

Conversion of *cis*-polyacetylene to *trans*-polyacetylene during doping

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An experimental study of the infrared properties of iodine-doped and ammonia-compensated polyacetylene has been carried out. Doping of *trans*-polyacetylene leads to strong absorption lines at 870 and 1390 cm^{-1} along with a broad "midgap" absorption at higher frequencies. Compensation reduces all of these features in equal proportion. The doping-related absorption in *cis*-polyacetylene as well as the effects of compensation are essentially identical to that in the *trans* form. This result shows that the doping in *cis* samples occurs in *trans* regions present in the sample or created in it by the doping process.

The discovery¹ that the electrical conductivity of polyacetylene $(\text{CH})_x$ increases by a factor of 10^{11} when the polymer is doped with donor or acceptor molecules has led to considerable interest in this substance over the past five years.² In the beginning, similar results were obtained by doping either the *cis*- $(\text{CH})_x$ form or the *trans*- $(\text{CH})_x$ form; in fact, even though *trans*- $(\text{CH})_x$ is more stable thermodynamically,³ *cis*- $(\text{CH})_x$ yields a somewhat higher conductivity at maximum doping levels.¹

The doping mechanism and the nature of the insulator-metal transition have been the subject of controversy. Optical and magnetic measurements⁴⁻⁹ of doped *trans*- $(\text{CH})_x$ have been interpreted within a soliton model.^{10,11} In this model, doping causes the formation of charged solitons on the polymer chain. Alternatively, magnetic and electric field dependent transport studies¹²⁻¹⁴ have been interpreted within a metallic-islands model. According to this model, a heavily doped metallic phase exists as islands or particles within the undoped polymer; the insulator-metal transition is a percolation transition that occurs when these metallic particles become interconnected. Other measurements^{5-7,15} have provided evidence for a nonuniform dopant distribution, although a percolation threshold has not been invoked in these cases. Many experiments¹⁶⁻¹⁹ suggest that heavily doped *cis*- $(\text{CH})_x$ has been converted to the *trans* form. In fact, iodine-doped *cis*- $(\text{CH})_x$ and *trans*- $(\text{CH})_x$ have nearly identical x-ray diffraction patterns.¹⁹

This paper describes measurements of the doping-induced infrared absorption in *cis*- $(\text{CH})_x$ and *trans*- $(\text{CH})_x$. We find that this absorption is essentially identical for the two isomers, although the infrared spectra of the undoped materials are quite different. This result reveals that the doping of *cis*- $(\text{CH})_x$ sam-

ples occurs in *trans* regions present in the sample or created by the doping process.

Polyacetylene films were prepared by the Shirakawa technique.³ The as-grown *cis*-polyacetylene films were stored at low temperatures ($\sim 80^\circ\text{C}$) until optical measurements were made. *Trans*-polyacetylene was prepared by heating the film in vacuum at 190°C for 2 h. All samples were doped *in situ* in the infrared spectrometer to progressively higher doping levels by exposure to iodine vapor at pressures below 1 Torr. It typically took an hour to increase the doping level y in $[\text{CH}(\text{I}_3)_y]_x$ by a step of 0.003. The total time for a doping run was ~ 20 h with maximum y values being ≈ 0.02 ; our doping was a "slow doping" procedure.⁷ The dc resistance of the sample was monitored during the doping process; iodine levels were estimated from the conductivity of the sample.²⁰ For one sample the weight uptake was also measured yielding a doping level that agreed with the estimate from conductivity to within 10%, confirming the reliability of the latter technique. Several samples were compensated by adding ammonia gas to the cell. The ammonia concentration was estimated from the conductivity by assuming that each ammonia molecule compensated one $(\text{I}_3)^-$ unit. Compositions are represented by $[\text{CH}(\text{I}_3)_y(\text{NH}_3)_z]_x$.

