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FORMATION OF THE STABLE INTERMEDIATE COMPLEXES IN THE HALOGENATION OF POLYACETYLENE

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Stable charge-transfer π complexes $[-(CH{=}CH)_n-(CH{=}CH-\cdots X^+)X_3^--]_m$ X = Cl, Br, and I, are formed between both trans- and cis-polyacetylene $[-(CH{=}CH)_n-]$ with chlorine, bromine, and iodine, which have strong absorptions in near i.r. to i.r. region, and show a large increase in electrical conductivity.

We have observed that a dramatic decrease in i.r. transmission (4000 - 400 cm^{-1}) occurs without visible change in appearance of the films at the initial period of the reaction of polyacetylene films[1-4] with chlorine and bromine. We have recently reported that all of the dark films to i.r. ray show a large increase in electrical conductivity.[5-8] In order to clarify the structure of the intermediate complexes, which were believed to be a charge-transfer π complexes of the type suggested to explain both the kinetic[9,10] and spectroscopic[11-18] behaviour in the electrophilic addition of halogens to unsaturated systems, we have examined their Raman scattering and electronic spectra.

Raman spectra were taken by the front surface reflection method in the region of 50 - 1700 cm^{-1} with 5145 A excitation of argon ion laser using spinning film samples in order to avoid thermal decomposition and thermal cis → trans isomerization of the conjugated skelton of the intermediate complexes. Intense Raman bands were observed in the lower frequency region 100 - 400 cm^{-1} as well as in the medium range 1000 - 1600 cm^{-1} in the complexes; thus, 250 cm^{-1} (s) in cis-$(CHCl_{0.15})_n$, 158 (s) and 316 cm^{-1} (w) in cis-$(CHBr_{0.31})_n$, 157 (s) and 310 - 315 cm^{-1} (w) in trans-$(CHBr_{0.28})_n$, 172 (s), 342 (m), and 515 cm^{-1} (w) in cis-$[CH(IBr)_{0.09}]_n$, and 106 (s), 213 (m), 315 (w), and 430 cm^{-1} (vw) in cis-$(CHI_{0.01})_n$. Typical spectrum is shown in Figure 1. The vibrational assignment of the various trihalide ion has been carried out by Evans and Lo,[19] Person et al.,[20] Maki and Forneris,[21] and Parrett et al.[22] According to them, Raman active symmetric stretching vibrations of X_3^- were found at 268 cm^{-1} $(n\text{-}Pr_4NCl_3)$,[19] 162 cm^{-1} (Me_4NBr_3),[20] 163 cm^{-1} $[Bu_4N(IBr_2)]$[21] and 107 cm^{-1} (Me_4NI_3).[22] Comparing these with the observed bands, we assigned these bands to the symmetric stretching vibrations and their overtones of the X_3^- (X = Cl, Br, and I) and IBr_2^- ions. It is interesting to note that the bands in the iodinated polyacetylene became weak as increasing iodine content and were extremely difficult to find in case of $(CHI_{0.25})_n$. This result suggests that observed spectra may be due to resonance-enhanced Raman effect, as observed for starch-iodine,[23] poly(vinyl alcohol)-iodine,[24,25] and amylose-iodine[25] complexes. In fact, the iodinated

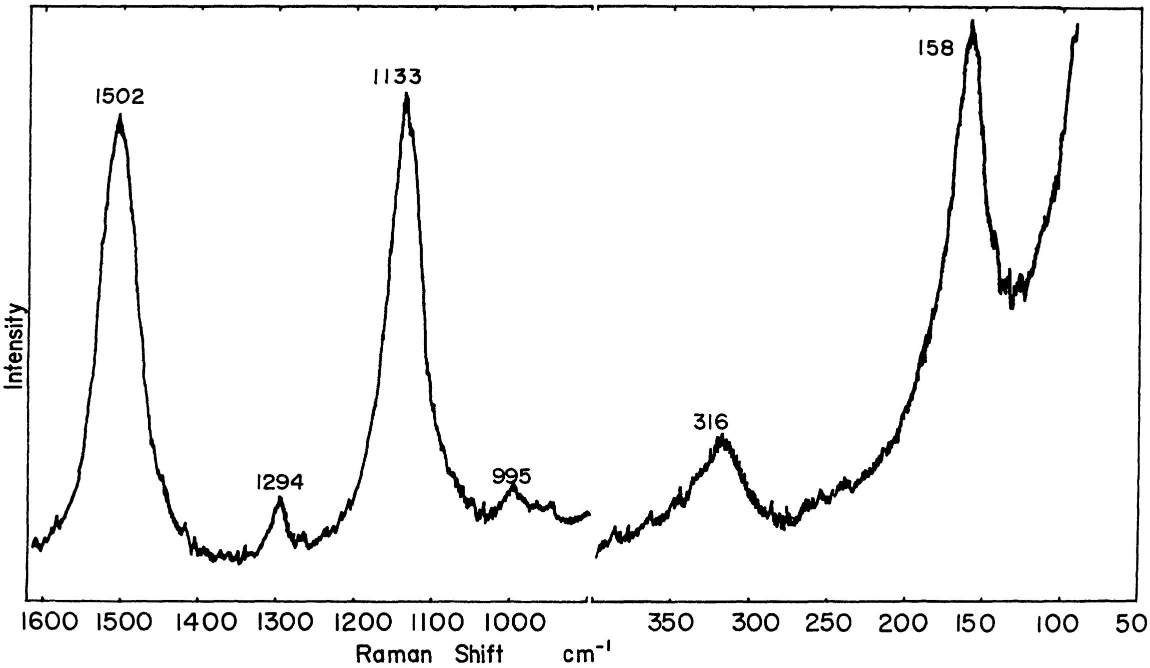

Fig. 1. Raman spectrum of $(CHBr_{0.31})_n$ taken with the 5145 A excitation.

