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STRUCTURAL CHANGES OF DOPED POLYACETYLENE DURING THE ELECTROCHEMICAL CHARGE AND DISCHARGE PROCESS

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Abstract Results of in situ Raman scattering during the electrochemical p-doping of cis- and trans-polyacetylene are reported. Doping the cis-isomer led to a complete cis-trans isomerization. During the discharge process, a down-shift of the Raman line for the C=C stretch mode without any increase of intensity was observed. Starting the doping process with trans-polyacetylene, the disordered parts dope first whereas the crystalline parts undope first.

1. INTRODUCTION

Polyacetylene ((CH)) has attracted very strong interest in chemical and physical research work. This is mainly due to the very strong enhancement of conductivity upon doping. Raman spectroscopy has proved to be a very useful tool to study undoped and doped polyacetylene. Since e.g. the spectra of the cis-and of the transisomerare different, the isomerization process can be analysed in detail. In addition the strong resonance enhancement of several modes for the transisomer in connection with a photo selection of the scattering process allows to determine the distribution of undisturbed series of conjugation on the chain, and to analyse details of the doping mechanism.

2. EXPERIMENTAL TECHNIQUES

High quality cis-polyacetylene was prepared according to the Shirakawa method. The original trans-contamination after preparation was about 20 %. Raman scattering experiments were carried out in situ through a quartz window of an electrochemical cell. Excitation of the spectra was performed throughout with a 4579 Å

laser line (20 mW, line focus). The scanning time for the spectra was kept below 20 minutes to reduce laser induced cis-trans isomerization to a minimum and to prevent laser induced sample damage. In the electrochemical cell polyacetylene was clamped to a nickel contact at the working electrode. Lithium strips were used as reference and counter electrode. The electrolyte consists of 0.3 Mol dried LiClO₄ in propylen-carbonat. In all doping experiments polyacetylene was p-doped by increasing the positive potential of the working electrode to about +3,9 V versus Li.^{6,7} Potentials will always be given versus the Li-reference electrode.

3. EXPERIMENTAL RESULTS

High quality cis-(CH) $_{\rm X}$ was measured during the doping process. The original trans-contamination after preparation was about 20 %.

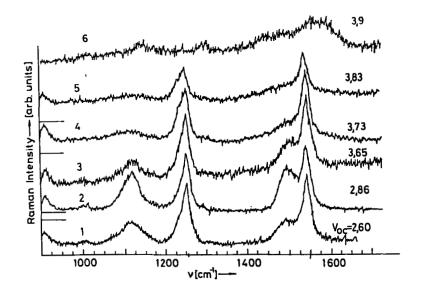


FIGURE 1 Doping of cis-polyacetylene

Trace 1 of Fig.1 shows the spectra of the sample at 77 K. The strong lines at 1540 cm $^{-1}$, 1250 cm $^{-1}$ and 910 cm $^{-1}$ are the off resonance Raman lines of the cis isomer whereas the broad features around 1500 cm $^{-1}$ and 1120 cm $^{-1}$ refer to the trans contamination. Inserting the polymer into the chemical cell and checking the spectra again results in an increase of the lines from the trans-

isomer. Charging the polymer at 3,9 V for various time intervals yields succesively the Raman spectra 3 to 6. These spectra show, that the trans Raman-lines vanish first, which is definite evidence, that the trans part of the polymer dopes first. Only after 4 % doping ($V_{\rm OC}=3,73$ V) the cis part of the polymer gets doped as well. Trace 6 shows the spectra of the highly doped polymer. The resonance enhancement of the lines disappeared and the spectra finally developed into a composition of weak and broad superposed lines with an upshifted mode for the C=C stretch mode towards nearly $1600~{\rm cm}^{-1}$.

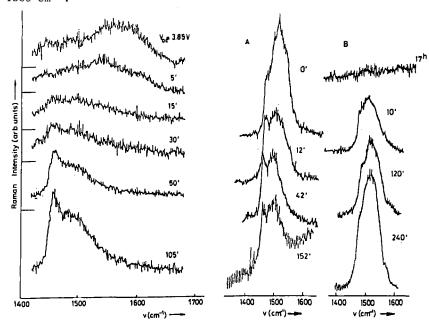


FIGURE 2 Undoping of cis- FIGURE 3 Doping and undoping of polyacetylene trans-polyacetylene

Detailed studies of the undoping process are shown in Fig.2. In the initial part a well pronounced down shift of the C=C stretch mode from 1560 cm⁻¹ to 1470 cm⁻¹ without any increase of the line intensity was observed. We suggest that this doping induced upshift of the line position for the C=C stretch mode is due to mechanical deformation of the chain by the dopand. The deformation is relaxed in the initial process of undoping. Another interesting fact is, that the cis-line at 1540 cm⁻¹ has disappeared. A complete cistrans isomerization had occured. Fig.3 shows the change of the C=C stretch mode during the doping process of trans (CH). The result (part A) clearly shows that the high frequency part of