

OPTICAL PROPERTIES OF SEGMENTED POLYACETYLENE

X.Q. YANG and D.B. TANNER

Department of Physics, University of Florida, Gainesville, FL 32611 (U.S.A.)

G. ARBUCKLE and A.G. MACDIARMID

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104 (U.S.A.)

A.J. EPSTEIN

Department of Physics, Ohio State University, Columbus, OH 43210 (U.S.A.)

ABSTRACT

Infrared and optical studies have been made on a segmented polyacetylene in which up to 17% of the CH units have been replaced by (sp^3 -hybridized) CHD units. The valence-to-conduction band transition in the segmented polymer is shifted to slightly higher frequency and reduced by half in intensity. Treatment with iodine produced strong doping-induced infrared absorption at 900, 1290 1400 cm^{-1} and midgap. The maximum dopant concentration achieved appeared to be smaller than in ordinary $(CH)_x$.

INTRODUCTION

This paper describes the optical and infrared absorption by a "segmented" polyacetylene. Segmented polyacetylene is made by forming sp^3 -hybridized carbon sites on a polyacetylene chain in a controlled manner, so that chains initially having average conjugation lengths of order 500-1000 C-H units can be chopped into shorter segments. Various average conjugation lengths can be obtained by controlling the concentration of sp^3 sites. Assuming that (1) the sp^3 sites are homogeneously distributed and (2) that a sp^3 site is a severe interruption to conjugation, this segmentation should have a drastic effect on extended defects, such as solitons, when the average conjugation length becomes shorter than the coherence length of the defect. Our data show that the infrared signatures of solitons persist at sp^3 concentrations up to 17%, suggesting that one or both of these assumptions is incorrect.

EXPERIMENTAL DETAILS

The method of preparation of segmented samples has previously been described [1,2]. Briefly, Shirakawa polyacetylene was first n-doped with sodium, using a sodium naphthalide solution. Then, after washing and drying, the sodium-doped sample was compensated by deuterated alcohol. This two-step method introduces in its second step an extra deuterium atom, bonded to a carbon of the polyacetylene as an sp^3 CHD site, for each sodium ion present after the first step. The deuterium concentration, y , in $(CHD_y)_x$ can be determined by titration of the alcohol solution after compensation.

We were able to dope the samples with iodine to concentrations $z=0.033$ in $[CHD_y(I_3)_z]_x$. The doping was done in situ in the infrared spectrometer. The concentration was determined by measurement of the resistance of the sample during both the doping process and the subsequent optical measurements. The conductivity versus dopant concentration scale was calibrated by weight uptake measurements. The 3.3% maximum concentration is only about half the maximum doping level achievable in ordinary polyacetylene.

Upon doping the conductivity increased by six orders of magnitude, much as in ordinary iodine-doped trans-polyacetylene. The principal difference is that the magnitude of the conductivity (measured with current perpendicular to the thin dimension of the film) was at all dopant concentrations a factor of 3000-5000 times smaller than in the ordinary case.

The 100 μ sample thickness limited transmission measurements to frequencies below $4000\text{ cm}^{-1}/0.5\text{ eV}$, on account of the much increased absorption coefficient as the semiconducting gap is approached. The high-frequency limit decreased upon doping; the most highly-doped samples were opaque almost everywhere. We did reflection measurements for the high frequencies and the doped samples. Kramers-Kronig analysis gave the optical properties of these samples.

RESULTS

Undoped samples

Fig. 1 shows the absorption coefficient (from the Kramers-Kronig analysis) of $(CHD_y)_x$ at zero, low (2%) and high (17%) deuterium concentrations. The effect of the deuteration is threefold: (1) The peak of absorption coefficient shifts a small amount to higher energies. (2) There is a substantial broadening of the absorption to the high frequency side. (3) The overall intensity or oscillator strength of the absorption is reduced by about a factor of 2.

