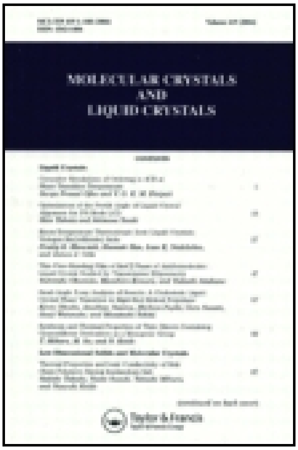

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Cis-Trans Isomerization During the Electrochemical Doping of Cis-$(CH)_x$: In Situ ESR Study

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CIS-TRANS ISOMERIZATION DURING THE ELECTROCHEMICAL DOPING OF Cis-$(CH)_x$: IN SITU ESR STUDY

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Abstract An in situ Electron Spin Resonance (ESR) study has been carried out during the electrochemical n-type doping of cis-$(CH)_x$. The cis-trans isomerization is observed after a doping-undoping cycle. The doping level at which the isomerization can be achieved is in the range $\sim 0.3 \rightarrow 0.8$ %. Our results show that this level depends on the rate at which the polymer is doped and that the isomerization process implies a collective motion of the chains at the scale of the fibrils.

INTRODUCTION

The cis-trans isomerization of $(CH)_x$ can be attained by a thermal treatment[1] or via a doping-undoping cycle[2] (chemical or electrochemical). No agreement has been reached yet concerning the doping level at which isomerization starts or the level at which it is complete[2]. For this reason we have performed in situ ESR experiments in order to study continuously the kinetics of the isomerization process during the electrochemical doping and undoping of cis-$(CH)_x$.

EXPERIMENTAL TECHNIQUE

The electrochemical cell consisted of a cis-$(CH)_x$ film as one electrode and a lithium (Li) metal slab as the counter electrode with 1 M $LiClO_4$ in THF as the electrolyte solution. The two electrodes were introduced in a 5 mm ESR tube with the $(CH)_x$ electrode in the bottom and the Li electrode 1 cm above.

RESULTS AND DISCUSSION

Figure 1 shows that before doping the ESR spectrum had a broad

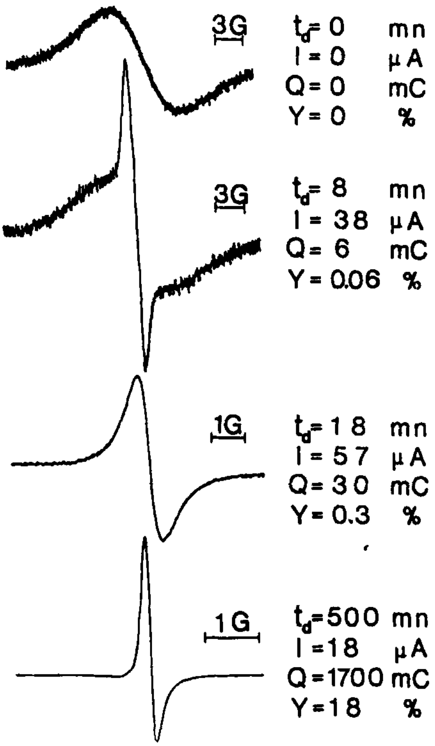

FIGURE 1 Evolution of the ESR signal of cis-(CH)$_x$ during the electrochemical Li doping for various time, current, charge and doping level.

signal (Gaussian shape) with a peak to peak line width ΔHpp $\sim$ 7 G characteristic of cis-(CH)$_x$[1]. A superposition of two signals (broad with ΔHpp $\sim$ 7 G and narrow with ΔHpp $\sim$ 1 G) has been observed for a doping level as low as $y \sim 0.06$ %. The superposition is due to the inhomogeneous distribution of current density on the (CH)$_x$ film and so of the dopant distribution (the upper part of the film being more doped than the lower) as a consequence of the geometry of the cell. For doping levels higher than y_i ($y_i \sim 0.3$ to 0.8 % depending on the experimental conditions) the broad signal completely disappeared and the ESR spectrum consisted of a single narrow line

