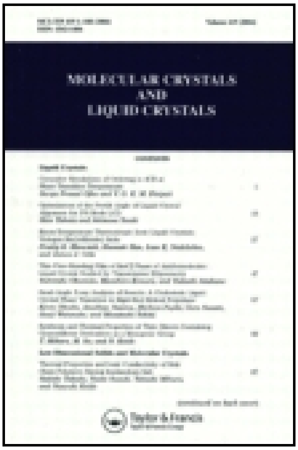

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Optical studies on the mechanism of electrical conduction of doped polyacetylene

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OPTICAL STUDIES ON THE MECHANISM OF ELECTRICAL CONDUCTION OF DOPED POLYACETYLENE

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Optical spectra are measured with the AsF_5 and Br_2 doped polyacetylene films. By the doping, the $\pi \rightarrow \pi^*$ band located in the 19000 cm^{-1} region is disappeared, while the new bands are observed at 870, 1370 and 5000 cm^{-1} regions. In addition, other new absorption bands are found around 570 - 660 cm^{-1} region by decreasing the temperature of the doped thin films, which may be assigned to the transitions between the levels of the electron-hole pair. The reflection spectrum of the AsF_5 doped film shows a metallic behavior and it is analysed assuming a presence of free carrier. The conductivity estimated by the optical data is in good agreement with the measured one. The reflectivity of the bromine doped film is less metallic presumably because the chemical reaction may take place. The logarithm of the conductivity shows $T^{-1/4}$ dependence, indicating that the conductivity is dominated by the hopping of the carrier between the chains.

INTRODUCTION

Polyacetylene $(CH)_x$ is a large band gap semiconductor. However, the polymer increases its electrical conductivity dramatically upon exposure to vapors of chlorine, bromine (Br_2), iodine and aresenic pentafluoride (AsF_5).[1] For the heavily doped samples with AsF_5,[2] the room temperature conductivity reaches almost $10^3\ \Omega^{-1}cm^{-1}$ and the conductivity increases slightly between the room temperature and 250 K, then decreases slowly as the temperature is decreased. On the other hand, the conductivity of the heavily doped film with Br_2[3] is in the order of 10 - 100 $\Omega^{-1}cm^{-1}$ at 300 K and it decreases gradually with decreasing temperature.

The color of the film changes from the silver black to the golden or reddish cupric luster with doping. Such color change was taken as an evidence of the creation of free carrier[4,5,6] in the one-dimensional polyacetylene chain. Actually the metallic reflection observed in the IR to visible region may be correlated with the conductivity of the doped films.

In the present paper, we report the IR and visible absorption and reflection spectra of AsF_5 and Br_2 doped $(CH)_x$ films and discuss about the conduction mechanism of these doped polymers. In addition, we report the temperature dependent new IR absorption band of thin films doped with Br_2 and AsF_5 in the 500 - 800 cm^{-1} region.

ABSORPTION SPECTRA OF THIN $(CH)_x$ FILMS DOPED WITH AsF_5

Pure $(CH)_x$ film has a strong $\pi \rightarrow \pi^*$ band in the 19000 cm^{-1} region besides the C-H out-of-plane (740 cm^{-1} for *cis*-$(CH)_x$ and 1015 cm^{-1} for *trans*-$(CH)_x$) and the C-C-C deformation (446 cm^{-1} for *cis*-$(CH)_x$). Figures 1 and 2 show the change

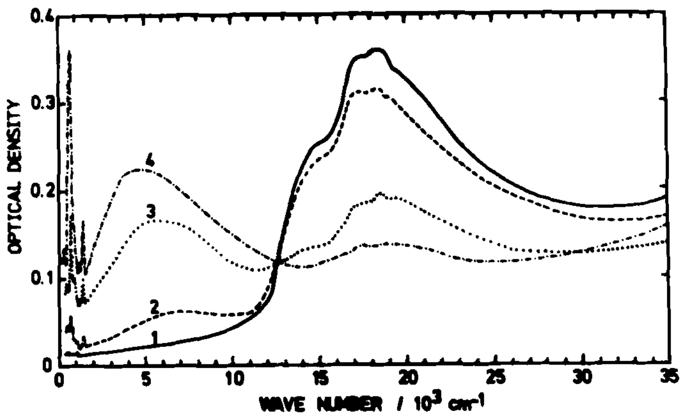

FIGURE 1 Absorption spectra of *cis*-rich $(CH)_x$ films doped with AsF_5.

