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ELECTRICAL PROPERTIES OF POLYACETYLENE DOPED WITH BF_3, H_2SO_4, AND $ClSO_3H$

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The conductivity of BF_3, H_2SO_4, and $ClSO_3H$ doped polyacetylene films is measured as a function of dopant concentration and temperature. The conductivity at 295 K of the heavily doped film is σ_{295K}= 220 $\Omega^{-1}cm^{-1}$ for BF_3, 130 $\Omega^{-1}cm^{-1}$ for H_2SO_4, and 245 $\Omega^{-1}cm^{-1}$ for $ClSO_3H$, respectively. The conductivity of $ClSO_3H$ doped film is metallic between 295 and 250 K.

Shirakawa et al.[1)] have found that the electrical conductivity of polyacetylene, $(CH)_x$, can be increased over seven orders of magnitude by doping with iodine. This remarkable effect is due to oxidizing the $(CH)_x$ film with Lewis acid dopant. We intended to obtain metallic $(CH)_x$ films by using such powerful oxidizing dopants as BF_3, H_2SO_4, and $ClSO_3H$, and examined the dependence of the conductivity upon dopant concentration and temperature.

Films of cis-rich polyacetylene were produced in the usual way from gaseous acetylene in a liquid Ziegler-Natta catalyst.[2)] Four platinum wires were attached to films by means of silver paste and were connected to an apparatus for measuring their d.c. conductivity by the four probe method and the sample was mounted in a glass vessel. After that, the polymer was exposed to gaseous BF_3, H_2SO_4 or $ClSO_3H$ at room temperature. The level of doping was determined by the measurement of the conductivity of $(CH)_x$. The final dopant content of the sample was determined by chemical analysis from the elemental analysis center of Kyoto university. The doped films were pumped for about one hour before the conductivity measurement. Room temperature conductivity was measured,

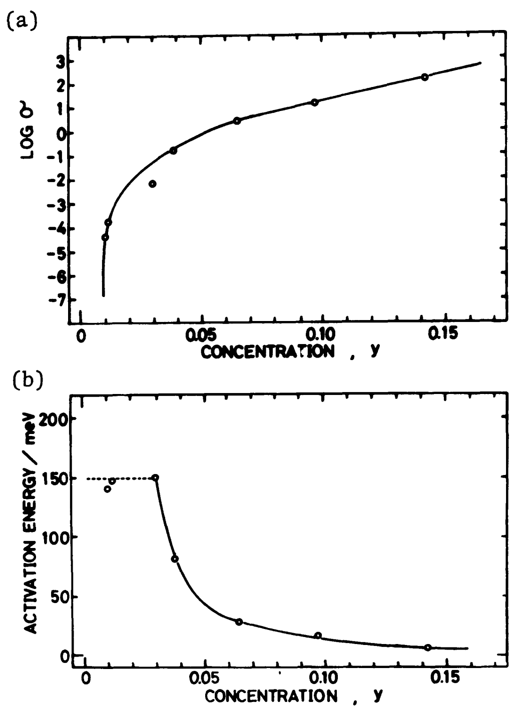

Fig. 1 Electrical conductivity and activation energy of BF_3 doped polyacetylene, $[CH(BF_3)_y(H_2O)_w]_x$, as a function of BF_3 concentration determined by C and H analyses.

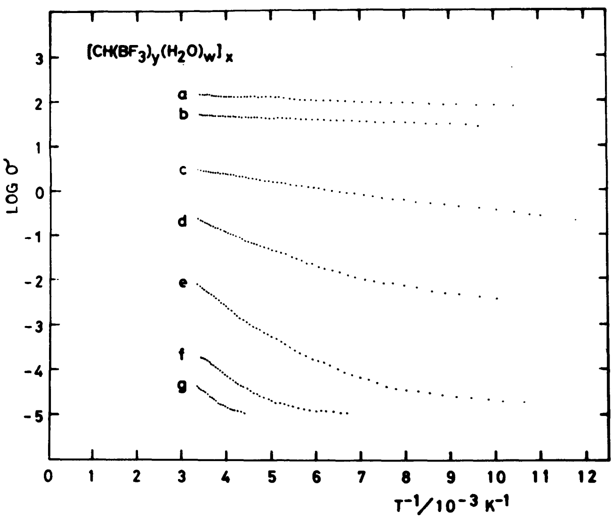

Fig. 2 Log σ vs 1/T of $[CH(BF_3)_y(H_2O)_w]_x$ [8) for various concentrations, y, of BF_3.