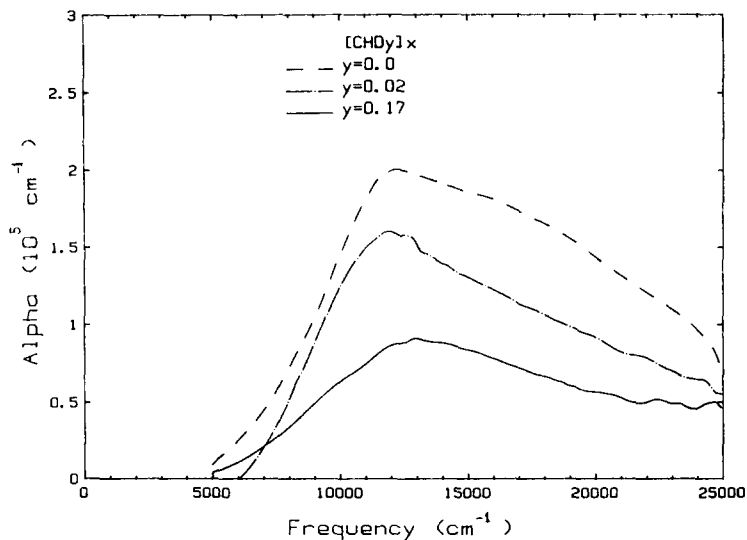


Fig. 1. The absorption coefficient of segmented polyacetylene at two deuterium concentrations. The absorption coefficient of ordinary polyacetylene is also shown.

Doping-induced absorption

Fig. 2 shows the absorption coefficient (from transmission measurements) of highly segmented polyacetylene, $(\text{CHD}_{0.16})_x$ at four levels of iodine doping. With doping, new absorption features [3] appear at 900, 1290, and 1400 cm^{-1} . The low frequency edge of a broad "midgap" absorption [4] is seen also in Fig. 2.

This feature is more clearly seen in Fig. 3, where the absorption coefficient (from Kramers-Kronig) is plotted for three iodine concentrations over 800-22000 cm^{-1} (0.1-2.8 eV).

DISCUSSION

Conjugation length

The shift to higher energies of the peak in the absorption coefficient of the segmented samples (Fig. 1) is consistent with a reduction of the conjugation length, L . However, the peak position indicates that the assumption of $L=1/y$ is not correct. (Here, L is in units of the carbon-carbon spacing.) Our results are shown in Table 1, where we list y , $1/y$, the estimated energy gap, E_g from the peak shift, and the conjugation length inferred from this gap, $L(E_g)$. In making this last estimate, we have used the estimates of gap versus conjugation length of Brédas *et al.* [5] who find that (approximately) $E_g = (1.4 + 7.5/L)$ eV.

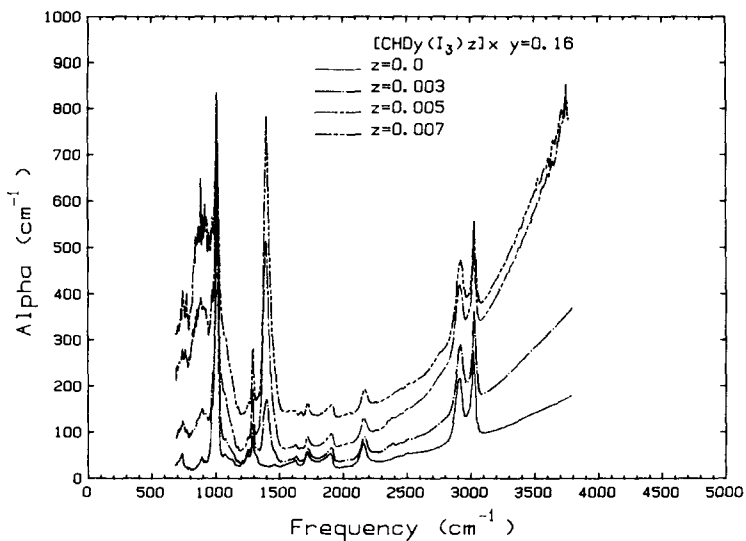


Fig. 2. The infrared absorption coefficient of $(\text{CHD}_{0.16})_x$ at four levels of iodine doping.

