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NMR INVESTIGATIONS OF NATIVE AND DOPED POLYACETYLENE FILMS

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Résumé - Nous avons mesuré le second moment de la raie RMN du proton et les temps de relaxation spin-réseau du proton, du deutérium et du carbone 13 dans des échantillons de polyacétylène normaux, deutérés et enrichis en ^{13}C . Pour les échantillons cis et trans normaux, progressivement dopés à l'iode ou au sodium, la variation du second moment met en évidence l'isomérisation induite par le dopage et le gonflement du réseau dû à l'intercalation du dopant entre les chaînes polymères. La variation du temps de relaxation du proton s'explique par l'évolution du nombre et de la mobilité des solitons neutres au cours du dopage. Pour le deutérium et le carbone 13, par contre, la relaxation n'est pas monoexponentielle et elle s'explique parfaitement en deux exponentielles de constantes de temps 1,5 et 8,6s pour ^2H et 0,3 et 1,5s pour ^{13}C .

Abstract - Our results concern the second moment of the proton NMR line and the relaxation time T_1 of protonated, deuterated and ^{13}C enriched polyacetylenes. For the protonated cis and trans samples, progressively doped with iodine or sodium, the changes in the second moment reveal doping induced isomerization and further swelling of the lattice; the T_1 measurements are consistent with a decrease in number and mobility of neutral solitons upon doping. Our preliminary results on deuterated and ^{13}C enriched samples show that, whereas proton magnetization recovers in an exponential way, ^2H and ^{13}C relaxations are well fitted by a double exponential function with time constants 1.5 and 8.6s for the deuterated samples and 0.3 and 1.5s for ^{13}C nuclei.

All our samples were prepared according to Shirakawa's technique : the exact procedure has been described in another report from our laboratory (1).

NMR measurements were performed on a Bruker SXP spectrometer working at 60MHz for the proton and on a Bruker CXP 200 at 30.7 and 50.3MHz for the deuterium and ^{13}C . The signal was processed on a Nicolet BNC 12 minicomputer, after acquisition and digitalization by an 8 bit - 10MHz Bruker BC 100q converter.

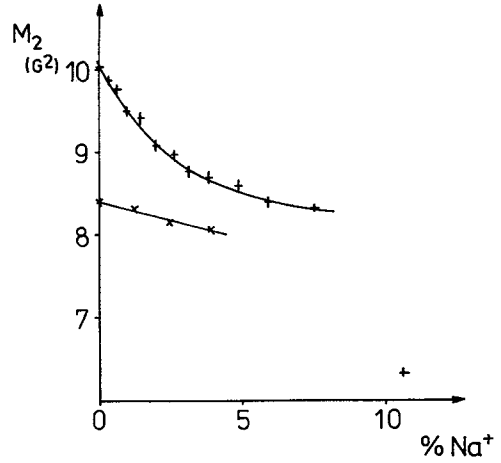
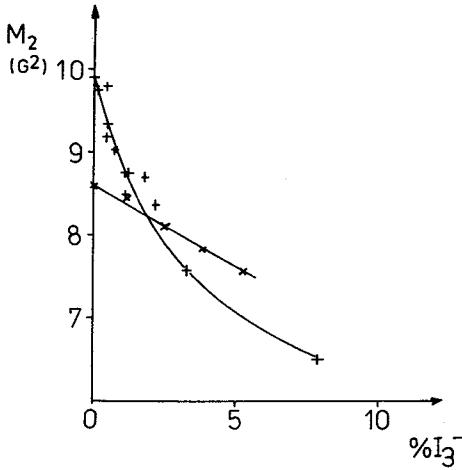
The second moment of the proton line was measured by fitting the free induction decay (FID) following the spectrometer deadtime (typically $5\mu\text{s}$) to an even polynomial of degree 10, and extrapolating it to time 0 taken at the middle of the pulse (2).

The relaxation curves, obtained by the inversion-recovery technique, were fitted to one or two exponentials, according to the best fit.

I - IODINE AND SODIUM DOPED SAMPLES

We performed these experiments in order to check the amount of dopant necessary to isomerize an initially cis-sample and we compared the structural effects of the dopants, benzophenone sodium being known to be a mild and easily controllable doping agent.

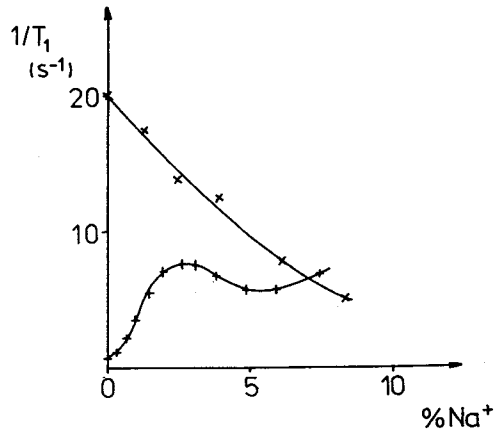
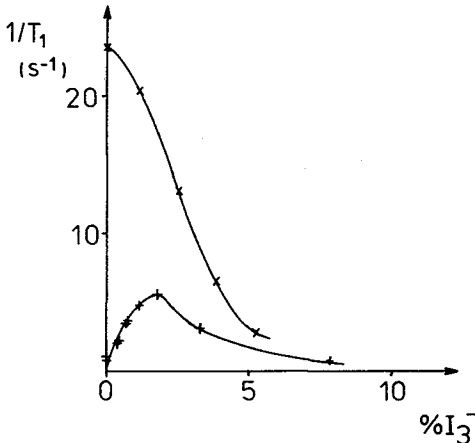
The second moments and proton relaxation rates of progressively doped samples have been measured at 200K.



