

## ESR STUDIES ON POLYMERS WITH PARTICULAR ELECTRONIC AND MAGNETIC PROPERTIES

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Abstract: Measurements on insulating and conducting polymers from the polyaniline (PANI) family and investigations on semiconducting poly(tetrathiafulvalenes) (PTTF) have been used for illustration and discussion of some methodical questions of electron spin resonance (ESR). This concerns especially the new possibilities of the recently developed high-resolution ESR in the 2 mm wave band. It was applied for the study of the nature and dynamics of paramagnetic centres (PC) and charge carriers in PANI and PTTF. The rate of the quasi-one-dimensional (1D) intrachain electron motion and of the three-dimensional (3D) interchain electron hopping has been estimated separately. In iodine-doped PTTF the maximum electrical conductivity is  $10^{-4} \text{ S cm}^{-1}$ . It is almost identical with the 3D-conductivity estimated by ESR and shows the typical temperature dependence of a semiconductor. The quasi-1D-conductivity is several orders of magnitude higher and shows in its dependence on temperature similarities with a metal. The PANI samples show in the highly doped form a maximum conductivity of about  $10 \text{ S cm}^{-1}$  and relatively small differences between the 1D- and 3D-conductivity, supporting the model of metallic islands.

### 1. Introduction

Electron spin resonance (ESR) is a unique spectroscopic method with a broad application field in polymer sciences (Ref.1). It is very sensitive in the study of the behaviour of paramagnetic molecules or molecule segments in polymers. Especially, it allows to get singular information about principal properties of polymers with particular electronic and magnetic properties like conducting polymers and polymers with antiferro-, ferri- and ferromagnetic properties. The study of such systems requires the use of all potentialities of ESR spectroscopy including the electron spin echo (ESE) detection and the high-field (and high-frequency) ESR. This will be shown in connection with our studies on semiconducting poly(tetrathiarulvalencs) and in connection with measurements on insulating and conducting polyanilines.

## 2. Eiperimental

### 2.1. The investigated polymers

Poly(tetrathiafulvalene) PTTF is a sulfur-organic polymer which shows long-term stability and a significant increase in electrical conductivity upon doping. In the studied poly(tetrathiafulvalenes) the TTF units are linked via phenyl groups or via tetrahydroanthracene bridges (Ref.2). The PTTF is doped with oxygen and with iodine, respectively. The electrical conductivity strongly depends on the temperature as typical for semiconducting materials. The chemical structure of the polymers investigated is the following:

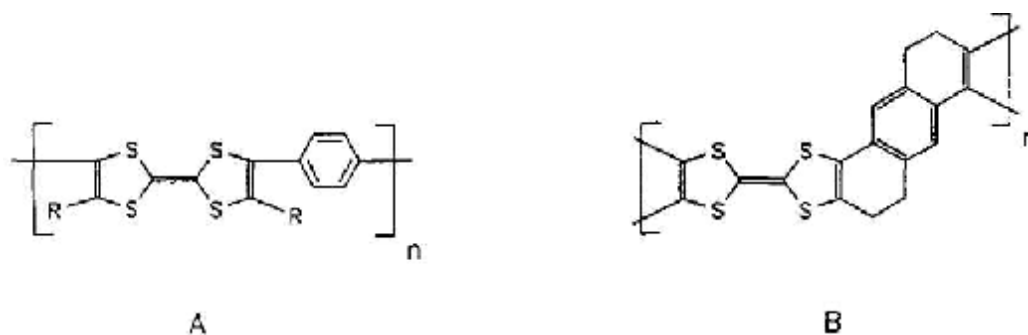


TABLE 1

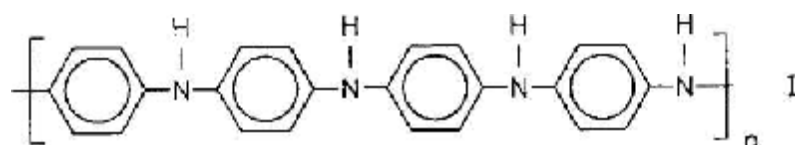
The substituents  $R$ , the average molecular weights  $m$  and the average number of monomeric units  $n$  of the investigated compounds

Compound	Structure	$R$	$m$	$n$
A.1	A	-H	7150	25
A.2	A	-CH <sub>3</sub>	7660	25
A.3	A	-CH <sub>2</sub> CH <sub>3</sub>	7800	25
B.1	B		6810	20