a) y=0.142, w=0.299 b) y=0.097, w=0.230
c) y=0.065, w=0.090 d) y=0.038, w=0.076
e) y=0.030, w=0.050 f) y=0.011, w=0.052
g) y=0.011, w=0.041

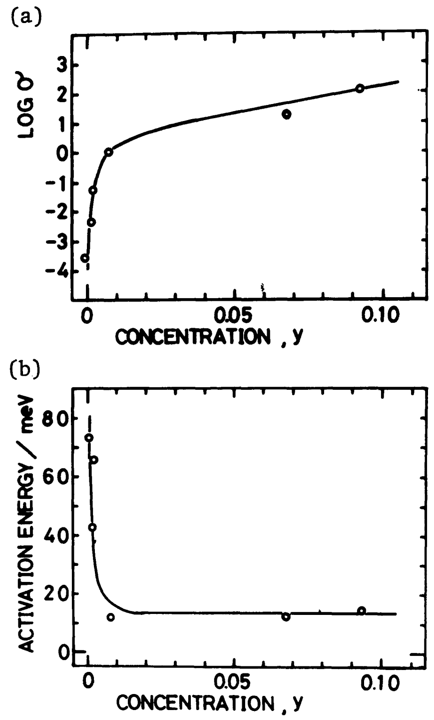

Fig. 3 Electrical conductivity and activation energy of H_2SO_4 doped polyacetylene, $[CH(H_2SO_4)_y(H_2O)_w]_x$, as a function of H_2SO_4 concentration determined by C, H, and S analyses.

and then the sample was cooled to about 100 K (or 4.2 K) in vacuo and the temperature dependence was measured as the sample was slowly warmed.

BF_3 doped $(CH)_x$ film ; The room temperature conductivity of BF_3 doped $(CH)_x$ is shown in Fig. 1-a as a function of dopant concentration. BF_3 doped films are very unstable in air. Therefore, the doped films were not exposed to air until after the electrical measurement had been performed. The films had the size of $0.8\times0.2\times0.005$ cm^3. As shown in Fig. 1-a, the conductivity increases rapidly in the region of the concentration of 0%(y=0) to 1%(y=0.01) BF_3 and saturates to the maximum value for the concentration of more than 5% (y=0.05) BF_3. The conductivity at 295 K of the heavily doped film was σ_{295K} = 220 $\Omega^{-1}cm^{-1}$ which is comparable with the value (σ = 100 $\Omega^{-1}cm^{-1}$) obtained by Gau et al.,[3] and the optically determined one (σ = 1070 $\Omega^{-1}cm^{-1}$).[4] The temperature dependence of the conductivity of BF_3

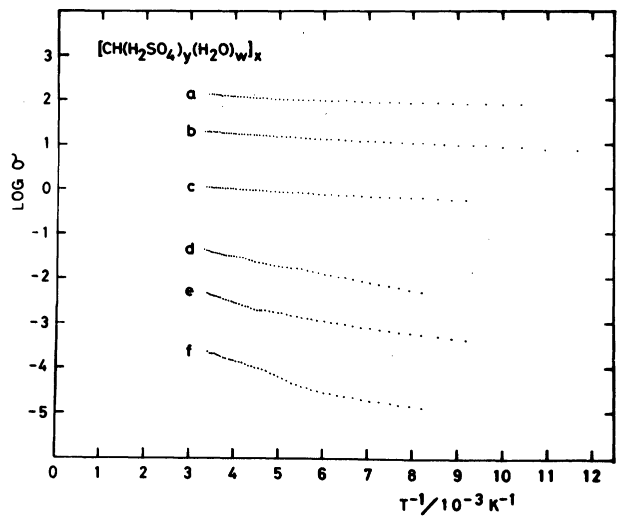

Fig. 4 Log σ vs 1/T of $[CH(H_2SO_4)_y(H_2O)_w]_x$ for various concentrations, y, of H_2SO_4.

