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To cite this version:

F. Devreux, G. Bidan, A.A. Syed, C. Tsintavis. Solid state 13C NMR in conducting polymers. Journal de Physique, 1985, 46 (9), pp.1595-1601. 10.1051/jphys:019850046090159500 . jpa-00210106

J. Physique 46 (1985) 1595-1601 SEPTEMBRE 1985, PAGE 1595

Classification
Physics Abstracts
71.50 — 76.60C — 76.70F

Solid state ^{13}C NMR in conducting polymers

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(*Reçu le 2 janvier 1985, révisé le 6 mai, accepté le 9 mai 1985*)

Résumé. — Nous présentons une étude par RMN du carbone-13 du polythiophène, du polypyrrole et de la polyaniline. Les résultats ont été obtenus par polarisation croisée, avec découplage des protons et rotation à l'angle magique. En effectuant des polarisations sélectives, il a été possible de séparer les raies de résonance des carbones non équivalents et d'évaluer leur déplacement chimique. Les résultats permettent de déterminer la structure de la polyaniline et de préciser les effets de charge sur la chaîne polymérique dans le polythiophène et le polypyrrole. Nous discutons également l'importance du déplacement paramagnétique du carbone-13 dans ces systèmes.

Abstract. — We present a ^{13}C NMR study of polythiophene, polypyrrole and polyaniline. The results have been obtained by cross-polarization with proton decoupling and magic angle sample spinning techniques. Using selective polarization, we have been able to separate the lines of inequivalent carbons and to estimate their chemical shift. From the results, we determine the structure of polyaniline and we discuss the oxidation scheme of the polymeric chain in polythiophene and polypyrrole. We also give an estimate of the ^{13}C paramagnetic shift.

1. Introduction.

Structural characterization of conducting polymers presents a real challenge. Because of amorphous nature of these materials, information obtained from X-ray and neutron diffraction is quite limited, while their insolubility prevents the use of the standard characterization techniques for classical polymers. As pointed out by Clarke *et al.* [1], the so-called solid-state high-resolution ^{13}C NMR (CMR) could be a promising way to investigate the structure of this type of materials. It has been used previously for polyacetylene (undoped [2, 3] and doped [4, 5]) polyparaphenylene [6], polypyrrole [7] and polythiophene [8-10]. Concerning these materials, the term « high-resolution » is, however, overstated. Because of the morphological disorder and the localized nature of the charged excitations (impurity-like states), the CMR lines are inhomogeneously broadened. Moreover, in compounds containing nuclei with $I \geqslant 1/2$ (such as ^{14}N), there is an extra broadening coming from the incomplete averaging of the dipolar coupling with the quadrupolar nuclei [11, 12]. Thus, it is often difficult to separate the inequivalent carbon lines and to make unambiguous line assignments. To overcome this difficulty, we have used different pulse sequences resulting in selective carbon polarization. This allows us to distinguish different ^{13}C lines, which would have overlapped otherwise, and to estimate their chemical shift. This determination provides valuable information on the chemical structure of the polymer. Moreover, by comparing the results for neutral and charged polymers, it is possible to get an insight into the oxydation scheme of the polymer chain. In this paper, we present results for two widely studied heterocyclic polymers, polythiophene and polypyrrole, and for the recently re-discovered polyaniline which seems to be a promising material for battery applications.

2. Experimental.

High resolution CMR is achieved in solids by averaging the interactions which cause anisotropic inhomogeneous broadening by two ways :

- the strong carbon-proton dipolar interaction is suppressed by saturating the proton resonance line, while recording the ^{13}C free induction decay ;

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- the weaker dipolar interactions with other nuclei and the anisotropic chemical shift are removed by magic angle sample spinning.

Moreover, one generally uses a sensitivity enhancement procedure which consists in polarizing the ^{13}C spins through a transfer of the ^{1}H polarization in the rotating frame. The expected gain in sensitivity is $^{1}\gamma/^{13}\gamma \simeq 4$. Also this allows to accumulate at a rate which is fixed by the proton relaxation rate instead of being determined by the generally longer carbon relaxation rate. Moreover, this procedure makes possible selective ^{13}C polarization by changing the polarization time or letting the proton-coupled ^{13}C spins to relax before recording the ^{13}C signal.

