Spectral Studies on the Charged Soliton of Polyacetylene

Jiro Tanaka [a] , Masashi Tanaka [b] , Hitoshi Fujimoto [a] , Koji Kamiya [a] , Yasuyoshi Saito [a] & Tohru Kishi [c]

[a] Department of Chemistry, Nagoya University, Chikusa, Nagoya, 464, Japan

[b] Faculty of Science and College of General Education, Nagoya University, Chikusa, Nagoya, 464, Japan

[c] National Research Institute of Police Science, Chiyoda, Tokyo, 102, Japan
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SPECTRAL STUDIES ON THE CHARGED SOLITON OF POLYACETYLENE

JIRO TANAKA, MASASHI TANAKA*, HITOSHI FUJIMOTO, KOJI KAMIYA,

YASUYOSHI SAITO AND TOHRU KISHI**
Department of Chemistry, Faculty of Science and College of
General Education*, Nagoya University, Chikusa, Nagoya, 464
and National Research Institute of Police Science,** Chiyoda,
Tokyo, 102, Japan

Abstract   The optical spectra of polyacetylene doped with
iodine (p type) or sodium (n type) are investigated in the
infrared and visible region. The change of spectra with
doping is measured quantitatively. Model structures of the
charged soliton lattice are suggested for p and n type chains
of the highest doping levels. The reflection spectra of
$(CHI_y)_x$ and $(CDI_y)_x$ for heavy doped films are measured and
analyzed by five transitions existing in 0 - 24000 cm^{-1} region.
By lowering the temperature to 30 K, the gapless transition
is disappeared presumably because the lattice with the
charged soliton is frozen.

INTRODUCTION

The optical spectra of polyacetylene (PA) provides most important

information on the electronic and the molecular structures of the

polymer chain.   The concept of the charged soliton is very useful

to understand the change of spectra upon doping.   However, a

quantitative aspect of spectra and doping has not been fully

explored except that Feldblum et al.[1] have found a linear relation

between the spectral change and the perchlorate doping by opto-

electrochemical method.   In this study absorption spectral changes

upon iodine and sodium dopings are investigated by determining the

dopant concentration quantitatively with radio activation analysis

for iodine and sodium or flame spectrochemical method for sodium.

A structural aspect on the charged soliton lattice will be

presented. The main excited states of the doped PA are character-
ized by reflection spectroscopy and temperature dependence of
reflectance is measured to correlate the spectra with a motion of
the charged soliton in the doped PA chain.

DOPANT CONCENTRATION DEPENDENCE OF SPECTRAL CHANGES

By doping PA with electron acceptors such as AsF_5[2] and Br_2[3] or
electron donor such as Na[4], the peak of PA visible band at 18500
cm^{-1} is decreased and a new peak appears at about 6000 cm^{-1} (a mid
gap absorption band), which is a characteristic of an odd chain
carbonium ion structure. The chemical stoichiometry of iodine
doping suggests that three iodine molecules accept two electrons
from PA to form two triiodides ions and the oxidized PA and a pair
of charged soliton (a bipolaron) will be formed in the chain.
Absence of esr signals in the initial stage of p and n dopings is
in accordance with a bipolaron formation. A thin PA film is
synthesized by Shirakawa's method on quartz plate; the thickness
of film has been determined by the absorption coefficient at
18500 cm^{-1}. The spectra have been obtained after doping with
iodine vapor and the iodine content is determined by radio
activation analysis.

The spectral changes occurred by iodine doping is shown in
Fig.1. Compared with spectral changes by other dopants, the
decrease of the visible peak is small because the absorbance of I_3^-
is significant in this region. On the other hand, the intensity
of the mid gap band increases with doping. The correlation between
the spectral changes and the dopant concentration is illustrated in
Fig.2, where a linear relation is found to the level of 10 $\pm$ 1 %
(Similar values have been found in AsF_5 doping[2] as well as
ClO_4^- doping.[1])