Figs. 1 and 2 - Dependence of the second moment M_2 of $(\text{CH})_x$ cis(+) and trans(x) films with iodine (Fig. 1) and sodium (Fig. 2) contents.

In both cases, for the initially cis-samples, the second moment decreases faster in the initial range of doping (up to 5% of atomic iodine and 3% of sodium) and reaches values typical of the cis-trans content of such doped samples. These values are in good agreement with IR determinations of the cis-trans content of such doped samples. The further decreases are most probably due to swelling of the lattice by the dopant.

Notice also that the second moment of cis and trans films decreases faster in the case of iodine doping, because the doping agent I_3^- is much larger than Na^+ .



Figs. 3 and 4 - Dependence of relaxation rate T_1^{-1} of $(\text{CH})_x$ cis(+) and trans(x) films with iodine (Fig. 3) and sodium (Fig. 4) contents.

The recovery of the longitudinal magnetization is exponential over one decade in the whole doping range.

For the trans isomer, the relaxation rate reveals a monotonic variation, which can be explained by the change in number and mobility of neutral solitons, which are transformed into spinless charged solitons upon doping.

Cis samples show a non monotonic variation of T_1 , the mechanism of relaxation being complicated by the initial isomerization. At the highest doping ratio, the relaxation rates are similar for both isomers.

II - ^{13}C ENRICHED POLYACETYLENE

These experiments result from a collaboration with F. Masin (Bruxelles) who reported earlier measurements of proton T_1 in ^{13}C enriched polyacetylene (3) which differed significantly from our results on ^{13}C natural abundance samples (4). A 45% ^{13}C enriched sample was then prepared in our laboratory, avoiding all contact with air.

The second moment of this sample is compared with our previous results (4) on unenriched cis and trans $(\text{CH})_x$

$M_2(200\text{K})$	^{13}C enriched	unenriched
cis	14 G^2	9.9 G^2
trans	12.5 G^2	8.5 G^2

In both enriched isomers, M_2 is 4G^2 higher than in natural abundance samples. This higher value can be attributed to the dipolar broadening due to the heterogeneous interaction between the proton and its first neighbour carbon, calculated from :

$$\Delta W_{IS} = \left(\frac{4}{15}\right) \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \sum_j r_{ij}^{-6} \quad (5)$$

where r_{ij} is the distance between I and S spins. This contribution is found to be on the order of 3G^2 for the given ^{13}C enrichment and is sufficient to explain the observed difference.

The proton follows an exponential relaxation with a time constant of 48ms in good agreement with our reported measurements (40ms) (4). This discrepancy with Masin's results might be explained by the poorer quality of his films which resulted from the presence of oxygen.

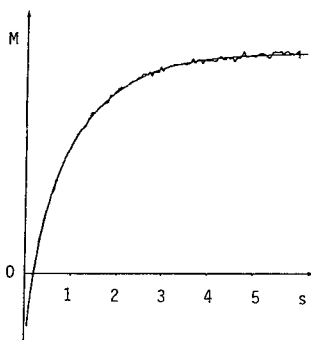


Fig. 5 - ^{13}C typical relaxation and its double exponential fitting.

^{13}C nuclei don't have the same relaxation behaviour as protons : their recovery is best fitted by a double exponential with a 1 to 2 amplitude ratio and time constants 0.3s and 1.5s.

More measurements are required to determine whether the different behaviours of the proton and ^{13}C can be explained by the presence or absence of nuclear spin transverse diffusion between chains with and without solitons.

III - DEUTERATED POLYACETYLENE

Quadrupolar interaction is usually dominant for nuclei with spin $> 1/2$. One can therefore expect the deuterium signal to be most susceptible to fluctuations of electric field gradients induced by the presence of a charged soliton on the carbon backbone. Quadrupolar spectra and relaxation behaviour can thus reveal interesting information about charged solitons and their mobility.

The spectra of pure cis and trans deuterated polyacetylene are very similar : the measured quadrupolar splitting is exactly the same for pure and lightly iodine doped samples (126kHz).

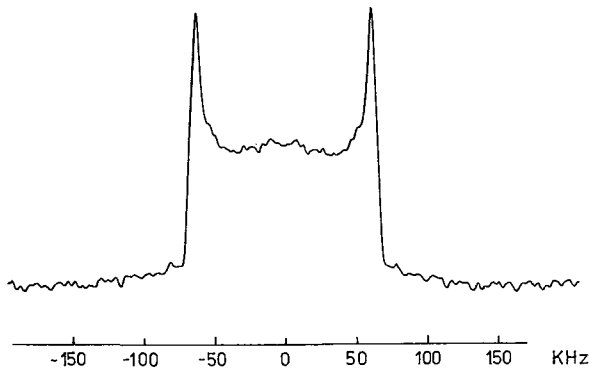


Fig. 6 - ^2H spectra of a deuterated cis-sample at 200K.

For the pure trans sample, ^2H 's relaxation is best fitted by a double exponential. The fast relaxation concerns about 20% of the spins.

time constants.

room temperature	1.4s	6.5s
low temperature (200K)	1.6s	9s

Experimental problems mainly involving band width and detuning of the probe-head have kept us from performing T_1 measurements on doped samples.

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