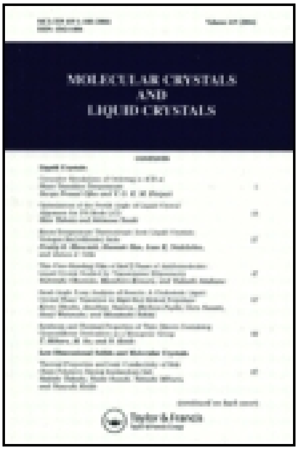

Molecular Crystals and Liquid Crystals

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

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M. Ziliox [a] , B. Francois [a] , C. Mathis [a] , B. Meurer [a] , G. Weill [a] & K. Holczer [a] [b]

[a] Centre de Recherches sur les Macromolécules, C.N.R.S., 6, Rue Boussingault, 67083, Strasbourg, Cedex, France

[b] Central Research Institute for Physics, POB 49, H-1525, Budapest, Hungary

To cite this article: M. Ziliox , B. Francois , C. Mathis , B. Meurer , G. Weill & K. Holczer (1985): Proton Magnetic Resonance in Partially Deuterated Trans - Polyacetylene, Molecular Crystals and Liquid Crystals, 117:1, 483-486

To link to this article: http://dx.doi.org/10.1080/00268948508074670

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 483-486
0026-8941/85/1174-0483/$10.00/0

PROTON MAGNETIC RESONANCE IN PARTIALLY DEUTERATED TRANS - POLYACETYLENE

M. ZILIOX, B. FRANCOIS, C. MATHIS, B. MEURER, G. WEILL and K. HOLCZER[x]
Centre de Recherches sur les Macromolécules, C.N.R.S.,
6, Rue Boussingault, 67083 Strasbourg Cédex, France.

Abstract Proton NMR measurements as a function of ^{1}H concentration in partially deuterated trans-$(CH_zD_{1-z})_x$ show that at high ^{1}H content the proton relaxation is homogeneous and reflects the dynamics of electronic spins. At low concentration, protons of residual catalyst (about 6% per CH unit) dominate the NMR results, misleading earlier analysis.

The nature of the paramagnetic centers observed in trans-polyacetylene continues to be a subject of controversy, particularly regarding their description as highly mobile bond alternation defects (solitons).[1] The proton relaxation rate T_1^{-1} revealed an inverse square root dependence on the Larmor frequency.[2] This characteristic behaviour may arise either from direct relaxation by one-dimensional diffusion of the electronic spin, or from three-dimensional nuclear spin diffusion towards localized paramagnetic centers. The first interpretation was supported by the observation of an Overhauser effect in trans-$(CH)_x$. However, W.G. Clark and coworkers[3] tried to test which description was the more appropriate, by checking whether T_1^{-1} changed when the proton diffusion coefficient was reduced. If the former interpretation was correct, T_1^{-1} should not depend on the proton concentration. They therefore measured ^{1}H spin-lattice relaxation rate in trans-$(CH_{.08}D_{.92})$.

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x Permanent address : Central Research Institute for Physics, H-1525 Budapest, POB 49, Hungary.

The change they observed led them to the conclusion that nuclear spin diffusion plays an important role in the relaxation mechanism which questions the high value earlier inferred for the electronic spin diffusion constant.

We report here NMR measurements on a series of different degrees deuterated $(CH)_x$. The real proton concentration y, measured by the NMR signal amplitude, is found higher than the unlabelled monomer content z of the gas mixture used for synthesis (labelled monomer contained less than 1% of protons). The difference between y and z corresponds to 6 - 8 % of extra protons. Interpreting their results, W.G. Clark et al. implicitly supposed that these protons result from an isotopic exchange, i.e. that they are on the polymer backbone. The second moment M_2 of the samples, measured as a function of monomer's ^1H content (Figure 1.), shows that the extra protons have a different origin. Were they on the chains, their second moment should decrease monotonically (as it does as long as their relative concentration is negligible) to a value