A Michelson interferometer²¹ was used to measure the transmission of the samples for 20 to 700 cm^{-1} (0.0025–0.09 eV) while a grating monochromator²² was used for 700 – $15\,000\text{ cm}^{-1}$ (0.09–2 eV). The absorption coefficient α of the samples was calculated from these transmission measurements using

$$\alpha = -\left(\frac{1}{d}\right) \ln(T) + \left(\frac{2}{d}\right) \ln(1-R) \quad (1)$$

where d is the thickness of the film, T is the transmittance, and R is the reflectance. The latter quantity was estimated from the far-infrared refractive index.

Figure 1 shows the absorption coefficient of undoped *trans*-polyacetylene as the solid line. Our relatively thick sample ($\sim 50 \mu\text{m}$) was not transparent above 4000 cm^{-1} . The absorption coefficient of this sample doped with iodine to $y = 0.008$ is shown as the dashed line, while the absorption coefficient of the doped sample compensated with ammonia to $z = 0.0064$ is shown as the dotted line. After doping with iodine, two strong absorption lines appear in the spectrum: at 870 cm^{-1} (0.11 eV) and 1390 cm^{-1} (0.17 eV). In addition, the absorption edge which begins around 3000 cm^{-1} in the undoped material shifts to around 1500 cm^{-1} . The doping-induced features at 870 and 1390 cm^{-1} have been observed⁴ in doped $(\text{CH})_x$ and have been associated^{8,23} with internal vibrational modes of a charged soliton in *trans*- $(\text{CH})_x$. The increased absorption at higher frequencies (of which we see only the edge) is also observed in the doped *trans*- $(\text{CH})_x$ and is interpreted as resulting from a midgap soliton state.⁶ Compensation with ammonia reduces in equal proportion the strength of all three of the doping-induced absorption features.

Figure 2 shows the absorption spectra of undoped, iodine-doped ($y = 0.009$), and ammonia-compensated ($z = 0.007$) *cis*-polyacetylene. Although the thickness of this sample was also $\sim 50 \mu\text{m}$, the undoped sam-

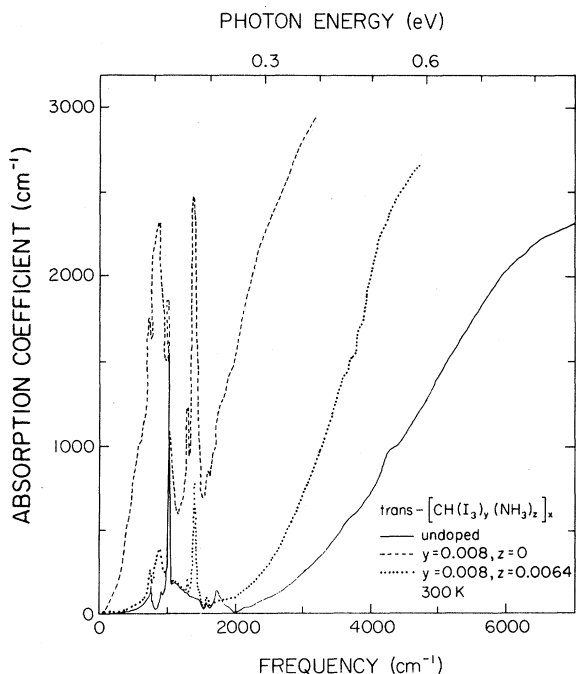


FIG. 1. Absorption coefficient for *trans*-polyacetylene.

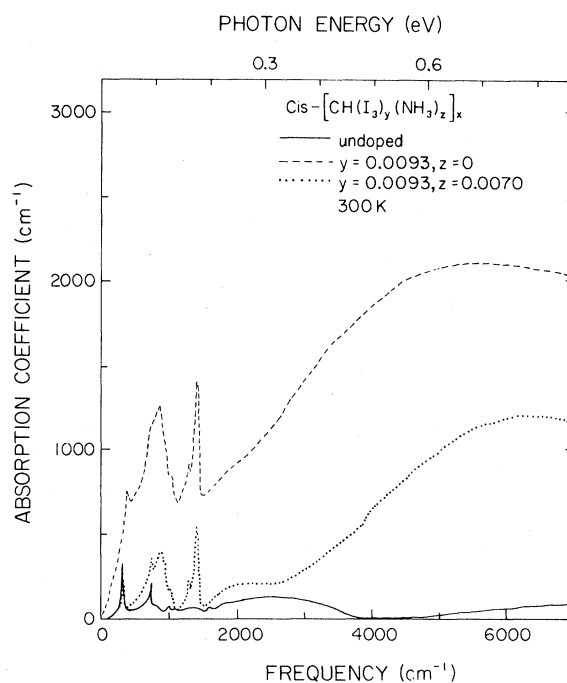


FIG. 2. Absorption coefficient for *cis*-polyacetylene.