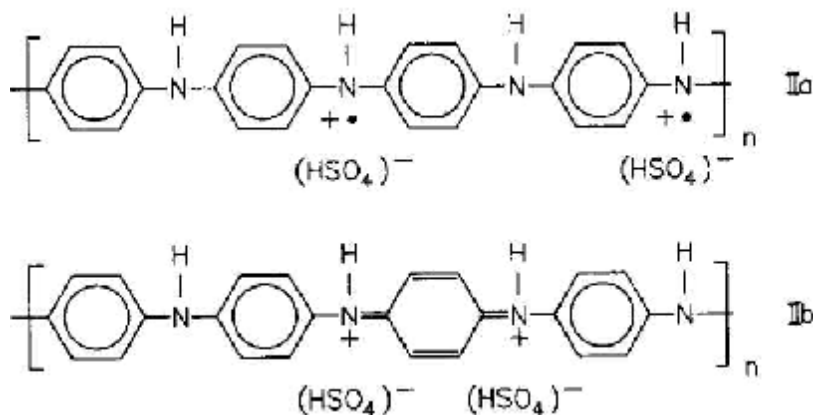
Details of the synthesis are given in Refs.2,3. All these amorphous polymers are usually obtained in powder form. The samples were doped with iodine dissolved in chloroform using different concentrations of the dopant. The iodine content is referred to the TTF unit (iodine per monomeric unit).

Polyaniline (PANI) is one of the most important electrically conducting polymers because of the unique combination of high conductivities, environmental stability and good processibility. The molecular structure and some properties of this polymer depend on the synthesis route. The studied PANI have been synthesized by Lux (Ref.4) via a modification of the general route with  $(\text{MH}^+\text{BrO}_3$  in 1.0 M hydrochloric acid as described, e.g., by Cao and Tan(Refs.5,6).

After the synthesis the PANI powder was neutralized in 1.0 M  $\text{NH}_4\text{OH}$ . The basic polymer (PANI I in the undoped form ( $y = 0$ )) is a poly(phenylenamine) or a leucoemeraldine base polymer ( $y$  is the doping level) .



The applied doping process is an oxidation. The highly doped PANI (predominantly PANI II at  $y > 0.1$ ) is a polyaniline with sulfate ions as counter ions (Ref.4). It contains probably as well positively charged radical ions (polarons) as bipolarons.



The aim of the ESR measurements is to obtain more information about the kind and properties of spins and charge carriers in poly(tetrathiafulvalenes) and polyaniline.

## 2.2. Basic requirements of ESR spectroscopy

A basic requirement for the application of ESR techniques to the polymer characterization is the presence of molecules containing unpaired electron spins. Most conducting polymers contain several types of paramagnetic centres (PCs) which differ in mobility and other

properties. Frequently one part of the charge carriers responsible for the electrical conductivity owns a spin, that is they are paramagnetic species. Other unpaired electron spins can be fixed on segments of the polymer chains. Their mobility is determined predominantly by the motions of the chain segments.

Both groups of paramagnetic centres are to be found in the conducting polymers PANI and PTFE. They will be used for a deeper characterization of the conducting polymers included the intrachain electron diffusion, interchain hopping and anisotropic slow segment motions.

### 2.3. Advantages of high-field ESR demonstrated in connection with measurements on PANI

In the 3 cm wave band the ESR spectra of organic free radicals are registered in a narrow range of the magnetic field where the exchange rate between distinguished spin packets is high in comparison with its width and an overlapping effect exists. As shown in previous papers (Refs.7-10), in the 2 mm wave band the spectral resolution and information content of the ESR method increases considerably and allows more complete investigations of the structure and dynamic properties of paramagnetic centres (PCs) in conjugated polymers. The ESR experiments on PANI have been performed by Krinichnyi et al. (Ref.11) using a 3 cm wave band PS-100X and 2 mm wave band ESR-05 (Ref. 12) spectrometers with 100 kHz field *a.c.* modulation for phase lock detection. The total spin concentration in the samples was determined using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  single crystal as a standard. Another standard,  $\text{Mn}^{2+}$  with  $g_{\text{eff}} = 2.00102$  and  $a = 8.74$  mT, was used for the determination of the *g*-factor as well as for the magnetic field sweep scale calibration in the 2 mm wave band.