The pulse sequence, we have used, is shown in figure 1. Three kinds of experiments can be done by varying the polarization time t_p and the relaxing time t_r :

i) $t_p = 1$ ms and $t_r = 0$: these are the standard conditions which allow observation of all the ^{13}C spins.

ii) $t_p = 30$ to 100 μs and $t_r = 0$: these conditions select the proton-bonded ^{13}C, which polarization is fast because of the strong proton-carbon dipolar coupling.

iii) $t_p = 1$ ms and $t_r = 30$ to 100 μs : these conditions favour the ^{13}C spins which are not bonded to protons, by letting the others relax with the protons by spin-spin relaxation during t_r.

Experiments have been performed at room temperature using a BRUKER CXP 200 spectrometer working at 4.7 T (^{13}C Larmor frequency of 50.3 MHz). The sampling time was 10 μs (spectral width of 50 kHz) and the number of scans was typically of the order of 10^4. The decoupling time t_d was 2 ms, except for polythiophene where it was 5 ms. These values were chosen after checking that larger decoupling times do not improve the resolution. The proton rf field was limited to 0.6 mT because of flashing in the probe head. It has been checked that this low field does not cause a loss of resolution ; however, it is probable that this decreases the efficiency of the polarization transfer and thus the sensitivity. The Andrew-type rotor in perdeuterated poly-methylmethacrylate was loaded with about 100 mg of the powdered sample and rotated at 3.9 ± 0.2 kHz. For polypyrrole and polythiophene samples, the rotor was loaded under argon in dry box and spun with dry nitrogen gas. Finally, there was a broad and quite important probe head signal on the high field side of the sample signal, which has been substracted or suppressed in the results shown below. This prevents any detailed observation in the range 10 to 80 ppm from TMS.

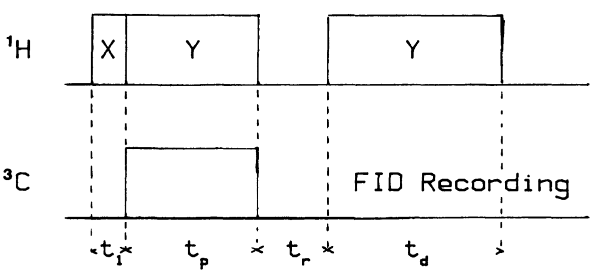


Fig. 1. — Pulse sequence timing. t_1 is the duration of the $\pi/2$ pulse, t_p is the polarization time, t_r the relaxing time and t_d the decoupling time. ^{13}C signal recording starts at the beginning of the decoupling time.

3. Results.

3.1 POLYTHIOPHENE. — Polythiophene-tetrafluoroborate (PTh-BF$_4$) has been synthesized electrochemically following the method of Tourillon and Garnier [13] from a solution of 2,2'-bithiophene (0.06 M) in CH_3CN using $(C_2H_5)_4NBF_4$ (0.1 M) as electrolyte. The doping level (0.12 BF_4 per thiophene ring) was estimated from the ^{19}F to ^{1}H NMR signal ratio. The room temperature conductivity, as measured on pressed pellets, was 13 $(\Omega cm)^{-1}$. The CMR results are shown in figure 2. While the spectrum (i) obtained in standard conditions indicates the presence of a double peak structure, the spectra (ii) and (iii) allow us to clearly distinguish and assign the two lines :

- a rather broad line with a low field shoulder (ii)

