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POLARIZED ABSORPTION IN ORIENTED "NEW" $(CH)_x$

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Abstract

We have measured the temperature and polarization dependence of the infrared absorption in $\sim$ 500%-stretched highly-conducting *trans*-$(CH)_x$, doped chemically with iodine to levels up to 6% (I_3^-). The dc conductivity for the 6%-doped sample was $\sim$ 10 000 $\Omega^{-1}cm^{-1}$ at 300 K. These samples have highly anisotropic infrared conductivity, with substantially greater $\sigma_1(\omega)$ for polarization parallel to the chain direction. The 300 K frequency-dependent conductivity has a narrow Drude-like peak at zero frequency above which is a broad "midgap" band with the usual doping-induced vibrational modes superimposed. When the temperature was lowered, the far-ir conductivity decreased (in accord with dc measurements). The Drude-like peak was not seen below $\sim$ 200 K.

1. Introduction

About four years ago, Naarmann and Theophilou[1] described a method of preparing high-density $(CH)_x$ which, when doped, has conductivity considerably higher than that of Shirakawa[2] $(CH)_x$. Several variations for preparing this "new"-$(CH)_x$ have been reported, giving stretch-oriented samples conductivities in the 10 000–100 000 $\Omega^{-1}cm^{-1}$ range.[1,3,4,5] In this paper we present the infrared properties of "new"-$(CH)_x$.

2. Experimental

Free-standing "new"-$(CH)_x$ films were prepared at Penn as previously described.[3] The undoped polymers were mechanically stretched up to 5.5× (550%). The doping was carried out at Florida, immediately prior to the infrared measurements. We tried both vapor-phase and solution-phase doping. With vapor-phase doping we were only able to reach dopant levels of $\approx$ 2% I_3^-, well below the 6% levels achieved in Shirakawa $(CH)_x$ by the same technique. Solution-phase doping, from a I_2/CCl_4 saturated solution, was much more successful. One hour immersion in this solution, followed by a 1 minute wash with CCl_4 and 5–10 minutes drying in a weak Ar stream, led to dopant levels of 6%, measured by weight uptake. Typical

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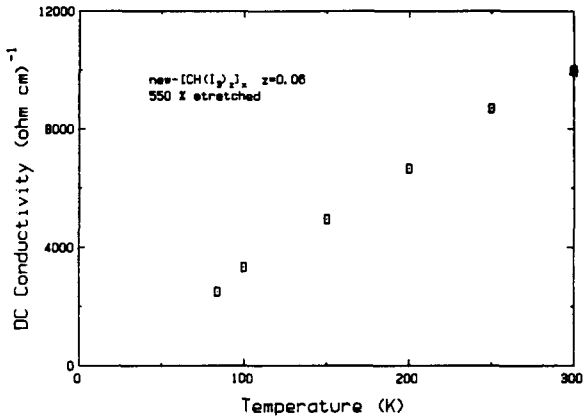

Fig. 1. Temperature dependence of the dc conductivity of oriented "new"-$(CH)_x$.

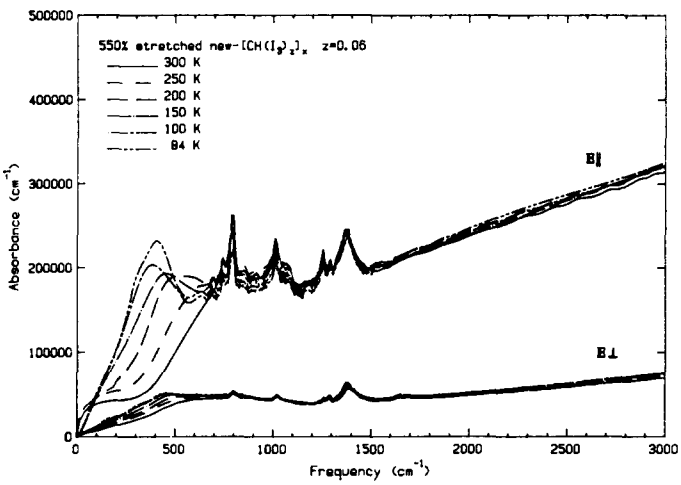

Fig. 2. Absorption coefficient of "new"-$[CH(I_3)_{0.06}]_x$ for $\vec{E}$ || and $\vec{E}$ ⊥ to the stretching direction.

