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GENERATION AND CHARACTERIZATION OF CHAIN DEFECTS IN POLYACETYLENE

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ABSTRACT: Investigations of defects of carefully prepared trans-$(CH)_x$ are presented. The dependence of conjugation length on the generation of various types of defects was observed by resonance Raman scattering. In the case of sample oxidation a quantitative comparison of these results combined with a determination of weight uptake leads to a distinction between oxygen interrupting chains and oxygen reacting at chain ends.

1. INTRODUCTION:

One of the main problems in the field of conducting polymers is the strong dependence of many physical properties of the polymer on mostly unknown defects generated during sample preparation and sample handling. This situation is particularly dramatic for polyacetylene($(CH)_x$). One possibility to study this problem at least for the latter material in its trans form is the application of resonance Raman scattering to characterize sample qualities[1,2,3,4]. This technique is based on the relation between the number of carbons in an undisturbed segment of a chain and several physical properties like $\pi\pi^*$ electron transitions or vibrational mode frequencies. It has recently been developed to an useful tool in order to study the distribution of undisturbed conjugation lengths in polyacetylene[5,6].

As reported previously a careful preparation of trans-$(CH)_x$ yields long segments of undisturbed conjugations characterized by a double peak structure of the C=C stretch Raman profile if the Raman spectrum is excited with the 4579 Å line of an Argon laser[3,7]. The high frequency part of this double peak profile may be as small as 65% of the corresponding low frequency part[6]. A polymer of this high quality appears to be a promising starting material to study the influence of artificially induced defects, which, in turn, can be expected to be a powerful tool to learn more about the nature of chain defects induced by sample preparation and sample handling.

In this paper we report on properties of trans-polyacetylene at which defects have been introduced artificially by sample compactation, exposure to air and irradiation with laser light. To characterize the samples resonance Raman scattering in combination with weight uptake during exposure to air and preliminary results on irradiation induced luminescence were used. From the compactations experiments we conclude, that the dispersion effects of the C=C stretch mode is indeed related to defects along the backbone and is not of pure extrinsic nature. Thus, these results confirm the model of interrupted conjugations. The effect of oxidation on physical properties of polyacetylene like isomerization, line width of ESR, conductivity, infrared absorption etc. has been studied previously[8-13]. However, the dependence of conjugation length on the oxidation process has not been investigated before and, certainly, it is a very helpful method learning more about the reactions of oxygen with polyacetylene chains.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES:

Polyacetylen films were prepared using a Ziegler-Natta cathalyst. Great care was taken to avoid any contamination of the samples with oxygen and humidity. The peak intensity ratio of the low frequency part of the Raman line of the C=C stretch mode at 1450 cm^{-1} and the high frequency part of the same mode at 1500 cm^{-1} was as high as 1.5 and the ESR line width was only 0.4 G. All Raman experiments were performed at nominally 77K with the 4579 Å laser line using a line focus and an intensity of 40 mW.

3. GENERATION OF DEFECTS AND EXPERIMENTAL RESULTS:

3.1 Compactation of Polyacetylene

Polyacetylene samples were compacted in Argon atmosphere using unaxial pressure up to 90 bar. As a typical result fig. 1 shows Raman spectra for samples compacted at various unaxial pressures. The Raman lines of the C-C stretch mode at about 1100 cm^{-1} and the Raman lines of the C=C stretch mode at about 1500 cm^{-1} show a very similar behaviour: the low frequency side decreases whereas the high frequency side increases. Increasing the pressure from 24 bar to more than 90 bar showed

