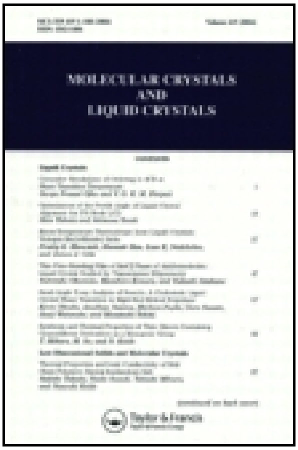

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

^{13}C -MAS-NMR of Conjugated Polymers: Preliminary Results on LI-Doped Cis-$(CH)_x$

M. Audenaert [a] & P. Bernier [a]
[a] GDPC - USTL, Place Eugéne Bataillon, 34060, MONTPELLIER, Cédex, FRANCE

To cite this article: M. Audenaert & P. Bernier (1985): ^{13}C -MAS-NMR of Conjugated Polymers: Preliminary Results on LI-Doped Cis-$(CH)_x$, Molecular Crystals and Liquid Crystals, 117:1, 83-86

To link to this article: http://dx.doi.org/10.1080/00268948508074600

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 83-96
0026-8941/85/1174-0083/$10.00/0

Printed in the United States of America

^{13}C -MAS-NMR OF CONJUGATED POLYMERS : PRELIMINARY RESULTS ON LI-DOPED CIS-$(CH)_x$

M. AUDENAERT, P. BERNIER.
GDPC - USTL, Place Eugène Bataillon, 34060 MONTPELLIER
Cédex, FRANCE

Abstract We have investigated the ^{13}C nuclear magnetic resonance of lithium-doped cis-polyacetylene by using the MAS-NMR spectroscopy technique. The highly-resolved spectra show that the measured intensity ratios of the cis and trans peaks strongly depend on the cross polarization time. Thus our conclusion is that high resolution NMR is not a good tool to check the cis to trans content of doped polyacetylene.

Several authors have reported experimental results on the ^{13}C magnetic resonance of doped polyacetylene, obtained with high resolution NMR[1-4]. It has been stated that a substancial cis/trans isomerization does not occur with doping, even at high doping levels.[3,4] In this work, we show that one has to be very careful when drawing such a conclusion from the measured intensity ratio of the resolved cis and trans NMR peaks. Indeed, among the different parameters which enable us to obtain highly resolved carbon NMR spectra of solids, the cross polarization time T_{cp} plays an important role. During this period of time (typically 1 ms), the Hartmann-Hahn condition[5] is fulfilled and allows the carbon spin system to exchange energy with the proton spin system with the result that the S/N ratio is enhanced by a factor of 4. However, within the rotating frame, the proton spins are relaxing while the cross polarization takes place such that the net magnetization due to the carbons goes through a maximum as a function of T_{cp}. The equation which governs the evolution of the magnetization M as a function of T_{cp} is given by[6] :

$$M(T_{cp}) = M_0 \left\{ 1 - \exp(-\lambda T_{cp}/T_{CH}) \right\} \exp(-T_{cp}/T_{1\rho H})$$

where $\lambda = (1 + T_{CH}/T_{1\rho C} - T_{CH}/T_{1\rho H})$, T_{CH} is the characteristic cross polarization time and M_o is a constant proportional to the number of carbons.

Carbons can be differently surrounded by protons or equally surrounded by protons having different relaxation times $T_{1\rho H}$. In both cases, the intensity ratios of the resonance peaks of these different carbons do generally not reflect their relative proportion.

Our paper has the purpose to illustrate the latter case, which we observed for Li-doped polyacetylene. Circular disks were cut in a 500 μm thick cis-$(CH)_x$ film in order to fit into the cylindrical-shaped rotor used for the MAS experiment. These samples where doped for 48 h in a solution of Lithium-Benzophenone in THF, then washed and pumped out for 40 h. By this thoroughly used doping procedure[7], we expect the Lithium concentration to be about 4 mol%. The samples were then transferred into the rotor under an argon atmosphere. At the very beginning of the experiment, the conducting $(CH)_x$ yield no signal at all in a frequency range covering 1000 ppm and centered at about 120-140 ppm from TMS, i.e. the chemical shift of the cis and trans ^{13}C peaks. After a couple of hours of spinning, the S/N ratio increased, which pointed to an air leakage at the rotor's cap. The doped and subsequently air-compensated samples allowed us to obtain a highly-resolved spectrum of Li-doped $(CH)_x$. The cross polarization time was then varied from 0.1 ms to 8 ms. The spectra, that we obtained with a Brüker CXP 200 spectrometer, are shown in Fig. 1, as a function of T_{cp}. The cis to trans ratios were then calculated from the relative intensities of the cis and trans peaks and are plotted in Fig.2.