dc conductivity data are shown in Fig. 1. The conductivity decreases on cooling, as has been previously reported.[1,3,4]

We measured the absorbance or the reflectance (depending on frequency and doping level) at temperatures between 80 and 300 K and at frequencies between 80 and 24 000 cm^{-1} (0.01–3 eV). To correct for scattering from rough surfaces, the reflectance of Al-coated samples was used for normalization. Kramers-Kronig analysis of the reflectance gave the optical constants.

3. Results

Fig. 2 shows the absorption of heavily-doped "new"-$(CH)_x$ for two polarizations. A strong peak at 790 cm^{-1}, mostly polarized along the chain, is introduced by the doping. The usual doping-induced vibrational modes at 900 (quite broad) 1290, and 1380 cm^{-1} can also be seen.[6,7,8] The intensity of these modes increases linearly upon doping up to 6 %.

A strong broad band is seen around 500 cm^{-1}, increasing in intensity with decreasing temperature. Tanaka *et al.*[9] have observed similar behavior in I_3-doped Shirakawa $(CH)_x$. The

band is present only in doped samples. The polarization dependence implies that this band is characteristic of the polymer chain. We speculate that it is a pinning mode, due to trapping of charge carriers by Coulomb interaction with the dopant ions and by barriers along the chains. The increase in infrared oscillator strength with decreasing temperature is accompanied by a decrease in the dc conductivity.

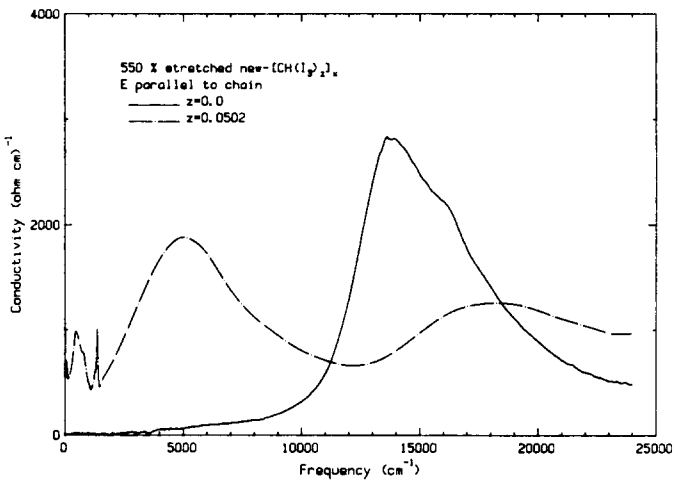

Fig. 3. $\sigma_1(\omega)$ ($\vec{E}$ || to the stretching direction) for undoped and doped "new"-$(CH)_x$.

Fig. 3 shows the chain-axis $\sigma_1(\omega)$ over 80–24 000 cm^{-1} for an undoped and a 6% doped sample. Above the doping-induced modes there is a "midgap" band at 5000 cm^{-1} (0.6 eV, somewhat smaller than half the 1.4–1.8 eV gap). A midgap absorption[10] is a universal feature of doped-$(CH)_x$, even at the highest doping levels.[8,11] This midgap band decreases the oscillator strength of the interband transitions of the undoped polymer (in some cases to zero[8]) and shifts it to higher energies.

Fig. 4 shows the low-frequency part of the conductivity for 6% doping. Data are shown at 300 K for two polarizations. The anisotropy ($E \parallel / E \perp$) at 1380 cm^{-1} is ≈ 26.

