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# Very High Field EPR Study of *Cis*- and *Trans*-Polyacetylene

**V. I. Krinichnyi[1], A. E. Pelekh[1], Ya. S. Lebedev[1], L. I. Tkachenko[1], G. I. Kozub[1], A. L. Barra[2], L. C. Brunei[2], and J. B. Robert[2]**

[1] Institute of Chemical Physics, Chernogolovka, Russian Federation [2] Services National des Champs Intense, CNRS, Grenoble Cedex, France

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**Abstract.** Some neutral *cis*- and *trans*-polyacetylene samples have been studied at 30 - 0.7 mm wave band EPR. A higher spectral resolution allows one to determine the principal values of anisotropic ***g***-tensor of localized paramagnetic centers in polyacetylene, attributed to pinned neutral solitons. The Very High Frequency EPR allows us to observe the increase of a number of such centers and the appearance of soliton diffusion along the polymer chains after the *cis-trans* isomerization.

## 1. Introduction

Conducting polymers attract considerable attention during the last decade due to their perspective application in molecular electronics [1,2]. Polyacetylene (PA) is the simplest among them. It can exist in *cis*- and *trans*-forms, and the latter is thermodynamically more stable. The transition between C—C and C=C bonds does not require energy change in *trans-PA,* therefore this Peierls distortion opens up a substantial gap in the Fermi level [3]. This twofold degeneracy leads to the formation of nonlinear excitations, namely solitons possessing spin $S$= 1/2 in *trans-PA* chains [4], whose energy level is localized at a mid-gap, thus stipulating the fundamental properties of the semiconductor. Short *trans-PA* chains exist in as-prepared *cis-PA* resulting in paramagnetic susceptibility of this sample as well.

As the original properties of PA are related to the existence of paramagnetic centers (PCs) in the polymer chains, a great number of EPR studies were performed at conventional ($\lambda$ = 3 cm) wave band EPR during the last years [5, 6]. It was shown that PCs in *cis-PA* are characterized by a weak and broad (7-9 G) single line with $g$ = 2.0026. In the case of thermal *cis-trans* isomerization, the concentration of unpaired electrons increases from ~$10^{18}$ spin per gram (or one spin per ~44000 CH-units) in *cis-PA* up to ~$10^{19}$ spins per gram (or one spin per ~3000 – 7000

CH-units) in *trans-PA* during the process. This is accompanied by the linewidth decrease down to 2 - 0.3 G depending on the average length of *trans-PA* chains. In order to explain such a transformation of the spectrum, the defrosting of quasi-one-dimensional (Q1D) on-chain diffusion of the most of solitons was proposed by Goldberg *et al.* [7]. The effective diffusion rate $v_{1D}$ of the mobile solitons was determined experimentally by EPR method to vary in ~ $10^{-11}$—$10^{-13}$ $s^{-1}$ range [8, 9]. The major source of such a difference seems to arise from a weak sensitivity of the method to the ratio of the number of pinned spins to that of mobile spins in the sample under study [10].

It is obvious that the EPR line shapes of localized and delocalized PCs in PA must differ due to their different mobility. However, the low spectral resolution does not permit one to separate the lines of these PCs with different mobility at low operation frequencies. Holczer *et al.* [11] have shown that a signal from a small amount of localized spins can completely mask a spectrum from mobile ones in *trans-PA.* Besides, the strong cross-relaxation processes exist in this sample due to spin-spin exchange. Therefore, a correct determination of magnetic, dynamic and other properties of PCs in PA is complicated at these bands.

Earlier we have shown [12-15] that the accuracy and informativity of the method increase considerably at investigating the conducting polymers at 2-mm wave band EPR. This paper reports the results of investigating *cis-* and *trans-PA* at millimeter and submillimeter (down to $\lambda_e$ = 0.7 mm) wave band EPR.

## 2. Experimental

Shirakawa *cis-PA* films of 90-350 μm thickness were synthesized according to the method described in [16]. *Trans-PA* samples were obtained by heating *cis-PA* samples at 450 K in vacuum for 30 min.

