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Transient effects during the electrochemical doping of cis-(CH)_x : *in situ* ESR study

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Résumé. — Nous avons étudié le dopage de type n et p *in situ* du polyacétylène cis-(CH)_x par voie électrochimique en utilisant la RPE. Une isomérisation partielle a été mise en évidence par l'observation de deux raies de RPE superposées pour un taux de dopage très faible ($Y \simeq 0,06\%$). Pour $Y \simeq 0,3\%$ une raie singulet étroite a été observée suggérant qu'un état d'isomérisation complète ou presque complète a été atteint. Le coefficient de diffusion D des contre-ions de la surface vers l'intérieur des fibres a été déduit : ($D \sim 5 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$). Nos résultats montrent que cette diffusion n'intervient pas pour déclencher le processus d'isomérisation. Nous proposons un modèle dans lequel on tient compte des informations existant sur la microstructure des fibres pour comprendre cette situation.

Abstract. — An *in situ* electron spin resonance (ESR) study has been carried out during the electrochemical doping (n and p type) of cis-(CH)_x. Partial cis-trans isomerization was deduced from the observation of two superposed ESR lines at very light doping level ($Y \simeq 0.06\%$). For $Y \simeq 0.3\%$ a single sharp line was observed suggesting that a state of complete or almost complete isomerization was reached. The diffusion coefficient D of the counterions (dopants) from the surface to the interior of the fibrils has been deduced ($D \sim 5 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$). Our results show that this diffusion which is very slow in the volume of the fibrils is not required to trigger the isomerization process. A model is proposed in order to understand this situation taking into account the existing information on the fibril microstructure.

1. Introduction.

Polyacetylene can be doped chemically [1] or electrochemically [2] through the semiconducting to the metallic regime. An enormous amount of work has been carried out with chemical doping using electron acceptors species (p-type dopants) [3]. Recently the chemical n-type doping with alkali metals has attracted attention and intense work has started [3-6].

The electrochemical doping of polyacetylene opens up a general, very simple and readily controllable means of doping with a wide variety of species which cannot be introduced by any

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obvious conventional chemical means [7]. The studies in this field present an extensive area for further research and technology especially rechargeable organic storage batteries [8]. Various *in situ* optical [9-11] and ESR [12, 13] studies have been carried out in order to investigate the cis-trans isomerization, the semiconductor to metal transition, the inhomogeneity of dopant distribution, the metallic regime, etc... during the electrochemical process. In spite of all these studies (chemical and electrochemical), the behaviour and characteristics of polyacetylene upon doping are still poorly known. In particular there is practically no information about the kinetics of the evolution of the physical properties during the doping process. Such information is needed to clarify the role played in this evolution by charge injection and molecular diffusion in the solid state. In our study, we have used an *in situ* ESR technique to investigate the modification of the magnetic properties during the electrochemical doping of cis-rich $(\text{CH})_x$.

2. Experimental techniques.

The electrochemical doping was carried out in a cell specially designed to monitor the ESR spectra during the *in situ* doping procedure. The electrochemical cell consists of a cis- $(\text{CH})_x$ film as one electrode and a lithium (Li) metal foil as the counter electrode with a 1M lithium perchlorate (LiClO_4) in tetrahydrofuran (THF) for n-type doping (propylene carbonate (PC) for p-type doping) as the electrolyte solution.

Anhydrous LiClO_4 was purified while pumping by heating gently with a smokey flame until the LiClO_4 had melted, then it was allowed to cool to room temperature before use. The preparation and construction of the electrochemical cell were carried out in a dry box under argon. The oxides on the surface of the Li ribbon were removed mechanically by scraping it with a knife. A rectangular piece of cis- $(\text{CH})_x$ (ca. 1 cm $\times$ 0.3 cm $\times$ 0.007 cm) was attached to one of the platinum wires while a piece of Li ribbon (ca. 1 cm $\times$ 0.3 cm $\times$ 0.038 cm) was attached to the other one. The two electrodes were introduced in a 5 mm ESR tube with the $(\text{CH})_x$ electrode in the bottom of the tube and the Li electrode 1 cm above. The electrolyte solution was added and the tube was sealed under vacuum.

The current and voltage were measured using Hewlett-Packard digital multimeters while the ESR spectra were recorded on a Bruker spectrometer ER200D with cavity mode TE102, microwave frequency 9.8 GHz and maximum hyperfrequency power 200 mW.

