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In Situ Raman and Epr Investigations of A Cis-(Ch)_x Electrode

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IN SITU RAMAN AND EPR INVESTIGATIONS OF A $\text{CIS}-(\text{CH})_x$
ELECTRODE

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Abstract In situ Raman and EPR experiments have been performed on a $\text{cis}-(\text{CH})_x$ electrode in an electrochemical cell $\{[(\text{CH})_x]/1\text{M LiClO}_4 \text{ in THF/Li}\}$. After a n-type doping with Li, the Raman spectra exhibit new features at $\approx 1600 \text{ cm}^{-1}$ and 1270 cm^{-1} , comparable to those obtained with $(\text{CH})_x$ films Li doped via a chemical treatment. The evolution of the EPR signal is followed in a doping-dedoping cycle, showing both the reversibility of the process as well as the evidence for a metallic behavior at the maximum doping concentration.

The electrochemical cell was used in this study built at the University of Pennsylvania in a purified argon atmosphere dry box. One electrode was made of a cis-rich $(\text{CH})_x$ film mechanically pressed onto a platinum grid. The second one was made of a lithium plate. The two electrodes were separated by a kiln - dried glass filter paper and the entire assembly was inserted into a small rectangular glass cell in which a 1.0 M $\text{LiClO}_4/\text{THF}$ electrolyte was added.

The open-circuit voltage V_{OC} of the as prepared cell was 2.30 V as typically observed (1). The n-doping of the $(\text{CH})_x$ film was achieved by lowering the potential of the cell down to $\approx 1.2 \text{ V}$

and the dedoping by increasing it back to 2.3 V. The average dopant concentration y was determined by measuring the charge passed during the dedoping process. The result was confirmed by the V_{OC} voltage measured after doping from the V_{OC} versus y curves determined previously for this system (2). The Raman spectra were taken after the first doping process and the EPR experiments were performed during the second doping-dedoping cycle.

The Raman spectra were recorded using standard equipment, with all the conventional wavelengths (λ_L) emitted either from a krypton or an argon cw laser. At the beginning of the doping process, no change in the Raman spectrum was detected (until $y \approx 0.02$ %), the Raman lines assigned to the cis isomer, together

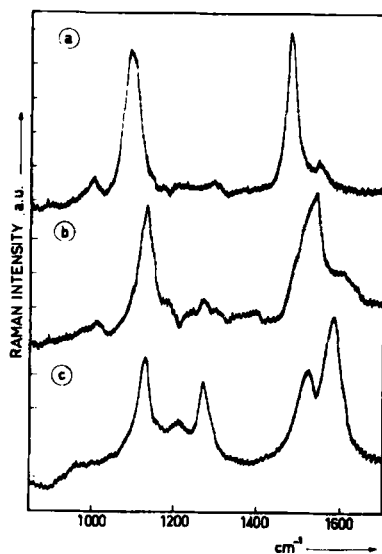


FIGURE 1 Raman spectra of $\{Li_y^+(CH)^{-y}\}_x$ taken in situ in the electrochemical cell at $20^\circ C$; ($y \approx 0.04$).
 a) $\lambda_L = 676.4$ nm ; b) $\lambda_L = 457.9$ nm ;
 c) $\lambda_L = 514.5$ nm.

with the bands characteristic of a small amount of trans being

observable. After a doping evaluated to $y \approx 4\%$, the Raman spectra obtained are presented Figure 1 for different excitation wavelengths. Two peaks are observed at 1070 and 1460 cm^{-1} for $\lambda_L = 676.4$ nm, shifted to 1136 and 1544 cm^{-1} for $\lambda_L = 457.9$ nm. For $\lambda_L = 514.5$ nm, strong additional bands are seen at ≈ 1570 – 1600 cm^{-1} and 1270 cm^{-1} . These new features are a general result of a n-type doped $(\text{CH})_x$ system as reported by Eckhardt et al. (3) and observed in Na-doped $(\text{CH})_x$ (4). These additional bands disappear completely after an electrochemical dedoping and only the Raman bands due to a trans isomer are still observed.

On Figure 2 are presented successive ESR spectra obtained

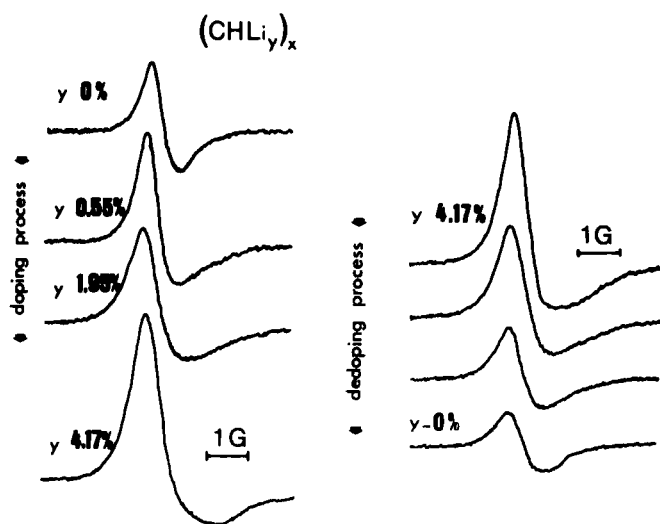


FIGURE 2 Successive EPR spectra of $\{(\text{CH})^{-y}\text{Li}_y^{+}\}_x$ during the doping and the dedoping processes.

during the doping and the dedoping processes. We started from an ESR spectrum characteristic of the trans isomer resulting from a first doping-dedoping cycle [the A/B ratio was about 1.7 due to the presence of the electrolyte solution, and the ΔH_{pp} was about 1 G]. Then, an increase of the A/B ratio, as well as the intensity

of the ESR signal are observed upon doping. For the highest concentration, $y \approx 4.17\%$, we found $A/B \approx 3.6$. Upon dedoping, the signal intensity and the A/B ratio decrease to come back to their initial value after the complete cycle.

The combined in situ ESR and Raman experiments, of a Li-doped $(CH)_x$ electrode yield important information about the n-type doping process. From the ESR experiments, it is proved that for $y \approx 4.17\%$, a metallic state has been reached and the reversibility of the process is demonstrated, once the isomerization has occurred (2nd cycle). In Raman experiments, the new features already seen in $(CH)_x$ chemically doped with Li are again observed with the appearance of two additional mode at 1600 cm^{-1} and 1270 cm^{-1} . The Raman mode at 1600 cm^{-1} seems to characterize any doped system since it appears even in p-doped $(CH)_x$ (5). The mode at 1270 cm^{-1} does not depend upon the n-type dopant. Its assignment is not quite clear, but it must be noticed that an IR mode at this wavenumber is seen in the IR absorption of doped systems. An alternative explanation can be given by ab initio calculations performed by Zerbi et al. who showed that a mode at 1260 cm^{-1} is predicted for an undimerized chain. Finally, upon dedoping, a spectrum of a good trans isomer can be recorded, and this result confirm the good reversibility of the process. This reversibility was also shown by similar Raman experiments on electrochemically p-doped $(CH)_x$, as shown recently(6).

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