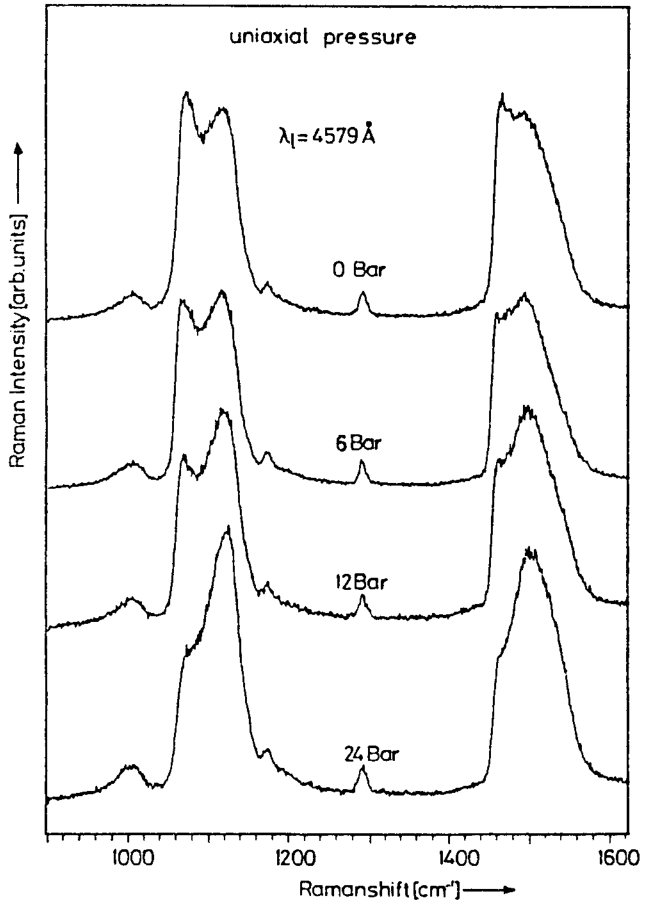

FIGURE 1 Dependence of line shapes on compactation

no further change of the lines. The change of the Raman line shape with uniaxial pressure is as expected from the interrupted conjugation model since compactation is expected to induce bending, kinking and, may be, squeezing of fibers. These processes will in turn induce stress fields and kinks on the individual chains and thus reduce the length of undisturbed conjugation by intrinsic defects. This proves that the dispersion effect of the C=C stretch mode in trans-$(CH)_x$ is due to intrinsic chain defects and not due to any other extrinsic defects not related to the chain. Thus, these experiments strongly support the proposed model of defect interrupted conjugations on the polymer chains.

3.2 Oxidation of polyacetylene.

High quality samples of trans-$(CH)_x$ were exposed to ambient air for several time intervalls. After each exposure the polymer was pumped for at least on hour before it was cooled to liquide nitrogen temperature in order to take Raman spectra. Thus, only oxygen really incorporated into the fibers by a nonreversible process remained in the material. In fig. 2 the results of the Raman measurements are shown. Exposure times indicated in the figure refer to total exposure. Similar to the experiments with uniaxial pressure a strong decrease of the low frequency side of the Raman lines is observed. This is a consequence of a decrease of the length of undisturbed conjugations due to the interaction of oxygen with the chains. It is interesting to note that it needs a total exposure time of 45 days in order to degrade the samples to an average conjugation length equal to samples measured previously[2,14]. After this very strong oxidation the samples were very brittle. From these results it may be concluded that interruption of conjugation is not the only process

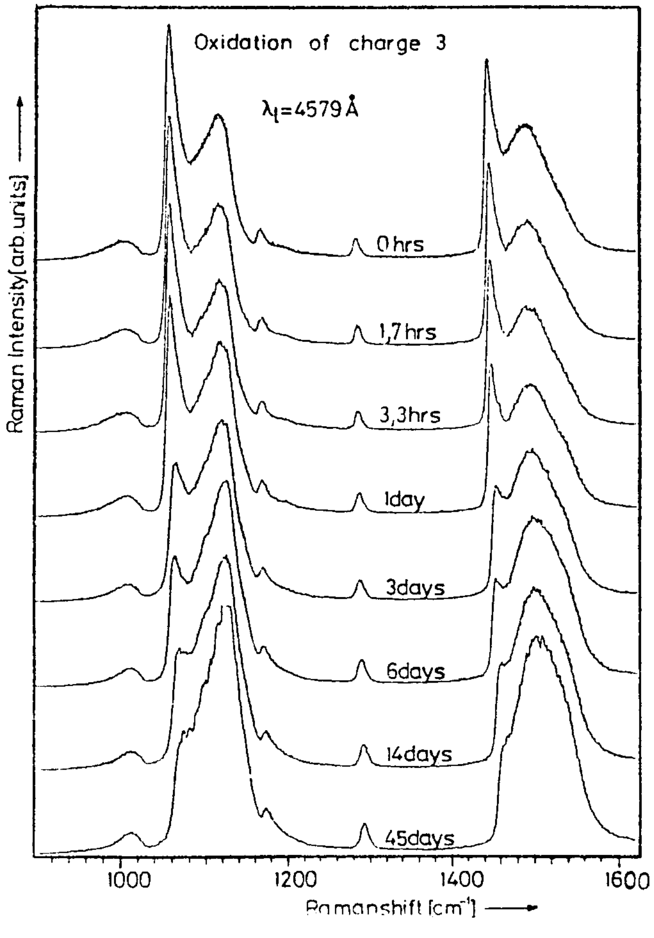

FIGURE 2 Dependence of line shapes on exposure to air

during oxidation.

