# CONTRIBUTION TO EPR STUDIES
# OF TRANSPOLYACETYLENE

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The temperature dependences of EPR spectrum parameters of undoped poly-
acetylene have been studied in the temperature interval from 300 K to 473 K. The
extinction of the paramagnetic species at 460 K and 473 K, respectively, have been
measured. In the same temperature range the linewidth changes of the doped poly-
acetylene were evaluated.

## I. INTRODUCTION

During the last years a large number of experimental and theoretical works
have been done for the understanding of the conjugated polymer chains because
of their unconventional properties. One of such conjugated polymers is trans-
polyacetylene.

The polyacetylene (CH)$_x$ is in the first approximation the one-dimensional
organic matter having cis and trans isomers. By the thermal isomerization
cis-(CH)$_x$ is transformed to trans-(CH)$_x$. During the cis/trans isomerization
magnetic defects, so-called neutral solitons, are created [1—7]. EPR is one of the
various techniques in magnetic resonance which has been applied to study the
properties of neutral solitons [1—7, 10—23]. Our EPR investigation on trans-
polyacetylene contributes to that type of studies.

## II. EXPERIMENTAL PART

### II.1. Preparation of the samples

Polyacetylene was prepared according to the technique of Shirakawa et
al. [8]. Iodine doping was carried out by immersing (CH)$_x$ into (2.65 g I$_2$ in a

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100 ml $CCl_4$) — solution at 25°C. After standing in it one hour, the sample was rinsed three times by pure $CCl_4$ for 5 minutes.

The so prepared samples were kept in a nitrogen atmosphere. Powdered samples were used in all EPR experiments.

## II.2. Measurement of EPR spectra

The EPR spectra of the polyacetylene samples were measured by means of the Bruker 200E-SRC spectrometer with a 100 kHz modulation in the X-band.

The spectrum EPR is a simple symmetrical line. Such singlets are formed as a result of an absorption of energy at the reorientation of an isolated spin. The resonance condition is:

$$hf = g\beta B,\qquad(1)$$

where $h$ is Planck's constant, $f$ — the frequency of the microwave field, $g$ — the spectroscopic splitting factor, $\beta$ — the Bohr magneton, $B$ — the induction of the magnetic field. A complete analysis of such spectra includes the evaluation of the lineshape, the linewidth, the g-factor and the concentration of paramagnetic centres.

The lineshapes were determined by a direct comparison of the experimental spectra with the theoretical Lorentzian lines.

The linewidth $\Delta B_{max}$ is defined as a peak-peak distance of an absorption derivative line.

The g-factor is obtained from Eq. (1):

$$g = \frac{hf}{\beta B_0},\qquad(2)$$

where $B_0$ is the magnetic induction coordinated to the maximum of an absorption line.

The concentrations of the paramagnetic centres in polyacetylene samples were estimated by the comparison of the EPR spectra in these materials with the standard EPR spectrum. The EPR standard with a defined number of spins $10^{15}$ cm$^{-1}$ of the effective length with a Lorentzian lineshape was used.

The spectra were compared under the same experimental conditions. The number of paramagnetic centres in the investigated samples is defined by [9]:

$$N_x = N_n \cdot \frac{(I_0' \Delta B_{max}^2)_x}{(I_0' \Delta B_{max}^2)_n},\qquad(3)$$

where $I_{0x}$, $I_{0n}$ are the amplitudes of the absorption derivative lines of the sample and the standard, respectively.

The changes of the relative concentrations of the paramagnetic centres observed during the temperature increase were evaluated as the products of $(I_0' \Delta B_{max}^2)_x$.

