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NMR OBSERVATION OF PROTON EXCHANGE IN THE CONDUCTING POLYMER POLYANILINE

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Résumé
Nous donnons des résultats de RMN qui montrent l'existence d'un échange rapide de protons entre la matrice rigide du polymère et une phase d'eau adsorbée mobile.

Abstract
We report NMR experiments which supply direct evidence for fast proton exchange between the polymer skeleton of polyaniline and adsorbed water.

Although polyaniline has been known as a conducting polymer for a long time, a renewed interest for this material has arisen recently, in particular related to its potential applications. One of the most fascinating features of polyaniline is the very high sensitivity of its transport properties to the presence of mobile protons. As other conducting polymers polyaniline needs to be doped—or oxidized—to present conductivity, but in addition the degree of protonation is also a determinant parameter. A kind of metal-insulator transition has been reported to occur as a function of the pH at which the polyaniline samples have been equilibrated. This effect has been observed on conductivity, thermopower, and spin dynamics properties. Furthermore proton-exchange processes are also probably involved in the high redox activity of polyaniline. The proton-exchange mechanism has been qualitatively described as an acid-base reaction as follows:

\[ \text{In this letter we present a direct proof for the proton-exchange mechanism in polyaniline and we report preliminary NMR experiments which open the way to quantitative studies.} \]

The samples have been obtained by oxidation of aniline by ammonium persulfate in a fluorhydric acid medium. They were washed in acetonitrile in a Soxhlet, equilibrated in a sulfuric acid solution of pH = 0, and dried under vacuum. They were introduced into an NMR sample holder tube in a dry box. The NMR tube was connected to a line which enabled us to monitor the water vapor pressure, \( P_{\text{H}_2\text{O}} \), on the sample while observing the NMR signal. We used a pulsed NMR spectrometer (Bruker SXP) at the frequency of 54MHz.

As shown in Fig. 1, the signal of the proton free induction decay is the superimposition of two components with different \( T_2 \)

\[ \begin{align*}
\text{a) a short } T_2 \text{ signal, or } S\text{-signal, } (T_2^{(S)} = 20\mu s), \\
\text{b) a long } T_2 \text{ signal, or } L\text{-signal, } (T_2^{(L)} = 300\mu s), 
\end{align*} \]

which is partly masked in the dead time of the spectrometer and that we attribute to the protons of the rigid polymer skeleton,

\[ \begin{align*}
\text{corresponds to protons in a mobile phase.} 
\end{align*} \]

We will call "solid" or S, and "liquid" or L, the types of protons corresponding to a) and b), respectively. With the time scale used in Fig. 1 the L-signal appears as a pedestal for the S-signal. As its amplitude is reversibly governed by \( P_{\text{H}_2\text{O}} \), we attribute the L-signal to mobile, water adsorbed at the polymer surface.

The L-signal can be removed by pumping. After one hour pumping (10⁻⁴ torr at the pump level) its amplitude is reduced to a few percents of that of the S-signal. For \( P_{\text{H}_2\text{O}} \) close to saturating vapor pressure the L-signal amplitude is about half that of the S-signal, which corresponds to about one \( \text{H}_2\text{O} \) adsorbed molecule per aniline monomer. However, accurate estimate of the amount of adsorbed water is difficult due to the fact that the starting of the signal is lost in the dead time. Detailed studies of the kinetics of water adsorption and desorption are in progress and will be published subsequently.

We have measured the proton spin-lattice relaxation time (\( T_1 \)) for the S- and for the L-signals. It turns out that they are equal (within 10%). This equality is not fortuitous. For different samples prepared in somewhat different conditions, and also for a given sample measured at different frequencies, the value of \( T_1 \) can vary. We have found values in the range 8 to 40ms. But in all cases we have obtained the same \( T_1 \) value for the two signals. This equality in \( T_1 \) shows that there is a single spin temperature for the protons, either in the solid, or in the liquid phase. Hence, a strong coupling should exist between S- and L-protons. This situation is quite similar to that described by Goldman and Shen (GS) in
LaF$_3$ \(^8\). In this material two types of fluorine are present: one type is mobile and the other is quasi-motionless. Furthermore, there exists a strong cross-relaxation between the two fluorine types. In the general case two mechanisms contribute to the cross-relaxation: spin flip-flop due to spin-spin dipole interactions and exchange of nuclei between the two phases. These mechanisms also contribute to the linewidth of the \(L\)-protons. Taking into account motional narrowing one may write:

\[
T_2^{-1} (L) = (D_{LL})^2 \tau_M + (D_{LS})^2 \tau_M + (N_A/N_L) \tau_{ex}^{-1}
\]