1. $\sigma = 10^{-9}\ \Omega^{-1}cm^{-1}$ 2. $\sigma = 20\ \Omega^{-1}cm^{-1}$
3. $\sigma = 50\ \Omega^{-1}cm^{-1}$ 4. $\sigma = 100\ \Omega^{-1}cm^{-1}$

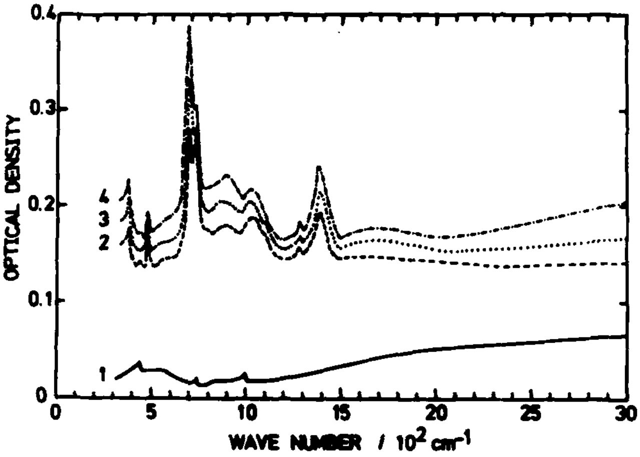

FIGURE 2 IR absorption spectra of *cis*-rich $(CH)_x$ doped with AsF_5.
1. $\sigma = 10^{-9}\ \Omega^{-1}cm^{-1}$ 2. $\sigma = 50\ \Omega^{-1}cm^{-1}$
3. $\sigma = 100\ \Omega^{-1}cm^{-1}$ 4. $\sigma = 300\ \Omega^{-1}cm^{-1}$

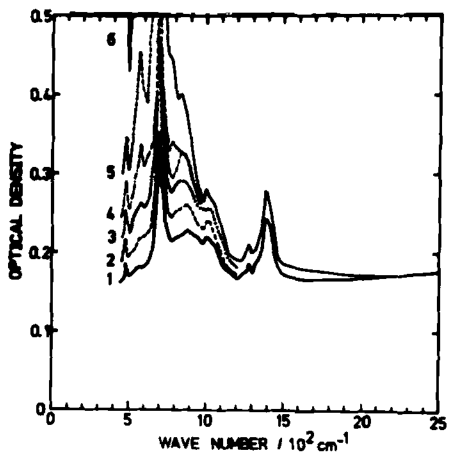

FIGURE 3 Temperature dependence of the IR absorption spectra of *cis*-rich $(CH)_x$ film doped with AsF_5 ($\sigma = 300\ \Omega^{-1}cm^{-1}$).
1. 300 K 2. 280 K
3. 260 K 4. 220 K
5. 200 K 6. 140 K

of the spectra with doping: the free carrier absorption band is observed over the wide region from 300 to 25000 cm^{-1}, while the $\pi \rightarrow \pi^*$ band at 19000 cm^{-1} is diminished. Several new vibrational peaks are found at 1370, 1280 and 870 cm^{-1}, two of which were assigned by Mele and Rice[7] as the carbon-carbon skeltal stretching vibration intensified through the coupling with the motion of free electron. Another peaks at 696 and 393 cm^{-1} are assigned to the AsF_6^- anion by comparison with model compounds.[8,9] Furthermore, the 1015 cm^{-1} band, which is the C-H out-of-plane band of *trans*-$(CH)_x$, is intensified because the *cis*-$(CH)_x$ isomerizes to *trans*-$(CH)_x$ on doping.

In figure 3 the temperature dependence of the IR absorption spectra of the heavily doped thin $(CH)_x$ films is illustrated. The thin films were polymerized on the teflon frame with a 5 × 5 mm^2 hole and doped with AsF_5 and then measured *in situ in vacuo*. In the lower frequency region (400 - 1100 cm^{-1}) the intensity becomes stronger and the new peak appears at 570 cm^{-1} upon cooling. The origin of this band will be discussed later.