## III. RESULTS AND DISCUSSION

In the first place the EPR spectrum of the powdered undoped polyacetylene at room temperature was recorded. Then the temperature dependences of the EPR spectra in the temperature range of $T \in \langle 300\ \text{K}, 460\ \text{K}\rangle$ with the step of 40 K were measured. At 460 K and 473 K, respectively, the time-dependent extinction of the EPR signal was observed. In both experiments the total measurement time was 30 minutes and the step of the spectrum record was 2 minutes. After this temperature treatment the sample was cooled down and the EPR spectrum was recorded once more at room temperature.
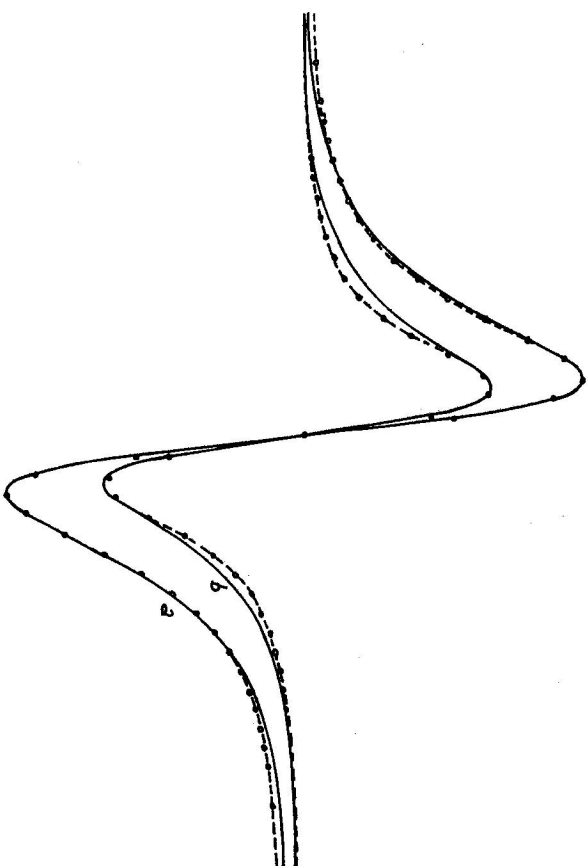


Fig. 1. Experimental EPR spectrum of undoped polyacetylene (solid lines) compared with the theoretical Lorentzian curve (broken lines): a) record at room temperature; b) record of the re-cooled sample

All the measured spectra (with good approximation) had a lineshape of the Lorentzian type. The characteristic EPR spectrum of the tested sample is shown in Fig. 1a and compared with the theoretical Lorentzian curve. The Lorentzian

nature of the lineshape is usually interpreted as a consequence of the 3-dimensionality of the investigated system [10].

The calculated value of the g-factor of the undoped sample is $g \doteq 2.0027$. This value differs only very little from the g-factor of an isolated spin.
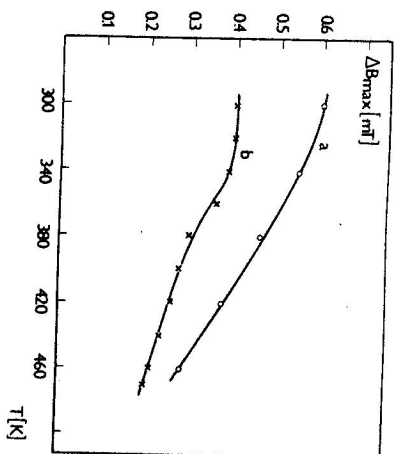


Fig. 2. Dependence of the linewidth on temperature: a) in the undoped sample; b) in the doped sample

The linewidth measured at room temperature is $\Delta B_{max} = 0.6$ mT. Fig. 2a shows the linewidth dependence on the temperature in the undoped sample. In the temperature range from 300 to 460 K the value of the linewidth decreases up to 0.29 mT. After the sample had been heated up to 460 K it was maintained at this temperature. The variations of the EPR spectrum parameters were measured. The linewidth increases with time monotonically, as shown in Fig. 3a. Then followed the re-heating of the sample up to 473 K. At this temperature the time dependence of the EPR parameters were measured again. An increase of
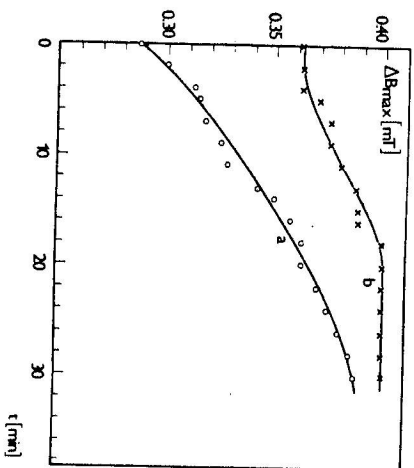


Fig. 3. Time dependence of the linewidth in the undoped sample: a) at T = 460 K; b) at T = 473 K

