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Absorption and Reflection Spectra of Pure and $ClSO_3H$ Doped Polyacetylene Films

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Optical absorption and reflection measurements are carried out on pure and $ClSO_3H$ doped polyacetylene films over a wide wavelength region (350—35000 cm^{-1}). In the doped polymer, the transition from the valence band to the impurity level is observed at 870 cm^{-1} and the free carrier absorption band appears over the wide region of 350 to 20000 cm^{-1}, while the interband transition located in the region of 15000 cm^{-1} disappears. This means that doping removes the bond alternation leading to a uniform bond length and all π-electrons contribute to the transport. For the heavily doped films, the d.c. conductivity of polyacetylene films is obtained by the optimum fit of the theoretical curve to the observed absorption and reflection spectra. The obtained values are comparable with the d. c. conductivity ($\sigma \simeq 280$—250 Ω^{-1} cm^{-1}) obtained by the four probe method.

Polyacetylene, $(CH)_x$, is one of the simplest linear conjugated polymers with a single chain structure. The theoretical studies upon the electronic structure of pure $(CH)_x$ polymer showed that the alternant structure was found to have the lowest energy and the energy gap between the π and π^* bands was too high.[1-4] The observation[5,6] of the $\pi \rightarrow \pi^*$ transition band at about 16000 cm^{-1} also showed that the bond alternation is present in the polymer and $(CH)_x$ would be expected to make semiconducting behavior.[7] However, Shirakawa, Heeger, and MacDiarmid and co-workers found that AsF_5 doped $(CH)_x$ films have the high conductivity of about 10^3 Ω^{-1} cm^{-1} [8] and they observed the new absorption bands in the lower frequency region by the absorption and reflection measurements.[9-11] Tanaka *et al.* estimated the optical conductivity by measuring the free carrier absorption band of BF_3 doped film[12] and also showed that $ClSO_3H$ is a good dopant by the d.c. conductivity measurement of $ClSO_3H$, H_2SO_4, and BF_3 doped films.[13]

In the present paper, we report the absorption and reflection spectra in the 350—35000 cm^{-1} region of $(CH)_x$ films doped with $ClSO_3H$ and discuss about the electronic structure of the heavily doped $(CH)_x$ films.

Experimental

The polyacetylene films were prepared from acetylene gas by treatment of the Ziegler catalyst in hexane at −80 °C as described by Shirakawa, Ikeda, and co-workers.[14-16] The films were doped by exposure to the vapor of $ClSO_3H$ *in vacuo*. The dopant level were determined by the measurement of the four probe d.c. conductivity.

After the thin $(CH)_x$ films were polymerized on the KBr plate or the polyethylene film and doped with $ClSO_3H$, the absorption spectra of $(CH)_x$ films were measured with Hitachi IR 260-50 (350—4000 cm^{-1}) and Carl Zeiss M4Q (4000—35000 cm^{-1}) spectrophotometers. For the study of the *cis-trans* isomerization of $(CH)_x$ films, the thin films were polymerized on the inner surface of the 1 cm quartz cell and the absorption spectra of the films kept *in vacuo* were measured with a Carl Zeiss spectrophotometer after heating at 60 °C. The reflection measurement of pure and doped thick films were taken with Hitachi IR 260-50 and a microscopic spectrophotometer (4000—35000 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 tube, and an Intel 8080 microcomputer for data processing.

The Kramers-Kronig (K-K) transformation[17,18] of the reflection spectra of pure $(CH)_x$ films and the best fit of the calculated absorption and reflection spectra of $ClSO_3H$ doped films to the observed spectra were made on a FACOM M-200 computer of Nagoya university.

Results and Discussion

Absorption and Reflection Spectra of Pure $(CH)_x$ Films. The thin $(CH)_x$ film polymerized at −80 °C shows the reddish cupric color and the film becomes blue on heating it *in vacuo*. This color change was explained by the analysis of IR-vibration spectra[14-16] to be due to the *cis-trans* isomerization of $(CH)_x$. In Fig. 1 is shown the visible absorption spectral change of the thin $(CH)_x$ film at 60 °C and *in vacuo*. *cis*-Rich $(CH)_x$ has two vibronic peaks at 17100 and 18300 cm^{-1} and the second peak (18300 cm^{-1}) is the most intense. On heating the *cis*-rich thin film at 60 °C, the broad band in the region of 15000 cm^{-1} becomes more intense and the