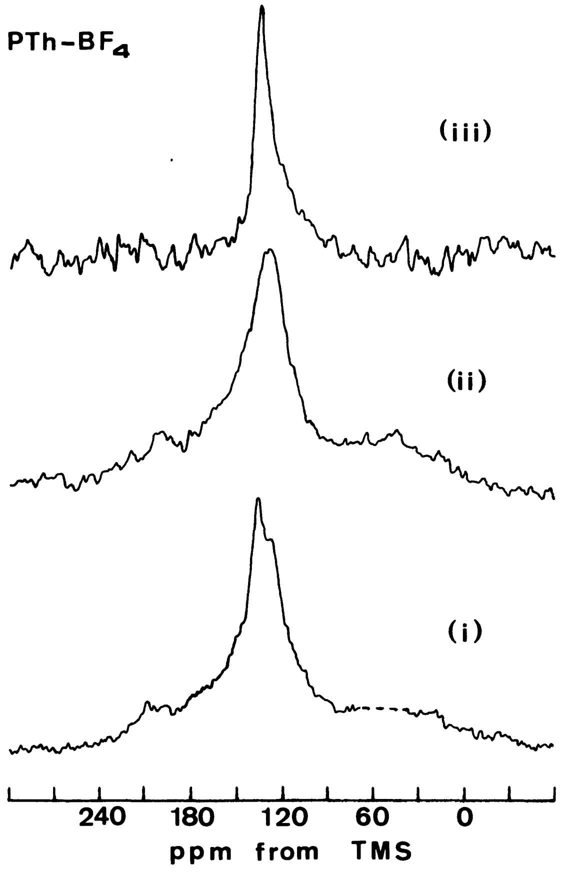


Fig. 2. — CMR spectra of polythiophene-tetrafluoroborate with different experimental conditions : (i) $t_p = 1$ ms and $t_r = 0$, (ii) $t_p = 30$ μs and $t_r = 0$ and (iii) $t_p = 1$ ms and $t_r = 100$ μs.

which corresponds to the proton-bonded ^{13}C spins (β-carbons);

- a sharp line (iii) due to the non proton-bonded ^{13}C spins (α-carbons).

The chemical shifts, taken as the position of the line maximum, are 126.5 and 134.2 ppm with a precision better than 2 ppm, for β- and α-carbons, respectively. These results desagree with the previous determination by Hotta *et al.* [8] in PTh-ClO$_4$ (120 and 127 ppm). They are compared in table I with the chemical shift in thiophene, 2,5-dimethylthiophene and neutral polythiophene [10]. The results for neutral and charged polythiophene agree remarkably well with that in α-substituted dimethylthiophene. This is strong evidence in favour of a regular α-polymerization. On the other hand, it is puzzling that there is practically no deshielding in PTh-BF$_4$ with respect to neutral polythiophene. This result will be discussed in section 4.

Table I. — *Chemical shift in thiophene, α-substituted dimethylthiophene, neutral polythiophene and polythiophene-tetrafluoroborate.* (*) *From reference* [10].

	α-carbon	β-carbon
	—	—
Thiophene	125.6	127.4
2,5-dimethylthiophene	137.4	125.3
PTh (*)	136.5	124.8
PTh-BF$_4$	134.2	126.5

3.2 POLYPYRROLE. — Electrochemically as well as chemically prepared polypyrrole has been studied. Electrochemical polypyrrole-tetrafluoroborate film (PPy-BF$_4$) has been synthesized following a slight modification of the method of Diaz *et al.* [14] from a solution of 0.1 M pyrrole, 0.1 M $(C_2H_5)_4NBF_4$, 0.01 M HBF$_4$ (35 % in H$_2$O) in CH$_3$CN. The elemental analysis (found : C = 53.6, N = 16.4, H = 3.5, B = 2.6, F = 19.9) is consistent with the formula $C_4NH_3(BF_4)_{0.22}$ (calculated : C = 57.1, N = 16.6, H = 3.6, B = 2.8, F = 19.9). Chemical polypyrrole-perchlorate powder (PPy-ClO$_4$) has been obtained by reaction of pyrrole with Fe(ClO$_4$)$_3$ in CH$_3$CN. As it is difficult to obtain by electrochemical reduction the large amount of sample required for CMR, neutral polypyrrole (PPy) has been prepared by chemical reduction of PPy-BF$_4$ film and PPy-ClO$_4$ powder, using, respectively, SnCl$_2$ in CH$_3$CN and $Li_2(C_6H_5)_2CO$ in THF as reducing agent [15].