For a more quantitative analysis of the Raman line shapes shown in fig.2 the distribution of chain length P(N,t) as a function of exposure time t must be considered. If α_1 is the average probability that oxygen interrupts one carbon double bound, the change ∂P of the number of conjugations with N double bounds is determined by a creation and annihilation term of the form:

$$\partial P(N,t)=2\ \alpha_1\int_N^\infty P(n,t)\ \partial n\ \partial t+\alpha_1 N\cdot P(N,t)\partial t \qquad (1)$$

Since it is difficult to solve this equation analytically, the two limiting cases for very short ($N_{<<}$) and very long chains ($N_{<<}$) were evaluated. For very long chains the creation term can be neglected, which yields

$$P(N_{>>},t)=P(N_{>>},0).e^{-N_{>>}\alpha_1\cdot t} \qquad (2)$$

For very short chains ($N_{<<}$) the annihilation term is neglected. The integral, which represents the number or chains larger than $N_{<<}$, can be expressed by the total number of chains $A(t)=\int_0^\infty P(N,t)dN$ reduced by the number of chains with length $N_{<<}$. The dependence of A(t) on time is given by the fact that every oxygen interrupting a chain increases the total number of chains by one.

$$A(t)=A(O)+(A(\infty)-A(O))\cdot(1-e^{-\alpha_1 t}) \qquad (3)$$

A(O) and A(∞) are the total number of chains unexposed and after infinite time, respectively. Using equation 3 the number of very short chains is given by:

$$P(N_{<<},t)=A(\infty)-(A(\infty)-A(O)).e^{-\alpha_1 t}-(A(0)-P(N_{<<},O))^{-2\alpha_1 t} \qquad (4)$$

For a comparison of the calculation with experiments the number of long and short chains must be determined from the experimental results shown in fig.2. According to the interrupted conjugation model the Raman intensity of the peak at 1450 cm^{-1} is proportional to the number of long chains e.g. longer than about 100 double bonds. Thus, the behaviour of this peak is expected to follow equation 2 with $N_{>>}=100$, as there are only very few segments longer than 100 double bonds[5]. On the other hand, the high frequency limit of the Raman line for the C=C mode is about 1550 cm^{-1}, which corresponds to a segment length of 8 double bonds. Thus, the behaviour of the intensity at 1550 cm^{-1} must be described by equation 4 because more than 90% of the material is in chains longer than 8 double bonds[5]. In order to be independent of absolute scattering intensity, the ratio of the intensities at 1450 cm^{-1} and at 1550 cm^{-1} was taken from fig.2 and was compared with calculated results given by equation 2 and 4. As fig.3 shows there is very good agreement between experimental result (full circles) and calculation (full drawn line). The time constant for oxygen interrupting a chain was determined as $\alpha_1=1\cdot 10^{-4}$ $days^{-1}$. As mentioned earlier oxygen mainly reacts with the polymer without interrupting chains. The low value of α_1 is in good agreement with this assumption. In order to prove this behaviour the weight uptake of the sample was determined which is shown in fig.4. As the longest exposure time is short with respect to a complete oxidation, a linear approximation was used in order to determine a time constant α_2 averaged over all possible oxygen reactions. As expected, the "overall" time constant α_2 is larger than α_1

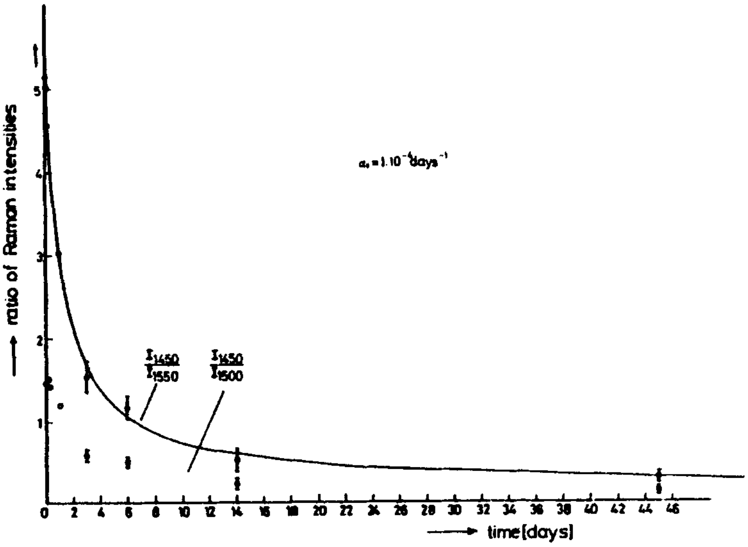

FIGURE 3 Calculated and measured chain shortening during oxidation

by more than an order of magnitude. This means that oxygen does not prefer interrupting chains but mainly reacts with original defects or chain ends, where electrons are much more localized as compared to undisturbed parts of the chain.