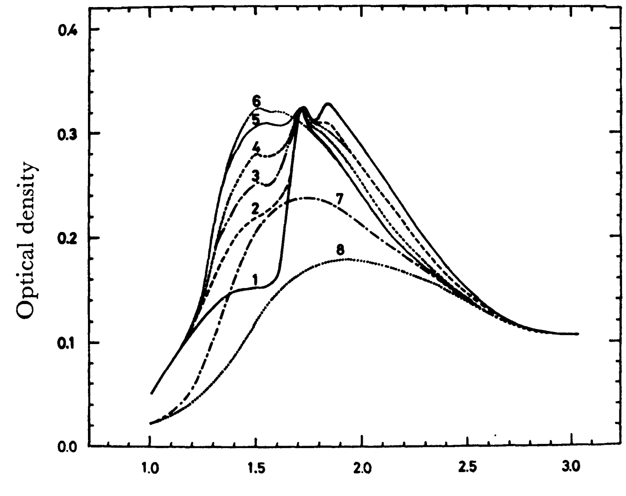

Fig. 1. The visible absorption spectral change due to the *cis-trans* isomerization of the thin $(CH)_x$ film at 60 °C and *in vacuo*. 1) 0.0 h, 2) 3.2 h, 3) 8.2 h, 4) 14.5 h, 5) 2.0 d, 6) 4.9 d 7) 16.3 d, 8) 22.2 d.

18300 cm^{-1} peak of *cis*-$(CH)_x$ becomes weaker. Finally, the 15000 cm^{-1} band of *trans*-$(CH)_x$ has the same absorption intensity as that of the 17000 cm^{-1} band of *cis*-$(CH)_x$ before heating. This means that *cis*-$(CH)_x$ transforms completely to *trans*-$(CH)_x$. After that, the absorption intensity of *trans*-$(CH)_x$ becomes weaker and the maximum peak shifts to the higher frequency region. This fact seems to be due to the formation of the bridge between the $(CH)_x$ chains and the decrease in the C=C conjugated system.

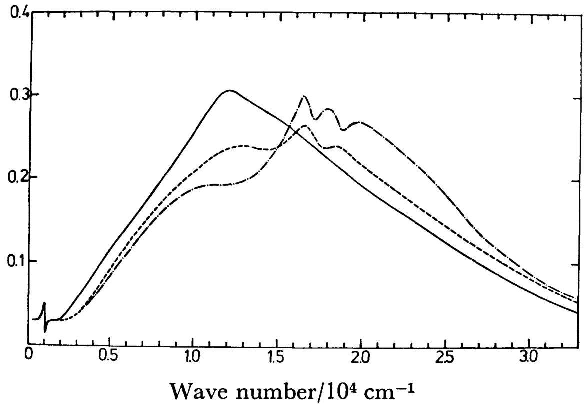

Fig. 2. The reflection spectra of the thick $(CH)_x$ films. —·—·: 80% *cis*-$(CH)_x$, ------: 55% *cis*-$(CH)_x$, ——: 85% *trans*-$(CH)_x$.

In Fig. 2 is shown the reflection spectral change of the thick $(CH)_x$ films at about 200 °C. The *cis,trans*-content of $(CH)_x$ films was determined by measuring the optical density of *cis* (740 cm^{-1}) and *trans* (1015 cm^{-1}) C–H out-of-plane vibrations.[16] The reflection spectrum of 80% *cis*-$(CH)_x$ film has the vibronic structures at 16400 and 18000 cm^{-1} as is observed in the absorption spectra of thin $(CH)_x$ films and the 16400 cm^{-1} peak has a reflectivity of 30%. For the 85% *trans*-$(CH)_x$ film, the reflection spectrum has the broad band at 12000 cm^{-1} and the sharp peak at 1015 cm^{-1} corresponding to the C–H out-of-plane mode of *trans*-$(CH)_x$. The main band at 12000 cm^{-1} has a reflectivity of 30.6%. The absorption spectra of $(CH)_x$ film are obtained by the K-K transformation of the reflection spectra as is shown in Fig. 3. The 16400 cm^{-1} band of 80% *cis*-$(CH)_x$ has the maximum absorption coefficient, α, of 2.59×10^5 cm^{-1} and the 12000 cm^{-1} band of 85% *trans*-$(CH)_x$ has $\alpha=2.33\times10^5$ cm^{-1}. On comparison between Figs. 1 and 3, the absorption maxima of thick $(CH)_x$ films are shifted to the lower frequency region than those of the thin films. This may be explained by the difference of the conjugated system length.