For the standard 3-cm and 8-mm wave band EPR studies using EPR-V and RE-1308 spectrometers, 10x2 mm thin film samples were introduced into quartz ampoules and sealed under vacuum. The concentration of PCs was measured at 3-cm wave band EPR using single crystal (TCNQ)pyrimidine as a standard.

The 3-mm wave band EPR spectra were registered using a home-made spectrometer at the Illinois University.

For the 2-mm wave band EPR studies at 90-320 K, 3x0.3x0.1 mm needle shape samples were introduced into 0.5 mm diameter and 7 mm long quartz capillaries and then into the cylindrical $H_{001}$ type cavity of a 2-mm wave band spectrometer described in [17]. The smallest dimension of the samples did not exceed the value of the wavelength used ($\lambda_e$ ~ 2.2 mm), thus the quasi-unimodal oscillation conditions of the magnetic field were fulfilled. Magnetic field sweep and $g$-factor measurements were carried out using another standard, namely $Mn^{2+}$ in MnO with $g_{eff}$ = 2.00102 and the hyperfine splitting constant $a$ = 87.4 G. HF modulation and microwave field phase tuning, and the measurement of the relative concentration of PCs were performed using a single crystal $(DBTTF)_3PtBr_6$ standard with $g$ = 2,00471 and a 4.4 G peak to peak linewidth ($\Delta H_{pp}$). The microwave phase adjustment was achieved by making the second harmonic of the absorption signal symmetrical at a low rate of field sweep. The value of the microwave field $H_1$ was not greater than 10 mG at the place of the sample location, the field sweep rate did not exceed 0.7 $G \cdot s^{-1}$, and the field modulation amplitude was equal to 0.6 G.

Because it is difficult to obtain good vacuum in small quartz capillaries, PA samples were studied at 2-mm wave band EPR in the presence of a small but unknown amount of oxygen. The smallest quantity of oxygen was obtained by placing a capillary with the sample in an air-free ampoule, which was in turn put into a Dewar flask with liquid nitrogen. Then the ampoule was removed and the capillary with the sample was placed into the cavity, being itself in a Dewar flask. Such a procedure allows one to avoid the contact of PA with air, after it had been placed in vacuum.

The spectra at higher frequencies were registered using a home-made spectrometer with a unit-quality factor of the sensitive cell described in [18]. In this spectrometer the signal was registered optically as an absorption of a pumped far infrared light guide $CO_2$-laser, providing emission lines at several wavelength from 570 nm to 2 mm. The magnetic field was induced by a resistive coil system with a homogeneity of about 3 G in a sphere of 8 mm diameter.

## 3. Results and Discussion

*Cis*- and *trans*-PA samples at 3-cm wave band EPR are characterized by a single symmetric line with $g$ = 2.0026 and peak to peak linewidth $\Delta H_{pp}$ equal to 6.7 and 2.2 G, respectively (Fig. 1, spectra a and d). The *trans-PA* sample shows $\Delta H_{pp}$ value slightly greater than that reported earlier [5] probably due to a higher oxygen contamination in the sample. A slight EPR linewidth increase ($\delta\Delta H_{pp}$ = 1 G) is observed at 77 K probably due to a smaller libration of the different fragments of the polymer chains. A linewidth is observed to increase by about 1 G if the sample is exposed to air.

At 8-mm wave band EPR an insignificant increase in the linewidth of PA samples is observed.

At 3-mm wave band *cis-PA* sample demonstrates the increase in $\Delta H_{pp}$ up to 8.4 G, with the analogous broadening of the high field peak attributed to the anisotropy of the $g$-factor. The *trans*-PA spectrum shows a line characterized by $g$ = 2.00270, $\Delta H_{pp}$ = 3.7 G and an asymmetry factor (the ratio of the high field to low field peak intensities) equal to 1.1.