Figures 3a and 3b show the CMR results for chemically synthesized neutral PPy (reduced by $Li_2(C_6H_5)_2CO$) and electrochemically synthesized PPy-BF$_4$ [16]. The room temperature conductivities were $6 \times 10^{-7}\ (\Omega\text{cm})^{-1}$ and $12\ (\Omega\text{cm})^{-1}$ for PPy and PPy-BF$_4$, respectively. Neutral PPy clearly shows a double peak structure and the selective polarization experiments allow us to attribute the low and high field peaks to the α and β carbons, respectively. However, because of the presence of the nitrogen proton, the C_α signal cannot be completely suppressed by reducing the polarization time, as in polythiophene. It may also be noticed that the intensity of the C_α and C_β lines are not equal, as expected; this may be due to our low proton saturating field, which allows the proton-bonded carbons to relax, broadening the line and weakening its apparent intensity. The spectrum of PPy-BF$_4$ does not show any structure (Fig. 3b(i)).

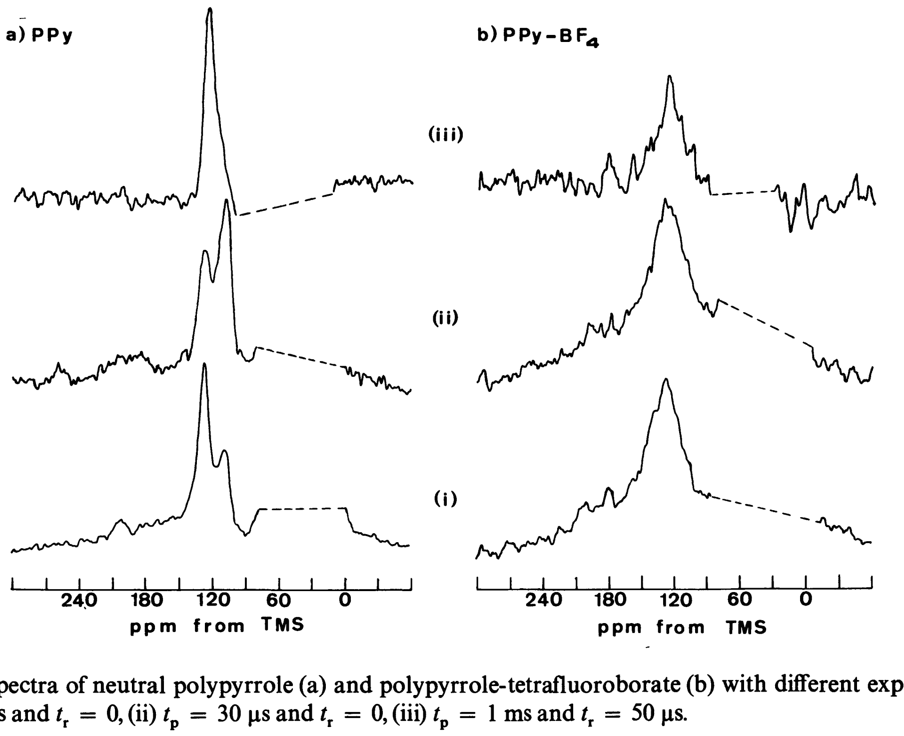


Fig. 3. — CMR spectra of neutral polypyrrole (a) and polypyrrole-tetrafluoroborate (b) with different experimental conditions : (i) t_p = 1 ms and t_r = 0, (ii) t_p = 30 μs and t_r = 0, (iii) t_p = 1 ms and t_r = 50 μs.

This feature is well explained by the selective polarization experiments which reveal that the C_α and C_β lines have their maximum at nearly the same position.

