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ESR study of the electrochemical doping of polyacetylene with potassium

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In this study we present the first experimental evidence of staging during doping of $(CH)_x$ with potassium, obtained from ESR measurements. For that purpose, we have followed the peak-to-peak linewidth of the ESR signal during successive electrochemical doping-undoping cycles. We have also measured the open-circuit potential difference V_{oc} of the cell. The behavior of the linewidth related to V_{oc} shows that doping and undoping occur via a sequence of successive ordered phases corresponding to various intercalation stages: A simplified model of a pseudobiphasic system can explain qualitatively the variations of the linewidth. However, the observed behavior demonstrates the existence of an ordered phase at a doping level of 2%, during the undoping process, which is not revealed from the variations of V_{oc}.

INTRODUCTION

The existence of well-organized structures in polyacetylene $(CH)_x$ doped with alkali metals has been previously demonstrated: Ion intercalation is suggested to occur via a sequence of crystalline phases and not randomly along and among the polymer chains.[1,2]

For the *n*-type doping, the dopant species is well defined. Furthermore, in the case of potassium, the diameter of the K^+ ion is a good match for the available space in $(CH)_x$.[1] The technique of electrochemical doping allows us to dope and undope (reversibility studies), knowing at any time the doping level. For these reasons, the electrochemical doping of $(CH)_x$ with K is of particular interest for the investigation of the mechanism of ion intercalation in $(CH)_x$.

Recent experiments have shown that ESR can provide information about the specific effects of the dopant on the properties of the doped system. For instance, the ESR linewidth is very sensitive to the nature of the dopant, varying from 0.1 G for Li to more than 300 G for Cs.[3] It has been shown that the origin of such widely spread values is the spin-orbit coupling of the conduction electrons with valence electrons on the dopant site.[3,4] In the case of $(CH)_x$ heavily doped with potassium, a linewidth in the range of 20 to 50 G has been measured by various authors.[5,6] Therefore, during electrochemical doping, the linewidth is expected to vary from $\sim$1 G, characteristic of the undoped state, over more than one decade to the highest doping level. We therefore use the spin-orbit coupling as a probe of the local electronic properties on the dopant site, with the purpose of investigating the likely transitions occurring during intercalation of potassium in $(CH)_x$. The present paper describes preliminary results of such a study performed using an electrochemical cell designed for *in situ* ESR measurements.

EXPERIMENTAL TECHNIQUE

The electrochemical cell consisted of a cis-rich (85% cis–15% trans) polyacetylene $[(CH)_x]$ film (380 μm thick) as one electrode, of metallic potassium as the counter electrode, and of a 1*M* solution of potassium cyanide (KCN) in tetrahydrofuran (THF) with 1*M* triethyl boron $[(C_2H_5)_3B]$ as the electrolytic solution. The triethyl boron is needed to solubilize the potassium cyanide in the solvant; it does not play any role in the electrolytic process. A detailed description of the cell construction has been presented elsewhere.[7]

Prior to doping, the potential difference between the $(CH)_x$ electrode and the alkali metal was in the range 1.6 to 1.8 V. The electrochemical doping occurred during a galvanic process, involving a spontaneous current flowing between the two electrodes via an external circuit, leading to the system $(CHK_y)_x$. The doping level y was determined from the charge injected into the $(CH)_x$ (or removed during the undoping process) and the weight of the polymer film. The electrochemical cell was placed in the ESR cavity of a Bruker ER200D spectrometer operating at room temperature, and ESR spectra were recorded continuously during doping or undoping.

Measurements of the open-circuit potential difference, V_{oc}, between the $(CH)_x$ electrode and the K electrode, versus the dopant concentration, were taken at incremental doping levels. The doping level was stepped in 0.3–0.5% increments (doping) or decrements (undoping). During each step a current in the range 4–6 μA/mg was used. After each step, the circuit was opened for $\sim$20 h and then the potential difference V_{oc} was recorded.