The weight uptake of our sample is much smaller as compared to results reported by H.W. Gibson et al[12]. This fact may be due to the high quality of our sample material and to the fact that we used an all transpolymer through out. A material with long conjugations has less chain ends and the weight uptake is mainly determined by oxygen interrupting chains, which is a very

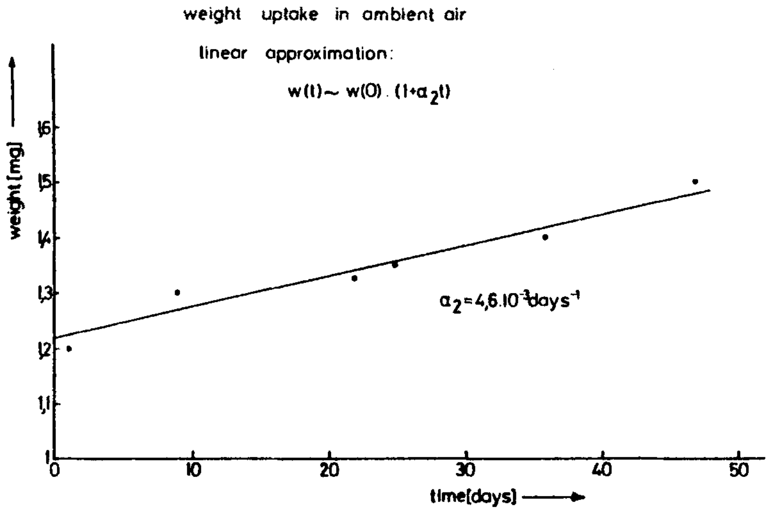

FIGURE 4 Weight uptake during oxidation

slow process.

3.3 Generation of defects by irradiation

Irradiating trans-$(CH)_x$ at room temperature with a 100 mW line focused laser at 4579 Å also leads to a change in Raman line shape as shown in fig.5. However, the observed effect was small as compared to changes of line shapes after compactation and oxidation. The ratio of long to short chains (I_{1450}/I_{1550}) and the ratio of long to medium long chains (I_{1450}/I_{1500}) were determined from the C=C Raman profile (circles). The full drawn lines are guide lines for the eye. The influence of irradiation on conjugation length is particularly small for the ration I_{1450}/I_{1500}

whereas the ratio I_{1450}/I_{1550} exhibits a considerable decrease at least at the begining of the irradiation process. Within the model of interrupted conjugations this means, that irradiation at this wave length has a small efficiency of defect generation and prefers interrupting conjugations close to defects or chain ends. At this time no further details on the nature of the defect generation process can be analysed.

Besides the influence of laser irradiations on the Raman line shape a strong irradiation induced luminescence peaking at 2,4 eV was observed. A detailed study of polymer samples prepared in other laboratories showed that this effect is hardly observable in these materials. Exposure of all samples to ambient air led to a strong enhancement of laser irradiation induced luminescence. Details of this investigation will be published elsewhere[15].

4. CONCLUSION

Resonance Raman scattering on high quality trans-$(CH)_x$ in conjunction with the interrupted conjugation model was shown to be a very useful tool in studying chain defects. Compactation and oxidation were found to cause considerable changes of the defect structure of the polymers. For compactation the creation of intrinsic defects like chain bends and chain kinks are assumed. In the case of oxidation a distinction between chain end reaction and chain interruption was found by comparing Raman results with measurements of weight

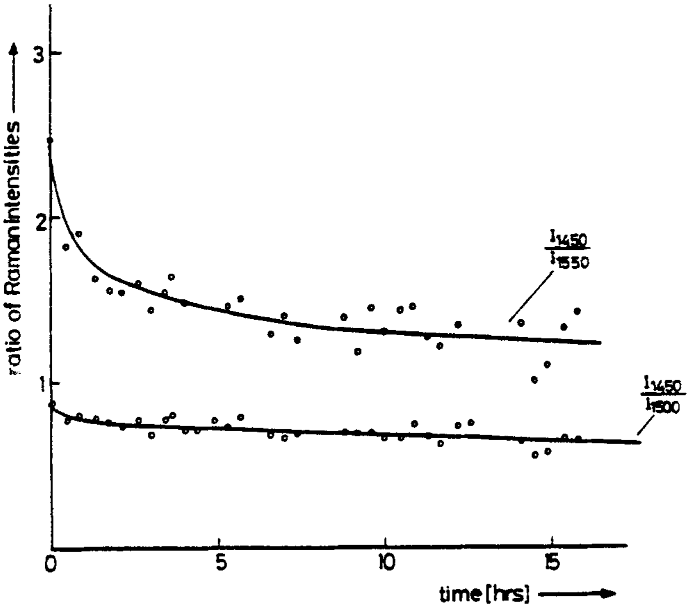

FIGURE 5 Decrease of chain length during irradiation

uptake upon exposure of the polymer to ambient air.

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