Our results are consistent with those of Street *et al.* [7]. However the selective polarization experiments provide new insight by allowing to follow the effect of doping on each carbon line. The experimental shifts are given in table II. We estimate the precision to be of the order of 2 ppm for PPy, but only 6 ppm for PPy-BF_4 because of the important line broadening. Again the complete agreement between the values for 2,5-dimethylpyrrole and neutral PPy is strong evidence in favour of α-polymerization. On the other hand, from neutral to positively charged polypyrrole, it turns out that there is no change in the chemical shift of the α-carbon within the limits of the experimental precision, while there is a definite downfield shift of 21 ± 6 ppm for the β-carbons. The deshielding of the β-carbon upon oxidation can be clearly seen in figure 4, where we compare the previous results with two other spectra obtained at standard conditions. The first one is that of the previously studied neutral PPy after 24 hours in air and the second one is that of PPy reduced by mild reducing agent $SnCl_2$. Probably, because of insufficient reaction time the reduction was not complete in the latter compound, which room temperature conductivity was $1.5 \times 10^{-3}\ (\Omega cm)^{-1}$. From figure 4, it is clear that the oxidation and increasing conductivity are associated with a continuous downfield shift of the C_β line toward the position of the C_α line and, meanwhile, to the appearence of a low field shoulder reminiscent of that of polythiophene.

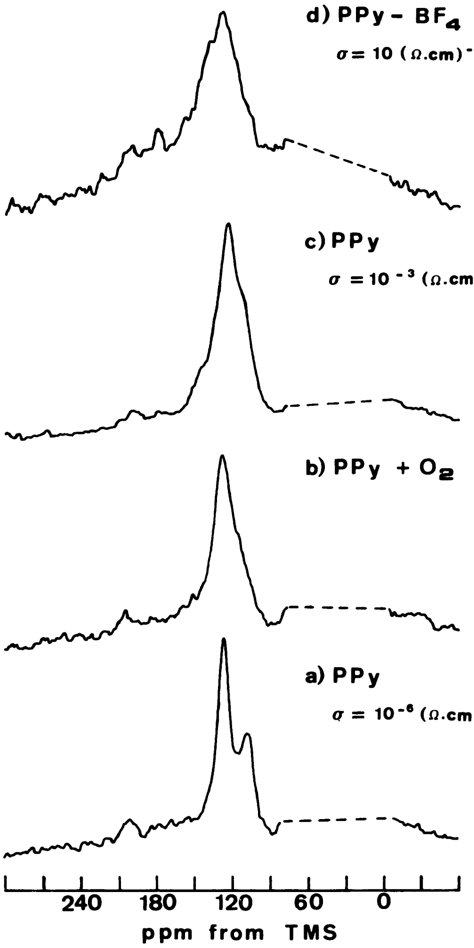


Fig. 4. — CMR spectra of different polypyrrole with standard conditions (t_p = 1 ms and t_r = 0) : a) neutral polypyrrole reduced by $Li_2(C_6H_5)_2CO$, b) the same sample after 24 h in air, c) polypyrrole reduced by $SnCl_2$, d) polypyrrole-tetrafluoroborate.

3.3 POLYANILINE. — In case of polythiophene and polypyrrole, the transition between conducting and insulating states is usually monitored by the oxydoreduction of the polymer. But, another mechanism based on acido-basic reactions has been shown to be working also in polyaniline [17-21]. We have thus studied protonated and deprotonated forms of polyaniline. Polyaniline-sulfate (PAn-SO_4) has been synthesized upon oxidation of aniline using $Na_2S_2O_8$ in sulfuric acid medium. The elemental analysis (found : C = 49.4, N = 9.3, H = 4.8, S = 8.9, O = 27.0) is consistent with the formula $C_6NH_5(SO_4)_{0.4}(H_2O)_{0.8}$ (calculated : C = 50.1, N = 9.7, H = 4.6, S = 8.9, O = 26.7). A deprotonated neutral compound (d-PAn) has been obtained by equilibrating PAn-SO_4 in a solution of pH 10 for 24 hours. The final pH value reached by the sample-solution was 7.6. The room temperature conductivities were $2.5\ (\Omega cm)^{-1}$ for PAn-SO_4 and $1 \times 10^{-8}\ (\Omega cm)^{-1}$ for d-PAn [20].