The decrease in the EPR wavelength down to 2 mm leads to the further increase in $\Delta H_{pp}$ of *cis*- and *trans*-PA samples up to 11 and 5 G, respectively. Moreover, the $g$-factor anisotropy of PCs in *cis*-PA and the asymmetry factor (about 1.3) for

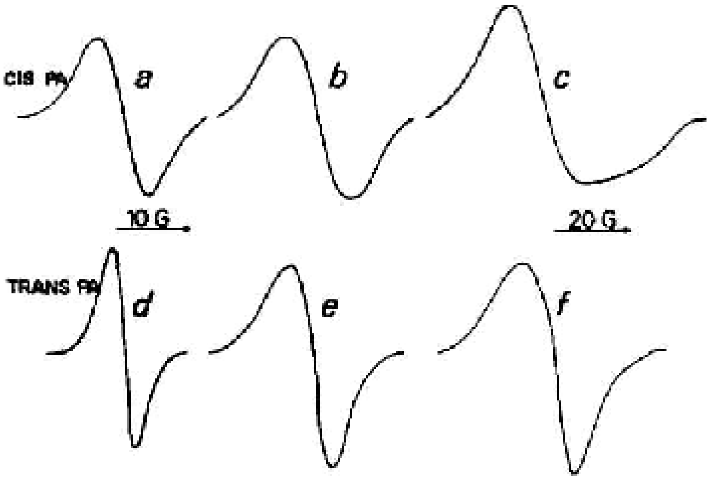

**Fig.** 1. Experimental EPR absorption spectra of *cis-* (*a-c*) and *trans-* (*d-f*) polyacetylene registered at 3-cm (*a*, *d*), 2-mm (*b*, *e*) and 0.7-mm (*c*, *f*) wave bands at room temperature.

*trans*-PA are displayed more evidently (Fig. 1, spectra *b* and *e*). The magnetic susceptibility of all the samples slightly decreases at cooling, it reaches a minimum at about 180-210 K (about 0.6 of its room temperature value), and then increases again with further cooling. This effect is not yet interpreted.

At higher frequencies the anisotropy of the *g*-factor of PCs becomes more evident in *cis-PA* sample (Fig. 1, spectrum *c*). The line shape must be attributed to the localized PCs. By analyzing the spectrum as described in [19], the following values are obtained for the *g*-tensor components: $g_\perp$ = 2.00283 ($\pm 5 \cdot 10^{-5}$) and $g_\parallel$ = 2.00236 ($\pm 5 \cdot 10^{-5}$); thus $g_{iso} = (2g_\perp + g_\parallel)/3 = 2.00267$ is obtained for $g_\perp$ value of localized PCs

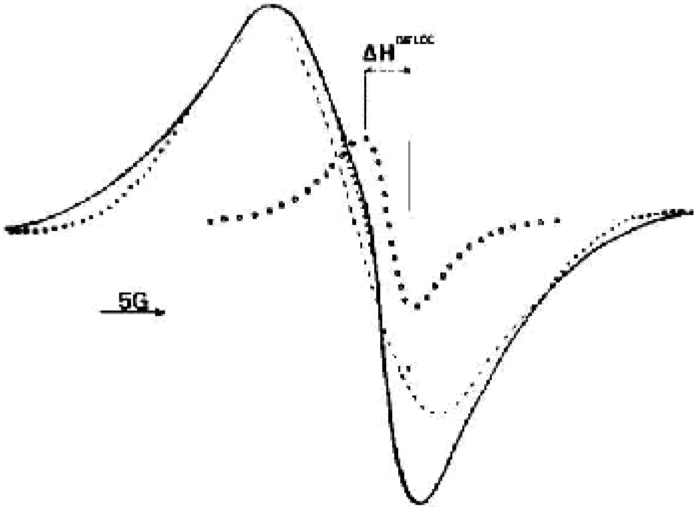

**Fig.** 2. Experimental 2-mm absorption spectra of *trans*-polyacetylene shown in Fig. 1, spectrum *e* (solid line) and calculated ones (dashed squares) taken as a superposition of spectra of localized (dotted line) and mobile (circles) paramagnetic centers.

differs from the $g$-factor for free electron $g_e$ by $\Delta g = 5 \times 10^{-4}$. According to the perturbation theory such a difference corresponds to the unpaired electron transfer from $\sigma_{C\text{-}C:}$ orbital to an antibinding p* orbital with an energy difference $\Delta E_{\sigma p^*} = 2\lambda_C / \Delta g = 14$ eV, where $\lambda_C = 3.6$ meV is the spin-orbit coupling constant for a carbon atom. As a matter of fact, the calculated $\Delta E_{\sigma p^*}$ value is equal to 14.5 eV for ***n***-conjugated systems in the case of normal C-C bond [20]. The other electron transitions with a greater $\Delta E_{ij}$ do not influence $\Delta g$. Thus, the spectrum line shape and the agreement between the calculated and measured $\Delta E_{\sigma p^*}$ values support the idea about the existence of localized PCs in PA.