Spectral changes with doping is also studied on Na doped PA,
and the results are shown in Figs. 3 and 4. An important
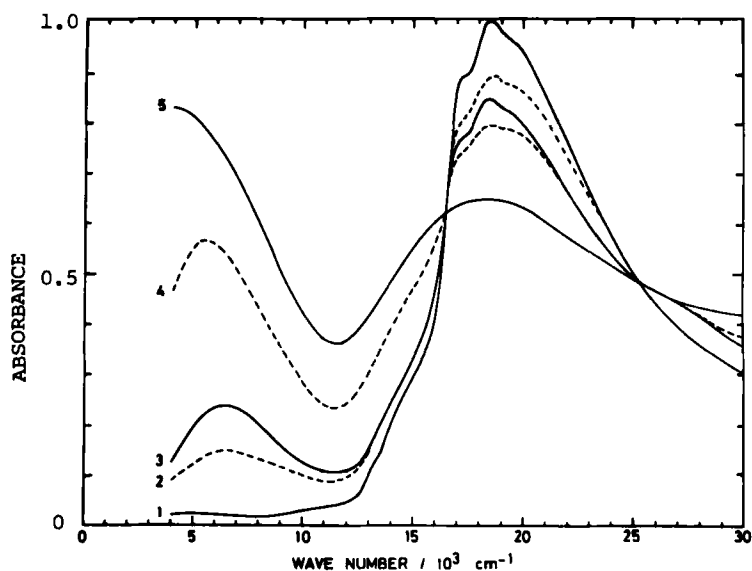consequence is that the n doping proceeds to the level of higher

FIGURE 1 Absorption spectra of cis-polyacetylene doped with iodine $(CHI_y)_x$. 1. y = 0, 2. 0.044, 3. 0.084, 4. 0.18, 5. 0.33.
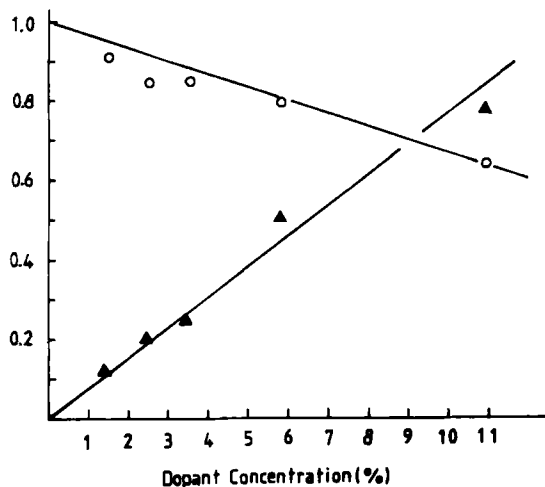

FIGURE 2 Dopant (I_3^-) concentration dependence of the cis peak (o) normalized at 18500 cm^{-1} and the intensity of the mid gap band at 6000 cm^{-1} ($\blacktriangle$).
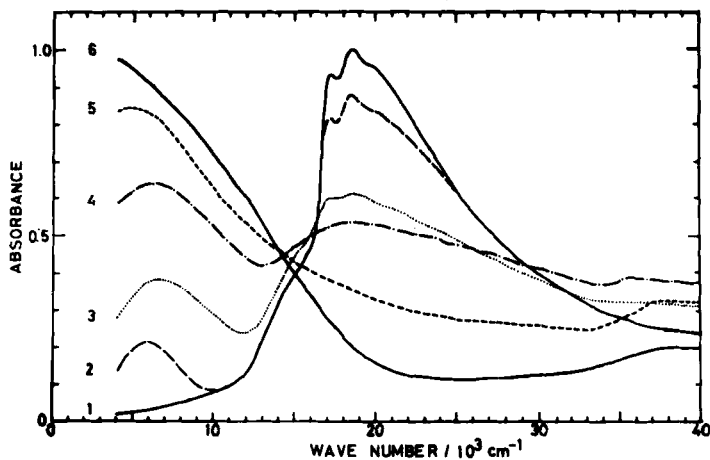
FIGURE 3 Absorption spectra of cis-polyacetylene doped with sodium $(CHNa_y)_x$. 1. y = 0, 2. 0.04, 3. 0.094, 4. 0.141, 5. 0.171, 6. 0.196.
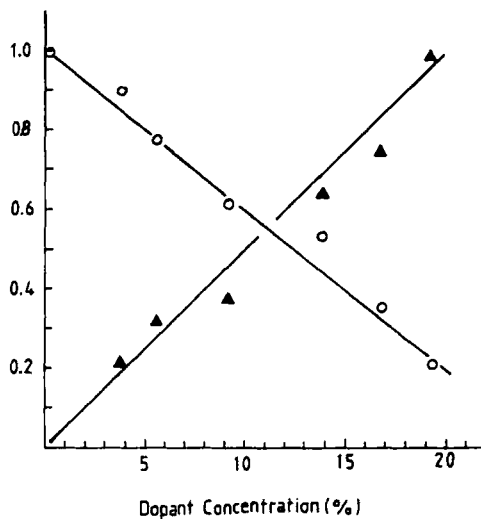