$\Delta B_{max}$ with time up to a certain constant value is observed (Fig. 3b). This constant value of $\Delta B_{max} = 0.4$ mT has been obtained in 18 minutes. The measured linewidth of the re-cooled sample at room temperature is 0.46 mT.
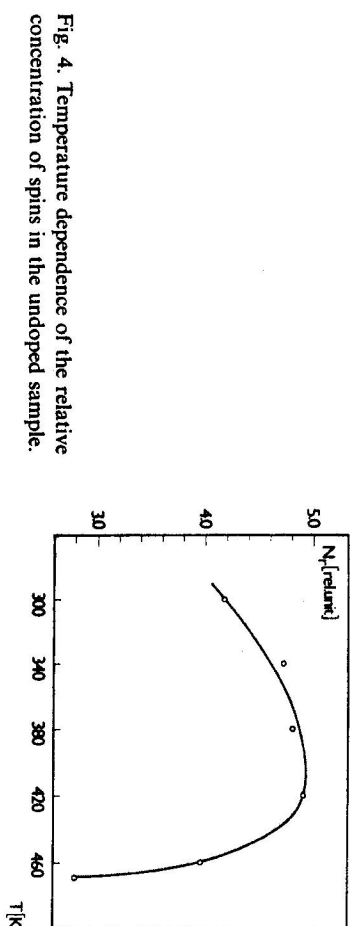


Fig. 4. Temperature dependence of the relative concentration of spins in the undoped sample.

The approximate evaluation of the concentration of paramagnetic centres according to Eq. (3) gives the value of $N_x \doteq 9.10^{18}$ spin/g at 300 K. The concentration $N_x$ increases slowly with the increase of temperature in the range of $\langle 300$ K, 420 K$\rangle$ but at the temperature of 460 K the value of $N_x$ strongly decreases. The temperature variation of a relative concentration of spins is shown in Fig. 4.

The time dependences of a relative concentration of spins at the temperature of 460 K and 473 K are in Fig. 5a and 5b, respectively.
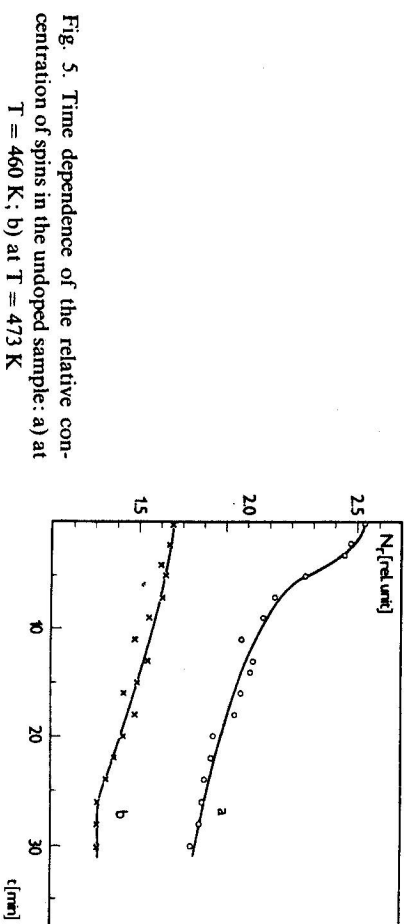


Fig. 5. Time dependence of the relative concentration of spins in the undoped sample: a) at T = 460 K; b) at T = 473 K

The spin concentration measured at 473 K after 30 minutes is three times smaller than the initial value of $N_x$ at room temperature. The measured spin concentration of the re-cooled sample at room temperature is $N_x \doteq 3.7 \cdot 10^{18}$ spin/g. The $g$-factor of this sample is the same as the primary value. The EPR lineshape of the re-cooled sample differs from the Lorentzian curve. (Fig. 1b) more than the primary recorded EPR spectrum at 300 K (Fig. 1a). It is obvious that such a temperature treatment of the sample causes its irreversible changes.
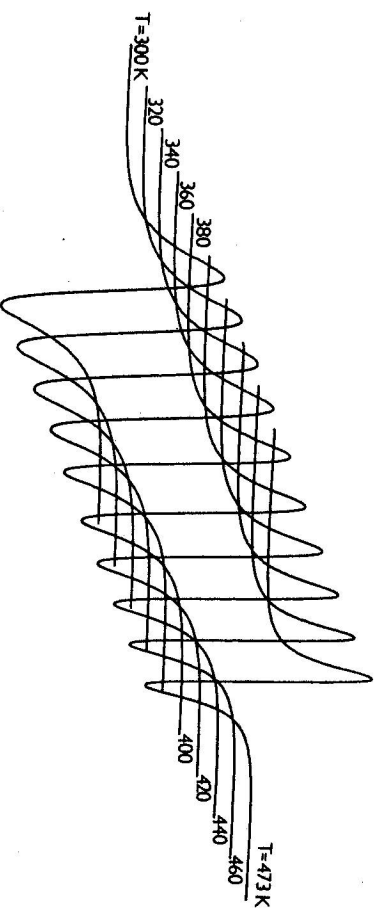