The line shape of *trans-PA* spectrum remains almost unchanged with the increase in the operation frequency. One only notices the further increase in both the linewidth and the asymmetry factor (Fig. 1, spectrum *f*).

The transformation of PA line shape at *cis-trans* isomerization apparently indicates the appearance of mobile PCs in PA during this process. The close values of the isotropic $g$-factor of the localized PCs and $g$-factor of the delocalized PCs shows that the averaging of the $\boldsymbol{g}$-tensor components of the delocalized PCs due to their mobility occurs with the rate [21]

$$\nu_{1D}^{0} \geq (g_{\perp} - g_e)\mu_B H_0 / h, \qquad (1)$$

where $\mu_B$ is the Bohr magneton, $H_0$ is the applied magnetic field strength and $h$ is the Planck constant. Such a change in the shape of PCs spectra has already been observed for doped poly(tetrathia-fulvalene) [14], polyaniline [15] and poly(*p*-phenylene) [22]. Thus, neutral solitons pinned on short *trans-PA* chains are the dominant PCs in as-prepared *cis-PA* sample. At the same time two types of PCs exist in *trans-PA*, namely neutral pinned solitons and neutral solitons moving along the long polymer axes with $\nu_{1D}^{0} \geq 1 \times 10^{8}$ s$^{-1}$ rate.

In order to examine this assumption, a simulation of *trans-PA* spectrum, which is considered as a superposition of spectra of localized PCs with $g_{||}$ and $g_{\perp}$ values and delocalized PCs with $g_{iso}$ value determined above was performed according to the method described in [23]. The concentration ratio of localized ($n_1$) and delocalized ($n_2$) PCs was taken as $n_1/n_2 = 18$ (or $1.1 \times 10^{-3}/6 \times 10^{-5}$ spin per CH-unit). The localized PCs linewidth $\Delta H_{DD}^{loc}$ was assumed to be twice as large as that of the low field peak, while the delocalized PCs linewidth was assumed to be equal to the distance between the slight hump near the spectrum center and the high field peak of *trans-PA* (Fig. 2). As seen from Fig. 2, the simulated spectrum is in good agreement with the experimental one. Note that $n_2$ estimated using spectrum simulation is two orders of magnitude smaller than that reported by Goldberg *et al.* [7].

As the operation frequency increases from $\nu_e = 35$ GHz, the linewidth of the PCs increases (see Table). Such a change can be explained in the frame of the Portis conception of interacting spin-packets (single spins or groups of spins) which are

**Table.** Linewidth *AH* (in G) and distance (in MHz) between the spin-packets in neutral polyacetylene as a function of the operation frequency $\nu_e$ (in GHz) and wavelength $A_e$ (in mm) at room temperature.

| $\nu_e$ | 10.0 | 37.5 | 94.3 | 139 | 250 | 349 | 428 |
|---|---|---|---|---|---|---|---|
| $\lambda_e$ | 30 | 8 | 3.2 | 2.16 | 1.2 | 0.86 | 0.7 |
| | | | Localized PCs in *cis-PA* | | | | |
| $\Delta H_{pp}^{loc}$ | 7.0 | 7.5 | 8.5 | 9.5 | 18 | 24 | 25 |
| $\Delta\omega_{ij}$ | 27.1 | 28.6 | 30.2 | 36.6 | 44.6 | 50.9 | 52.5 |
| | | | Localized PCs in *trans-PA* | | | | |
| $\Delta H_{pp}^{loc}$ | 2.5 | 3.0 | 4.5 | 6.1 | 16 | 25 | 19 |
| $\Delta\omega_{ij}$ | 15.9 | 19.2 | 22.3 | 35.0 | 44.6 | 55.7 | 49.3 |
| | | | Delocalized PCs in *trans-PA* | | | | |
| $\Delta H_{pp}^{deloc}$ | 0.6* | **1.1*** | 1.8 | 3.0 | 5.0 | 6.0 | 8.1 |
| $\Delta\omega_{ij}$ | 12.7* | 20.7" | 27.1 | 35.0 | 46.2 | 50.9 | 58.9 |