3. Experimental results.

The electrochemical n-type doping can result from a spontaneous (galvanic) process. The potential difference between the undoped $(\text{CH})_x$ electrode and the Li electrode $V_{(\text{CH})_x} - V_{\text{Li}}$ usually varies between 2.2 and 2.6 V [9]. This value depends on the method of cell construction, presence of impurities (specially oxygen), relative ratio of electrolyte to $(\text{CH})_x$ etc. [7]. A constant voltage 0.5 V (corresponding to a given doping level) was applied between both electrodes to avoid the degradation of the electrolyte solution [14].

During the doping process, the current has an instantaneous initial value $\simeq 80 \mu\text{A}$, it then dropped rapidly to $\simeq 15 \mu\text{A}$ for a few seconds and started to increase gradually to a maximum value of 100 μA , reached after 1 $\frac{1}{2}$ h. After long doping times $\simeq 7$ h the sample was heavily doped and the current decreased and reached a value $\simeq 20 \mu\text{A}$.

Before doping the ESR signal of the cis-rich $(\text{CH})_x$ film ($\simeq 85\%$ cis, 15% trans) had a single Gaussian line shape (Fig. 1) with peak to peak line width $\Delta H_{\text{pp}} \simeq 7.5$ G (Fig. 2). After the doping time $t_d = 8$ min, two superposed ESR lines were observed with similar g values but different line widths (a broad line width $\Delta H_{\text{pp}} \simeq 7.5$ G and a narrow line width $\Delta H_{\text{pp}} < 1$ G). The doping level, the charge and the instantaneous current necessary for the appearance of the narrow signal superposed on the broad one were 0.06 %, 6 mC and 38 μA respectively. After the doping time

$t_d = 18$ min, the broad signal had completely disappeared and the ESR spectrum had a single Lorentzian line shape with $\Delta H_{pp} \simeq 0.6$ G. The corresponding doping level, charge and instantaneous current necessary for the complete disappearance of the broad signal were 0.3 %, 30 mC and 57 μA respectively. Figure 2 shows that for doping levels in the range 0.3 % to 10 %, which

Fig. 1. — Evolution of the ESR signal of $\text{cis}-(\text{CH})_x$ during the electrochemical Li doping for various times, currents, charges and doping levels.

Fig. 2. — Variation of the peak to peak ESR line width of $\text{cis}-(\text{CH})_x$ with Li doping level.

correspond to doping times from 18 min to 3 hours, the peak to peak line width was approximately constant but the form of the signal (Fig. 1) had changed to a Dysonian one [15, 16]. For high doping level $\approx 18\%$ the peak to peak linewidth decreased to a remarkably small value $\Delta H_{pp} \approx 0.2$ G.

During the transition from the broad to the narrow line of the ESR spectrum the spin concentration did not change significantly. On the other hand it varied continuously and increased by nearly a factor of two for the high doping level $Y = 10\%$ if compared with the concentration at $t_d = 0$.

At the end of the doping process, the colour of the film had changed from silvery for the undoped $\text{cis}-(\text{CH})_x$ to golden for the heavily doped one. We had also observed an important increase in the length of the film, approximately 30 % of the original length, more significant than usually observed [17].

In another experiment, using a second electrochemical cell as described in section 2 and starting with $\text{cis-rich } (\text{CH})_x$ ($\Delta H_{pp} \approx 7.5$ G), two superposed ESR lines were observed upon doping with similar characteristics to the above. The doping process was stopped ($I = 0$) and the variation of the two superposed lines with time was recorded (Fig. 3). The narrow signal was observed to decrease gradually with time and completely disappear after ≈ 20 hours, while the broad signal had not changed.

Fig. 3. — Evolution of the ESR signal with the doping time t_d and the time t spent after doping.

In a third experiment, preliminary studies have been carried out on the electrochemical p-type doping of polyacetylene $[(\text{CH}^{+Y})(\text{ClO}_4)_Y^-]_x$.

The superposition of the two ESR lines has also been observed and the isomerization achieved at about the same doping levels as for the n-type doping $[\text{Li}_Y^+(\text{CH}^{-Y})]_x$. These studies are still underway.

4. Discussion.

During the electrochemical doping of cis-(CH)_x , two fundamental characteristic features have been observed.

- i) The sudden transition from a symmetric broad ESR spectrum to a symmetric narrow one for light doping levels.
- ii) The slow and gradual evolution of the symmetric narrow spectrum towards a Dysonian shape for high doping levels.