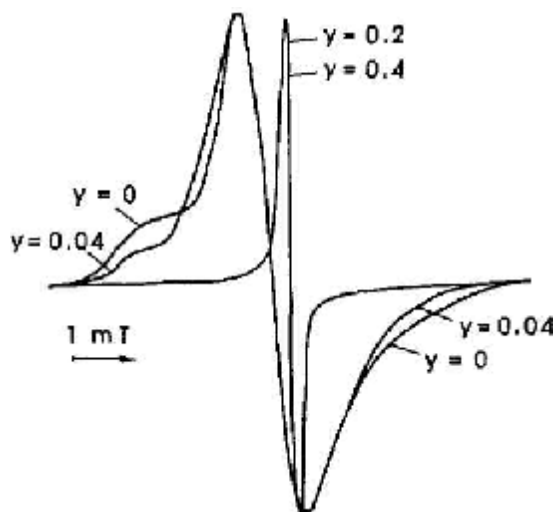


Fig 1: 3 cm wave band ESR spectra of four PANI samples with various doping levels  $y$  measured at room temperature and normalized to equal amplitudes.

The 3 cm ESR spectra are superpositions of two signals with different anisotropy caused by two types of spins with various mobilities. The strong asymmetric signal components seen in the low field region of the ESR spectra of the undoped and very low doped samples ( $y \leq 0.04$ ) decreases by oxidation to zero if the  $y$ -values become higher than 0.1 and the main ESR signal becomes narrower and is shifted to higher fields if  $y \geq 0.2$ . This might be due to an increase of mobility of PCs and to bipolaron formation. The averaged  $g$ -factor changes from  $g = 2.0036$  to  $g = 2.0027$ . This is accompanied by a strong increase of the amplitude of the narrow signal. It reflects an increase of spin carriers with high mobility which fits very well with the increase of electrical conductivity by doping.

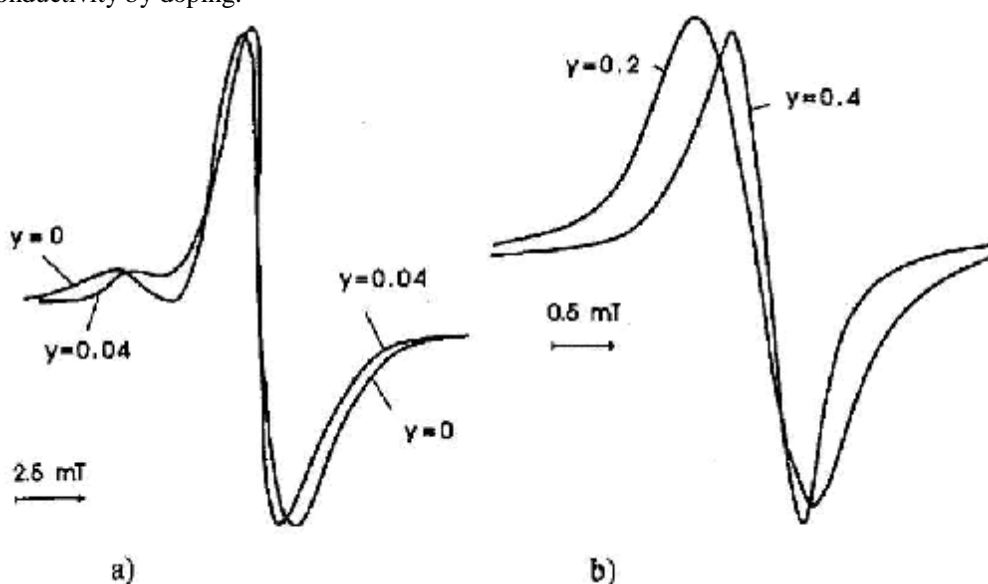


Fig. 2: 2 mm wave band ESR spectra of PANI samples with various doping levels measured at room temperature; a) undoped and very lowly doped samples, b) highly doped samples.