* Determined from extrapolation.

characterized by the spin-lattice $T_1$, spin-spin $T_2$ relaxation times and the resonant frequency $\omega_i$ in the paramagnetic system [24]. At low fields the distance between the different spin-packets $\Delta\omega_{ij}$ does not exceed their exchange rate $\nu_{EX}$, thus the resulting signal of such spin-packets is in the conditions of fast exchange and may be described by a Lorentzian function. If $H_0$ value increases, the spectral resolution between the spin-packets increases and when the $\nu_{EX} << \Delta\omega_{ij}$ condition is satisfied, the spectrum can be described by a convolution of the Gaussian and Lorentzian functions. Moreover, the cross-relaxation rate between the spin-packets decreases at high field according to the $W = k_1\exp(-k_2H_0^2)$ power law [25], where $k_1$ and $k_2$ are the normalization factors. Therefore, the spin-packets may be considered as noninteracting in these conditions.

The analysis of the line shape of *cis-* and *trans-PA* samples performed according to the method described in [26] shows that their low field parts can be described by a Lorentzian function in the center and by a Gaussian one in the wings at $\nu_e \geq 139$ GHz. At the same time the high field parts of the spectra are Lorentzian. The exchange frequency between spins obtained from the analysis is equal to $3.0\times10^7$ and $1.2\times10^8$ $s^{-1}$ for localized PCs in *cis-* and *trans-*PA, respectively. These values are in agreement with the estimation $\nu_{EX} \geq 10^7$ $s^{-1}$ made in [11] for *trans-*PA. Therefore, the condition $\nu_{EX} < \Delta\omega_{ij}$ holds and the spin-packets become noninteracting at the frequencies higher than 16 GHz. Then the linewidth varies according to the equation [27]

$$\Delta H_{\perp} = \frac{1}{\gamma_e T_2} + \frac{\Delta\omega_{ij}^2}{8\gamma_e \nu_{EX}}, \tag{2}$$

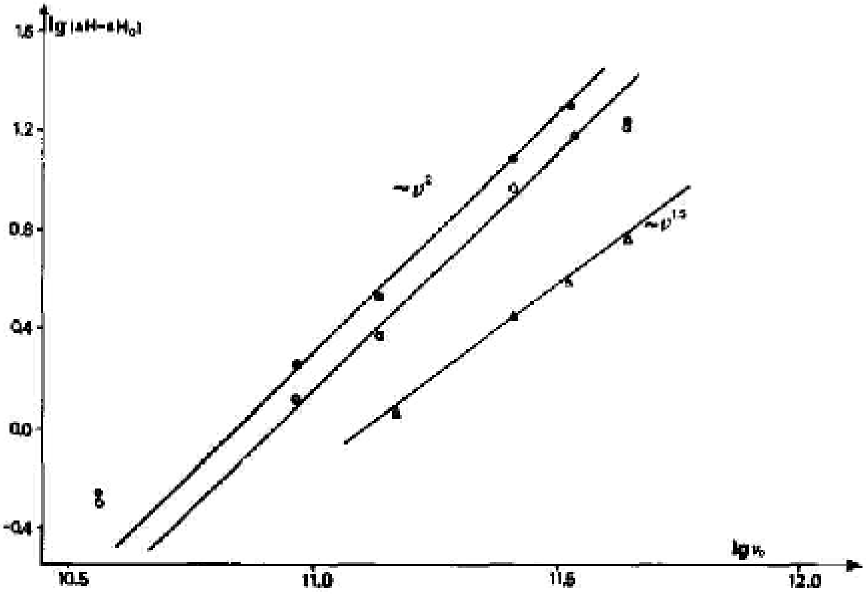

**Fig.** 3. Logarithmic dependences of EPR line broadening $\Delta H - \Delta H_0$ for paramagnetic centers localized in *trans*- (dashed circles) and *cis*- (open circles) polyacetylene samples (with respect to $\Delta H_0$ at 10 GHz) and for mobile paramagnetic centers in *trans*-polyacetylene (triangles) (with respect to $\Delta H_0$ at 94.3 GHz) versus operation frequency $\nu_c$ at room temperature.