REFLECTION SPECTRA OF $(CH)_x$ FILMS DOPED WITH AsF_5

The IR reflection spectra of AsF_5 doped $(CH)_x$ films are

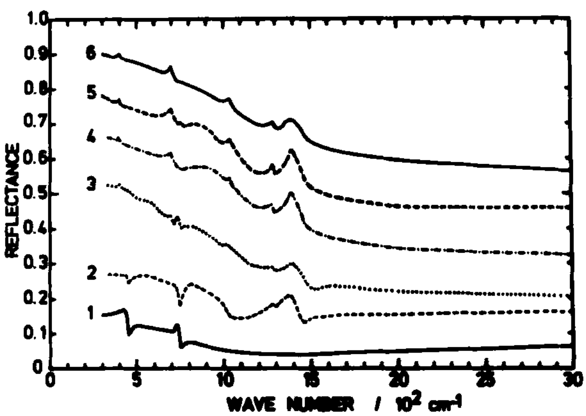

FIGURE 4 IR reflection spectra of *cis*-rich $(CH)_x$ doped with AsF_5.

1. $\sigma = 10^{-9}\Omega^{-1}cm^{-1}$ 2. $\sigma = 16\ \Omega^{-1}cm^{-1}$
3. $\sigma = 27\ \Omega^{-1}cm^{-1}$ 4. $\sigma = 120\ \Omega^{-1}cm^{-1}$
5. $\sigma = 300\ \Omega^{-1}cm^{-1}$ 6. $\sigma = 800\ \Omega^{-1}cm^{-1}$

shown in figure 4. The most conductive film shows the metallic behavior; the reflectivity increases with lowering the frequency attaining a value of approximately 90 % at 300 cm^{-1}. With the less conductive films, the reflectivity remains small even at lower frequency and the sharp peak is observed at 1370 cm^{-1} with a dip in the nearby region. Furthermore, the peaks due to the AsF_6^- ion and the *trans*-$(CH)_x$ are observed at 696, 393 and 1015 cm^{-1}, respectively.

The complex dielectric function of the metallic film may be given approximately by the sum of the contribution of the free carrier and 1370 cm^{-1} bands as follows,

$$\varepsilon(\omega) = \varepsilon_{core} - \frac{\omega_p^2}{\omega^2 + i\gamma_0\omega} + \frac{\Omega^2}{\omega_1^2 - \omega^2 - i\gamma_1\omega} \quad . \qquad (1)$$

Here, ω_p is the plasma frequency of the free carrier and γ_0 is the band width. Ω and γ_1 are the parameters for the 1370 cm^{-1} band. The reflection spectra of the heavily AsF_5 doped film are simulated by equation 1 with the following parameters and the result is shown in figure 5. (ω_p = 37450 cm^{-1}, γ_0 = 18700 cm^{-1}, Ω = 743 cm^{-1}, γ_1 = 42 cm^{-1}, ε_{core} = 5.13) The agreement between the calculated and observed results is fairly satisfactory.

By using these parameters the number density (N)of the free carriers in the heavily doped film can be estimated to be about 1.4×10^{22} cm^{-3} by assuming that $m^* = m$ with the following formula[6];

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

The obtained value is approximately equal to the total number of π-electron density (2×10^{22} cm^{-3}) in the $(CH)_x$ chain. This result clearly indicates that the band gap in the chain is closed by the heavy doping and a 1-D metallic state is formed. The dc conductivity, σ_0, is given by the following formula[6];

$$\sigma_0 = \frac{\omega_p^2}{4\pi\gamma_0} \quad , \qquad (3)$$

and it is calculated by the above mentioned parameters. The obtained value (σ_0 = 1250 $\Omega^{-1}cm^{-1}$) is in good agreement with the measured value (σ_0 = 800 $\Omega^{-1}cm^{-1}$) by the four probe method.

The change of reflection spectra with increasing the concentration of free carrier is also simulated as shown in figure 6, where the parameters γ_0, Ω, ω_1 and γ_1 were fixed but only ω_p is varied. The obtained curve indicates that the 1370 cm^{-1} band is accompanied with a dip in the higher energy region as is observed for the low concentration of the carrier and the reflectivity increase below 500 cm^{-1} is a characteristic of the metallic behavior. The conductivities of the films guessed from the reflection spectra are in reasonable agreement with the measured values.

ABSORPTION SPECTRA OF $(CH)_x$ FILMS DOPED WITH Br_2

Absorption spectra of the Br_2 doped films are shown in figures 7 and 8. The general feature of the spectra is similar to those of AsF_5 doped films shown in figures 1 and 2, except that the absorption band of the Br_3^- ion appears in the 23000 - 35000 cm^{-1} region in the heavily doped film. The temperature dependence of the absorption spectra of the heavily Br_2 doped film for the 140 - 300 K range is shown in figure 9. The absorption intensity in the lower frequency region becomes stronger and the new peaks appear at 570 and 660 cm^{-1}. The peak at 570 cm^{-1} is also observed in the AsF_5 doped films. The 1370 cm^{-1} band and the free carrier absorption above 2000 cm^{-1} does not change the intensity apprecia-