a) y=0.093, w=0.170 b) y=0.068, w=0.189
c) y=0.008, w=0.063 d) y=0.002, w=0.032
e) y=0.002, w=0.022 f) y=0.001, w=0.011

doped films is shown in Fig. 2. The conductivity of BF_3 doped $(CH)_x$ decreases with decreasing temperature and the plots of log σ vs 1/T give straight line behavior near room temperature. Therefore, the approximate thermal activation energy, Eg, can be determined by the initial slope of the 1/T plots. The resulting activation energies are also shown in Fig. 1-b as a function of BF_3 concentration. The activation energy, Eg, is 0.15 eV in the range of 1%(y=0.01) to 3%(y=0.03) BF_3 and decreases rapidly at a concentration y=0.03 - 0.05. At higher values, Eg is only weakly dependent on concentration and reaches a value as low as 15 meV at about 14%(y=0.14) BF_3. The sudden change in the concentration dependence of the activation energy near y=0.03 is correspondent with the behavior of the conductivity (Fig. 1-a) which corresponds to a semiconductor to metal transition. The critical concentration, n_c = 0.03, is in good agreement with the values obtained for AsF_5 and I_2 doped films.[5)]

H_2SO_4 and $ClSO_3H$ doped films ; The $(CH)_x$ film becomes metallic when the vapor from H_2SO_4(98%) is pumped over the films for one day at room temperature. Chlorosulfonic acid ($ClSO_3H$) is more volatile than sulfuric acid (H_2SO_4). Therefore, the film is more quickly doped with $ClSO_3H$ than with H_2SO_4. Both golden films doped with H_2SO_4 and $ClSO_3H$ are so stable that they undergo almost no change in appearance and conductivity after two day exposure to air. The films of the size $3.5\times1.0\times0.01$ cm^3 were pumped for about one hour after doping and used for the conductivity measurement. The room temperature conductivity of H_2SO_4 and $ClSO_3H$ doped films is shown in Figs. 3-a and 5-a as a function of the concentration. These figures show that the

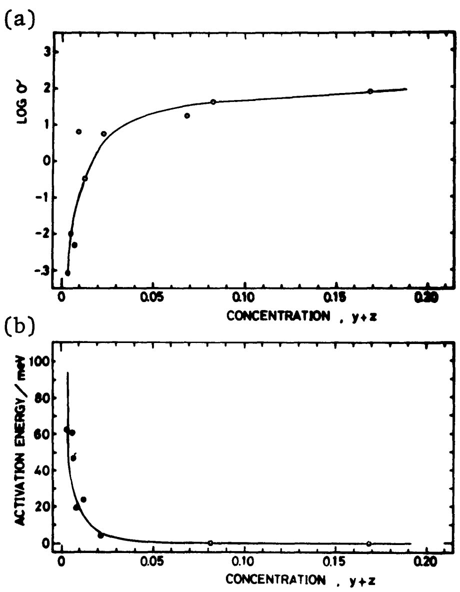

Fig. 5 Electrical conductivity and activation energy of $ClSO_3H$ doped polyacetylene, $[CH(H_2SO_4)_y(ClSO_3H)_z(H_2O)_w]_x$, as a function of H_2SO_4 and $ClSO_3H$ concentrations determined by C, H, S, and Cl analyses.

