In situ Raman spectroscopy of the electrochemical doping process in polyacetylene

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(Received 31 January 1984)

Results of *in situ* Raman scattering experiments during the electrochemical *p* doping of *cis*- and *trans*-polyacetylene are reported. Doping the *cis*-isomer led to a complete isomerization, and a phase separation between the doped and the undoped parts of the samples is observed. The disordered *trans*-polymer dopes faster as compared with the *cis*-isomer and the crystalline *trans*-isomer. During the discharge process the crystalline parts of the *trans*-isomer undope first.

Raman spectroscopy has proved to be a very useful tool to study undoped and doped polyacetylene $(CH)_x$.[1-9] Since, e.g., the spectra of the *cis*- and the *trans*-isomer are different the isomerization process can be analyzed in detail.[6,9] In addition, for the *trans*-isomer the strong resonance enhancement of several modes in connection with a photoselection of the scattering process allows determination of the distribution of undisturbed series of conjugations on the chain.[2-4,8] Doping the polymer was shown to lead to a quenching of the resonance effect and experimental results of Raman scattering from doped cis-$(CH)_x$ suggested that doping induces *cis-trans* isomerization.[2,7] More recently additional evidence for doping-induced isomerization was obtained from infrared and from optical absorption measurements.[10-12]

In this paper *in situ* Raman experiments during electrochemical doping are reported for the first time. We show that valuable information on the doping and dedoping process, on the structure of the polymer, and on the doping-induced isomerization can be obtained.

High-quality *cis*-polyacetylene was prepared according to the Shirakawa method. The original *trans*-isomer contamination after preparation was about 20%. Raman scattering experiments were carried out *in situ* through a quartz window of an optical cell filled with the electrolyte. 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 min to reduce laser-induced *cis-trans* isomerization to a minimum. The electrochemical cell consisted of a glass tube with a quartz window and polyacetylene clamped to a nickel contact as the working electrode. Lithium strips were used as reference and counter electrode, respectively, together with an electrolyte of 0.3 mol dried $LiClO_4$ in propylene carbonate.[13] Charging and discharging the cell was controlled potentiostatically by a Jaissle potentiostat, Mod 1001 T-NC. In all doping experiments polyacetylene was *p* doped (oxidized) by increasing the positive potential of the working electrode to about +4 V vs Li. Thus, the ClO_4^- ions enter the polymer during the doping process and act as counterions to preserve charge neutrality. Potentials will always be given versus the Li-reference electrode. Charge and discharge currents were monitored and plotted

versus time. Experiments were repeated several times and showed quantitative agreement in all details to be discussed.

Figure 1 shows Raman spectra of *cis*-polyacetylene after various stages of the electrochemical doping process. Spectrum 1 is for the original, mainly *cis*-polymer as measured in an optical cryostat at 77 K. The strong lines at 1540, 1250, and 910 cm^{-1} are the off resonance Raman lines of the *cis*-isomer whereas the broad features around 1500 and 1120 cm^{-1} refer to the *trans*-isomer contamination. Inserting the polyacetylene sample into the electrochemical cell and checking the spectrum again resulted in an increase of the lines from the *trans*-isomer and in a slight decrease of the lines from the *cis*-isomer (spectrum 2). Obviously some isomerization had occurred. This laser-induced isomerization was checked explicitly and found to be equivalent to a thermal isomerization at 100 °C. Charging the polymer at +4 V for various time intervals yields successively the Raman spectra 3–5 of Fig. 1. The open circuit voltage (V_{oc}) indicated was measured 5 min after interruption of the charging process. The lines of the *trans*-isomer clearly decrease whereas the lines of the *cis*-component slightly increase up to $V_{oc} = 3.8$ V. The behavior of the *cis*-lines is shown more explicitly in Fig. 2. Here the in-
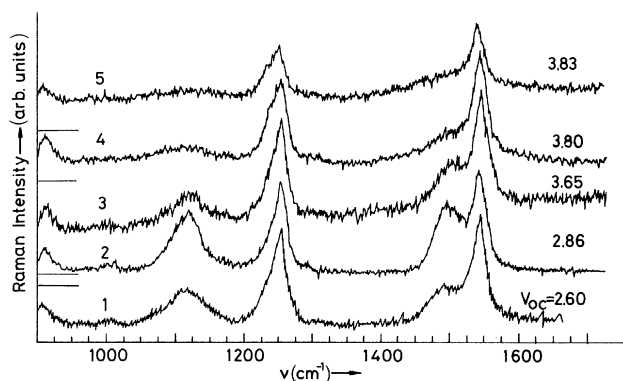

