

¹³C NMR STUDIES OF IODINE DOPED POLYACETYLENE

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Résumé. - Nous décrivons des expériences de RMN sur le ¹³C, utilisant la polarisation croisée et la rotation à l'angle magique, sur des échantillons de cis et trans (CH)_x en fonction du taux de dopage avec l'iode. Deux signaux nouveaux apparaissent au cours du dopage sont attribués à la formation de solitons chargés sans spins et à l'addition chimique d'iode sur les doubles liaisons. L'isomérisation cis-trans n'apparaît pas même pour des taux de dopants élevés.

Abstract. - Natural abundance ¹³C NMR experiments using cross-polarization and magic angle spinning are reported for cis- and trans-polyacetylene as a function of iodine doping level. Two new signals appearing on doping are attributed to the formation of spinless charged solitons and the chemical addition of iodine to double bonds. The substantial cis/trans isomerization does not occur even at high iodine doping levels.

High resolution ¹³C NMR spectra of the polyacetylene (CH)_x were studied for the first time in [1]. Then the method was used to study the thermal cis/trans isomerization [2,3]. For high-conductive AsF₅ doped polyacetylene the appearance of Knight shift for doping levels higher than 7 mol % was reported [4]. However, the reexamination of the results showed that the shift is primarily a chemical shift appearing from the polymer oxidation on doping [5].

Experiment. The cis-(CH)_x film was synthesized at -78°C using the Sira-kawa technique [6]. The product was carefully washed in toluene, THF and methanol and dried in vacuum. The trans-polyacetylene was achieved by heating the cis-isomer at 130°C during two hours in vacuum. Doping with iodine was carried out at ambient temperature by exposure the polyacetylene samples to iodine vapor carried by argon gas flow. The exposition times up to 30 hours were used to obtain heavily doped samples. The doping was followed by the vacuum pumping of the sample during two hours in order to remove any residual iodine absorbed on the surface. The iodine content was subsequently determined by weight uptake. The powdered sample was packed into the cylindrical NMR rotor and closed airtight with a plastic cap. The 9 mm O.D. rotor has about 0.5 cc for the sample and is mad from glass ceramics to avoid any background carbon signal. All manipulations with the polymer have been done in an inert atmosphere dry box. The NMR spectra were recorded at room temperature on a Bruker CXP-200 spectrometer (50.3 MHz for ¹³C) using proton decoupling, cross polarization and magic angle spinning of the sample. Shifts are given with respect to the external TMS.

¹³C NMR spectra of (CH_{1y})_x. Dependence of spectra on iodine content is given in Fig. 1 and 2 for cis- and trans-isomer, respectively. The starting spectra (y = 0, bottom curves) show a single narrow line of the principal isomer together with the weaker one representing the presence of the small amount of the other isomer. The chemical shifts were found to be 127 and 136 ppm for cis- and trans-(CH)_x, respectively, and

agree with previous data [1-5]. Achieved high resolution (5 ppm FWHH) and the absence of additional lines in spectra, indicate relatively high chemical homogeneity of our $(\text{CH})_x$ films.

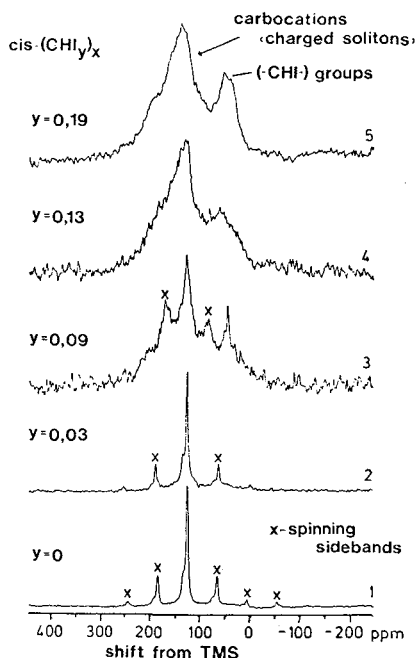


Fig. 1.

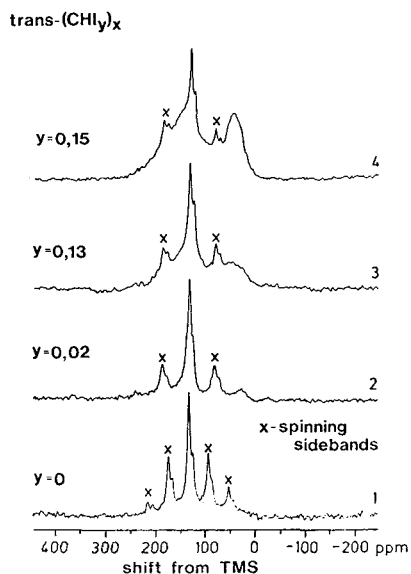


Fig. 2.