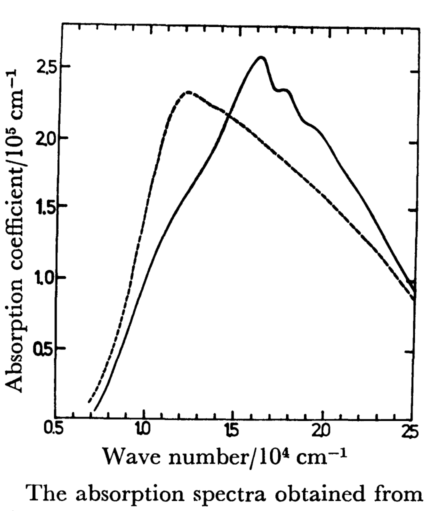

Fig. 3. The absorption spectra obtained from the K-K transformation of the reflection spectra of the thick $(CH)_x$ films. ——: 80% *cis*-$(CH)_x$, ------: 85% *trans*-$(CH)_x$.

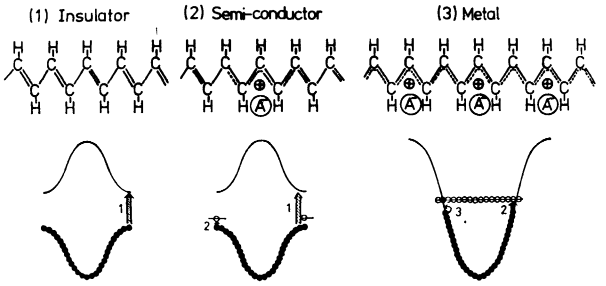

Fig. 4. The electronic structure of the $(CH)_x$ film.

$(CH)_x$ is one of the simplest linear conjugated polymers with a single chain structure and has the configuration of alternating the single and double bonds. Then, the π-electrons on each carbon atom form two separate bands as shown in Fig. 4-1. The one is the bonding π band (valence band) and the other is the antibonding π* band (conduction band). Accordingly, the complex dielectric constant of $(CH)_x$ is given by the following equation,[19]

$$\varepsilon(\omega) = \varepsilon_{\text{core}} + \sum_{\text{k}} \frac{(4\pi Ne^2/m)\hbar^2 f_{\pi\text{k},\pi^*\text{k+q}}}{(\varepsilon_{\pi^*}(\text{k+q})-\varepsilon_\pi(\text{k}))^2-\hbar^2\omega^2-\text{i}\hbar^2\omega/\tau_0} \quad (1)$$

where N is the number density of π-electrons, m is the electron mass, and $f_{\pi\text{k},\pi^*\text{k+q}}$ is the oscillator strength of the πk→π*k+q transition. $\varepsilon_{\pi^*}(\text{k+q})$ and $\varepsilon_\pi(\text{k})$ are the energy of π and π* bands. When the momentum of photon, q, is neglected, the imaginary part $\varepsilon_2(\omega)$ of the complex dielectric constant is derived from Eq. 1 as follows,

$$\varepsilon_2(\omega) = \frac{\pi}{2}\,\frac{4\pi Ne^2}{m}\bar{f}_{\pi,\pi^*}\sum_{\text{k}}\frac{\hbar}{\omega}\delta(\varepsilon_{\pi^*}(\text{k})-\varepsilon_\pi(\text{k})-\hbar\omega). \quad (2)$$

Here, $\bar{f}_{\pi,\pi^*}$ is the average of the oscillator strength of the πk→π*k transition. The sum rule of $\varepsilon_2(\omega)$ is defined for a finite range from the absorption edge $E_g=\hbar_{\omega g}$ to the energy $E_0=\hbar_{\omega o}$,

$$\begin{aligned}\int_{\omega_g}^{\omega_o}\omega\varepsilon_2(\omega)\text{d}\omega &= \frac{\pi}{2}\,\frac{4\pi Ne^2}{m}\bar{f}_{\pi,\pi^*}\sum_{\text{k}}\int_{E_g}^{E_o}\delta(\varepsilon_{\pi^*}(\text{k})-\varepsilon_\pi(\text{k})-E)\text{d}E \\ &= \frac{\pi}{2}\,\frac{4\pi Ne^2}{m}\bar{f}_{\pi,\pi^*}G(E_o) \quad (3)\end{aligned}$$

where $G(E_0)$ is the integral of the joint density of state $\rho(E)$ over the energy region of E_g to E_o,

$$G(E_o) = \int_{E_g}^{E_o}\rho(E)\text{d}E \quad (4)$$

and

$$\rho(E) = \sum_{\text{k}}\delta(\varepsilon_{\pi^*}(\text{k})-\varepsilon_\pi(\text{k})-E). \quad (5)$$