FIG. 1. Raman spectra of *cis*-polyacetylene at various stages of the electrochemical doping (4579-Å laser, 20 mW).
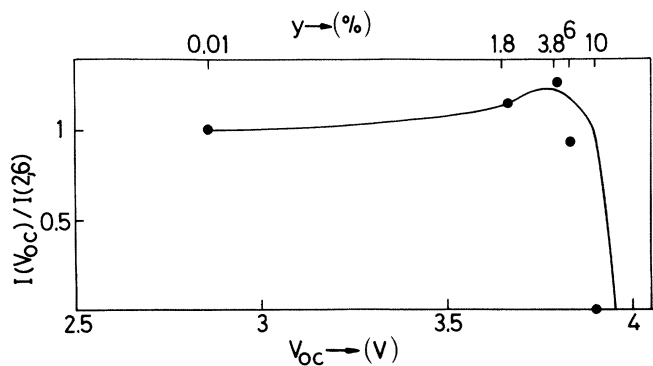
FIG. 2. Relative values of integrated intensity for the 1250-cm^{-1} Raman line of *cis*-(CH)$_x$ vs open circuit voltage V_{oc} after electrochemical doping as measured ($\bullet$) and as calculated from Eq. (4) (——).

tegrated intensities for the mode at 1250 cm^{-1} of the *cis*-isomer in relative units are plotted as a function of V_{oc}. By continuing the doping process for 14 h V_{oc} increased to 3.90 V. The Raman spectrum now shows the features for heavily doped *cis*-(CH)$_x$ or *trans*-(CH)$_x$, i.e., broad and upshifted lines characteristic for an off resonance spectrum of *trans*-(CH)$_x$ (spectrum 1 in Fig. 3). The similarity between *cis*-(CH)$_x$ heavily doped electrochemically and *cis*-(CH)$_x$ heavily doped from the gas phase is demonstrated by spectrum 2 which refers to 12% AsF$_5$ doped *cis*-(CH)$_x$, as reported in Ref. 2.

Discharging the polymer was generally performed at a potential of 2.6 V in order to avoid *n* doping of the polymer. The discharge current dropped rapidly in the first 10 min and continued to drop slowly later. During this process the open circuit voltage decreased correspondingly. Trace 3 of Fig. 3 shows the spectrum after a 35-min discharge. It is typical for an undoped high-quality *trans*-isomer. In particular the high-frequency part of spectrum 2 around 1600 cm^{-1} has completely disappeared. Continuing the discharge
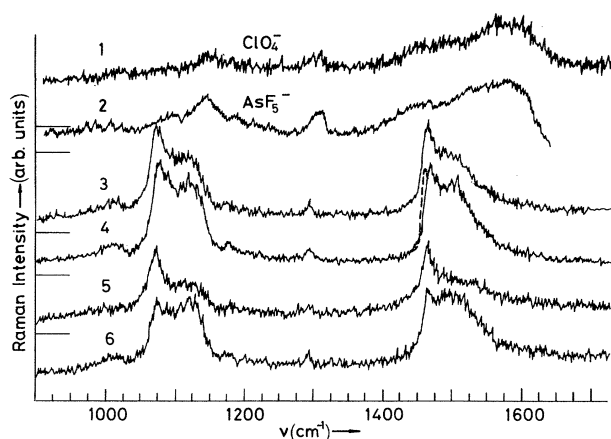

FIG. 3. Raman spectra for (CH)$_x$: (1) spectrum for heavily ClO$_4^-$ doped polymer; (2) spectrum for heavily AsF$_5$ doped *cis*-(CH)$_x$ from Ref. 2; (3) as (1) after fractional discharge; (4) as (1) after complete discharge; (5) as (4) after redoping to $V_{oc} = 3.83$ V; and (6) as (5) after redischarge.

process at a slightly reduced voltage for another 10 h yielded a final V_{oc} of 2.6 V and the spectrum 4. This spectrum is similar to number 3, but the high-frequency components of the *trans*-isomer lines have increased relative to the narrow lines at 1070 and 1460 cm^{-1}. Redoping the sample led to spectrum 5. The Raman lines are again reduced and the high-frequency parts of the lines disappear more rapidly as compared to the low-frequency parts. Undoping the samples a second time restored the initial spectrum for the *trans*-polymer (spectrum 6). However, the relative intensities of the high-frequency parts of the lines to their low-frequency parts have increased.

