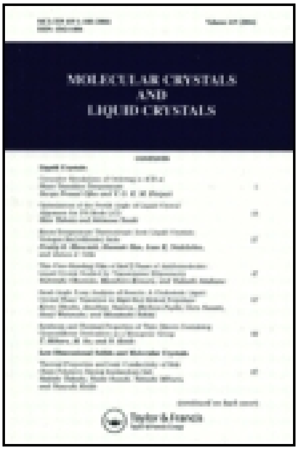

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

NMR Studies in Polypyrrole

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To cite this article: H. Lecavelier, F. Devreux, M. Nechtschein & G. Bidan (1985): NMR Studies in Polypyrrole, Molecular Crystals and Liquid Crystals, 118:1, 183-186

To link to this article: http://dx.doi.org/10.1080/00268948508076208

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 183-186
0026-8941/85/1184-0183/$10.00/0

Printed in the United States of America

NMR STUDIES IN POLYPYRROLE

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Abstract We present the results of proton and fluor NMR studies in the conducting polymer, polypyrrole-BF_4. The fluor nuclear relaxation is dominated by the rotation of the BF^-_4 ions, while the proton nuclear relaxation is controlled by the electronic spin motion on the polymer backbone.

Apart from the starring polyacetylene, polypyrrole is one of the most studied conducting polymers. It can be prepared by electrochemical way[1] and presents the advantage to be stable in air[2], at least in its oxydized form. Novel spinless conducting mechanisms involving bipolarons have been invoked to explain its transport and magnetic properties[3]. Moreover, recent in-situ ESR experiments demonstrate that the creation of polarons with spins and bipolarons without spins can be reversibily controlled by electrochemical methods[4]. On the other hand, little is known about the ion dynamics, which should nevertheless play a major role in the electrochemical applications of these conducting polymers. However it is highly suspected that electrochemical cycling result in a more complicated process than a simple coming and going of the initial ions [5,6].

In order to get an insight into the ion dynamics, we have measured the temperature and frequency dependence of the ^{19}F nuclear relaxation rate in polypyrrole-BF_4. It is compared to the proton relaxation rate in the same compound and completed by the temperature dependence of the ^{19}F NMR second moment and by a dynamic nuclear polarization experiment on the protons.

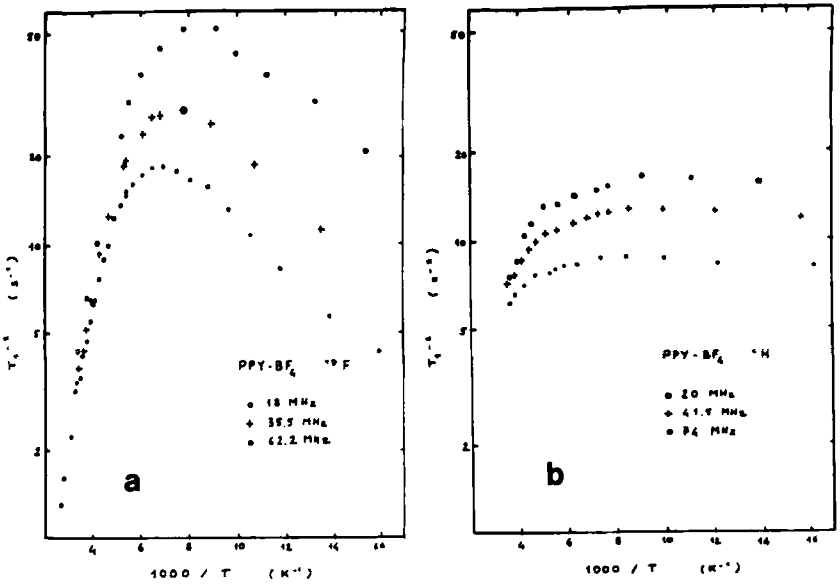

Figure 1 ^{19}F (a) and ^{1}H (b) nuclear relaxation rates vs reciprocal temperature

