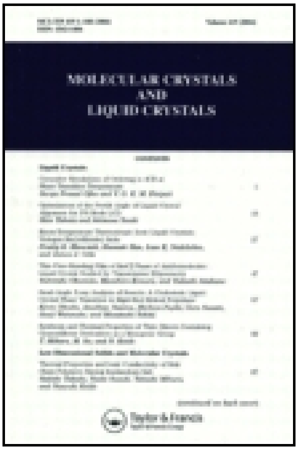

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Optical Spectra and Neutral Soliton in Segmented Polyacetylene

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Version of record first published: 04 Oct 2006.

To cite this article: H. S. Woo , D. B. Tanner , G. Arbuckle & A. G. Macdiarmid (1996): Optical Spectra and Neutral Soliton in Segmented Polyacetylene, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 280:1, 163-168

To link to this article: http://dx.doi.org/10.1080/10587259608040326

Mol. Cryst. Liq. Cryst., 1996, Vol. 280, pp. 163–168
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OPTICAL SPECTRA AND NEUTRAL SOLITON IN SEGMENTED POLYACETYLENE

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We have measured the doping induced optical absorption in segmented polyacetylene, $[CDH_y]_x$, in which either 15% or approximately 27% sp^3-bonded CDH units. These sp^3 defects, which can be called "conjugation-interrupting" defects have an average spacing considerably less than the length of a soliton. In order to introduce the charged soliton excitation, all samples were doped with iodine by in-situ vapor doping technique with various dopant levels. For a sample with 27% sp^3 hybridization, we have found a new broad band around 1.12 eV with relatively lower intensity for lower sp^3. We assigned this band as an absorption due to the neutral solitons. The optical properties of deuterated polyacetylene with sp^3 defects including the comparison with ordinary polyacetylene, $(CH)_x$, will be discussed.

INTRODUCTION

Soliton in polyacetylene can have neutral or charged states with spin-charge reversal relation.[1] Recently, in order to investigate the effects on transport and optical properties in *trans*-polyacetylene from specific defects, a controlled number of sp^3 defect, which can be called "conjugation-interrupting" defects, have been introduced onto the polyacetylene chain.[2] This segmentation in polymer chain leads to shorter conjugation length and high order of crosslinks, thus, reducing the electrical conductivity.

In this report, we prepared the partially deuterated polyacetylene, $[CDH_y]_x$, and presents the role of sp^3 defects on electrical conductivity and optical spectra, doping induced infrared active vibrational(IRAV) modes, and, optical evidence of neutral soliton in highly sp^3 defected polyacetylene.

EXPERIMENTAL

The introduction of sp^3 defects[2] was followed after synthesizing the deuterated polyacetylene, $(CD)_x$, by usual Shirakawa method.[3] For 15 % sp^3 defects in $(CD)_x$, the reactions invoved are

$$(CD)_x + xyNa^+Naphth^- \text{------->} [Na^+_{0.16}(CD)^-_{0.15}]_x + xyNaphth$$
$$[Na^+_{0.15}(CD)^-_{0.15}]_x + xyCH_3OH \text{---->} (CDH_{0.15})_x + xyCH_3ONa.$$

In order to introduce a larger amount of defects, the composition of rehydrogenerated $(CDH_{0.15})_x$ film as determined by titration of the CH_3OH/CH_3ONa washing solution leads to give $(CDH_y)_x$ with y=0.27, about 27 % sp^3 defects in $(CD)_x$.

The change in dc conductivity and optical properties of $(CDH_y)_x$ films were measured after the iodine vapor doping to the films by *in-situ*, where the iodine concentration was determined by weight uptake. For the IR spectra in the range of 25 - 5000 cm^{-1}, the Bruker IR/98 FTIR was used with liquid He cooled Bolometer(IR lab. NN-6/C) as a detector and polyethylene and KCl as windows respectively. The Perkin-Elmer type monochromator was used to measure the optical spectra ranging from mid-IR to visible region.

RESULTS AND DISCUSSION

The doping induced IRAV modes in $(CDH_y)_x$ at 745 and 1140 cm^{-1} with various dopant levels were shown in Figures 1 and 2 for y=0.0 and 0.27 respectively.

These modes correspond to those in $(CH)_x$ at 900 and 1380 cm^{-1}, C=C and C-C vibrations repectively.[4] Figure 1(y=0.0) shows, however, a strong enhancement of oscillator strength for these modes, beginning at dopant levels as low as about 0.4 %. In contrast, as shown in Figure 2, the sample with higher sp^3 defects required higher dopant levels for the same amounts of enhancement. This difference simply indicates that the absorption is samller for sample with higher sp^3 defects at same dopant level due to the loss of π-electrons by introducing these defects.

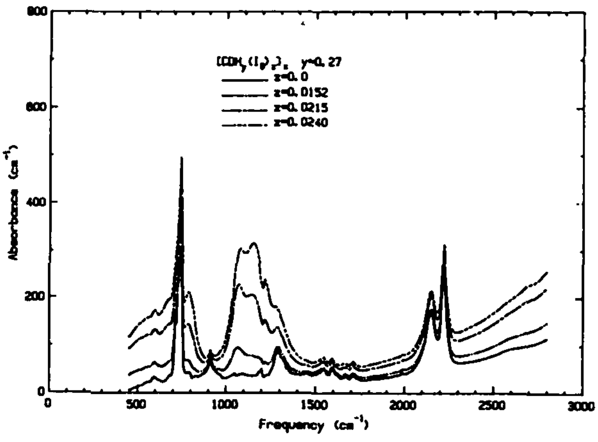

Figure 1. IR absorbance for $[CDH_y(I_3)_z]_x$ with y=0.27 and various doping levels.

