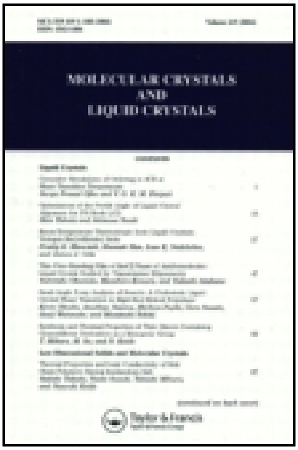

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Structural Changes of Doped Polyacetylene During The Electrochemical Charge and Discharge Process

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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 ($(CH)_x$)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.[1-3] Since e.g. the spectra of the cis-and of the trans-isomer are different, the isomerization process can be analysed in detail. In addition the strong resonance enhancement of several modes for the trans-isomer in connection with a photo selection of the scattering process allows to determine the distribution of undisturbed series of conjugation on the chain,[4] and to analyse details of the doping mechanism.[5]

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 $LiClO_4$ 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-$(CH)_x$ was measured during the doping process. The original trans-contamination after preparation was about 20 %.

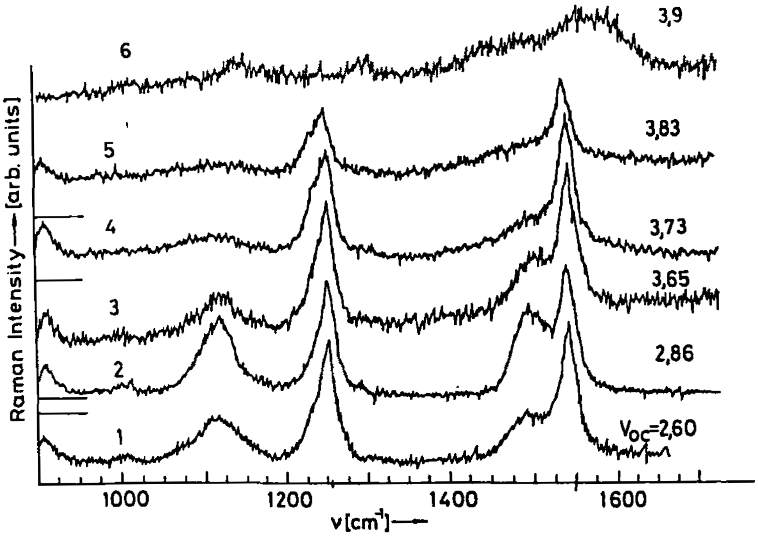

FIGURE 1 Doping of cis-polyacetylene

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 ($V_{OC} = 3,73$ 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 cm^{-1}.

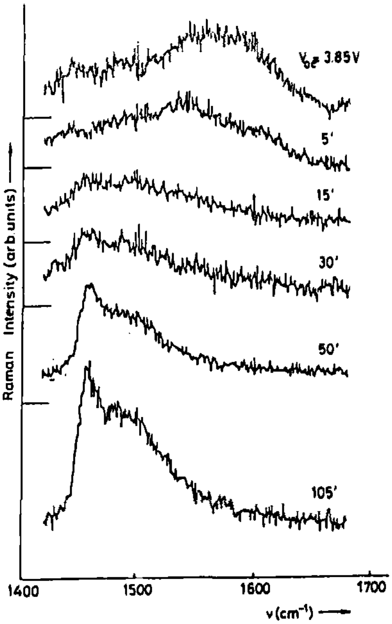

FIGURE 2 Undoping of cis-polyacetylene

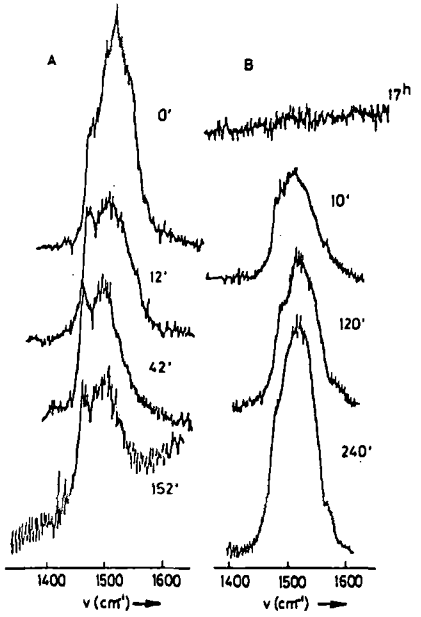

FIGURE 3 Doping and undoping of trans-polyacetylene

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 cis-trans isomerization had occured. Fig.3 shows the change of the C=C stretch mode during the doping process of trans $(CH)_x$. The result (part A) clearly shows that the high frequency part of