The second feature, corresponding to the evolution of the doped system from the semiconducting to the metallic state, will be discussed extensively in a further publication.

The first feature can be interpreted in terms of cis-trans isomerization of the film. The broad spectrum ($\Delta H_{pp} \simeq 7.5$ G) is characteristic of the cis-rich $(\text{CH})_x$ [18, 19] while the narrow one ($\Delta H_{pp} \simeq 0.6$ G) is coherent with the values reported for the trans- $(\text{CH})_x$ [5, 6, 18]. The cis-trans isomerization induced by chemical doping has been verified by many authors using various spectroscopic techniques [4-6, 9]. Recently electrochemical n-type and p-type doping have been shown to lead to the same result [9, 10, 20-22]. Our present work is the first study of the kinetics of the isomerization process using the *in situ* ESR technique during the electrochemical doping.

Figures 1 and 2 show that in a small range of Y values (0.06 to 0.3 %) there is a superposition of two ESR lines. Such a behaviour has already been observed during the chemical doping of cis-(CH)_x with Na [5] and Li [6] for short doping time. This suggests the coexistence of two phases in the polymer, one being already isomerized to trans- (CH) (narrow line) while the other remains as cis- (CH) (broad line) which can be attributed to the doping induced cis-trans isomerization in the doped regions (partial isomerization of the film). The phenomenon is well recognized as due to inhomogeneous distribution of current density on the $(\text{CH})_x$ film and consequently of the dopant ions. This inhomogeneity is unavoidable due to the geometry of the cell as the charge is injected at the upper part of the film (where the platinum wire is wound) and to the doping time which is only 8 minutes. The lower part is lesser doped because the resistance of the electrolyte solution is proportional to the distance between the upper part of the film (platinum contact) and the lower one. Such effect is significantly observable mainly at low doping levels ($Y < 1$ %) where almost all the properties of the polymer strongly depend on the dopant concentration. For instance it was observed that the change of colour of the $(\text{CH})_x$ film at the beginning of the doping process was non uniform (dark purple at the top and silvery at the bottom).

More evidence of the inhomogeneous doping comes from the data of figure 3. When the doping process was stopped immediately after getting the two superposed (broad and narrow) ESR lines, a peculiar behaviour of the spectrum with time was observed. The broad signal remained unchanged while the narrow one decreased towards zero with a time constant τ of the order of 20 hours. This effect can be understood by the progressive diffusion of doping species (originally concentrated near the surface) in the volume of the fibril. During this process the neutral magnetic defects became charged and diamagnetic. Such a model has already been proposed in the case of chemical Li doping of cis-(CH)_x by Rachdi *et al.* [23]. Furthermore, using the time constant τ , a rough estimate of the diffusion coefficient D of the Li^+ counterions can be deduced using the following expression [24]

$$D = \frac{r^2}{(2.405)^2 \tau}$$

where $r = 150$ Å is the mean value of the fibril radius.

Our calculated value $D \sim 5 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$ is in good agreement with that deduced for the chemical Li doping of cis-(CH)_x [23].

The number of paramagnetic centres n_s , as deduced from the ESR spectra, does not show a significant variation during the electrochemically induced isomerization process. This suggests

that the doping induced isomerization does not appreciably modify the number of neutral defects already present in the cis-rich $(CH)_x$, while thermal isomerization is known to lead to a large increase in n_s [19]. Consequently, structural defects such as for instance cross links, which are known to be present as neutral defects in thermally isomerized $(CH)_x$ [25], are probably of little importance in the present case.

Doping induced isomerization is a definitive characteristic of cis- $(CH)_x$, while the concentration range at which this occurs varies considerably with the experimental technique used to study the process. Mihaly *et al.* [27], François *et al.* [5] and Rachdi *et al.* [6] have evidenced, from Magnetic Resonance measurements (NMR and ESR) on I_2 , Na and Li doped cis- $(CH)_x$ respectively, that the isomerization could be chemically induced either with a low concentration of dopant or after a short doping time. Such a conclusion was ascertained by Raman spectroscopy [6]. This was also recently confirmed by Nigrey [21] during electrochemical doping with ClO_4 . Our study shows that through electrochemical doping of cis- $(CH)_x$ (n- or p-type) a stable situation characterized by only one narrow ESR line is reached at a concentration as low as 0.3 %. This value is comparable with the value 0.5 % reported by Mihaly *et al.* [27] for an almost complete isomerization. This comparison, as well as our small value of ΔH_{np} obtained when $Y > 0.3$ %, suggests that in our case the polymer had converted to the trans form. The fact that the measured number of spins does not appreciably change during the transition from a broad to a narrow ESR line also favours the above suggestion of a conversion to the trans form. It means that roughly the same unpaired spins originally on short trans sequences in a cis-matrix (broad line) are now mobile on long trans sequences (narrow line).