EXPERIMENTAL RESULTS

The neutral cis-rich $(CH)_x$ has an ESR signal with a peak-to-peak linewidth $\Delta H_{p.p.} \sim 6$ G, characteristic of the cis-isomer. For very light doping levels a narrow signal of linewidth $\Delta H_{p.p.} \sim 1$ G (characteristic of the trans-isomer) was superimposed on the broad signal. At a doping level y of 0.3% the broad signal had almost totally disappeared, indicating a state of near total isomerization.[8,9] Subsequent spectra, obtained during the various cycles, showed only a single line. Up to 3%, this signal remained narrow with $\Delta H_{p.p.} \sim 1$ G (Fig. 1). Between 3% and 6% the

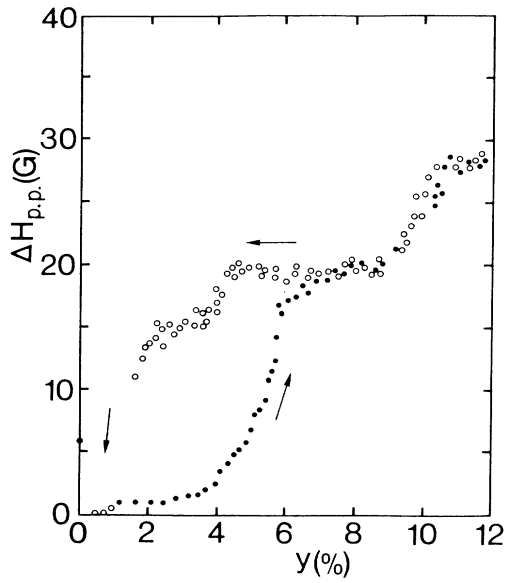

FIG. 1. Evolution of the peak-to-peak linewidth $\Delta H_{p.p.}$ vs the doping level y during the first cycle. Filled circles: doping. Open circles: undoping.

linewidth increased continuously from 1 to 17 G and then slowly increased (quasiplateau behavior) to 19 G at $y \sim 8\%$. Between 8% and 10% the linewidth increases again to 28 G and remained constant at this value for $y > 10\%$.

During the undoping process the behavior of $\Delta H_{p.p.}$, compared to the doping process, was totally reversible in the range 12% to 8% (Fig. 1). For undoping from 8% to 4%, the linewidth remained constant at the 19-G plateau.

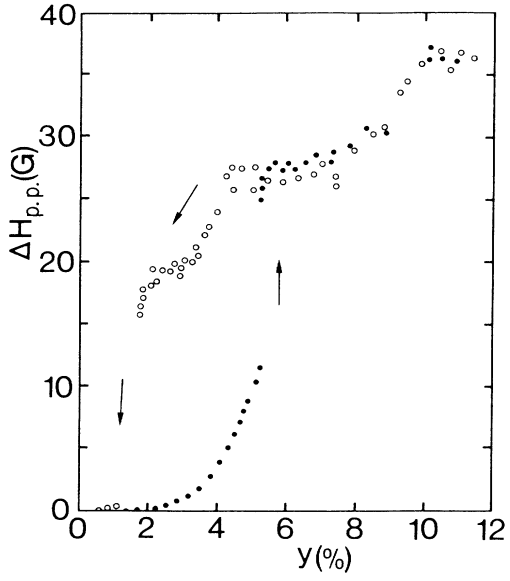

FIG. 2. Evolution of the peak-to-peak linewidth $\Delta H_{p.p.}$ vs the doping level y during the second cycle. Filled circles: doping. Open circles: undoping.

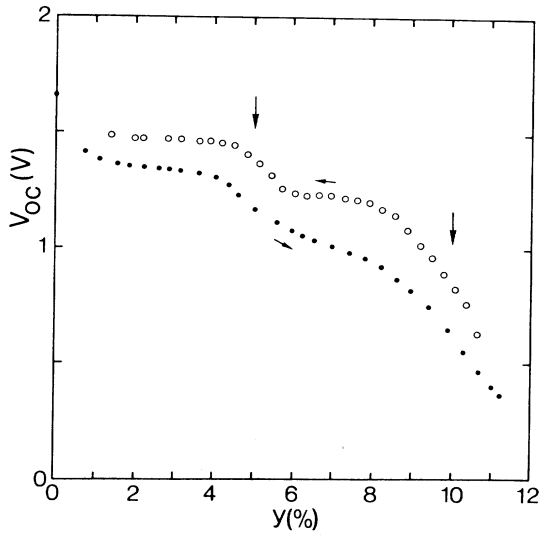

FIG. 3. Evolution of the open circuit potential V_{oc} vs the doping level y. Filled circles: doping. Open circles: undoping.

A decrease of $\Delta H_{p.p.}$ from 19 to 15 G was observed between 4.5% and 3%, followed by a quasi plateau of linewidth 15 G for doping levels from 3% to 2%. At a doping level less than 2%, the linewidth decreased sharply to 0.2G at $y = 0.5\%$; at this point the current was very small and the undoping process was stopped.

In order to test the possible existence of transient effects, we have observed the evolution of the linewidth after stopping the doping or undoping processes at several levels chosen in each range of concentration where a $\Delta H_{p.p.}$ plateau occurred. In such cases the linewidth values did not change with time, indicating that in each case the material was in a stable form.

