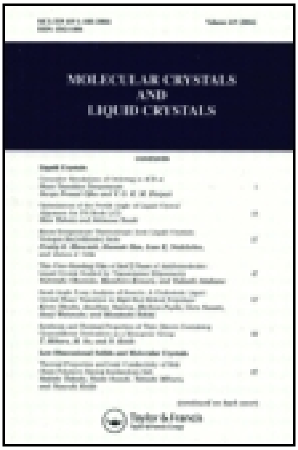

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Spectroscopic Investigation of Highly Oriented Polyacetylene

H. S. Woo [a] , D. B. Tanner [b] , N. Theophilou [c] & A. G. Macdiarmid [c]

[a] Electronic Materials Research lab., Institute for Advanced Engineering(IAE), C.P.O. Box 2849, Seoul, Korea

[b] Department of Physics, University of Florida, Gainesville, FL, 32611, U.S.A.

[c] Department of Chemistry, University of Pennsylvania, Philadelphia, PA, 19104, U.S.A.

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SPECTROSCOPIC INVESTIGATION OF HIGHLY ORIENTED POLYACETYLENE

H. S. WOO
Electronic Materials Research lab., Institute for Advanced Engineering(IAE),
C.P.O. Box 2849, Seoul, Korea

D.B. TANNER
Department of Physics, University of Florida, Gainesville, FL 32611 U.S.A.

N. THEOPHILOU, A.G. MACDIARMID
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104
U.S.A.

The doping induced infrared spectra in highly oriented Naarmann-Theophilou type polyacetylene, NT-$[CH]_x$, have been measured. All samples were doped with iodine chemically doping with various dopant levels. In 550% stretched NT-(CH)x, doped at level 6%(I_3^-), the dc conductivity was about 10^4 /Ω cm at 300 K, decreasing as temperature is lowered and reaching 2.5x10^3 /Ω cm at 84K. In contrast, the far-infrared oscillator strength in the 500 cm^{-1} region, where the "pinning" mode is usually seen, increased and shifted to lower frequencies with decreasing temperature. This effect was observed for polarization parallel and perpendicular to the stretching direction. All stretched samples displayed highly anisotropic behavior with substantially greater optical conductivity $\sigma_1(\omega)$ for polarization parallel to the chain direction. This $\sigma_1(\omega)$ at zero frequency was found to be 1.2x10^4/Ω cm, which is in good agreement with measured dc conductivity, 10^4/ Ω cm.

INTRODUCTION

Polyacetylene, where the π band is half filled with energy gap about 1.45 eV, is interesting for the possibility of metallic conductivity.[1] From optical measurement it is known that the charged soliton in heavily doped polyacetylene has a broad absorption band at midgap and IRAV modes are shown in infrared region.[2] The "pinning mode", a characteristic of oscillation of the charged solitons bounded by to ionized impurities, is seen 500 - 900 cm^{-1}.

Few years ago, a new technique has been developed by Naarmann and Theophilou to synthesize polyacetylene with fewer sp^3($<<$ 1 mol%) defects than in Shirakawa polyacetylene(S-$(CH)_x$).[3] This fewer sp^3 defects in NT-$(CH)_x$ implies that the polymer chain has longer conjugation length and fewer crosslinks, which leads to higher electrical conductivity. Naarmann and Theophilou have reported the dc conductivity of heavily doped film by iodine was about 20000 /Ω cm which is much higher than that of S-$(CH)_x$, 10-1000 /Ωcm.[3] The bulk density of stretched NT-$(CH)_x$ film is about .8 - 1.12 g/cm^3 , greater than one for S-$(CH)_x$, 0.4 g/cm^3.

In this report, we presents the electrical and optical properties of highly oriented (500 % stretched) NT-$(CH)_x$. On account of extremely high conductivity in NT-$(CH)_x$, the dc conductivity and optical properties under various condition, e.g. doping, temperature, and the polarization dependence etc., will be major points.