The discussion of the experimental results will be performed within the interrupted conjugation model (particle in the box model). This model gives a quantitative description of the resonance Raman scattering in *trans*-(CH)$_x$.[2–4] The polymer is considered as consisting of long chains on which the conjugation is statistically interrupted by defects. π electrons thus behave like particles in a box with a statistical distribution of box lengths. Since the energy $\Delta\epsilon$ for the π-π^* transition and the C=C stretch frequency ν_{C-C} depend critically on the box-length scattering is dominated by a photoselective resonance process. An estimation for the dependence of $\Delta\epsilon$ and ν_{C-C} on the number of double bonds N in the box can be obtained from Eqs. (1) and (2), respectively.[2]

$$\Delta\epsilon = h^2(2N+1)/32m_0N^2a^2 + V_0(2N-1)/2N , \qquad (1)$$

$$\nu_{C-C}(\text{cm}^{-1}) = 1450 + 720/(N+1) . \qquad (2)$$

In these equations V_0, m_0, and a correspond to the bond alternation potential, the free-electron mass, and the average carbon-carbon distance, respectively. Blue laser light is known to be the best choice to study long and short segments simultaneously[3] since in this case the Raman lines of good samples have a double-peak structure for the C=C stretch mode and the mode around 1120 cm^{-1}. The low-frequency part and the high-frequency part of the lines correspond to long (quasi-infinite) and short segments, respectively. Polymers corresponding to these two peaks will be described as crystalline and amorphous for convenience. According to Eq. (2) the broad shoulder around 1500 cm^{-1} in spectrum 1 of Fig. 1 roughly corresponds to a conjugation length of 14 double bonds. Little is known about details of the interruption of conjugations. Defects due to interaction of the polymer with oxygen,[14] cross links, or chain bending may be examples. In the model always rectangular boxes with infinite potentials at the boundaries are assumed. Recently Vardeni, Ehrenfreund, Brafman, and Horovitz[15] obtained a very similar description of the resonance scattering by replacing the distribution of box lengths by a distribution of electron-phonon coupling constants. Thus, in their work no specification on the type of boxes was necessary.

Since the laser-induced isomerization shown in Fig. 1 corresponds to a temperature where isomerization takes several days[6] this process cannot significantly influence the experimental results. Comparing spectrum 2 to 4 of Fig. 1 we conclude that the *trans*-isomer part of the sample dopes first and much faster than the *cis*-isomer part. The final result for the heavily doped sample (trace 1 of Fig. 3) is similar to the results for heavily AsF$_5$ doped samples. Thus, the final concentration after electrochemical doping should be of the same order as observed for doping from the gas phase and the structures in the broad features are intrinsic to the poly-

mer. The behavior of the lines from the cis-isomer is a result of the bleaching of the trans-isomer due to doping.[16]

The relative change of the intensity for these lines can be described in a quantitative form if some specifications for the doping process are accepted. If, e.g., a complete phase separation for the doping of the cis-isomer and trans-isomer part and homogeneous doping to a saturation concentration n_s within the trans-isomer parts of the sample is assumed, the relative scattering intensity $I(y)$ for the cis-line at 1250 cm^{-1} is given as

$$I(y) \propto |\alpha_{ZZ}|^2 [1 - R(y)]^2 / \alpha(y) \ , \tag{3}$$

where y, α_{ZZ}, $R(y)$, and $\alpha(y)$ are the doping concentration, the corresponding Raman tensor, the reflectivity, and the optical absorption, respectively. Saturation of doping is in principle determined by the new structure developing in heavily doped $(CH)_x$.[17] Since $R(y)$ in Eq. (3) is only slightly varying with y and α_{ZZ} is proportional to the concentration $C_{cis}(y) = 1 - C_{tr}(y)$, $I(y)/I(0)$ may be calculated from

$$I(y)/I(0) = [\alpha_{cis}(0)/\alpha(y)][C_{cis}(y)/C_{cis}(0)] \ . \tag{4}$$

According to the specification assumed the cis-isomer concentration remains constant at $C_{cis}(0)$ until y reaches $y_s = n_s C_{tr}(0)$. For this region $\alpha(y)$ is given by