The second and all subsequent cycles showed essentially the same features as the first one; in particular, the hysteresis during undoping was still evident (Fig. 2). Nevertheless, the values of $\Delta H_{p.p.}$ for the plateaus were systematically greater during the first cycle.

The behavior of V_{oc} during the doping process can be described by several plateaus (Fig 3). Vertical arrows mark two regions where the first derivative versus the doping level $-(dV_{oc}/dy)$ present a maximum: one main around 5% and a weaker one close to 10%. Note that the curve corresponding to the undoping process is significantly different in shape and amplitude, but the maxima of $-(dV_{oc}/dy)$ occur roughly at the same doping level.

DISCUSSION

It is now definitely accepted that for alkali-metal-doped $(CH)_x$ the spin-orbit coupling[3,4] is the dominant electronic relaxation process in which the dopant plays the main role. ESR studies performed on $(CH)_x$ doped chemically with Li to Cs have verified this proposition. Our result of a maximum of $\Delta H_{p.p.} = 37$ G, during the electrochemical doping with potassium, is also in good agreement with this model.

From Figs. 1 and 2 it is clear that, starting from less than 1 G for lightly doped $(CH)_x$, the evolution of $\Delta H_{p.p.}$ with y shows remarkable features, around 6% and 10% during the doping process and around 10%, 4.5%, and 2% during the undoping process. We suggest that this behavior is associated with the existence of intercalation stages as proposed by Shacklette and Toth.[2] Furthermore, the observation of V_{oc} vs y immediately shows that the features in $\Delta H_{p.p.}$ correspond reasonably (except for y 2%) to the arrows which mark the completion of given stages. It is then reasonable to suggest that the ESR linewidth of $(CHK_y)_x$ proceeds through a sequence of increasing values corresponding to successive stages of given composition when y increases. For each stage, there corresponds a specific ordered structure with a characteristic residence time of the conduction electrons on the dopant site. As the structure of the stage changed, the residence time, and therefore the ESR linewidth, is changed and then the linewidth. In Fig. 1, we identify three values of $\Delta H_{p.p.}$ at 15, 19, and 28 G; in Fig. 2 the observed values at the plateaus are 19, 27, and 37 G. The fact that the first cycle is quantitatively different from the others is probably associated with the doping-induced isomerization which needs a full cycle to be achieved. Incomplete isomerization results in a chain-to-chain distance slightly greater than in the pure trans $(CH)_x$ as shown by Elsenbaumer *et al.*[6] and, consequently, a less efficient spin-orbit interaction yielding a smaller linewidth. As the hysteresis has been observed during all successive cycles, it cannot be related to the isomerization process.

The general behavior of $\Delta H_{p.p.}$ can be understood in terms of a two-phase model. Let us consider that the ESR spectra are a combination of two components arising from each phase, say A and B, of the system. It can be shown that, due to the experimental determination of $\Delta H_{p.p.}$ (distance between the peaks of the absorption derivative), the measured linewidth does not have a linear dependence versus composition, but shows marked plateaus with sharp increases between them.[10] For instance, in the transition from the phase A with $\Delta H_{p.p.}=27$ G to the phase B with $\Delta H_{p.p.}=37$ G, the largest width was dominant only when 90% of the system was of the phase B.

One important consequence of the above model is that the doping of $(CH)_x$ with K (and probably with the other alkali metals) is intrinsically inhomogenous, in agreement with the most recent model concerning the structural and electronic properties of doped $(CH)_x$.[11]

To the contrary, the existence of staging is very often accompanied by hysteresis of the physical properties. Such an effect probably occurs in our case in the range 4%–6% where a significant delay is observed before the decrease of $\Delta H_{p.p.}$ from 27 G (from 19 G for the first cycle).

Staging is probably also the origin of the plateau at 19 G (at 15 G for the first cycle) appearing down to 2.5%. In effect, stages which do not appear during the *doping* process can be stabilized during the *undoping* process by dilution of stages present at high concentration. Such behavior has already been suggested by Shacklette and Toth[2] for the same systems. The reason why this stage does not appear in the variation of V_{oc} vs y is not understood at the moment.

These preliminary results clearly show that *in situ* ESR can be a very powerful technique to investigate staging during the doping of $(CH)_x$ with potassium. We are presently extending our measurements over various successive cycles, other types of dopants, and variable temperature. We are also studying in detail the evolution of the ESR line shape in order to obtain information on the dynamic properties of the conduction electrons.

ACKNOWLEDGMENTS

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