It has been shown that only the trans-isomerized regions are doped[8]. As the proton relaxation time drops upon doping[9,10], there must be a difference in relaxation times in the doped trans regions and in the cis regions, where $T_{1\rho H}$ remains the same as in pristine cis-$(CH)_x$. This explains the artificial variation observed for the cis over trans content of the Li-doped film as a function of T_{cp}.

On the other hand, by varying the cross polarization time within the same range, the cis/trans ratio of non-doped $(CH)_x$ didn't present a significant change. Thus, our results make uncertain the conclusions drawn by different experimentalists from the measured cis to trans ratios in doped cis-$(CH)_x$, using high resolution NMR. A detailed NMR study is in progress in order to investigate the electronic properties of alkalin-doped $(CH)_x$ with respect to their structural properties.

REFERENCES

1. M. Peo, H. Förster, K. Menke, J. Hocker, J.A. Gardner, S. Roth, K. Dransfeld, Solid State Commun., 38, 467 (1981).
2. L. Mihaly, S. Pekker, A. Janossy, Synthetic Metals 1, 349 (1980).
3. T.C. Clarke, J.C. Scott, Solid State Commun., 41, 389 (1982).
4. I. Heinmaa, M. Alla, A. Vainrub, E. Lippmaa, M.L. Khidekel, A.I. Kotov and G.I. Kozub, J. Phys. (Paris) Colloq. 44, C3-357 (1983).
5. S.R. Hartmann, E.L. Hahn, Phys. Rev., 128, 2042 (1962).
6. J.M. Dereppe, RMN ^{13}C Haute résolution de matériaux Fossiles Solides, GERM8, p 146 (La Grande Motte, France, 1984).
7. F. Rachdi, P. Bernier, E. Faulques, S. Lefrant, F. Schué, J. Chem. Phys., 80, 6285 (1984).
8. A. Feldblum, A.J. Heeger, T.C. Chung, A.G. MacDiarmid, J. Chem. Phys., 77, 5114 (1982).
9. F. Masin, G. Gusman, R. Deltour, Solid State Commun, 40, 513 (1981).
10. M. Ziliox, B. François, C. Mathis, B. Meurer, P. Spegt and G. Weill, J. Phys. (Paris) Colloq. 44, C3-361 (1983).

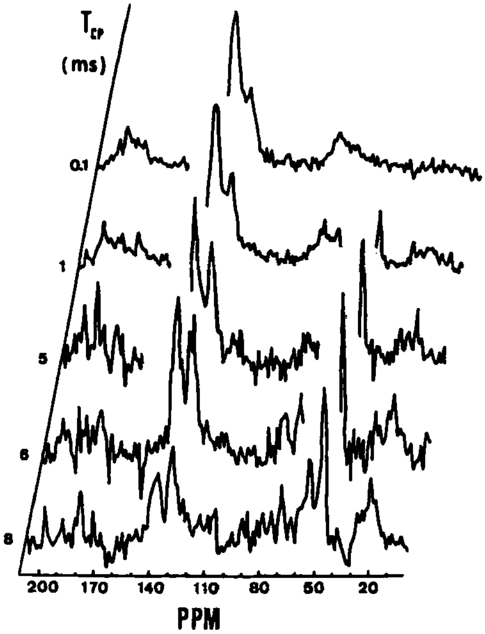

FIGURE 1

FT-NMR Spectra of Li-doped cis-$(CH)_x$ as a function of the cross polarization time.

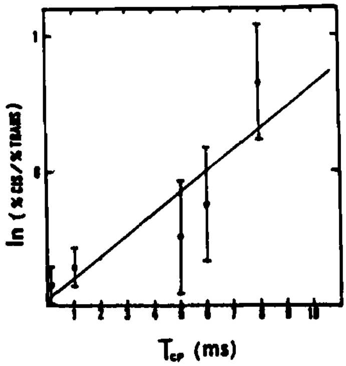

FIGURE 2

Log. of the cis to trans ratios measured from the spectra of Fig.1.