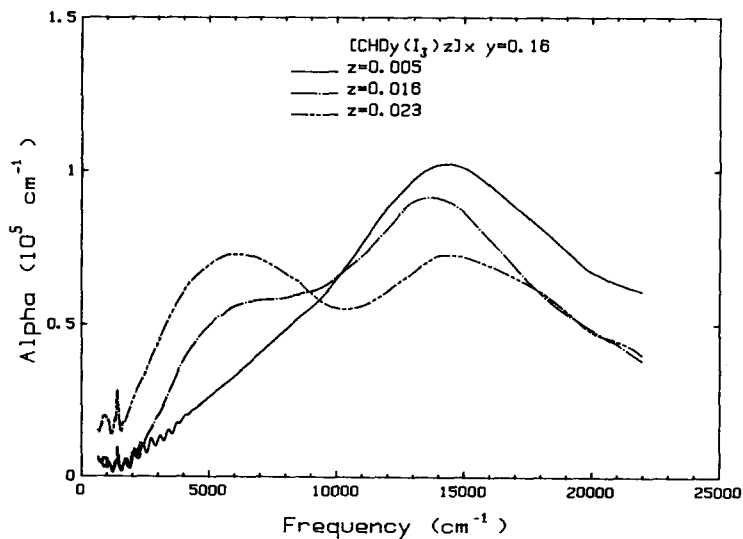


Fig. 3. Absorption coefficient in near infrared and visible of $(\text{CHD}_{0.16})_x$ at three levels of iodine doping.

The energy gap indicates a substantially longer conjugation length than inferred from the deuterium concentration. This discrepancy would occur if there were a bimodal distribution of conjugation lengths, with some fraction of the chains remaining substantially longer than the average while the rest

TABLE 1

Energy gap and conjugation length in $(\text{CHD}_y)_x$

y	1/y	E_g (eV)	$L(E_g)$
0.0	∞	1.4	∞
0.02	50	1.5	75
0.11	9	1.7	25
0.16	6.2	1.7	25
0.17	5.9	1.8	19

are much shorter. The reduction in the oscillator strength and the broadening of the gap absorption would be consistent with this picture, because the absorption by the short portion of the distribution would occur at frequencies higher than we are able to measure.

General features of doped polyacetylene are the strong 900, 1290 and 1400 cm^{-1} vibrational features [3] and the broad midgap [4] absorption at 6000 $\text{cm}^{-1}/0.7$ eV. These features have been associated with charged solitons [4,6,7]. All are seen in the doping-induced spectra of segmented polyacetylene.

The intensity of the vibrational modes grows with increasing dopant concentration but is substantially smaller than in ordinary polyacetylene [8]. Fig. 4 shows this difference. The integrated oscillator strength of the 1400 cm^{-1} mode are shown for the two materials. Lines are guides to the eye. The oscillator strength per dopant molecule in the segmented polyacetylene is reduced by about a factor of 5. This is much larger than the factor-of-2 reduction in the interband absorption coefficient.

The reduction may be viewed as either a reduction in the population of charged solitons per dopant molecule or as an increase in the effective mass of the solitons because they are confined by the sp^3 defect sites.

CONCLUSIONS

There are two possibilities for the interpretation of these data within the context of solitons in polyacetylene. First, if a bimodal chain-length distribution is assumed, then the long-chain segments would have no difficulty in containing a soliton. The second possibility is that the sp^3 defects are randomly distributed but that they are not severe interruptions of the conjugation [9]. The change of interband and doping-induced oscillator strength could be interpreted as caused by of narrowing of the conduction and valence bands, thereby increasing the effective mass, when the sp^3 defects reduce the effective overlap of the pi electrons.

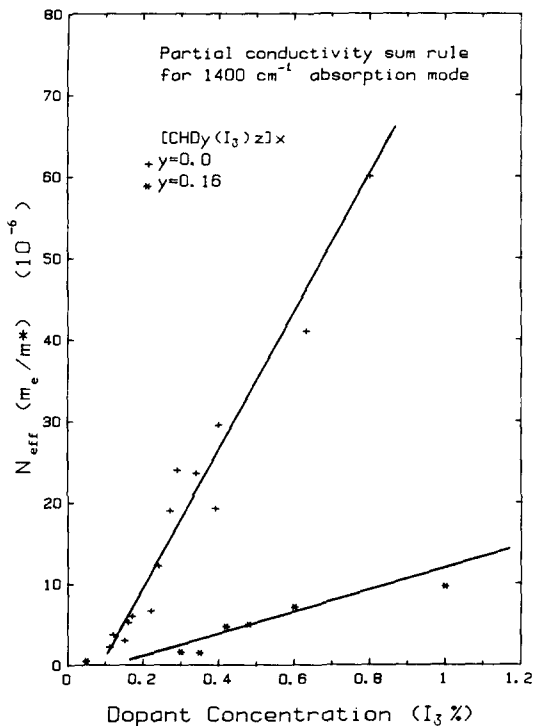


Fig. 4. Integrated oscillator strength of the 1400 cm^{-1} doping-induced oscillator strength in ordinary (+) and segmented (*) polyacetylene.

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