In the typical one-dimensional system of the length L, the band energy $\varepsilon_{\pi}(\mathrm{k})$ and $\varepsilon_{\pi}^{*}(\mathrm{k})$ can be approximated by the parabolic function,

$$\varepsilon_{\pi}(\mathrm{k}) = -\frac{\hbar^2}{2m_{\pi}}\left(\mathrm{k}-\frac{\pi}{2a}\right)^2 \tag{6}$$

and

$$\varepsilon_{\pi^*}(\mathrm{k}) = E_{\mathrm{g}} + \frac{\hbar^2}{2m_{\pi}}\left(\mathrm{k}-\frac{\pi}{2a}\right)^2. \tag{7}$$

Then, the joint density of state near the gap edge varies as

$$\rho(E) = \frac{L\sqrt{m_{\pi}}}{h}(E-E_{\mathrm{g}})^{-1/2} \tag{8}$$

and the integral of the joint density of state rises toward the square root as follows

$$G(E_0) = \frac{2L\sqrt{m_{\pi}}}{h}(E_0-E_{\mathrm{g}})^{1/2}. \tag{9}$$

In this case, $\varepsilon_2(\omega)$ is calculated from the K-K transformation of the reflection spectra (Fig. 2) of $(\mathrm{CH})_x$ films and the sum rule of Eq. 10 is found by integrating $\varepsilon_2(\omega)$,

$$\frac{m}{2\pi^2 Ne^2}\int_{\omega_{\mathrm{g}}}^{\omega_0}\omega\varepsilon_2(\omega)\mathrm{d}\omega = f_{\pi,\pi^*}G(E_0), \tag{10}$$

where the number of π-electrons per unit volume of the medium is taken to be $N \approx 2\times10^{22}\ \mathrm{cm}^{-3}$ from the measured density of $(\mathrm{CH})_x$ (0.4 g/cm^3).$^{20)}$ The obtained sum rule curves are shown in Fig. 5 together with the theoretical curve of $G(E_0)=A(E_0-E_{\mathrm{g}})^{1/2}$. The good agreement between the observed and theoretical curves indicates that $(\mathrm{CH})_x$ can be treated as the one-dimensional system and that the top of π band and the bottom of π^* band can be approximated as the parabolic function. Accordingly, the absorption band observed in the visible region can be assigned to the direct interband transition (type 1 shown in Fig. 4-1) from the π band to the π^* band.

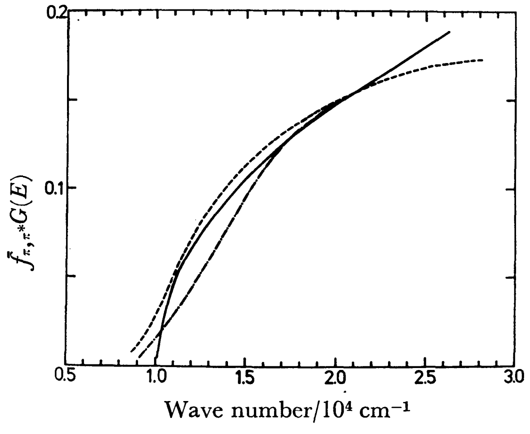

Fig. 5. The sum rule of $\varepsilon_2(\omega)$ obtained from the K-K transformation of the reflection spectra of the thick $(\mathrm{CH})_x$ films. -·-·-: 80% *cis*-$(\mathrm{CH})_x$, ------: 85% *trans*-$(\mathrm{CH})_x$, ——: $G(E)=A(E-E_{\mathrm{g}})^{1/2}$.

