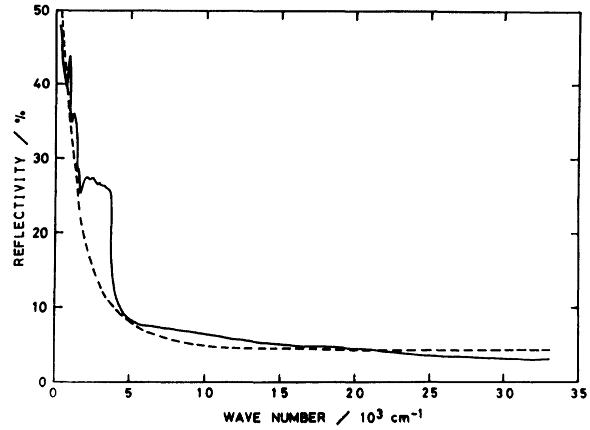

Fig. 3. Observed and calculated reflection spectra of polypyrrole film prepared by using Et_4NBF_4.
——: Observed spectrum, ------: calculated spectrum.

Then, the number density, N, of the free carrier in the polypyrrole film can be estimated as $3\times10^{21}\ cm^{-3}$ by substituting $m^*=m_e$ to the next equation,[10—12)]

$$N = \frac{\omega_p^2 m^*}{4\pi e^2}. \qquad (5)$$

This value corresponds to *ca.* 5% of the total π-electrons ($7\times10^{22}\ cm^{-3}$) which is estimated from the density of the film ($\rho=1.48\ g/cm^3$).[5)] This means that a few holes in the filled π-band contribute to the transport phenomenon.

Furthermore, the dc conductivity, σ_0, is given by the following equation,[10—12)]

$$\sigma_0 = \frac{\omega_p^2}{4\pi\gamma}. \qquad (6)$$

The value is calculated by using the observed plasma frequency, ω_p, and the band width, γ. The obtained value ($\sigma_0\simeq126\ \Omega^{-1}\,cm^{-1}$) is two order of magnitude larger than the observed value ($\sigma_0\simeq4.4\ \Omega^{-1}\,cm^{-1}$) of the d.c. conductivity of polypyrrole prepared by using Et_4NBF_4.

The difference between these two values may be

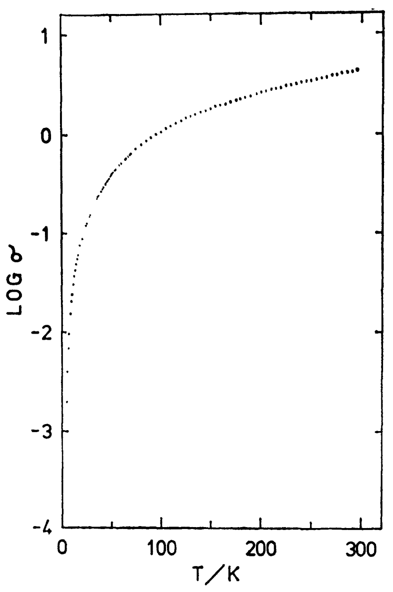

Fig. 4. Electrical conductivity of polypyrrole film prepared by using Et_4NBF_4 in the form of log σ *vs.* *T*.

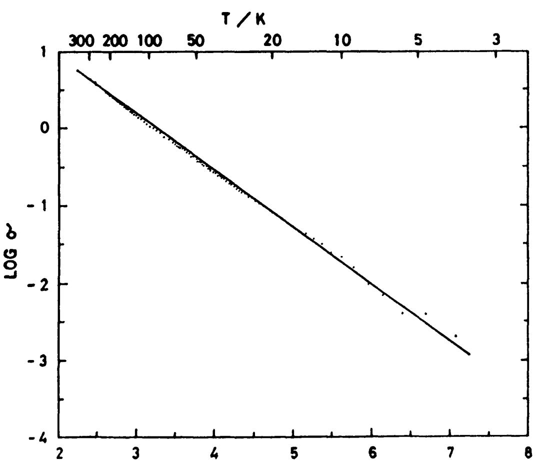

Fig. 5. Electrical conductivity of polypyrrole film prepared by using Et_4NBF_4 in the form of log σ *vs.* $T^{-1}/^4$.

explained by the mechanism as shown below. Namely the temperature dependence of the electrical conductivity was measured on the polypyrrole films prepared by using Et_4NBF_4 as shown in Fig. 4 in the form of log σ *vs* *T*. A plot shows a smooth curve from $\sigma_{295K}=4.4\ \Omega^{-1}$ cm^{-1} to $\sigma_{4.2K}=6.72\times10^{-4}\ \Omega^{-1}\ cm^{-1}$. In fact, a plot of log *vs.* $T^{-1}/^4$ gives a straight line over the temperature region of 4.2—300 K as is shown in Fig. 5. The straight line is expressed by

$$\log\sigma = -7.35\ T^{-1/4} + 2.385. \tag{7}$$

Such behavior suggests a hopping model for the conduction mechanism. That is, the resistivity ($\rho=1/\sigma$) of the film is composed of the sum of the resistivity ($\rho_0=1/\sigma_0$) in the polypyrrole chain and the resistivity ($\rho_h=1/\sigma_h$) between the chains,

$$\rho = \rho_0 + \rho_h. \tag{8}$$

The intrachain conductivity, σ_0, can be explained by

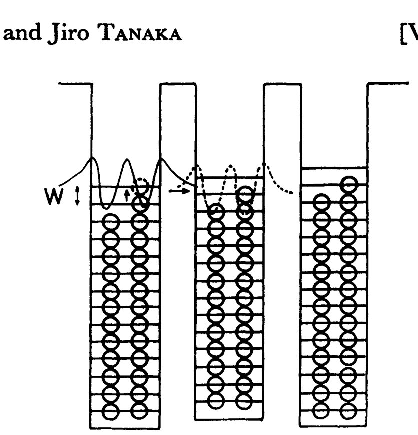

Fig. 6. A conduction mechanism of the hopping electron between the polypyrrole chain.