FIGURE 4 Dopant (Na) concentration dependence of the cis peak (o) and the mid gap band (▲) intensities.

concentration than the p doping. The highest doping level is estimated as large as 17 % for K doped PA film by Baughman[5] with the X ray method, however, the present result gives nearly 20 % for Na doping.

STRUCTURES OF THE CHARGED SOLITON LATTICES

The structures of the heavy doped PA chain are considered with following considerations. (1) the chain has an inversion symmetry to satisfy the mutual exclusion rule of infrared and Raman bands. (2) The charged soliton forms a pair or a bipolaron state. These considerations necessarily impose an odd number carbon chain in the charged soliton lattice. Accordingly, the structures of the doped PA chain are described as shown in Fig.5 with a simplest structural formula.

Although the bond alternation in the central CH chain is not accurately known yet, but the formation of short conjugation chain is supported by Raman spectra. Faulques and Lefrant[6] showed that the p doped PA exhibits characteristic bands at 1550 cm^{-1} and 1136 cm^{-1} (413 nm excitation) which are comparable to that of trans-octatetraene observed at 1608 cm^{-1} and 1185 cm^{-1}. A still short chain might be found in n doped PA; the Raman bands are found at 1600 cm^{-1} and 1275 cm^{-1} (515 nm excitation). However, the Raman spectra are not completely analyzed in terms of the chain length; the Raman bands of neat PA show a strange dispersion relation to the excitation wavelength. In spite of this, it seems certain that the long conjugation chain of PA is divided into short chain where the conjugation is disrupted by a presence of the charged soliton kink.

At the intermediate level of the doping, the short segment with a charged soliton kink is produced stoichiometrically, and the undoped chain coexist in equilibrium with the doped one and the dopant ion. It means that the perturbation due to the charged soliton extends about 9 and 5 carbons in p and n dopings.
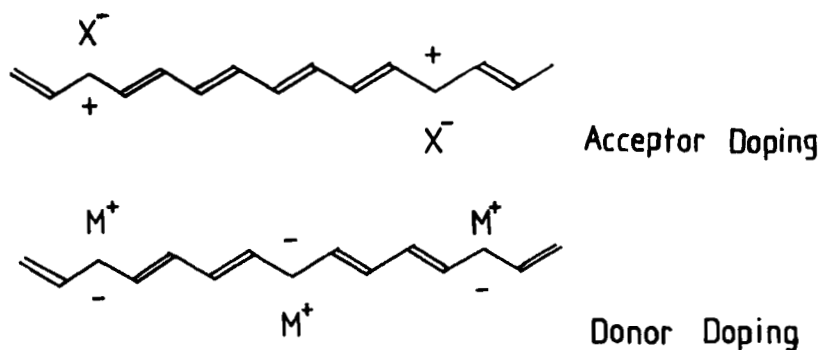
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X⁻