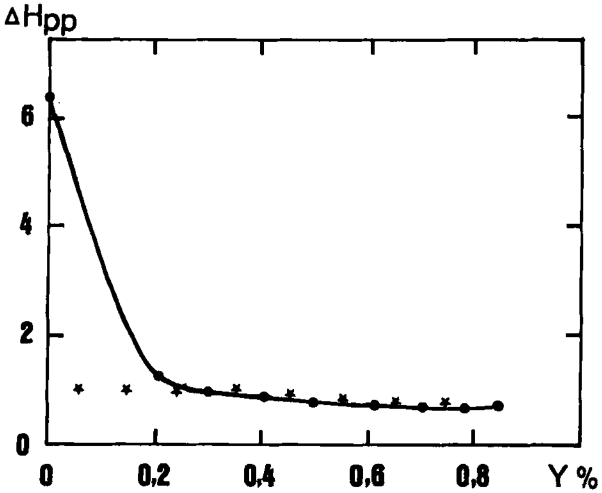

FIGURE 2 The variation of ΔHpp of cis-$(CH)_x$ with the doping level when ●doping ✱undoping

(Lorentzian shape) with ΔHpp ~0.8 G characteristic of trans $(CH)_x$[1,3,4]. The variation of ΔHpp with the doping level is shown in Figure 2. The doped film (y ~ 0.9 %) could be undoped by applying the potential characteristic of the parent $(CH)_x$. At the end of the undoping process, the ESR spectrum had the same Lorentzian shape and the same peak to peak line width ~0.8 G as in the doped case. The ESR intensity (undoped) was substantially smaller than in the doped case but not significantly different from the intensity of the initial cis-rich-$(CH)_x$. The sudden decrease of ΔHpp from ~7 G to ~0.8 G when doping is attributed to the isomerization process[9] and the constant value of ΔHpp ~ 0.8 G during undoping suggest that a state of complete or almost complete isomerization has been reached. y_i is then the doping level at which the isomerization is achieved and its value (0.3 to 0.8 %) is comparable with the value 0.5 % reported by Mihaly et al[5]. The short doping time (low doping level) reported by François et al[3] and Rachdi et al[4] for the isomerization is also consistent with our result.

On the other hand, our value is in strong apparent disagreement with Chung et al[2], Feldblum et al[6], Hoffman et al[7] and Tanaka et al[8] who have deduced that a high concentration ∿6 % is required for a complete isomerization. We think that this is only an apparent disagreement due to differences in doping techniques.

Two very important points must be clarified :

- Chemical doping[3,4] and our electrochemical doping were performed continuously. In this case the system is permanently far from equilibrium for high doping rates or high current densities. On the contrary optical measurements[2,6-8] used a step by step electrochemical process. During each step the system was close to its equilibrium and consequently current densities were small.
- Preliminary results show that the value of the doping level y_i depends on the doping current I(y_i increases when I 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 y_i at which the isomerization is achieved. We propose the following model to explain our experimental results :

* For short time, as the electrochemical doping is a surface effect, the majority of the charges injected at the surface of the fibrils has no time to diffuse inside the fibrils (the diffusion coefficient of Li^+ in the solid phase is ∿ 5×10^{-18} cm^2 sec^{-1} [9]).

* There is a given concentration of dopant ions at the surface of the fibrils (corresponding roughly to one dopant per chain of $(CH)_x$ [9]) at which the isomerization can occur as a collective process i.e. for the whole volume of the fibrils.

* For high doping current values, this concentration can be attained very rapidly (consequently at very low doping level) and the isomerization can be achieved.

* The doping level (obtained as a <u>mean value over the whole sample</u>) at which the isomerization can be achieved y_i is much less than the <u>local</u> dopant concentration close to the surface of the fibril.

* When the doping is performed very slowly the collective motion of the chains cannot be triggered. Parts of the fibrils which are already isomerized are preferentially doped and a total isomerization is reached only for high dopant concentration.

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