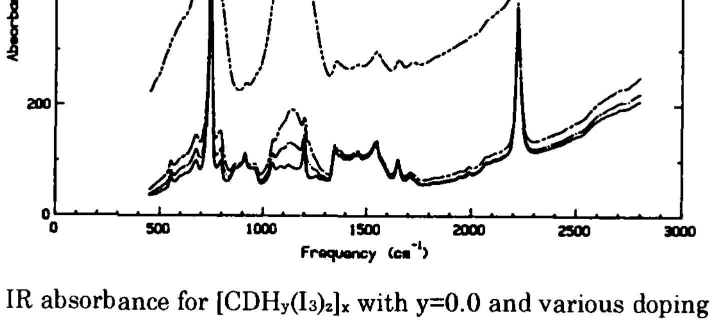

Figure 2. IR absorbance for $[CDH_y(I_3)_z]_x$ with y=0.0 and various doping levels.

	σ_{dc}(/ Ω cm)	Dopant levels: z (%)
(y=0)	1.6 x 10^{-6}	0.0
	3.9 x 10^{-6}	0.0034
	3.9 x 10^{-4}	0.0096
	4.9 x 10^{-1}	0.0187
(y=0.27)	1.2 x 10^{-7}	0.0
	7.2 x 10^{-6}	0.0169

Table 1. dc conductivity of $[CDH_y(I_3)_z]_x$

Table 1 shows, as expected, that dc conductivity is decreased by increasing the sp^3 defects. This can be viewed as, (i) the population of π-electrons is reduced by introducing the sp^3 defects, (ii) the effective charge carrier masses are increased as increasing the number of sp^3 defects, which results reducing the mobility of charge carriers, and (iii) the sp^3 defects might act as the scattering center of charge carriers.

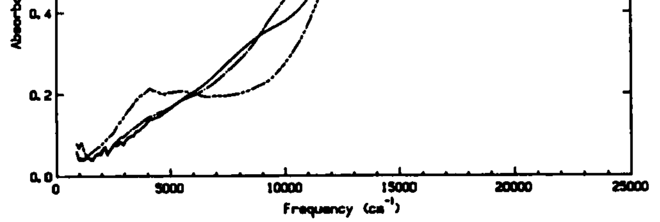

Figure 3. Absorbance in mid-IR and visible region for $[CDH_y(I_3)_z]_x$ with y=0.0 and various doping levels

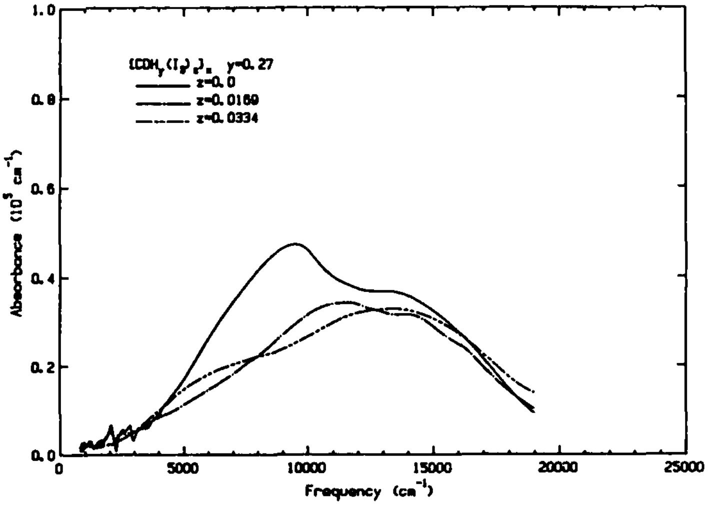

Figure 4. Absorbance in mid-IR and visible region for $[CDH_y(I_3)_z]_x$ with y=0.27 and various doping levels

Figures 3 and 4 show the usual mid gap band absorption at around 5000 cm^{-1} (upon doping $\geq$ z=2%) due to charged solitons. In Figure 4 (27 % sp^3 defected undoped sample), a broad band near 9000 cm^{-1} (1.12 eV) is shown, which is not clearly shown in sample without sp^3 defect (Figure 3). We assigned this new broad band as an absorption due to neutral soliton for following reasons:

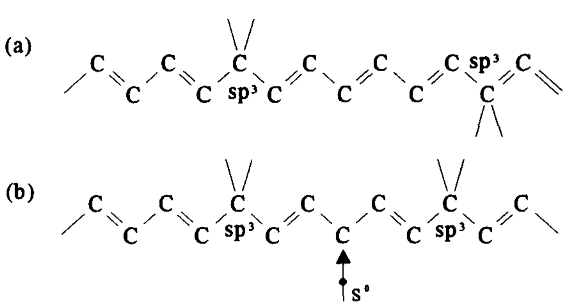

Figure 5. Schematic diagram of a *trans*-polyacetylene chain with two sp^3 defects by (a) an even number of sites 6; (b) an odd number of sites 5.

(i) Neutral solitons in undoped samples can be easily ionized upon doping to form charged solitons. Figure 4 shows that the band at 9000 cm^{-1} disappeared with about 2% doping. In fact, with more than 2% doping, the mid gap charged soliton band (5000 cm^{-1}) starts to grow.

(ii) The charged soliton occupies an mid-gap state. For the neutral soliton, however, the repulsive electron-electron interaction will push this mid-gap state up towards the conduction band. Our measurement does find a peak at 1.12 eV, near the inter-band edge 1.45 eV, in agreement with this prediction.

(iii) There must be at least one neutral soliton between two sp^3 defects separated from the first by an odd number of carbon atoms because the phase of the bond alternation pattern in segmented polyene.[5] Figure 5 shows an example, with two sp^3 defects separated by 5 and 6 carbon atoms. Thus, the introduction of sp^3 defects in the conjugated chain might give more chances to have neutral solitons.

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