Table II. — *Chemical shift in pyrrole, α-substituted dimethylpyrrole, neutral polypyrrole and polypyrrole-tetrafluoroborate.*

	α-carbon	β-carbon
	—	—
Pyrrole	118.7	108.4
2,5-dimethylpyrrole	126.0	106.2
PPy	125.2	105.2
PPy-BF_4	~ 123	~ 126

The CMR spectra are shown in figures 5a and 5b for d-PAn and PAn-SO_4, respectively. The insulating d-PAn shows a well defined structure with three peaks, while the conducting PAn-SO_4 gives a broad structureless line. For d-PAn, the selective polarization experiments prove that the high field peak (124.7 ppm from TMS) is originated from proton-bonded carbons, while the two other peaks (144.6 and 160.3 ppm) should be attributed to non proton-bonded carbons, which must be, therefore, bonded to nitrogen. It is well known that, in high resolution solid state NMR, the proximity of the quadrupolar ^{14}N spin can give rise to an asymmetric doublet structure for the ^{13}C line [11, 12]. However, this explanation can be ruled out in the present case, because the value

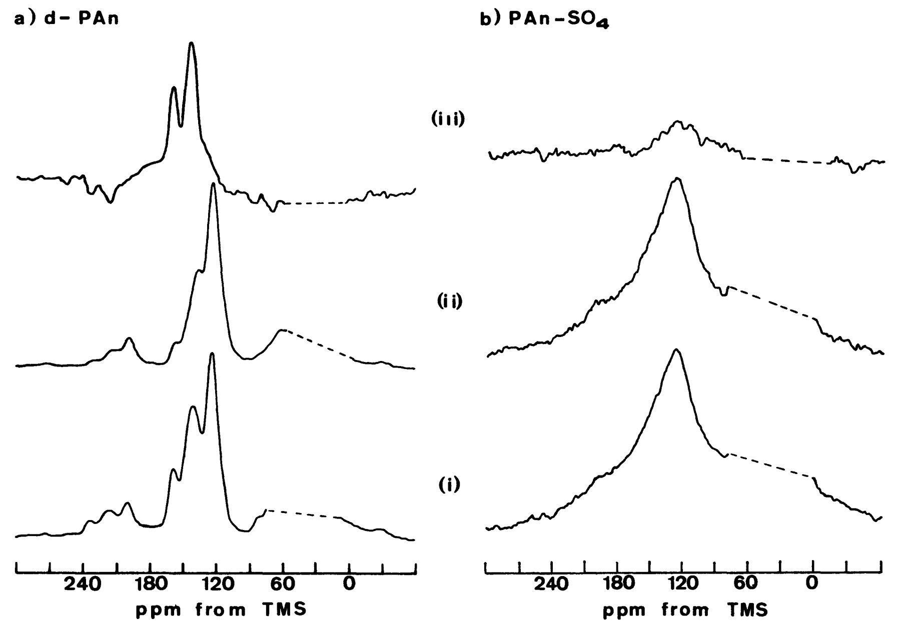
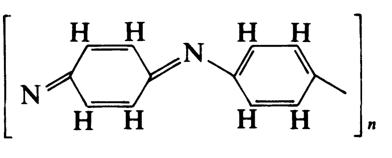


Fig. 5. — CMR spectra of neutral deprotonated polyaniline (a) and polyaniline-sulfate (b) with different experimental conditions : (i) $t_p = 1$ ms and $t_r = 0$, (ii) $t_p = 100$ μs and $t_r = 0$, (iii) $t_p = 1$ ms and $t_r = 100$ μs.

of the splitting between the two lines (about 800 Hz) would imply no average at all for the ^{14}N dipolar field, which, in turn, supposes an unreasonably large quadrupolar interaction at the nitrogen site. On the other hand, it may be observed that the positions of the two low-field peaks fall rather well in the range of the chemical shift for sp^2 carbons with C—N and C═N bonding, respectively [22]. As the intensity of both peaks are comparable (Fig. 5a(iii)), this leads one to suggest alternating benzenoid and quinoid rings, corresponding to the 2A form proposed by Mac Diarmid *et al.* [19], with the developed structure :



This is also consistent with the fact that the proton-bonded carbons have a chemical shift close to that of non-substituted aromatic carbons (124.7 ppm *vs.* 116.3, 130.0 and 119.2 ppm for ortho, meta and para carbons in aniline, respectively). However, although the para-polymerization shown above is most probable, partial polymerization in ortho position would be difficult to observe in the ^{13}C spectrum.