polyacetylene has a strong absorption in visible region as well as i.r. and far i.r. regions.$^{6)}$ Figure 2 shows the electronic spectra of cis-polyacetylene and the intermediate complexes of bromine and iodine. The spectra were recorded in the region of 210 nm (4.76×10^4 cm^{-1}) - 2600 nm (3.85×10^3 cm^{-1}) for extremely thin films which were polymerized at -78°C on a wall of 1-cm quartz cell and reacted with halogen vapour in situ. Characteristic absorptions to the complexes were observed in ultraviolet and visible region; thus, 253 nm in chlorine-, 280 and 338 nm in bromine-, 280 and 333 nm in monobromoiodine-, and 360 nm in iodine-complex. The iodine complex show a strong absorption at 630 nm. These absorptions may be connected with the trihalogen ions. All of these halogen intermediate complexes have an intense absorption in near i.r. to i.r. regions. The maximum wavelength of these absorption were not observed in the measured region, however, it must be in i.r. region. This strong absorption might quite possibly be explained in terms of a red shift of $\pi - \pi^*$ transition of polyacetylene conjugated skeleton by strong delocalization of the conjugated system coupled with charge-transfer between π electrons of the conjugated double bonds and halogen cations. These results suggest that the intermediate complexes can be express as follows;

$$[-(CH{=}CH)_n-(CH{=}CH-\cdots X^+)X_3^--]_m \quad X = Cl,\ Br,\ \text{and}\ I$$

In medium frequency region of Raman spectra, all complexes containing more than 1 atom-% of halogens exhibited two intense Raman bands at 1490 - 1520 cm^{-1} and 1110 - 1130 cm^{-1} which closely coincide with the bands at 1474 cm^{-1} ($\nu_{\text{trans } C=C}$) and 1080 cm^{-1} (ν_{C-C}) of trans-polyacetylene$^{2)}$ rather than with the bands at 1552 cm^{-1} ($\nu_{\text{cis } C=C}$) and 1262 cm^{-1} (ν_{C-C}) of cis-polyacetylene,$^{2)}$ indicating that a rapid cis → trans isomerization occurred during the complex formation even at room temperature.

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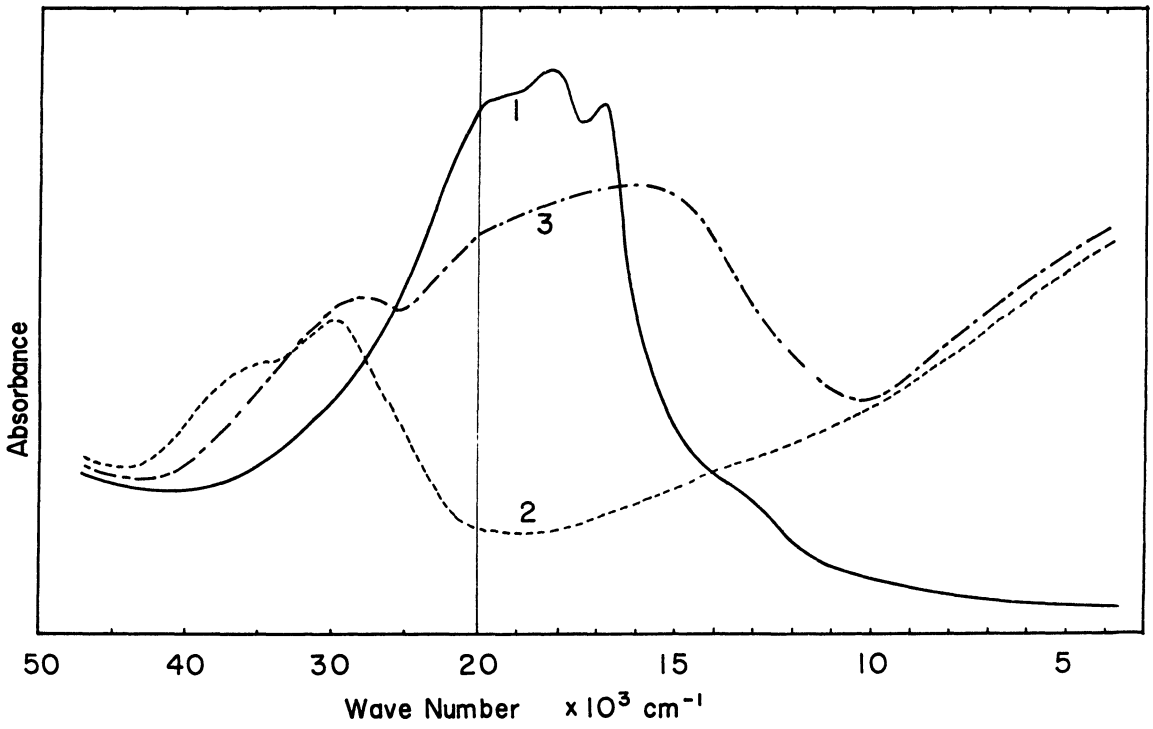

Fig. 2. Electronic spectra replotted from ultraviolet, visible, and near i.r. spectra of (1) cis-polyacetylene, (2) intermediate complex with bromine, and (3) intermediate complex with iodine.

measurement.

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