The most interesting feature in Fig. 4 is the upturn in $\sigma_1(\omega)$ at low frequencies. This is interpreted as a Drude-like peak in $\sigma_1(\omega)$, associated with the free carriers. (We note that at these low frequencies, the reflectance is large, > 95% and the error in absolute reflectance—or rather in $1-\mathcal{R}$ which is the "signal" in this case—is relatively large, so that the accuracy of the Kramers-Kronig results in this region is no better than ±25%.) The width of the free-carrier peak is very narrow, perhaps ~ 100 cm^{-1}. At $\omega = 0$, the conductivity is 7000 $\Omega^{-1}cm^{-1}$, a bit smaller than the measured room temperature conductivity of this sample, which was 10 000 $\Omega^{-1}cm^{-1}$. (See Fig. 1.) This free-carrier peak is not seen in ordinary $(CH)_x$ because the dc conductivity is so much smaller. With decreasing temperature, the dc conductivity of "new"-$(CH)_x$ decreases, and the oscillator strength of the free carrier absorption is transferred into the pinning mode, as shown in Fig. 2.

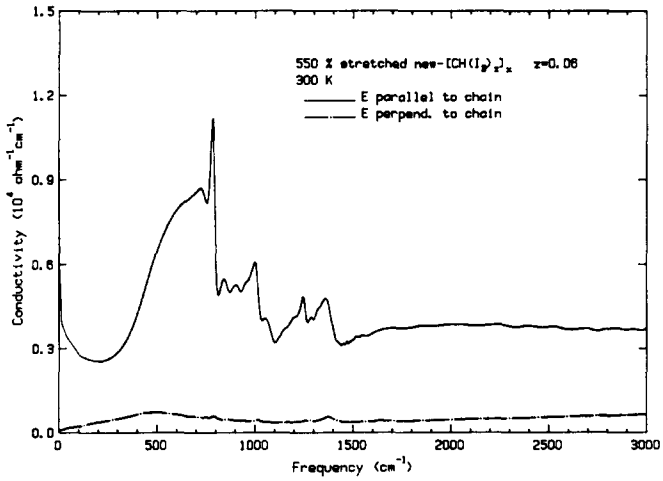

Fig. 4. $\sigma_1(\omega)$ for $\vec{E}$ || and $\vec{E}$ ⊥ to the stretching direction for 6% I_3-doped "new"-$(CH)_x$.

4. Discussion

Despite the significant differences in dc conductivity, the infrared absorption of "new"-$(CH)_x$ resembles closely that of ordinary $(CH)_x$. There is only a small amount of temperature dependence. The exception is in the far infrared, where at 300 K there is a narrow, Drude-like peak in $\sigma_1(\omega)$. With decreasing temperature, the oscillator strength associated with this peak moves into the pinning mode at 500 cm^{-1}.

Acknowledgements

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References

1. H. Naarmann and N. Theophilou, *Synth. Met.* **22**, 1 (1987).
2. K. Soga, S. Kawakami, and H, Shirakawa, *Macromol. Chem. Phys.* **71**, 4614 (1979).
3. N. Theophilou *et al.*, *Synth. Met.* **28**, D35 (1989).
4. N. Basescu *et al.*, *Synth. Met.* **28**, D43 (1989).
5. A.G. MacDiarmid and A.J. Epstein in *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics,* edited by J.L. Brédas and R.R. Chance (Kluwer Academic Publisher, Amsterdam, 1990), p. 53.
6. C.R. Fincher, Jr. *et al.*, *Phys. Rev. B* **19**, 4140 (1979).
7. A.J. Epstein *et al.*, *Phys. Rev. Lett.* **50**, 1866 (1983).
8. X.Q. Yang *et al.*, *Solid State Comm.* **61**, 335 (1987).
9. J. Tanaka *et al.*, *J. de Physique* **44**, C3-279, (1983).
10. H. Suzuki *et al.*, *Phys. Rev. Lett.* **45**, 1209 (1980).
11. D.B. Tanner *et al.*, *Synth. Met.* **28**, D141–D146 (1989).