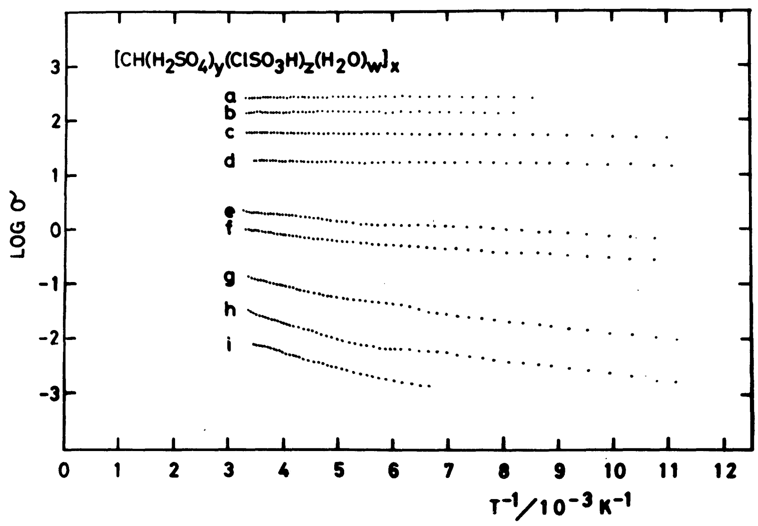

Fig. 6 Log σ vs 1/T of $[CH(H_2SO_4)_y(ClSO_3H)_z(H_2O)_w]_x$ for various concentrations, y+z, of H_2SO_4 and $ClSO_3H$.
a) y=0.119, z=0.050, w=0.195 b) y=0.067, z=0.015, w=0.292
c) y=0.054, z=0.014, w=0.170 d) y=0.019, z=0.004, w=0.000
e) y=0.005, z=0.004, w=0.016 f) y=0.000, z=0.013, w=0.022
g) y=0.000, z=0.007, w=0.000 h) y=0.000, z=0.006, w=0.000
i) y=0.000, z=0.004, w=0.010

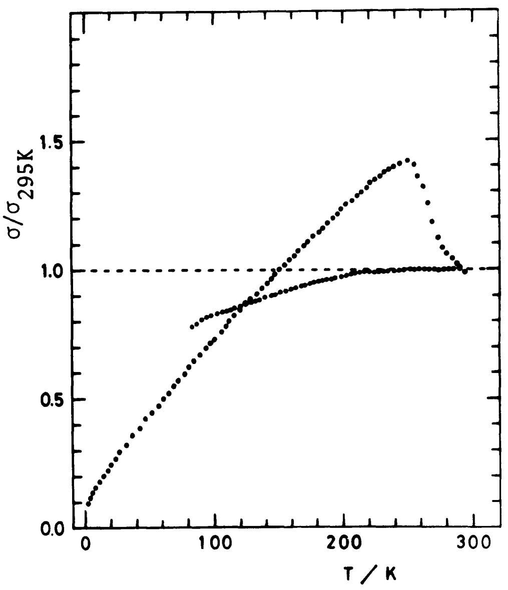

Fig. 7 Conductivity ratio - temperature dependence of $[CH(H_2SO_4)_{0.020}(ClSO_3H)_{0.014}(H_2O)_{0.039}]_x$ ooooo in helium gas, ••••• in vacuo.

conductivity increases rapidly and approaches to the maximum value in the region of less than 1% dopant concentration. The temperature dependence of the conductivity of H_2SO_4 and $ClSO_3H$ doped films are shown in Figs. 4 and 6, and the activation energies are shown in Figs. 3-b and 5-b. The critical concentration is observed to be less than 1% for both H_2SO_4 and $ClSO_3H$ doped films. The activation energy of $ClSO_3H$ doped film reaches to almost zero in the range of more than 5% $ClSO_3H$ while that of H_2SO_4 doped film reaches to about 15 meV. As shown in Fig. 7, the conductivity of $ClSO_3H$ doped film is found to be metallic between 295 and 250 K. The conductivity ratio has the maximum $\sigma_{MAX} / \sigma_{295K} = 1.43$ at 250 K for the film in helium gas while $\sigma_{MAX} / \sigma_{295K} = 1.01$ in vacuo. This kind of metal-like behavior has been reported only for AsF_5[3,6] and $FSO_2O\text{-}OSO_2F$[7] doped films.

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References and Note

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