EXPERIMENTAL

According to Naarmann and Theophilou[3] the NT-$(CH)_x$ was prepared by Theophilou at the University of Pennsylvania. In order to produce the stretched film, NT-$(CH)_x$ prepared on the surface of polyethylene was stretched (500% longer than its original length) inside the glove box after acetylene was polymerized. This oriented free standing film was doped chemically with saturated I_2 /CCl_4 solution, submerging the film in this solution for one hour. Afterward, this doped film was washed once with CCl_4 and then dried in a weak stream of argon.

In optical spectra, a Fourier transform infrared(FTIR) spectrometer, BRUKER IR/98, was used to cover frequencies ranging from 25 to 5000 cm^{-1}, with mercury arc and glowbar lamps as optical sources and a liquid He cooled bolometer(infrared lab. LN-6/C) and pyroelectric deuterated triglycine sulfate(DTGS) as detectors, for the far and mid- IR respectively.

In order to perform the measurement *in-situ*, optical, dc conductivity, and temperature dependence, a home made sample holder with 4-terminal electrode for resistance measurement and heater with silicon diode thermometer(Scientific Ins. Si-410A) was connected to the liquid N_2 cryostat which controls the temperature from 80 K to 300 K. The polyethylene and KCl were used as the windows for the frequency ranges 20-600 cm^{-1} and 450-25000 cm^{-1} respectively. In order to investigate the optical anisotropy of the stretched samples, the wire grid polarizers were used such that the electric field was polarized parallel and perpendicular to the stretching direction(thus polymer chain direction).

RESULTS AND DISCUSSION

	dc conductivity $(\Omega\ cm)^{-1}$	
Temperature(K)	Undoped TN-$(CH)_x$	Doped TN-$(CH)_x$
300	1.4×10^{-6}	1.0×10^{4}
250	2.0×10^{-7}	8.7×10^{3}
200	3.7×10^{-8}	6.7×10^{3}
150	1.1×10^{-8}	5.0×10^{3}
100	1.0×10^{-8}	3.3×10^{3}
84	8.3×10^{-9}	2.5×10^{3}

Table 1. dc.conductivity of TN-$(CH)_x$ as function of temperature

Upon doping TN-$(CH)_x$ with iodine, the maximum dopant level obtained by weight uptake was about 6%. The transport properties of heavily doped TN-$(CH)_x$ are metal-like except the dc conductivity which decreases with decreasing the temperature as shown in Table 1. Table 1 shows that dc conductivity of doped sample increased by factor of 10^{10} from undoped sample at room temperature, reaching dc conductivity that of metal. The temperature dependent dc conductivity of doped sample, however, is not metal-like because it does decrease with lowering the temperature. This may indicate, as reported previously, that phonon scattering does not contribute significantly to the sample resistance even at room temperature.[1]

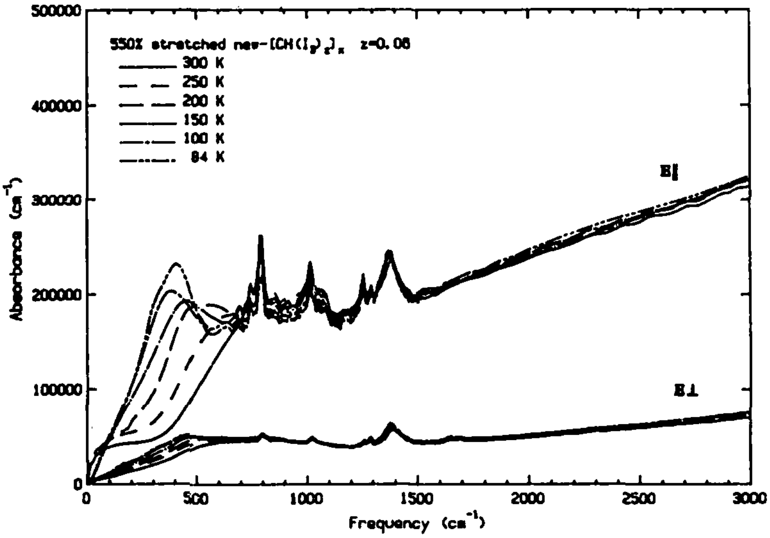

Figure 1. Temperature and polarization dependence of the IR absorbance of oriented TN-$[CH(I_3)_z]_x$ with 550 % stretching ratio and z=0.06