(1)

\[
T_{cr}^{-1} = (D_{LS})^2 \tau_M + (N_A/N_L) \tau_{ex}^{-1}
\]

(2)

where \(D_{LL}\) and \(D_{LS}\) are the spin-spin dipole interactions of protons in the \(L\)-phase, or between \(L\)- and \(S\)-phases, respectively; \(\tau_M\) is the correlation time for the motion in the \(L\) phase; \(\tau_{ex}\) is the proton exchange time between \(L\)- and \(S\)-phases; \(T_{cr}\) is the cross-relaxation time; \(N_L\) is the number of \(L\)-protons, and \(N_A\) the number of those which can be exchanged.

GS have proposed a pulse sequence to determine the cross-relaxation time. It consists in three \(\pi/2\) pulses. The first two pulses are used to prepare the spin system in such a way that the magnetization of the \(S\)-spins is zero, while the magnetization of the \(L\)-spins is not zero. The third pulse, which is sent after a variable delay \(\tau\), enables us to follow the rate at which the equality of the spin magnetizations is restored.

In Fig. 2 we see the amplitude of the \(L\)-signal as a function of \(\tau\). In the first 2 ms, the \(L\)-spin magnetization decreases because part of it is transferred to the \(S\)-spins, via cross-relaxation. Then, the magnetization increases due to spin-lattice relaxation \((T_1(L) = T_1(S) = 25 \text{ ms})\). Without the spin-lattice relaxation effect, the \(L\)-magnetization would decrease from \(M_0(L)\) to \(M_1(L) = M_0(L) \exp(-\tau_{ex})\). Determining \(M_1(L)\) by extrapolation, as shown in Fig. 2, we obtain a value for the ratio of \(S\)- to \(L\)-spins: \(N_S/N_L = 2.3\). With the assumption that the exchangeable proton spends half of the time in each phase we estimate the hydration rate to about 0.8 H$_2$O molecule per aniline ring.

From the data of Fig. 2 in the first 2 ms, we deduce the cross-relaxation time: \(T_{cr} \approx 0.7 \text{ ms}\). At the present stage it has not been established which one of the two contributions to the cross-relaxation -dipole interactions, or proton exchange- is dominant, but the reality of proton exchange has been proved as follows.

In order to visualize the proton-exchange phenomenon we have performed the experiment as shown in Fig. 3. The amplitude of the \(L\)-signal is measured as a function of time. The FID amplitude is taken during the aperture of a gate (1 ms), 45 \(\mu\)s after the end of the rf pulse (point \(t_L\) in Fig. 1). At time \(t_A\) the sample is pumped off. About 90% of the adsorbed water is removed by pumping for one hour. At time \(t_B\) a pressure of 9.2 torr of deuterated water is suddenly introduced. We observe that the proton \(L\)-signal increases.

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This is evidence that the following processes take place:

a) D$_2$O adsorption at the polymer surface. From the gaseous phase, D$_2$O molecules are condensed into the adsorbed, liquid phase, L.

b) Exchange between proton in the solid phase and deuteriums in the L-phase.

Hence, owing to the presence of D$_2$O, protons are transferred from the solid to the liquid phase and contribute to the L-signal. The rate at which the L-signal increases after introduction of D$_2$O is the same as after introduction of H$_2$O, which shows that the kinetics of the L-signal amplitude is governed by gas diffusion in the polymer matrix and not by proton exchange.

The L-signal reaches a maximum in about half an hour, and then decreases, with a time constant of ~3 hours. We attribute the decay to isotopic exchange between the liquid and the gaseous phase. Protons being exchanged with deuteriums are transferred into the gaseous phase and are lost for the L-signal.

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