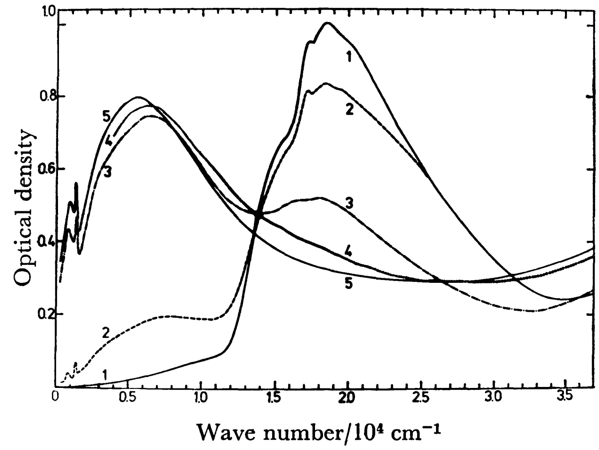

Fig. 6. The absorption spectra of *cis*-rich thin $(\mathrm{CH})_x$ films doped with $\mathrm{ClSO_3H}$.
1) Pure $(\mathrm{CH})_x$, 2) $\sigma_0 \simeq 2\times10^{-2}\ \Omega^{-1}\,\mathrm{cm}^{-1}$, 3) $\sigma_0 \simeq 2.6\ \Omega^{-1}\,\mathrm{cm}^{-1}$, 4) $\sigma_0 \simeq 10^2\ \Omega^{-1}\,\mathrm{cm}^{-1}$, 5) $\sigma_0 \simeq 250\ \Omega^{-1}\,\mathrm{cm}^{-1}$.

Absorption Spectra of Thin $(CH)_x$ Films Doped with $ClSO_3H$. In the lightly doped $(\mathrm{CH})_x$ film ($\sigma \simeq 2\times10^{-2}\ \Omega^{-1}\,\mathrm{cm}^{-1}$) polymerized on the KBr plate, two infrared peaks of the additional absorption are observed at 1370 and 870 cm^{-1} as shown in Fig. 6. In doping $(\mathrm{CH})_x$ with $\mathrm{ClSO_3H}$, the π-electrons transfer from $(\mathrm{CH})_x$ chain to $\mathrm{ClSO_3H}$. The resulting hole (cation) on the polymer chain is bound by the Coulomb potential to the region of the chain near the acceptor ion and the impurity state appears in the energy gap (Fig. 4-2). The band at 870 cm^{-1} can be assigned to the transition (type 2 shown in Fig. 4-2) from the valence band to the impurity 1s level according to Fincher *et al.*$^{9)}$ and Tanaka *et al.*$^{12)}$ In this model, the cation on the $(\mathrm{CH})_x$ chain delocalizes near the acceptor ion and a region of the uniform bond lengths occurs. This phenomenon is called "Soliton" and the possibility of the existence of soliton was theoretically recognized.$^{21,22)}$ The 1370 cm^{-1} mode appears at a frequency approximately intermediate between the single bond (C–C, 950 cm^{-1}) and double bond (C=C, $\simeq$1650 cm^{-1}) stretching mode and may be assigned to the stretching mode of the bond order 1.5 corresponding to the uniform bond lengths, while Harada *et al.*$^{23)}$ and Rabolt *et al.*$^{24)}$ concluded that the 870 and 1370 cm^{-1} peaks were the molecular vibration mode.

In addition to the 870 and 1370 cm^{-1} bands, a broad band appears in the region of 8000 cm^{-1} and the absorption intensity of the interband transition at about 17000 cm^{-1} decreases (Fig. 6). The fact that there is an isosbestic point at about 14000 cm^{-1} in the spectra clearly indicates that there is an equilibrium between two absorbing species of the 8000 and 17000 cm^{-1} bands.

In heavily doped $(\mathrm{CH})_x$ films polymerized on the polyethylene films, the 870 and 1370 cm^{-1} bands remain clearly. Furthermore, the absorption band corresponding to the interband transition disappears in the visible region and the broad band observed in the near IR region becomes more intense. The broad band has the maximum peak at about 5500 cm^{-1} and the absorption edge in the region of less than 300 cm^{-1}. This fact suggests that the energy gap between the π and π^* bands becomes zero in the heavily doped $(\mathrm{CH})_x$ and doping removes the bond alternation leading to a unform bond lengths. Accordingly, the electronic structure of heavily doped (CH)$_x$ consists of one π band and one impurity band. Figure 4-3 shows the observed intraband transition (type 3) and impurity band (type 2), although the transition energy to the impurity level seems to become zero due to the electron screening effect in the metallic state.