Figures 1a and 1b show the temperature variation of the nuclear relaxation rates at different frequencies for ^{19}F and ^{1}H, respectively. The ^{19}F and ^{1}H behaviours are clearly different. ^{19}F relaxation show a strong temperature dependence, reminiscent of the standart Bloembergen-Purcell-Pound (BPP) curve[7], which is known to result from a lorentzian correlation spectrum :

$$T_1^{-1} \sim 2\,\tau_c / 1 + (\omega\tau_c)^2$$

with an activated correlation time : $\tau_c = \tau_0 \exp(E/kT)$. However the slopes of $\ln T_1^{-1}$ versus T^{-1} in Figure 1a are not symmetrical : 910 K and 170 K on the high and low temperature sides, respectively. Moreover the frequency dependence of the relaxation rate on the low temperature side nearly follows an ω^{-1} law, instead of the ω^{-2}

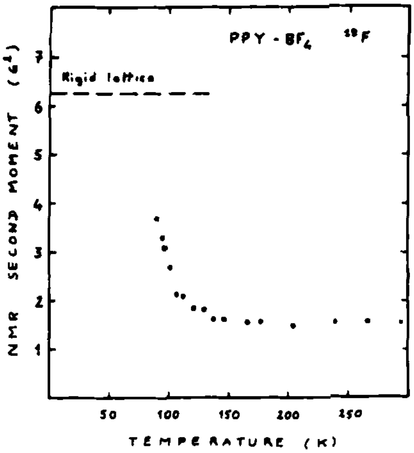

FIGURE 2 ^{19}F NMR second moment vs temperature

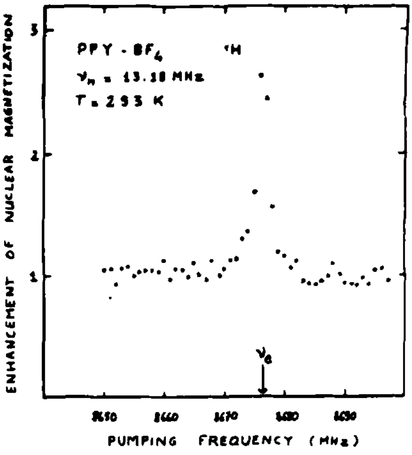

FIGURE 3 ^{1}H dynamic nuclear polarization

law expected from the simple BPP model. This can be accounted for by a distribution of the energy barrier E, due to the random environment of the ions in the amorphous polymer matrix.

The most probable origin for the ^{19}F relaxation is the modulation of the F-F dipolar interaction by the rotation of the ions. This is confirmed by the temperature dependence of the ^{19}F NMR second moment, which is shown in Figure 2. Second moment has been obtained by polynomial fitting of the free-induction-decay after a $\pi/2$ pulse[8]. Figure 2 shows that the room temperature value of the second moment is much less than the calculated rigid-lattice value for static BF_4. Moreover the increase of the second moment around 100 K is consistent with a progressive freezing of the rotation.

On the opposite, the ^{1}H nuclear relaxation (Figure 1b) is weakly temperature dependent. Moreover it is only 20 to 30 percent larger than that measured in polypyrrole-ClO_4[9], where no nuclear relaxation can be induced by ionic motion because of the absence of efficient nuclear spins in ClO_4. Thus it is likely that only a small -temperature dependent- part of the ^1H relaxation is due to the modulation of the H-F dipolar interaction by the ionic motion. The main contribution to the ^1H relaxation arises from the coupling with electronic spins on the polymer backbone as evidenced by the observation of a positive Overhauser effect -like in trans-polyacetylene[10]- in dynamic nuclear polarization experiment (Figure 3).

To conclude, it turns out that nuclear relaxation provides a way to study both electronic and ionic motion in polypyrrole-BF_4, by considering ^1H and ^{19}F NMR, respectively.

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