the conduction mechanism for the band model and corresponds to the optically determined value ($\sigma_0\simeq$ 126 $\Omega^{-1}\ cm^{-1}$), which is larger than the conductivity, σ_h, between the chains. Accordingly, the observed conductivity, σ, of the film may be correlated with the conductivity, σ_h, for the hopping electron between the chains. Mott[13] presented a conduction mechanism for a hopping process, which is depicted in Fig. 6. Every time an electron moves between the polymer chains, an electron just below the Fermi level jumps normally to a state just above it with energy *W*, and transfers from the one chain to the adjacent chain, of which the wave function overlaps that of the first chain. The hopping probability is then of the form,

$$\sigma \sim \nu_{ph}\exp(-2\alpha R - W/kT), \tag{9}$$

where α denotes the rate of a fall-off of the envelope of the wave function. The average spacing, *W*, between energy levels can be written by the density of state, *N*(*E*), and the mean distance, *a*, between atoms as follows,

$$W = 1/(4\pi/3)a^3N(E). \tag{10}$$

If $a\simeq R$, the maximum conductivity can be found at $R\simeq(9/8\pi\alpha kTN(E))^{1/4}$ and can be expressed by the following equation,

$$\sigma \sim A\exp\{-(Q/kT)^{1/4}\}, \tag{11}$$

where

$$Q = 1.5/\alpha^3N(E). \tag{12}$$

A good consistency between the observed and the theoretical relation of log σ *vs.* $T^{-1/4}$ means that the mechanism of the conduction of polypyrrole films can be expressed by a hopping model.

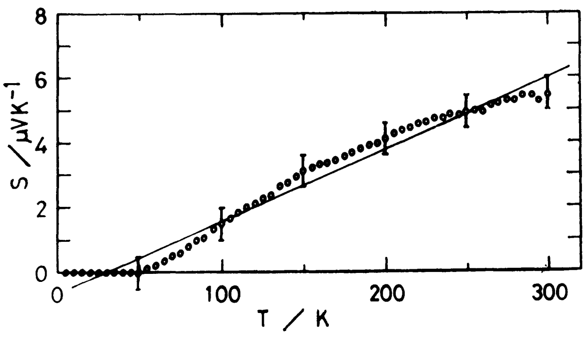

Fig. 7. Thermoelectric-power of polypyrrole film prepared by using Et_4NBF_4 in the form of *S* *vs.* *T*.

Thermoelectric-power, S, of the polypyrrole films is shown in Fig. 7, where S *vs.* T is plotted on a linear scale. The room temperature value of the thermoelectric-power is 6 μV/deg. The thermoelectric-power decreases with lowering temperature in a manner typical of a metal and the straight line in Fig. 7 is expressed by

$$S = 0.022\,T - 0.6 \qquad (\mu\mathrm{V/deg}). \tag{13}$$

The sign of S is positive in the range above 27.3 K indicating a p-type behavior. It means that the conduction occurs by the hole conduction.

For a nearly filled metallic band system (*i.e.* p-type), the thermoelectric-power can be written as follows,[13]

$$S = \frac{\pi^2}{3}\,\frac{k^2 T}{\mathrm{e}}\,\frac{\mathrm{d}\ln\sigma}{\mathrm{d}E}. \tag{14}$$

In the case that the interchain conduction occurs by hopping electrons, the thermoelectric-power can be expressed by using Eq. 9 as follows,[13]

$$S = \frac{\pi^2}{3}\,\frac{k}{\mathrm{e}}\left(kT\frac{\mathrm{d}\ln\sigma_0}{\mathrm{d}E} - \frac{\mathrm{d}W}{\mathrm{d}E}\right). \tag{15}$$

$|S|$ is linearly increasing with T, and it falls down at certain temperature given by

$$T = \left(\frac{\mathrm{d}W}{\mathrm{d}E}\right)\Big/\left(k\frac{\mathrm{d}\ln\sigma_0}{\mathrm{d}E}\right) \tag{16}$$

and these theoretical predictions are in good agreement with the observed tendencies. The same result was obtained by Kanazawa *et al.*[14]

References

1) M. M. Labes, P. Love, and L. F. Nichols, *Chem. Rev.*, **7**, 79 (1979).

2) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, **1977**, 578.

3) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, **1977**, 578.

4) A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, **1979**, 635.

5) K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, *J. Chem. Soc., Chem. Commun.*, **1979**, 854.

6) A. F. Diaz and J. I. Castillo. *J. Chem. Soc., Chem. Commun.*, **1980**, 397.

7) A. F. Diaz, W.-Y. Lee, and J. A. Logan, *J. Electroanal. Chem.*, **108**, 377 (1980).

8) N. S. Moe, *Acta Chem. Scand.*, **19**, 1023 (1965).

9) A. Kreutzberger and P. A. Kalter, *J. Phys. Chem.*, **65**, 624 (1961).

10) F. Wooten, "Optical Properties of Solids," Academic Press, New York (1972).

11) M. Tanaka, A. Watanabe, and J. Tanaka, *Bull. Chem. Soc., Jpn.*, **53**, 3430 (1980).

12) A. A. Bright, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **30**, 1328 (1974).

13) S. N. Mott, "Metal-Insulator Transitions," Taylor & Francis London (1974).

14) K. K. Kanazawa *et al.*, *Synthetic Metals*, **1**, 329 (1980).