where $\gamma_e$ is the gyromagnetic ratio for electron, $(\gamma_e T_2)^{-1}$ is the spin-packet line width in the absence of the spin-spin exchange. By assuming $T_2 = 1.8 \times 10^{-7}$ s for *trans-PA* at room temperature [13] and strong interaction between localized and mobile solitons in this sample, $\Delta H_{pp} = 0.32$ G may be calculated for a mobile soliton. Such a value is in good agreement with that proposed by Holczer *et al.* [11]. However, our data evidence that the sharp low-frequency-line narrowing at PA *cis-trans* isomerization attributed earlier [5-7, 9, 11] to the defrosting of the motion of most of the spins in the polymer, is indeed caused mainly by the increase in $\nu_{EX}$ and the decrease in $\Delta\omega_{ij}$ values during the process.

$\Delta\omega_{ij}$ of PCs of both *cis*- and *trans-PA* samples obtained by using Eq. (2) is also presented in Table. The dependences of line broadening of both localized and mobile PCs versus $\nu_e$ are shown in Fig. 3. It is seen from the figure, that the linewidth of PCs localized in *cis*- and *trans-PA* samples, changes quadratically with the registration frequency, and hence it can be described by Eq. (2). This is an additional evidence for a weak interaction of spin-packets in these polymers. At the same time the line of mobile PCs broadens with frequency as $\Delta H_{DD}^{deloc} \propto \nu_e^{1.5}$. This indicates a more strong spin-phonon interaction in *trans-PA* due to Q1D soliton motion.

By using the well known results for the random walk, the EPR linewidth of soliton with halfwidth $N$ in the Q1D motionally narrowed regime is given in the frames of the phenomenological model [28] by

$$\Delta H_{pp}^{deloc} = \nu_{1D}^{-1/3} (\Delta H_{\perp}^{loc})^{4/3} N^{2/3} \qquad (3)$$

in contrast to $\Delta H_{\mathrm{pp}}^{\mathrm{deloc}} = \nu_{\mathrm{3D}}^{-1}(\Delta H_{\perp}^{\mathrm{loc}})^2 N$ dependence, characteristic of Q3D spin motion. From the data of Table, $\Delta H_{\mathrm{pp}}^{\mathrm{deloc}} \propto (\Delta H_{\perp}^{\mathrm{loc}})^{4/3}$ dependence can be evaluated at least for $\nu_e \leq 139$ GHz region additionally favoring the Q1D soliton mobility in ***trans-PA*** under study. At higher frequencies such a dependence is not fulfilled probably due to the close values of $\nu_{\mathrm{1D}}/N^2 = 2\times10^{11}$ $\mathrm{s}^{-1}$ [13] and $\nu_e$.

## 4. Conclusions

Therefore, neutral solitons pinned on short ***trans-PA*** chains seem to be dominant PCs in ***cis-PA***. The possibility of an interchain electron transfer is very small being defined only by librations of ***cis-PA*** chains. The number of such PCs increases remarkably and mobile solitons appear during ***cis-trans-'isomerization***. The appearance of about 6 % of mobile solitons is accompanied by the drastic increase in ***trans-PA*** conductivity in this process. The change in $\Delta\omega_{ij}$ and $\nu_{\mathrm{EX}}$ values for the centers of both types leads to a sharp narrowing in its low-frequency EPR spectrum (e.g. by 4-5 times at $\nu_e \leq 10$ GHz) under the isomerization.

The registration of the spectra at a wide operation frequency range allows one to obtain complementary, more correct and complete information on various properties of PA and to testify the models, which describe the dynamic processes in this and other organic semiconductors.

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**Author's address:** Dr. V. **I.** Krinichnyi, Institute of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, M.D., Russian Federation