Also the 2 mm ESR spectra of the two PANI samples characterized by extremely low conductivity and  $y < 0.04$  are superpositions of two signals: of a weak, very asymmetric signal of strongly localized PCs  $R_I$  with the  $g$ -tensor components  $g_x = 2.00535$ ,  $g_y = 2.00415$ ,  $g_z = 2.00238$ , and the components of the hyperfine structure tensor  $A_x = A_y = 0.33$  mT and  $A_z = 2.3$  mT, and of a less asymmetric signal of higher intensity belonging to the more mobile PCs  $R_{II}$ . For the last the following magnetic parameters were obtained from the simulation:  $g^{\wedge} = 2.00351$ ,  $g_{\parallel} = 2.00212$  (Ref.11). The relative content of the PC  $R_I$  in the undoped sample is approximately 25% at room temperature.

Krinichnyi et al. showed earlier (Refs. 10,13,14) that the diffusion of paramagnetic centres with anisotropic  $g$ -factors in conjugated organic polymers leads to the averaging of the principle  $g$ -tensor components, if

$$n_{\text{diff}} \gg |g^{\wedge} - g_{\parallel}| \mathbf{b}B_0/h$$

where  $n_{\text{diff}}$  is the diffusion rate of paramagnetic centres,  $b$  is the Bohr magneton. It means, paramagnetic centres  $R_{\text{II}}$  giving rise to the narrow ESR line of figures 1 and 2b possess a relatively high diffusion rate along the polymer chains and may be attributed to mobile spin charge carriers, namely polarons, while at lowly doped samples ( $y < 0.1$ ) the predominant part of paramagnetic centres exhibiting asymmetric spectra is relatively strongly localized on segments of polymer chains.

The 2 mm spectra analysis undoubtedly confirms the existence of localized paramagnetic centres with anisotropic  $g$ -factors, especially in PANI samples with  $y < 0.1$ , and of mobile ones, diffusing along the chain with a rate of  $n_{\text{diff}} > 5 \times 10^{10} \text{ s}^{-1}$  (Ref. 11). The observed narrow ESR spectra at high doping level are evidence for the formation of areas with high spin density in which a strong spin-spin exchange occurs.

Fig. 2b shows the 2 mm ESR spectra of the highly doped PANI samples with  $y = 0.2$  and  $0.4$ , which in the 3 cm wave band gives rise to a narrow ESR signal almost identical for the two different samples. It shows best the effect of the higher spectral resolution of the 2 mm technique. The complete evaluation of these spectra and of other ESR measurements on PANI are still in progress and will be published soon in a separate paper (Ref. 11).

### 3. Studies on PTFE by ESR and ESE in the 3 cm waveband

#### 3.1. Results of ESR studies

Previous ESR studies (Refs. 15-17) have shown that the spectra of weakly doped PTFE are a superposition of a strongly asymmetric spectrum of immobile radicals  $R^i$  and of a symmetric spectrum caused by mobile cation radicals  $R^m$  (formula will be given further down). The dependence of the signal intensities on temperature and doping level has been interpreted by means of a model based on trapped radicals, mobile polarons and bipolarons (Refs. 16,17). In poly(tetrathiafulvalene) the measured  $g$ -factors of free radicals are with  $2.0068 < g < 2.0081$  larger than in PANI (see chapter 2.3.) and in poly(thiophene) with  $g = 2.0026$  (Ref. 18). The high value of the  $g$ -factor in PTFE refers to radicals with a large spin density near sulfur atoms. ESR spectra of two phenylene-bridged PTFE weakly-doped only with oxygen, which contaminated the polymers, are presented in Fig.3.

The asymmetric spectrum predominant in PTFE A.2 and A.3 assigned to immobile radicals  $R^i$ , has a typical powder pattern caused by an anisotropic  $g$ -tensor with a symmetry lower than axial. The mean  $g$ -factor is  $g = 2.0081$ . Simulation of the measured spectra of Fig. 3 by superposition of an asymmetric spectrum with  $g_x = 2.0147$ ,  $g_z = 2.0067$  and  $g_y = 2.0028$  and a symmetric one of mobile radicals  $R^m = R_2^m$  with  $g = 2.0071$  yields that the paramagnetic centres of the undoped samples consist at least to 10 % of the radicals  $R^i$ . In the samples A.2 and A.3 the portion of  $R^i$  radicals even amounts to 54 % and 75 %, respectively.