\+

\+

X⁻

Acceptor Doping

M⁺   −   M⁺

−

M⁺

−

Donor Doping

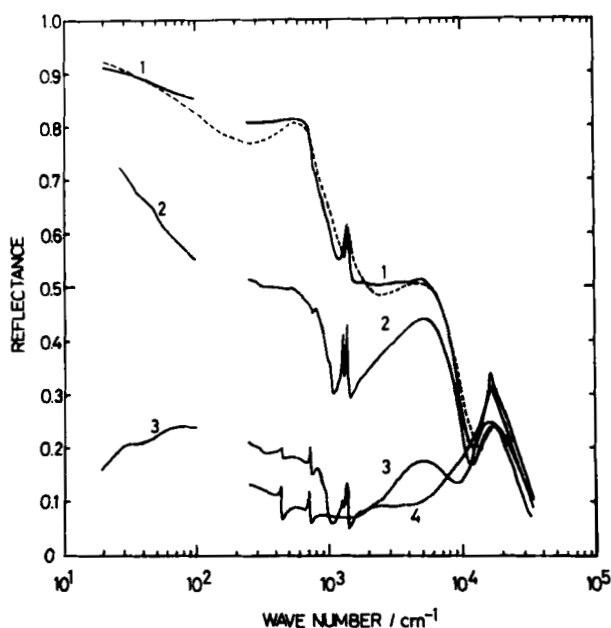FIGURE 5   Models of the charged soliton lattices
for acceptor (p) and donor (n) dopings.

FIGURE   6   Reflection spectra of I_2 doped $(CHI_y)_x$
1. y= 0.25, 2. 0.10, 3. 0.024, 4. 0
Calculated simulation curve (------).

REFLECTION SPECTRA OF THE DOPED POLYACETYLENE

The reflection spectra are measured with the doped PA films for $10 - 100$ cm^{-1} and $300 - 30000$ cm^{-1} range as shown in Fig.6. The reflectance curve of the heavy doped film at room temperature is simulated by using five main transitions, where the dielectric constant is given by the following formula.

$$\varepsilon(\omega) = \varepsilon_{core} - \frac{\Omega_o^2}{\omega^2 + i\Gamma_o\omega} + \sum_{j=1} \frac{\Omega_j^2}{\omega_j^2 - \omega^2 - i\Gamma_j\omega}$$

The second term represents a free carrier term and ω_j ($j=1,\cdots,4$) are 500, 1350, 5000 and 15800 cm^{-1}, respectively. The reflectance is represented by real (ε_1) and absolute values of ε as follows.

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

From the estimated parameter (Ω_o), the effective mass m* is estimated as 2.2 m$_e$ for (CHI$_{0.25}$)$_x$ and 5.3 m$_e$ for (CDI$_{0.24}$)$_x$ by using the relation $\Omega_o = (4\pi N e^2/m^*)^{1/2}$.

By lowering the temperature of the heavy doped film to 30 K, the reflectance at low energy region is reduced to 70 % of room temperature value as shown in Fig.7. A similar change was also found in (CDI$_{0.24}$)$_x$, and these results are explained only if the free carrier term is omitted. It means that a band gap is produced or the charged soliton sliding mode is pinned at low temperature. The metallic free carrier type band in the heavy doped PA film may be originated either by the sliding mode of the charged soliton or the broadening of the mid gap band as was suggested by Mele and Rice.[7] Temperature dependence of the free carrier band will be important to clarify the dynamics of the charged soliton motion in the doped PA chain.
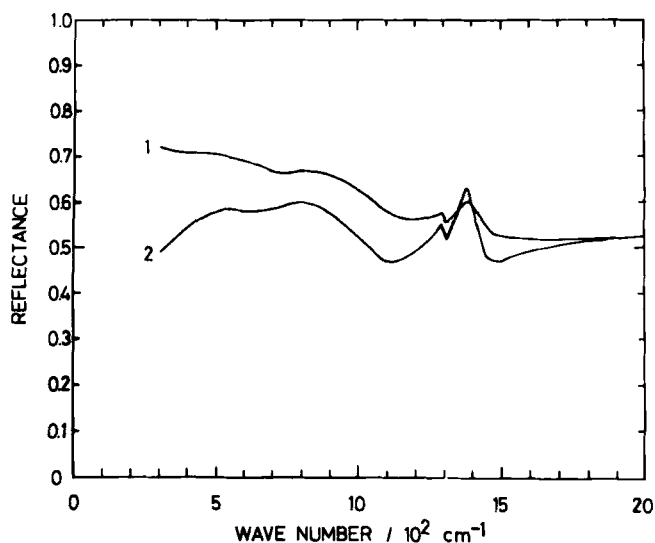
FIGURE 7   Temperature dependnece of reflection
spectra of $(CHI_{0.25})_x$. 1. 290 K. 2. 30 K.

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