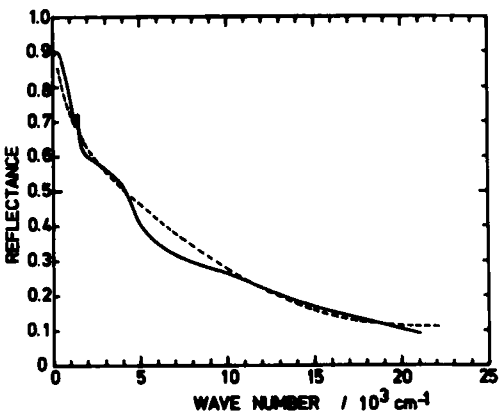

FIGURE 5 Comparison between the observed and calculated reflection spectra of $(CH)_x$ film heavily doped with AsF_5.
—— observed spectrum ---- calculated spectrum

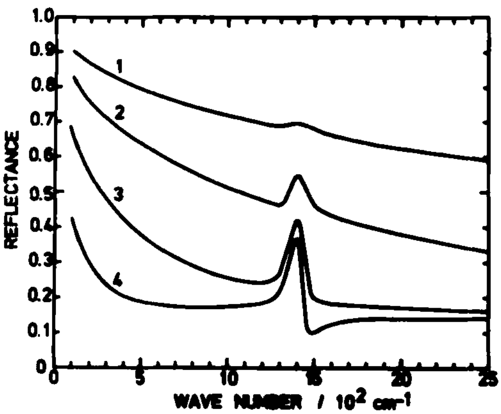

FIGURE 6 Calculated reflection spectral change due to the various concentration of free carriers.
1. ω_p = 37450 cm^{-1} (N ≃ 1.4 × 10^{22} cm^{-3})
2. ω_p = 20000 cm^{-1} (N ≃ 4.5 × 10^{21} cm^{-3})
3. ω_p = 10000 cm^{-1} (N ≃ 1.0 × 10^{21} cm^{-3})
4. ω_p = 5000 cm^{-1} (N ≃ 3.0 × 10^{20} cm^{-3})

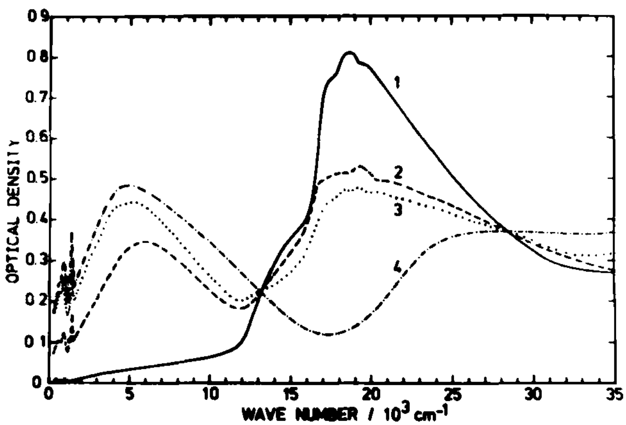

FIGURE 7 Absorption spectra of *cis*-rich $(CH)_x$ films doped with Br_2.
1. σ = 10^{-9} $\Omega^{-1}cm^{-1}$
2. σ = 6 $\Omega^{-1}cm^{-1}$
3. σ = 30 $\Omega^{-1}cm^{-1}$
4. σ = 40 $\Omega^{-1}cm^{-1}$

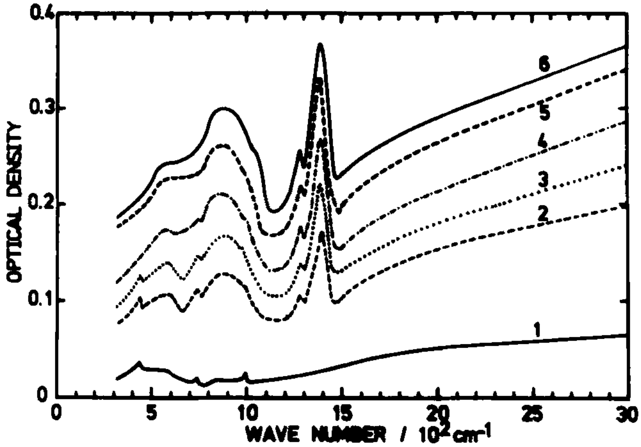

FIGURE 8 IR absorption spectra of *cis*-rich $(CH)_x$ films doped with Br_2.