In the system, the complex dielectric constant of heavily doped (CH)$_x$ can be easily derived from Eq. 1 by substituting the zero energy gap between the π and π^* bands

$$\varepsilon_{\pi^*}(\mathrm{k+q}) - \varepsilon_\pi(\mathrm{k}) \simeq 0 \tag{11}$$

and the oscillator strength of the intraband transition[19,25)]

$$\begin{aligned}\lim_{\mathrm{q}\to 0}\sum_{\mathrm{k}} f_{\pi\mathrm{k},\pi^*\mathrm{k+q}} &= \lim_{\mathrm{q}\to 0} f_{\pi\mathrm{k_F},\pi^*\mathrm{k_F+q}} \\ &= \frac{m}{\hbar^2}\left(\frac{\partial^2\varepsilon_\pi(\mathrm{k})}{\partial k^2}\right) \\ &= \frac{m}{m^*}. \end{aligned}\tag{12}$$

Here, m^* is the effective mass of the free carrier. The obtained dielectric constants are given in the following equations,

$$\varepsilon(\omega) = \varepsilon_{\mathrm{core}} - \frac{\omega_{\mathrm{p}}^2}{\omega^2 + i\omega/\tau_0}, \tag{13}$$

$$\varepsilon_1(\omega) = \varepsilon_{\mathrm{core}} - \frac{\omega_{\mathrm{p}}^2\tau_0^2}{1+\omega^2\tau_0^2}, \tag{14}$$

and

$$\varepsilon_2(\omega) = \frac{1}{\omega}\frac{\omega_{\mathrm{p}}^2\tau_0}{1+\omega^2\tau_0^2}, \tag{15}$$

where the plasma frequency ω_{p} is defined as follows

$$\omega_{\mathrm{p}}^2 = \frac{4\pi Ne^2}{m^*}, \tag{16}$$

and N is the number density of the free carrier. Then, the extinction coefficient $k(\omega)$ and the absorption coefficient $\alpha(\omega)$ are expressed by the next equations,[19)]

$$k(\omega) = \{(\sqrt{\varepsilon_1^2+\varepsilon_2^2}-\varepsilon_1)/2\}^{1/2} \tag{17}$$

and

$$\begin{aligned}\alpha(\omega) &= \frac{2\omega}{c}k(\omega) \\ &= \frac{\sqrt{2}\,\omega}{c}\{\sqrt{\varepsilon_1^2+\varepsilon_2^2}-\varepsilon_1\}^{1/2}. \end{aligned}\tag{18}$$

The maximum absorption coefficient of the interband transition is determined to be 2.58×10^5 cm^{-1} near 17000 cm^{-1} by the K-K transformation of the reflection spectra as is shown in Fig. 3. Accordingly, the absorption coefficient of the intraband transition of the heavily doped film ($\sigma\simeq250\ \Omega^{-1}$ cm^{-1}) can be estimated as is shown in Fig. 7. Then, the parameters of Eqs. 14 and 15 were determined by the optimum fit of Eq. 18 to the experimental data. The fit was obtained with $\hbar\omega_{\mathrm{p}}=31000$ cm^{-1}, $\tau_0=0.48\times10^{-15}$ s and $\varepsilon_{\mathrm{core}}=6$ (see Table 1). The calculated absorption spectrum based on these values is plotted for comparison with the experimental curves in Fig. 7.

Reflection Spectra of 85% trans-*(CH)$_x$ Films Doped with ClSO$_3$H.* Reflection spectra of 85% *trans*-(CH)$_x$ films doped with ClSO$_3$H are shown in Figs. 8 and 9.

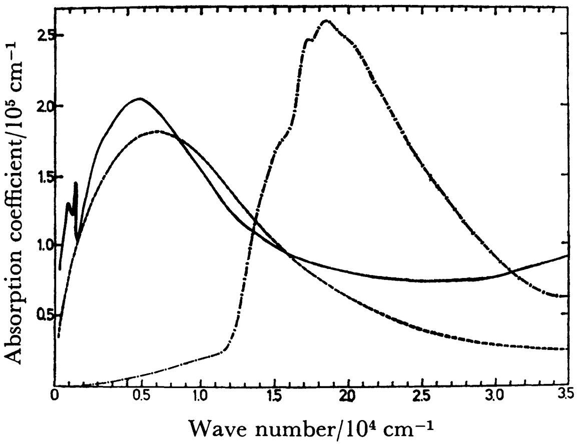

Fig. 7. Comparison between the observed and calculated absorption spectra of the thin (CH)$_x$ film ($\sigma_0\simeq250\ \Omega^{-1}$ cm^{-1}) heavily doped with ClSO$_3$H. ——: Observed, ------: theoretical, -·-·-: pure (CH)$_x$.