Figure 1 shows the temperature dependent polarized IR absorption spectra for heavily doped and undoped sample(both with 550% stretched) respectively. As can be seen from Figure 1, in heavily doped sample, a strong broad band was found around 500 cm^{-1} at 250 K with polarization parallel to chain direction ($E_{\parallel}$), in which the oscillator strength of this band is decreased as lowering the temperature down to 84 K, reaching its peak at 400 cm^{-1}. Same effect for this band was found for polarization perpendicular to the chain(E $\perp$) with substantially smaller change of oscillator strength. It should be, however, noted that the oscillator strength of other IRAV modes are not influenced by this temperature change.

Strong polarization dependence implies that this broad band is a characteristic of polymer chain. It is expected that the pinning mode increases its intensity on lowering the temperature because of reducing the screening of Coulomb interaction between charged soliton and counter-ions, which causes large dipole oscillation of the charged solitons. Thus, we assumed that the charged soliton introduced by doping are strongly involved in this broad band, which we assigned as a pinning mode in NT-$(CH)_x$, trapping oscillation of charged solitons due to Coulomb interaction with counter ions(I_3^-).

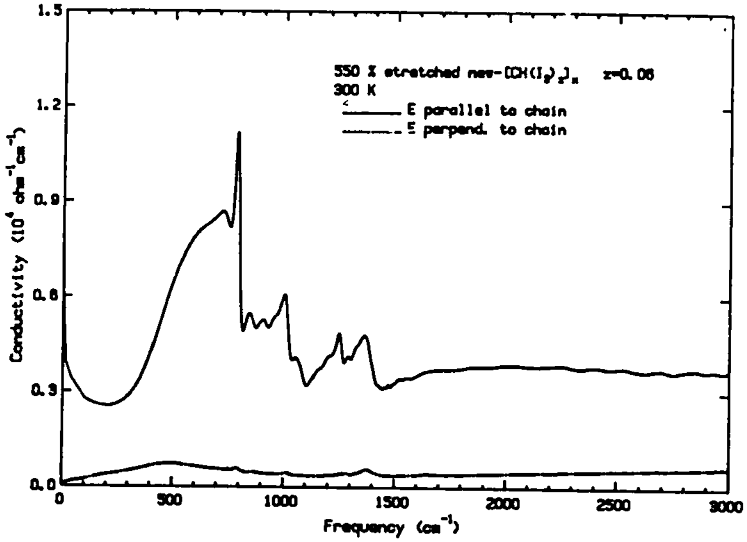

Figure 2. Polarization dependence of infrared conductivity for oriented TN-$(CH)_x$ with 550% stretching ratio and z=0.06

Figure 2 shows the polarization dependence of the $\sigma_1(\omega)$ for 550 % stretched sample in IR range, where the usual doping induced IRAV modes at 1283 cm^{-1} and 1389 cm^{-1} as shown in S-$(CH)_x$. For the two polarization, the ratio of oscillator strength at 1380 cm^{-1} was found to be about 28. This large anisotropy indicates, as mentioned earlier, that the doping induced IRAV modes are characteristic of the doped polymer chain, which implies the CC vibrations are strongly related to this modes. $\sigma_1(\omega)$ at zero frequency was found to be 12000 / Ω cm, which is in good agreement with measured dc conductivity, 10000 / Ω cm.

CONCLUDING REMARKS

It has been shown that the dc conductivity of highly oriented TN-$(CN)_x$ can be close to that of metal. However, the temperature dependence was not metal-like, decreasing with lowering of temperature. It may be possible to describe that the charge transfer is caused by tunneling through the conducting regions separated by a potential barrier, which will be influenced by thermal energy fluctuation, as proposed by Sheng *et al.*[4] The increasing of pinning potential by lowering the temperature can be viewed as large dipole oscillation of charged solitons due to decreasing of Coulomb screening (less phonon vibration at lower temperature) between charged solitons and counter ions.

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