Fig. 6. EPR spectra of doped polyacetylene at various temperatures.

Analogical temperature measurements were carried out with doped polyacetylene and compared with references [11—17]. The typical EPR spectra of doped polyacetylene at different temperatures are in Fig. 6. The temperature dependence of the linewidth in the doped sample is shown in Fig. 2b. The course of this dependence is analogical to the preceding one for undoped polyacetylene.

The $g$-factor of doped polyacetylene was $g \doteq 2.0028$.

The initial value of the spin concentration before the temperature treatment of the doped sample was $N_x \doteq 2 \cdot 10^{19}$ spin/g. The final value of the spin concentration for the re-cooled doped sample was $N_x \doteq 3.7 \cdot 10^{18}$ spin/g, the same magnitude as for the undoped sample.

The above results support the Holczer assumed two-spins model [18—20] in polyacetylene, containing both localized and diffused spins. The origin of the unmoving spins is probably due to the presence of the oxygen or of the other impurities. These impurities can cause the defects of the conjugation in the polyacetylene chain [21, 22]. Also at an imperfect polymerization there can arise regions in the polymer chains, where the spins are not able to move.

The number of localized immobile spins does not change considerably during temperature treatment, therefore the relative changes of the EPR linewidth, shape and spin concentration are characteristic of the behaviour of diffused spins.
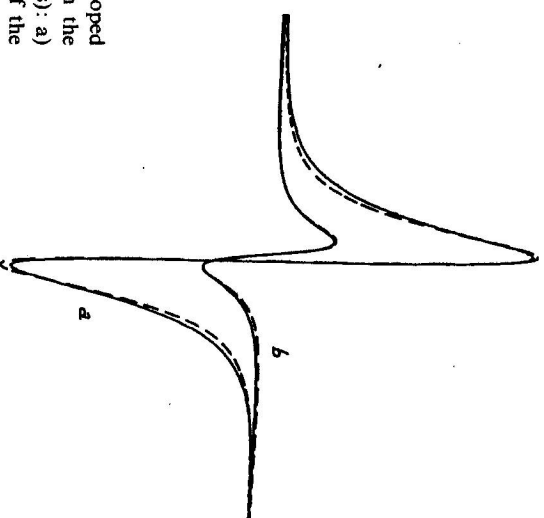


Fig. 7. Experimental EPR spectrum of doped polyacetylene (solid lines) compared with the theoretical Lorentzian curve (broken lines): a) record at room temperature; b) record of the re-cooled sample

The dynamic narrowing of the linewidth with temperature increase corresponds to the increase of the spin mobility. The spin mobility can be influenced by the degradation of the polymers as well. Probably, the degradation process occurs by the creation of the cross-bonds between chains, which are responsible for reducing the spin mobility.

The processes of degradation and isomerization co-exist [23]. Our measurements indicate that in the region of $T < 420$ K, where a decrease of $\Delta B_{max}$ and a simultaneous increase of $N$ are observed, the isomerization processes are dominant. The intense decrease of $N$ and the monotonous increase of $\Delta B_{max}$ in the region of $T > 460$ K point out the strong degradation process.

The optimal conditions — a complete isomerization and a small degradation — occur at $T \leqq 420$ K.

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# СООБЩЕНИЕ К ЭПР ИССЛЕДОВАНИЮ ТРАНСПОЛИАЦЕТИЛЕНА

Методом ЭПР исследованы температурные зависимости спектральных параметров в нелегированном и легированном полиацетилене в интервале температур (300 К, 473 К). Были измерены зависимости затухания парамагнитных центров от времени при температурах 460 К и 473 К.