Table 1. Optical parameters obtained from the best fit of the absorption and reflection spectra of the heavily doped (CH)$_x$ films

Optical parameter	Absorption spectra	Reflection spectra
$\varepsilon_{\mathrm{core}}$	6	1.81
$\hbar\omega_{\mathrm{p}}$/cm^{-1}	31000	28200
τ_0/s	0.48×10^{-15}	0.277×10^{-15}
N/cm^{-3}	1.2×10^{22}—1.8×10^{22}	1.0×10^{22}—1.5×10^{22}
σ_0/Ω^{-1} cm^{-1}	1450	690

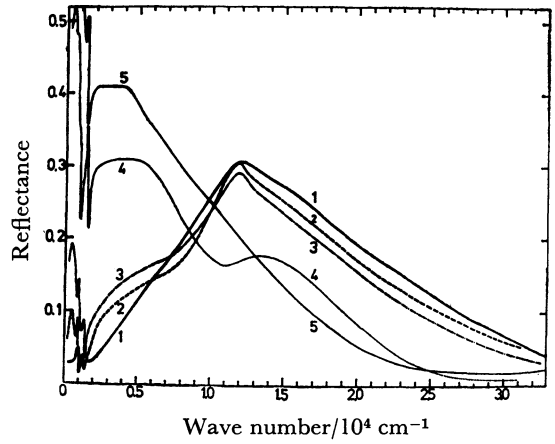

Fig. 8. The reflection spectra of thick 85% *trans*-(CH)$_x$ films doped with ClSO$_3$H. 1) pure (CH)$_x$, 2) $\sigma_0\simeq0.1\ \Omega^{-1}$ cm^{-1}, 3) $\sigma_0\simeq0.6\ \Omega^{-1}$ cm^{-1}, 4) $\sigma_0\simeq20\ \Omega^{-1}$ cm^{-1}, 5) $\sigma_0\simeq280\ \Omega^{-1}$ cm^{-1}.

Pure *trans*-(CH)$_x$ has the sharp dispersion peak of C–H out-of-plane mode at 1015 cm^{-1} in addition to the interband transition located in the visible region. Lightly doping of the film with ClSO$_3$H increases the reflectance below 10000 cm^{-1} and decreases the reflectance over the region of the interband transition. The shoulder at 800 cm^{-1}, the peak at 1400 cm^{-1} and the broad band in the region of 8000 cm^{-1} correspond to those observed in the absorption spectra of thin films

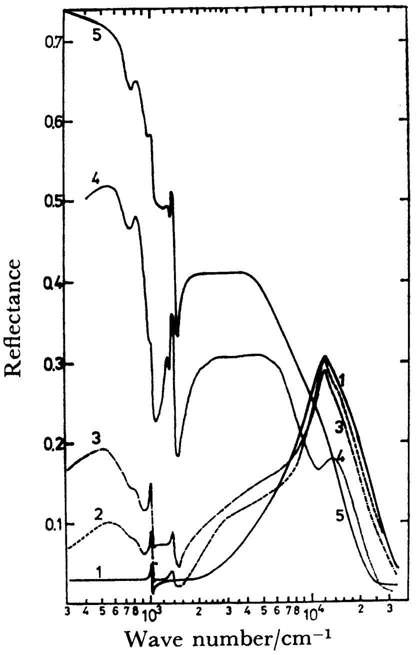

Fig. 9. The plot for the logarithmic wave number of the reflection spectra of thick 85% *trans*-$(CH)_x$ films doped with $ClSO_3H$. 1) Pure $(CH)_x$, 2) $\sigma_0 \simeq 0.1\ \Omega^{-1}\ cm^{-1}$, 3) $\sigma_0 \simeq 0.6\ \Omega^{-1}\ cm^{-1}$, 4) $\sigma_0 \simeq 20\ \Omega^{-1}\ cm^{-1}$, 5) $\sigma_0 \simeq 280\ \Omega^{-1}\ cm^{-1}$.