ple (shown as the solid line) was transparent to almost 15000 cm^{-1} . The increased transmission at higher frequencies in *cis*-polyacetylene results from a gap which is wider (1.9 as opposed to 1.5 eV) and sharper than the gap of the *trans* material.²⁴ When *cis*-polyacetylene is iodine doped (shown as the dashed line in Fig. 2), three strong features appear in the absorption coefficient: narrow lines at 850 and 1390 cm^{-1} and a broader, more intense peak at 6000 cm^{-1} (0.75 eV). Compensation (dotted line) reduces the strength of all three absorptions in equal proportion.

The doping-induced vibrational features seen in the *cis*-polyacetylene occur at the same frequencies as in *trans*-polyacetylene. The integrated absorption strength, normalized by the effective dopant concentration $y - z$, is also the same to within 8% for the two materials for all of the samples that we have studied. In addition, the "midgap" absorption in the *cis*-polyacetylene is at half the *trans*-polyacetylene band gap; midgap for *cis* would be at 8000 cm^{-1} . These infrared data demonstrate that the dopant is being taken up by *trans* regions in the *cis*-polyacetylene. No distinct signature of doped *cis* material is observed. These *trans* regions either exist already in the polyacetylene before doping or are a result of isomerization induced by the doping process.

The dopant level estimated for the *cis*-polyacetylene is an average for the entire sample; the *trans* portions of these samples must be doped to substantially higher levels than this average. The fraction of the sample doped can be estimated by examining the

cis-to-*trans* ratio for compensated samples. For example, a $\sim 90\%$ *cis*-polyacetylene sample doped to a nominal $y = 0.0093$ and subsequently compensated with ammonia was determined to be $\sim 30\%$ *trans*. The dopant concentration in the *trans* regions is then $y \sim 0.03$. The distribution of the doped *trans* regions with the host *cis*-polyacetylene is then a central issue.

If we assume that doped *cis*-(CH)_x is an inhomogeneous medium then we can model it by a two-component system with effective properties determined by the properties of the constituents, their concentrations, and their geometries. The absorption coefficient between 800 and 2000 cm⁻¹ for *cis*-polyacetylene doped to $y = 0.008$ is shown in Fig. 3 along with the results of an effective medium calculation for a two-component composite system. One component (representing the undoped *cis*-polyacetylene) was modeled with a real, constant dielectric function $\epsilon_c = 2.5$. The second component (the doped *trans*) was modeled with a narrow Lorentzian line combined with a very dirty (short relaxation time) metal, having dielectric function

$$\epsilon_t(\omega) = \epsilon_\infty - 4\pi\sigma_0\tau + i\frac{4\pi\sigma_0}{\omega} + \frac{\omega_L^2}{\omega_0^2 - \omega^2 - i\omega\Gamma} \quad (2)$$