Finally figure 3 clearly shows that during the doping process the isomerization process occurs first (appearance of the narrow line) while charging the magnetic defects (became diamagnetic) on the long sequence trans segments (disappearance of the narrow line) happens later slowly as it is controlled by the diffusion of the dopant ions in the fibrils.

Thus, the above discussion strongly supports the idea of an isomerization achieved for $Y \sim 0.3$ %, with our experimental conditions.

Nevertheless, this is in strong apparent disagreement with the conclusions of Feldblum *et al.* [9], Chung *et al.* [10], Hoffman *et al.* [22] and Tanaka *et al.* [26] who have deduced from optical studies of Li, Na, and I_2 doped cis- $(CH)_x$ that any dopant interacts preferentially with the already trans regions of the system, and that a high concentration (6 %) is required for a complete cis-trans isomerization. We want to suggest that this is only an apparent disagreement which is due to differences in doping techniques used by the different authors. Two points are of main importance for this discussion.

— Chemical doping and our present electrochemical doping were performed continuously. In this case the system is permanently far from equilibrium as far as the dopant concentration limit is not attained. This implies high doping rates or high current densities. On the contrary optical measurements used a step by step electrochemical process [9, 10, 22]. During each step the system was maintained close to its equilibrium and consequently current densities were small.

— Preliminary results show that the doping level at which the ESR broad line totally disappears increases when the doping current decreases. Taking into account these remarks we suggest that the rate at which the polymer is doped is of prime importance for the definition of the doping level at which isomerization is achieved. With a low doping rate, the doping process and the diffusion process of the ions in the fibrils take place simultaneously while at high doping rate diffusion can be neglected for short times. For the second case (high doping rates) a significant concentration of the dopant ions at the surface of the fibrils can be achieved very rapidly and at low doping level. Then, isomerization occurs when sufficient concentration allows the triggering of a collective process. For the first case of low doping rates, the dopant ions have sufficient time to diffuse inside the fibrils to preferentially dope the trans segments in the predominantly cis- $(CH)_x$. If there is insufficient trans segments, then doping will tend to induce partial isome-

rization to such a level in order for the former process to occur [9]. In this case the isomerization can be achieved but at higher doping levels. From the above discussion we find that the apparent disagreement between the optical studies and the magnetic studies can be attributed to the doping techniques used.

Finally we propose the following model to explain our experimental results :

— For a short time scale, electrochemical doping is a surface effect. Electrons or holes (coming from the external circuit) and counterions (coming from the electrolyte solution) interact primarily at the external surface of the fibrils.

— At the time doping occurs at the surface of the fibrils, isomerization (according to the models proposed by Yamabe *et al.* [28] and Chien [29]) takes place and propagates in the whole volume of the fibrils.

— The isomerization can be achieved for a sufficient concentration of the dopant ions at the surface of the fibrils corresponding roughly to the adsorption of at least one dopant molecule per chain of $(\text{CH})_x$ (taking 500 as a mean value for the number of carbon atoms per chain [30]). To explain this correspondance we must assume that a great majority of the chains in a fibril have a non negligible chance to be close to the surface somewhere on their path. This assumption is in agreement with the model which represents a fibril as consisting of a great number of micro-crystallites separated by more or less amorphous regions [31].

In conclusion, we have shown that the electrochemical doping *in situ* in the ESR cavity is a very interesting technique to study all the mechanisms which are initiated by the presence of a dopant and particularly the cis-trans isomerization.