as shown in Fig. 6. The appearance of the peak below 800 cm^{-1} seems to show that the hole carriers occur in the $(CH)_x$ chain and the $(CH)_x$ film becomes the p-type semiconductor. In heavily doped samples, the reflectance becomes larger and larger below 10000 cm^{-1} and the reflectivity reaches to 70% in the frequency region of lower than 500 cm^{-1} although the interband transition disappears in the visible region. It looks like the metallic reflection spectrum. Furthermore, the 1400 and 800 cm^{-1} bands can be also clearly observed. The increase in the intensity of the 1400 cm^{-1} band means that the region of the uniform bond lengths expands in the $(CH)_x$ chain and the observation of the 800 cm^{-1} implies that the impurity band exists in the metallic π band as shown in Fig. 4-3. The behavior of the reflection spectra of doped thick films is in good agreement with that of the absorption spectra of doped thin films.

The reflectance is given by the following equation[19,26]

$$R = \frac{|\varepsilon|+1-\sqrt{2(|\varepsilon|+\varepsilon_1)}}{|\varepsilon|+1+\sqrt{2(|\varepsilon|+\varepsilon_1)}} \tag{19}$$

and

$$|\varepsilon| = \sqrt{\varepsilon_1{}^2+\varepsilon_2{}^2}. \tag{20}$$

Accordingly, the best fit of Eq. 19 to the observed reflection spectrum of the heavily doped film ($\sigma \simeq 280\ \Omega^{-1}\ cm^{-1}$) can be obtained by using the parameters of $\hbar\omega_p = 28200\ cm^{-1}$, $\tau_0 = 0.277 \times 10^{-15}$ s and $\varepsilon_{core} = 1.81$ (see Table 1). The calculated reflection spectrum based on these values is depicted for comparison with the experimental curve in Fig. 10.

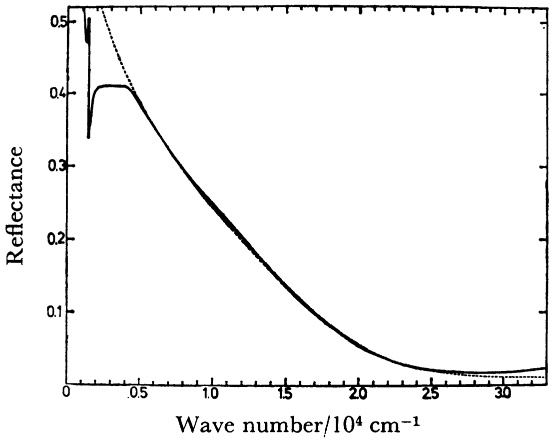

Fig. 10. Comparison between the observed and calculated reflection spectra of the thick $(CH)_x$ film heavily doped with $ClSO_3H$. ——: Observed, ------: theoretical.

Relation of the Obtained Optical Parameters with the Conductivity. The effective mass, m^*, of the free carrier in the $(CH)_x$ chain can be given in the tight binding approximation as follows,[26]

$$\frac{m}{m^*} = \frac{m}{\hbar^2}\left(\overline{\frac{\partial^2\varepsilon_\pi(\mathrm{k})}{\partial k^2}}\right) = \frac{4ta^2m}{\pi\hbar^2} \tag{21}$$

and can be estimated to be $0.6 < m/m^* < 0.9$ by using $a = 1.4$ Å and $t = 2.0$—2.5 eV. Then, the number density, N, of the free carrier contributing to the metallic conductivity is given as follows,

$$N = \omega_p{}^2m^*/(4\pi e^2). \tag{22}$$

The number density of the free carrier in the metallic $(CH)_x$ film can be extracted by substituting the observed plasma frequency and the effective mass, m^*, into Eq. 22 and is shown in Table 1. The observed number density, N, is comparable with the total π-electron number density ($N \simeq 2 \times 10^{22}\ cm^{-3}$) in the $(CH)_x$ film. This means that all π-electrons contribute to the transport and that heavily doping removes the bond alternation leading to a uniform bond lengths.

Furthermore, the d.c. conductivity, σ_0, is given by Eq. 23,[19]

$$\sigma_0 = \frac{\omega_p{}^2\tau_0}{4\pi} \tag{23}$$

and is calculated by using the observed plasma frequency, ω_p, and relaxation time, τ_0. The obtained values are comparable with the observed value ($\sigma \simeq 280$—$250\ \Omega^{-1}\ cm^{-1}$) of the d.c. conductivity of the heavily doped films as is shown in Table 1.

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