$$\alpha(y)/\alpha_{cis}(0) = C_{cis}(0) + C_{tr}(y)\alpha_{tr}(y/C_{tr}(y)) \ , \tag{5}$$

where α_{tr} is taken from experimental results or from soliton theory.[16] For $y > y_s$, $C_{cis}(y)$ and $\alpha(y)/\alpha_{cis}(0)$ become

$$C_{cis}(y) = C_{cis}(0) - (y - y_s)/n_s \tag{6}$$

and

$$\alpha(y)/\alpha_{cis}(0) = C_{cis}(y) + C_{tr}(y)\alpha_{tr}(y_s)/\alpha_{cis}(0) \ . \tag{7}$$

Using 0.8 and 0.125 for $C_{cis}(0)$ and n_s, respectively, the relative scattering intensity can be calculated from Eq. (4) as a function of y. Since the latter is directly related to V_{oc} (Ref. 18) experimental results and calculation can be compared. Very good agreement is obtained for the part where the scattering intensity increases with concentration. The discrepancy in the high doping region is probably due to inhomogeneous doping of our sample and to the difficulties in relating V_{oc} to the doping concentration at high values of y. However, the initial doping of the trans-isomer parts of the sample and the results from the calculation are evidence for the existence of closed areas of trans-$(CH)_x$ in the cis-matrix. From the position of the Raman peak for the C=C stretch mode in the undoped sample (trace 2 in Fig. 1) a high degree of disorder must be assumed for this area. Also, they must have direct access to the electrolyte. Thus, these areas are grain boundaries between crystalline parts of the fiber or areas at the surface of the fiber. Undoping the samples by discharging the cell revealed a spectrum characteristic for undoped trans-$(CH)_x$ with a high concentration of long noninterrupted conjugations. The broad feature around 1600 cm^{-1} has disappeared. However, the low-

frequency part of the line for the C=C stretch mode peaks at 1465 cm^{-1}. This is slightly higher than 1456 cm^{-1} observed for our best thermally isomerized samples. Also the slope on the low-energy side of the line is steeper for thermally isomerized samples as indicated in the figure by the dashed line. Thus, even though there is a high concentration of long segments they are considerably disturbed by the doping and dedoping process. This is consistent with the decrease of the slope of the absorption edge for trans-$(CH)_x$ after electrochemical doping and dedoping. The bleaching of the broad features around 1600 cm^{-1} upon dedoping implies that in this case conjugations are not interrupted by covalent bonds. Thus, this is the first experimental evidence that an upshift of the C=C stretch mode need not be due to a complete interruption of the conjugation but rather is due to a deformation of the chain by the dopand. This deformation disappears after the dopand is released.

Comparing spectrums 3 and 4 of Fig. 3 shows that crystalline parts of the sample dedope first. This result is not immediately consistent with a situation where the outer parts of a fiber are amorphous. An explanation may be based on an electrochemical inequivalence of the ordered and disordered polymer. In fact, since the electrochemical potential is given roughly by the difference between the voltage where oxidation starts (~ 3 V) and one-half of the gap voltage[16] shorter segments should have a lower electrochemical potential. Thus, the amorphous parts dope first and dedope later. However, for a detailed understanding of the discharge process a more extensive experimental and theoretical study is necessary.

Recharging the polymer and discharging again shows that the amorphous parts of the trans-polymer dope first in agreement with a higher diffusivity of the dopand in these areas and, in particular, agreement with a model where these areas are on the surface of the fibers. Finally, comparing spectrums 4 and 6 in Fig. 3 indicates that cycling induces some additional disorder.

In conclusion, we showed that in situ Raman spectroscopy is a valuable tool to reveal details of the electrochemical doping process of $(CH)_x$. In particular, trans-isomer areas in a predominately cis-isomer sample were found to dope first and heavily doping leads to a complete cis-trans isomerization. Good evidence for a phase separation between doped trans-$(CH)_x$ and undoped cis-$(CH)_x$ is obtained. In the case of trans-$(CH)_x$ disordered areas are doped first, probably due to the higher mobility of the dopand complexes in these regions and due to their location on the surface of the fibers. Undoping starts in the crystalline parts of the polymer.

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