As concerns PAn-SO$_4$, it is seen in figure 5b that the selective polarization experiments do not help to resolve the line. We observe that all the carbons are coupled to protons. This can be explained by the fact that the nitrogen-bonded carbons are close to the nitrogen proton because of the non-planar character of polyaniline and that the values of 100 μs chosen for t_m and t_r are too long to distinguish the different carbons in this case. Because of the large broadening, the origin of which is discussed below, the line collapses with the satellite spinning bands. Although this prevents a quantitative analysis, it seems that the centre of the line is not markedly changed with respect to that of d-PAn.

CMR experiments have been performed on other polyaniline samples prepared either by electrochemical polymerization or by changing the oxidant in chemical synthesis, and also by varying the acidic medium and the pH of the equilibrium solution [21]. The conducting compounds ($\sigma \geqslant 1\ (\Omega\text{cm})^{-1}$) show broad structureless lines similar to that in figure 5b, while the insulating compounds give a line with three peaks. Although these peaks are sometimes broader than those in figure 5a, their position, as far as it can be determined, remains the same. This suggest that these compounds prepared in various ways have the common structure shown above which corresponds to the state of first oxidation of polyaniline [19, 21] and that the transition from the conducting to the insulating form is well represented by the removing of a proton and an anion with no further alteration of the polymer structure [19].

4. Discussion : the ^{13}C shift in doped polymers.

The comparison of the ^{13}C shift between neutral and charged polymers is expected to give information on the charge repartition resulting from the doping. However the conclusions are limited by the precision of the experimental determination of the shifts. In this respect, the situation is quite different in our three compounds :

- in polythiophene, the comparison between our results for PTh-BF_4 and those in reference [10] for PTh clearly indicates that there is practically no shift for both C_α and C_β;

- in polypyrrole, the results are less precise; however, they seem to show a difference between the C_α which is not shifted and the C_β which is shifted downfield by about 20 ppm;

- in polyaniline, the selective polarization in inoperant to distinguish the different carbon contributions in the broad unresolved line of the doped polymer.

Furthermore, the interpretation of the data is complicated by the facts that the broadening of the line may imply an inhomogeneous shift distribution, that part of the observed shifts can be caused by spin paramagnetic contributions and that even the resulting chemical shift is not a direct measurement of the charge density on the carbon, because it is also sensitive to the charge on the neighbouring atoms. Keeping in mind these restrictions, we shall nevertheless examine and discuss the inferences from our results concerning the charge repartition. The problem of the spin paramagnetic shift and that of the line broadening will be addressed later in this section.

The absence of ^{13}C shift in charged polythiophene with respect to neutral polymer seems to imply that the main of the charge is born by the sulfur atom. On the opposite, by taking 160 ppm per π electron as a representative value for the carbon chemical shift in aromatic systems [23], the 20 ppm downfield shift observed in polypyrrole, would correspond to a charge of $0.12 \mid e \mid$ per β-carbon, implying that the whole charge is concentrated on these atoms. In the comparison between polythiophene and polypyrrole, it should be taken into account that PTh-BF_4 is less charged than PPy-BF_4 (0.12 *vs.* 0.22 charge per ring). Nevertheless our results suggest a marked difference in the charge repartition between these two polymers. Such a difference can be expected from the difference in electro-negativity between sulfur and nitrogen. It is also consistent with the comparison of the electrochemical behaviours of β-halogenated polythiophene [24, 25] and polypyrrole, which shows that the β-substitution induces non-equivalent effects, related to different positive charge distribution in these two polymers. Contrary we must mention that XPS results seem to lead to different conclusions : in these experiments, charge density is also observed at the nitrogen site in polypyrrole [26-28] and on the carbon atoms in polythiophene [29]. Finally it is not clear whether this charge repartition is consistent or not with the bipolaron picture. Unfortunately, no molecular orbital calculations for positively charged polymers are presently available for a direct comparison with the experimental results.