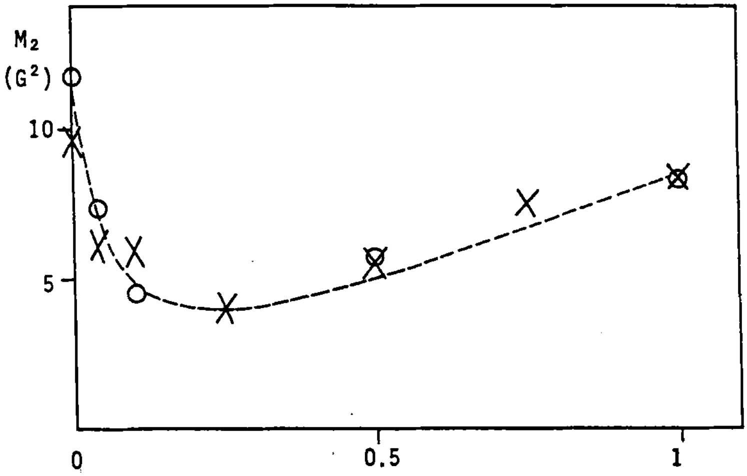

FIGURE 1 Second moment M_2 as a function of z, the fraction of protonated monomer, at 150 K : X 60 MHz , o 200 MHz.

less than or equal to 0.5 G^2, which is the M_2 calculated for a pair of protons on the backbone. If we take $M_2(0) = 11\ G^2$ (measured on the "fully deuterated" sample) as the second moment of the extra protons, the results shown in Figure 1 are well described by the sum of their contribution and of z% on-chain proton contribution:

$$M_2(z) = \frac{z^2 M_2(1) + (y - z) M_2(0)}{y}$$

where $M_2(1)$ is the second moment of undeuterated $(CH)_x$. It is commonly admitted that every polymer chain ends with a C-Ti or C-Al bond[4], these atoms being accompanied by $-C_2H_5$ or $-OC_4H_9$ groups. As a film usually contains about 0.2 % of Ti and Al, the proportion of protons associated with these metals can be estimated to 7 %, and 11 G^2 as a second moment of these groups seems a quite reasonable figure.

It is clear that protons in "fully deuterated" polyacetylene cannot experience any direct interaction with moving electronic spins confined to the conjugated sequences. Their contribution is sufficiently important in a relaxation time measurement up to 20 - 30 % proton concentration to make hopeless the quantitative experimental test attempted in ref. 3. On the other hand, at high proton

TABLE 1 Spin-lattice relaxation time for different proton concentrations. ★: deviation from exponential is observed.

z	60 MHz	200 MHz			
	T_1 (ms)	T_1 (ms)	T_{11} (ms)	T_{12} (ms)	$\frac{A_1}{A_1 + A_2}$
1.00	49	90	90		1
0.75	48				
0.50	68★	150★	97	240	0.51
0.25	77★				
0.10	161★	301★	85	330	0.12
0.04	275★	438★	89	470	0.06
0.00	345★	510★	89	590	0.17

concentration, the strong dipolar coupling between protons assures that these protons relax in the same way as all the others. Indeed the original interpretation of T_1 holds quantitavely as long as protons have a common well-established spin temperature.[5] Searching where inhomogeneity appears, relaxation curves were recorded up to 2 seconds and were carefully fitted with one or the sum of 2 exponentials. The results of these fits are given in table 1, where A_1 and A_2 are the respective amplitudes of the 2 exponentials. For ^1H concentrations $z \leq 0.5$, the double exponential fit is more accurate, i.e. relaxation is no longer homogeneous. We note that fitting with only one exponential in the time domain where it fits well (as one commonly does) would not give any deviation in T_1 down to about 10 % ^1H content.

In conclusion, studying a series of partially deuterated trans $(CH_zD_{1-z})_x$, about 6 % (per CH unit) of extra protons are observed in all samples, originating from chain-end located residual catalyst ($Ti(OC_4H_9)_4$ + $Al(C_2H_5)_3$). These protons cannot experience direct interaction with electronic spins on the chains, inhibiting any conclusion about soliton dynamics from measurements at low ^1H concentrations.[3] At high ^1H content, T_1 does not depend on z and is accurately homogeneous, confirming the existence of a well-established spin temperature and the validity of earlier T_1 interpretation.[2] A break down in the homogeneity of spin temperature is observed for $z \leq 0.5$.

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