The iodine doping leads to the formation of two new broad resonances at about 150 and 50 ppm of increasing intensity towards higher iodine content (upper curves in Fig. 1 and 2). The first band is similar to that reported for AsF_5 doped $(\text{CH})_x$ [5] and its position is quite insensitive to iodine/ AsF_5 doping level. The doping leads to the π -electron transfer from polyacetylene to iodine and thus to the formation of the oxidized polymer chain regions, i.e. polycarocations. Most probably, this band is due to the signal from polycarocations and since it lies in the typical region of the chemical shifts of aromatic carbocations [7] there is no remarkable paramagnetic or Knight shift one may expect for the highly conducting doped polyacetylene. This result supports the spinless character of charge carriers in doped $(\text{CH})_x$ and the soliton conception of the charge transfer [8,9].

The relative width of the band is about 100 ppm and does not depend remarkably on the polarizing magnetic field H ($H = 47$ kOe in our experiments and in [4] and $H = 15$ kOe in [5]) nor on the dopant type. This suggests that the width is primarily determined by the wide range of chemical shifts of unequivalent carbons in a polycarocation (charged soliton) consisting of about 15 $=\text{CH}-$ groups [8]. Similar chemical shift distribution is known for the aromatic carbocations with delocalized π -electrons [7].

Comparison of spectra in Fig. 1 and 2 shows that the iodine doping of $\text{trans}-(\text{CH})_x$ is less homogeneous than that of $\text{cis}-(\text{CH})_x$. In $\text{trans}-(\text{CHI})_x$, a sharp line at 136 ppm due to undoped regions of the sample is observed for all doping levels $y \leq 0.15$. For $\text{cis}-(\text{CHI})_x$ the sharp component disappears at iodine concentration $y = 0.13$.

The band observed at about 50 ppm in the doped polyacetylene is connect-

ed with the halogenation of double bonds with $-CHI-$ groups formation. The shift of this band is close to that of iodine-substituted paraffins [10]. For example, in $CHI(CH_2CH_3)_2$ the shifts are 43.9 and 33.2 ppm for $-CHI-$ and $-CH_2-$ carbons, respectively. The iodine addition interrupts the conjugated polymer chain that probably leads to severe decrease of the conductivity of the iodine doped polyacetylene as compared with AsF_5 doped material [11].

Undoping experiments. Iodine doping is partially reversible. Vacuum treatment of the heavily doped material leads to substantial removal of iodine. Even more complete undoping can be achieved by washing of

$(CHI_y)_x$ films in acetone. Fig. 3 shows the spectra of the same sample before doping, after doping and that of washed in acetone after doping. The initial configuration of the sample by the NMR spectrum was 60% cis-form. The spectrum recorded after the iodine doping up to the level of $y = 0.17$ consists of two broad lines at 150 and 50 ppm as described above. The sharp lines disappeared completely indicating the lack of undoped regions in the sample. The acetone washing of the sample reduced the iodine concentration to the level of $y = 0.06$ determined by the lost weight and the corresponding NMR spectrum indicates that the oxidizing iodine is mostly removed since the contribution of $-CHI-$ line at 50 ppm into the total intensity of the spectrum increases with undoping. Finally, the cis/trans ratio was determined using the intensities of sharp lines in the $y = 0.06$ spectrum.

Eliminating the broad component in the vicinity of narrow lines using the suitably scaled $y = 0.17$ spectrum we arrive that the cis/trans ratio in the undoped material is 2:3 (in starting material 3:2). The presence of the strong cis-line in the undoped sample spectrum cannot be explained assuming nearly complete cis-trans isomerization induced by iodine doping as detected in the case of AsF_5 doped cis-polyacetylene where the polymer was considered converted into the trans-form [12]. As a possible explanation for this effect we suggest the chemical addition of the dopant (iodine) to the polymer chains, that can make the isomerization mechanism proposed in [13] inefficient.

Summary. The results of our experiments are consistent with the spinless charged solitons model and show the chemical addition of iodine to the polymer on doping. No complete cis/trans isomerization was observed even for heavily doped samples.

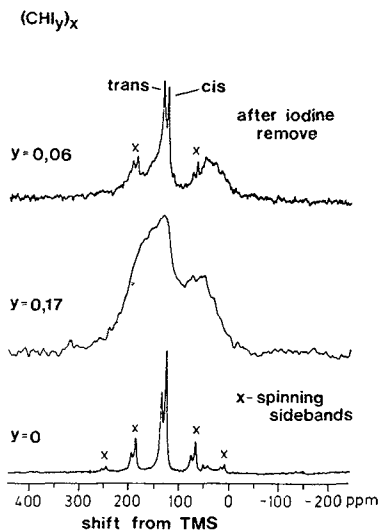


Fig. 3.

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