1. $\sigma = 10^{-9}\ \Omega^{-1}cm^{-1}$ 2. $\sigma = 1\ \Omega^{-1}cm^{-1}$
3. $\sigma = 6\ \Omega^{-1}cm^{-1}$ 4. $\sigma = 15\ \Omega^{-1}cm^{-1}$
5. $\sigma = 30\ \Omega^{-1}cm^{-1}$ 6. $\sigma = 40\ \Omega^{-1}cm^{-1}$

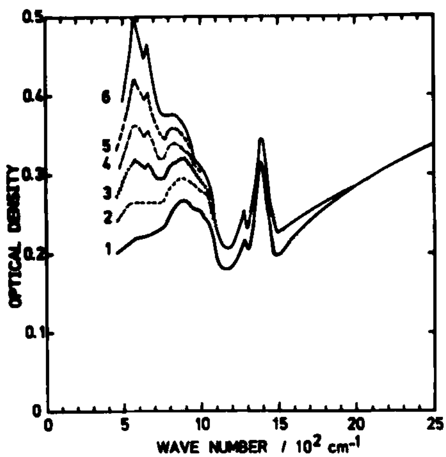

FIGURE 9 Temperature dependence of the IR absorption spectra of Br_2 doped $(CH)_x$ ($\sigma = 30\ \Omega^{-1}cm^{-1}$).

1. 300 K 2. 280 K
3. 260 K 4. 230 K
5. 200 K 6. 140 K

bly for these temperature range. Mele and Rice[7] inferred that a still lower energy phonon band might be found by doping in addition to the 1370 and 870 cm^{-1} bands. Presently found new bands around 570 and 660 cm^{-1} show strong temperature dependence, therefore they might be assigned rather to the energy levels of the electron-hole pair, which were first discussed by Fincher *et al.*[10] to be appeared at 900 cm^{-1} region. These bands might be appeared by a trapping of the charged soliton around the acceptor site at lower temperature and a bound electron hole state is created.

REFLECTION SPECTRA OF $(CH)_x$ FILMS DOPED WITH Br_2

The reflection spectra of Br_2 doped $(CH)_x$ films are shown in figures 10 and 11. The reflectivity of Br_2 doped film is lower than that of AsF_5 doped film and the 1370 cm^{-1} band has a deep dip even for the heavily Br_2 doped film. This means that the number of the free carriers is smaller in the Br_2 doped film than in the AsF_5 doped film. This fact may be explained by the decrease of the content of the unsaturated double bond by the addition of Br_2 to the $(CH)_x$ chain.

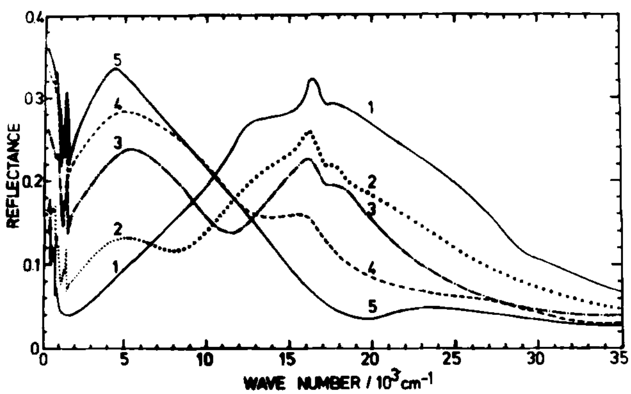

FIGURE 10 Reflection spectra of *cis*-rich $(CH)_x$ films doped with Br_2.

1. $\sigma = 10^{-9}\ \Omega^{-1}cm^{-1}$ 2. $\sigma = 0.3\ \Omega^{-1}cm^{-1}$
3. $\sigma = 2.6\ \Omega^{-1}cm^{-1}$ 4. $\sigma = 21\ ^{-1}cm^{-1}$
5. $\sigma = 33\ \Omega^{-1}cm^{-1}$

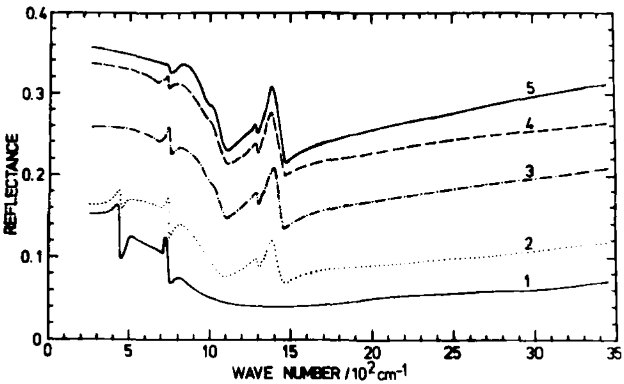

FIGURE 11 IR reflection spectra of *cis*-rich $(CH)_x$ films doped with Br_2.