In the analysis above, we have considered that the shifts in the charged polymers originate only from orbital contributions (chemical shift), neglecting possible spin contributions (hereafter referred to as paramagnetic shift). The basic reason for that rests on the fact that the fundamental charged species are believed to be spinless bipolarons [30]. However there is always a Curie-like spin susceptibility corresponding to about one spin per 100 cycles and recent electrochemical-ESR coupled experiments made in our laboratory seem to indicate that these spins are not due to extrinsic defects, but that they correspond to regular single-charged excitations (polarons) in thermodynamical equilibrium with bipolarons. These spins are likely to delocalize over a few rings and rapidly move from one site to another, as evidenced by their narrow ESR line. Depending on whether they are moving over all sites or only part of them, they give rise to an homogeneous or inhomogeneous paramagnetic shift. This isotropic paramagnetic shift is difficult to estimate, because the ^{13}C core-polarization hyperfine coupling is highly dependent on the precise spin distribution on the ring [31]. Resulting from a compensation of the positive contribution of the spin density on the considered carbon and a negative contribution of the spin density on the neighbouring atoms, it can be either positive or negative (although more likely positive, giving rise to a downfield shift). Assuming tentitatively 0.01 spin per ring, a uniform spin distribution over five atoms in the ring and a typical value of 10 MHz/spin for the hyperfine coupling, one obtains 2.1 ppm as a crude order of magnitude of the paramagnetic shift. This estimate shows that, if the spin contribution is expected to be small, it cannot be neglected in a quantitative interpretation of the observed shift.

Finally, a common feature in conducting polymers is the broadening of the CMR lines in the charged state. It is especially important for polyacetylene [4, 5] and polyaniline. In polyacetylene, it has been accounted for by Coulomb-induced charge density modulation around charged solitons [32]. In the compounds studied in the present paper, a possible explanation could be found in the localized nature of the charged bipolarons, giving rise to a distribution of the chemical shift over the bipolaron extension. However, one may wonder if such an inhomogeneity still exists when the bipolarons are moving ? Moreover, it should be noticed that, beside the isotropic hyperfine shift, there is an anisotropic dipolar shift, which is usually larger for ^{13}C. Using the same assumptions as before for the spin susceptibility and the spin distribution and a standard value of 90 MHz/spin for the dipolar coupling [31], the width of the shift distribution would be 57 ppm, i.e. 2 800 Hz at 50 MHz. In principle, this anisotropic interaction is averaged by the magic angle spinning; however, a larger spin susceptibility or a different spin distribution could rapidly give rise to an interaction exceeding the spinning rate. Then, the anisotropic paramagnetic shift would become an important cause of the line broadening. In particular, this seems to be the case in polyacetylene in the metallic regime. From the Pauli susceptibility, 5×10^{-6} emu/

mole [33], we deduce a width of 110 ppm for the distribution of the anisotropic dipolar Knight shift. Such a value, which is of the order of the observed linewidth, is larger than the spinning rate (4 kHz) in the experiment performed at 50 MHz by Peo *et al.* [4].

5. Conclusion.

Solid-state high-resolution CMR with selective polarization has been proved to be a powerful method to investigate the structural properties of the conducting polymers in their neutral state. It has been successful in confirming the regular α-polymerization in polypyrrole and polythiophene and giving the first experimental evidence in favour of alternating benzenoid and quinoid rings in polyaniline. In the charged state, the interpretation of the results is more difficult, but it may become quantitative, provided one can separate the spin and charge effects. This could be achieved by measuring the shifts as a function of temperature to distinguish, as in classical metals, the temperature dependent spin contribution from the constant orbital contribution.

Acknowledgments.

We thank J.-P. Travers for conductivity measurements and E. M. Geniès for stimulating discussions. The CMR experiments have been performed with the CXP 200 spectrometer of the Centre Grenoblois de Résonance Magnétique.

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