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References

- [1] SHIRAKAWA, H., LOUIS, E. J., MACDIARMID, A. G., CHIANG, C. K., HEEGER, A. J., *J. Chem. Soc. D* (1977) 578.
- [2] NIGREY, P. J., MACDIARMID, A. G., HEEGER, A. J., *J. Chem. Soc. D* (1979) 594.
- [3] « International Conference on the Physics and Chemistry of Conducting Polymers ». Les Arcs, Décembre 1982, *J. Physique Colloq.* **44** (1983) C3.
- [4] CHUNG, T. C., FELDBLUM, A., HEEGER, A. J., MACDIARMID, A. G., *J. Chem. Phys.* **74** (1981) 5504.
- [5] FRANÇOIS, B., BERNARD, M., ANDRÉ, J. J., *J. Chem. Phys.* **75** (1981) 4142.
- [6] RACHDI, F., BERNIER, P., FAULQUES, E., LEFRANT, S., SCHUE, F., *Polymer* **23** (1982) 173.
- [7] KANETO, K., MAXFIELD, M., NAIRNS, D. P., MACDIARMID, A. G., HEEGER, A. J., *J. Chem. Soc., Faraday Trans 1* **78** (1982) 3417.
- [8] NIGREY, P. J., MACDIARMID, A. G., HEEGER, A. J., *Mol. Cryst. Liq. Cryst.* **83** (1982) 1341.
- [9] FELDBLUM, A., HEEGER, A. J., CHUNG, T. C., MACDIARMID, A. G., *J. Chem. Phys.* **77** (1982) 5114.
- [10] CHUNG, T. C., MACDIARMID, A. G., FELDBLUM, A., HEEGER, A. J., *J. Polym. Sci., Polym. Lett. Ed.* **20** (1982) 427.
- [11] FELDBLUM, A., KAUFMAN, J. H., ETEMAD, S., HEEGER, A. J., CHUNG, T. C., MACDIARMID, A. G., *Phys. Rev. B* **26** (1982) 815.
- [12] KISPERT, L. D., JOSEPH, J., JAYARAMAN, T. V., SHACKLETTE, L. W., BAUGHMAN, R. H., *J. Physique Colloq.* **44** (1983) C3-317.
- [13] BERNIER, P., EL-KHODARY, A., RACHDI, F., *J. Physique Colloq.* **44** (1983) C3-307.

- [14] ARMAND, M., *J. Physique Colloq.* **44** (1983) C3-551.
 - [15] FEHER, G., KIP, A. F., *Phys. Rev.* **98** (1955) 337.
 - [16] BERNIER, P., BILLAUD, D., KULSZEWICZ, I., *C.R. Acad. Sci. Paris* **297** (1983) 231.
 - [17] FRANÇOIS, B., MERMILLIOD, N., ZUPPIROLI, L., *Synth. Met.* **4** (1981) 131.
 - [18] SHIRAKAWA, H., ITO, T., IKEDA, S., *Makromol. Chem.* **179** (1978) 1565.
 - [19] BERNIER, P., LINAYA, C., ROLLAND, M., ALDISSI, M., *J. Physique* **42** (1981) 295.
 - [20] LEFRANT, S., private communication.
 - [21] NIGREY, P. J., Ph. D. Thesis, Philadelphia, 1983.
 - [22] HOFFMAN, D. M., GIBSON, H. W., EPSTEIN, A. J., TANNER, D. B., *Phys. Rev. B* **27** (1983) 1454.
 - [23] RACHDI, F., BERNIER, P., FAULQUES, E., LEFRANT, S., SCHUE, F., *J. Chem. Phys.*, to be published.
 - [24] JOST, W., *Diffusion in solids, liquids and gases* (Academic Press, New York, 1960).
 - [25] BERNIER, P., *Mol. Cryst. Liq. Cryst.* **83** (1982) 1089.
 - [26] TANAKA, K., YOSHIZAWA, K., OHZEKI, K., YAMABE, T., *Solid State Commun.* **45** (1983) 391.
 - [27] MIHALY, I., PEKKER, S., JANOSSY, A., *Synth. Met.* **1** (1979) 349.
 - [28] YAMABE, T., AKAGI, K., SHIRAKAWA, H., OHZEKI, K., FUKUI, K., *Chem. Sci.* **17** (1981) 157.
 - [29] CHIEN, J. C. W., *J. Polym. Sci., Polym. Lett. Ed.* **19** (1981) 249.
 - [30] SHIRAKAWA, H., SATO, M., HAMANO, A., KAWAKAMI, S., SOGA, K., IKEDA, S., *Macromolecules* **13** (1980) 457.
 - [31] ROBIN, P., POUGET, J. P., COMES, R., GIBSON, H. W., EPSTEIN, A. J., *J. Physique Colloq.* **44** (1983) C3-77.
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