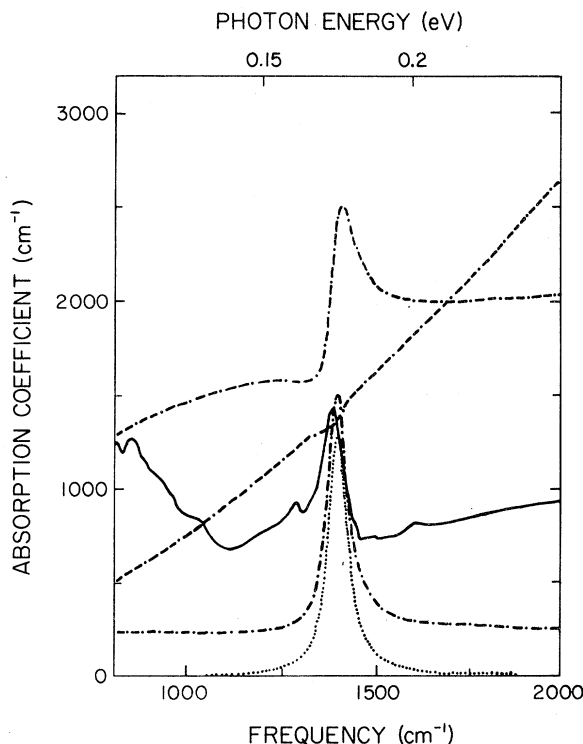


FIG. 3. Measured absorption coefficient of *cis*-polyacetylene doped to $y = 0.0093$ (solid line) with absorption coefficient calculated using Eq. (3) with $\sigma_0 = (\dots)$, $\sigma_0 = 10 \Omega^{-1} \text{cm}^{-1}$ (-.-.-), $\sigma_0 = 100 \Omega^{-1} \text{cm}^{-1}$ (- - -), and $\sigma_0 = 1000 \Omega^{-1} \text{cm}^{-1}$ (- - - -).

The first three terms in the right-hand side of Eq. (2) describe the metal; $\epsilon_\infty = 2.5$ is the core dielectric constant, σ_0 is the dc conductivity of the metal, and τ is the electronic relaxation time. In the fourth term, representing a narrow line, we have used $\omega_0 = 1390 \text{cm}^{-1}$ as the resonant frequency, $\Gamma = 60 \text{cm}^{-1}$ as the phenomenological linewidth, and $\omega_L = 450 \text{cm}^{-1}$ as the strength.

The effective dielectric function of the composite^{25,26} ϵ_{eff} is given by the solution to

$$0 = f \frac{\epsilon_t - \epsilon_{\text{eff}}}{g\epsilon_t + (1-g)\epsilon_{\text{eff}}} + (1-f) \frac{\epsilon_c - \epsilon_{\text{eff}}}{g\epsilon_c + (1-g)\epsilon_{\text{eff}}}, \quad (3)$$

where f is the volume fraction of doped *trans*-polyacetylene in the composite, $(1-f)$ is the volume fraction of *cis*, and g is the depolarization factor ($g = \frac{1}{3}$ for a sphere). Figure 3 shows the predictions of this model between 800 and 2000 cm⁻¹ when $f = 0.1$ and $g = \frac{1}{3}$ for four values of the dc conductivity of the metal. Use of $\sigma_0 \leq 1 \Omega^{-1} \text{cm}^{-1}$ produced results very similar to those for $\sigma = 0$. As the conductivity of the *trans*-(CH)_x increases, a broad background absorption builds up. The narrow line becomes distorted and eventually disappears, swamped by the metallic dielectric function. The comparison of the experimental data with the model shown in Fig. 3 suggests that the iodine-doped *trans* regions have a $10 < \sigma_{\text{dc}} < 100 \Omega^{-1} \text{cm}^{-1}$. The entire film with $y = 0.009$ had $\sigma_{\text{dc}} = 0.1 \Omega^{-1} \text{cm}^{-1}$.

The depolarization factor g appearing in Eq. (3) is determined by the shape of the inclusions; in addition, within the effective medium approximation the percolation transition occurs at a volume fraction $f = g$. We did the calculation for $g = \frac{1}{3}$ (spheres), where $f < g$, and also for $g = 0.001$ (very long needles), where $f \gg g$. In this second case the sample is well above the percolation point, leading to a multiply connected network of long metallic segments. For the parameters that we have used both cases predict essentially the same absorption, because the conductivity of the metallic inclusions is relatively low ($\sigma < 100 \Omega^{-1} \text{cm}^{-1}$). Therefore, although we are able to set an upper limit on the value of the conductivity, we are unable to distinguish between these two geometries.

In summary, we have shown that the doping-induced infrared spectra of *cis*-polyacetylene are characteristic *trans*-polyacetylene. This result suggests that the dopant is preferentially taken up by *trans* regions existing in the *cis* material or created by the doping process. At intermediate doping levels, there is a nonuniform distribution of dopant in the polymer.

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