1. $\sigma = 10^{-9}\ \Omega^{-1}cm^{-1}$ 2. $\sigma = 0.3\ \Omega^{-1}cm^{-1}$
3. $\sigma = 2.6\ \Omega^{-1}cm^{-1}$ 4. $\sigma = 21\ ^{-1}cm^{-1}$
5. $\sigma = 33\ \Omega^{-1}cm^{-1}$

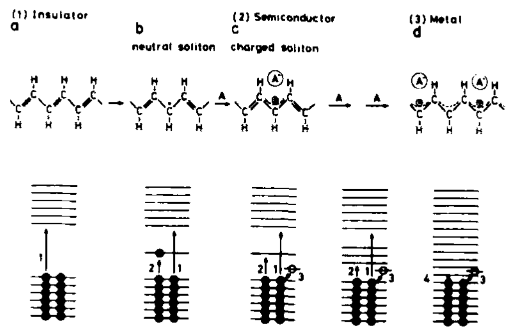

FIGURE 12 Electronic structure of pure and doped $(CH)_x$.

MECHANISM OF THE ELECTRICAL CONDUCTION OF AsF_5 AND Br_2 DOPED $(CH)_x$ FILMS

Pure $(CH)_x$ has a structure of alternating single and double bonds, and the π-electrons on each carbon atom form two separate energy bands as shown in figure 12-a. Upon doping *cis*-$(CH)_x$ tends to isomerize to *trans*-$(CH)_x$ and then neutral solitons are induced as defects on the chain. That is, the non-bonded localized state appears at the mid point of the energy gap (figure 12-b). Furthermore, an unpaired electron may be transferred to the acceptor by doping and the charged soliton is generated on the chain (figure 12-c).[11] Therefore,

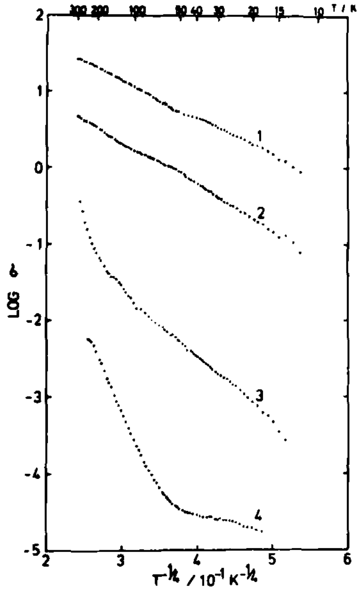

FIGURE 13 Temperature dependence of the electrical conductivity of Br_2 doped $[(CH)Br_y]_x$.
1. y = 0.21 2. y = 0.058
3. y = 0.034 4. y = 0.003

for lightly doped film, an intense broad absorption band with a peak at about 6500 cm^{-1} may be assigned to the chain involving the charged soliton. The hole state may delocalize over the 1-D chain, however, it may be trapped near the acceptor site at low temperature and a bound electronic state of a hydrogen like energy level is found at about 600 cm^{-1} region. Further doping leads to uniform bond length and closing of the band gap.

On the other hand, the heavily Br_2 doped films consists of aggregates of metallic parts and insulator segments as is noted in the previous section. Then, the resistivity (ρ = $1/\sigma$) of the film is composed of the sum of the resistivity in the metallic part ($\rho_0 = 1/\sigma_0$) and that of between the metallic chains ($\rho_h = 1/\sigma_h$) as $\rho = \rho_0 + \rho_h$, where $\rho_h > \rho_0$. Accordingly, the observed conductivity (σ) of the film may be correlated with the conductivity for the hopping electron between the metallic conjugated systems, because the hopping process can be considered as a rate-determining step. Mott[12] derived the following equation for the temperature dependence of a hopping conduction,

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

The electrical conduction was measured on the Br_2 doped $(CH)_x$ film. As is shown in figure 13, a plot of log σ *vs.* $T^{-1/4}$ gives a straight line over the temperature region of 10 - 300 K. 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 Br_2 doped $(CH)_x$ films can be explained by a hopping model between the metallic chains.

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