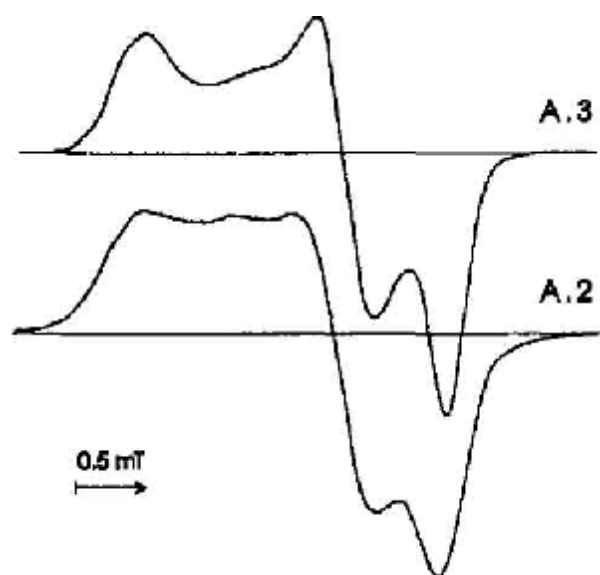
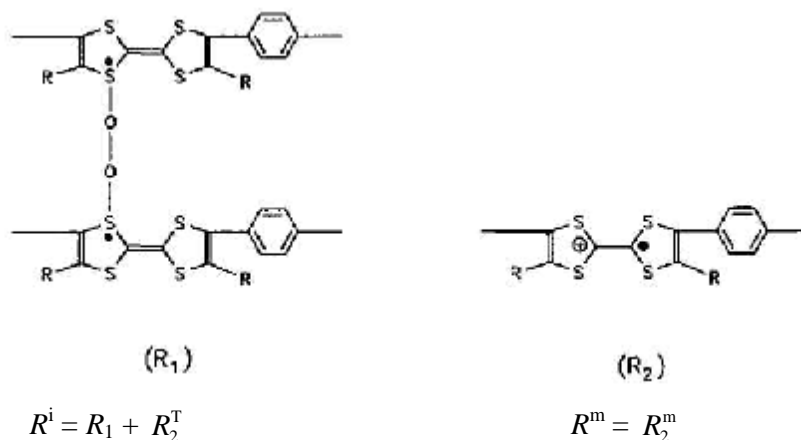


Fig 3: 3 cm wave band ESR spectra of two "undoped" PTF samples in which immobile radicals  $R^i$  predominate, measured at room temperature.

The mobile cation radicals  $R_2^m$  (or polarons  $P^{+*}$ ) have a  $g$ -factor between  $g = 2.0068$  (B.I) and  $g = 2.0078$  (A.I) depending on the molecular structure of the PTF (Ref.15). These values are in agreement with the  $g$ -factors of cation radicals in the tetrathiafulvalene (TTF) (Ref.19). The PTF A.1 and B.I have a nearly plane molecule structure. Due to this structure an electronic interaction occurs between the TTF units in the polymer, so that in an oxygen contaminated planar PTF an electron transfer from the PTF system to the  $^3O_2$  occurs, predominantly forming a TTF radical cation  $R_2$ , which has the same structure as a radical cation formed by doping with iodine (Ref.15). The structure of  $R^i$  can be realized by a homopolar bond between the oxygen and a sulfur atom of the TTF ring (forming a radical  $R_1$ ) or by an ion pair interaction between the cation radical  $R_2$  and the counterion  $O_2^-$  forming  $R_2^T$ , i.e., a trapped cation radical. A possible structure of  $R_1$ , and that of  $R_2$  can be represented by the following formulas (Refs. 16,17).



Because sulfur has a relatively large spin orbit coupling with  $l = 382 \text{ cm}^{-1}$ , an asymmetric spectrum is to be expected in trapped cation radicals  $R_2^T$ . Nevertheless, it cannot be excluded that the observed asymmetric spectrum is partly due to radicals of type  $R_1$  (Ref. 16). The addition of iodine as a dopant causes a drastic change of the line shape in outcome of a radical conversion. At very low dopant concentration the iodine atoms effect mainly a conversion of the localized radicals into mobile cation radicals. This results in the increase of conductivity without increasing the total spin concentration. The mobile radicals  $R_2^m$  directly contribute to the conductivity as polarons or indirectly by recombination to bipolarons, thus losing their spin paramagnetism. In the case of low dopant concentration the line shape of the ESR spectra shows that there are still localized paramagnetic centres in the samples. The simulation of ESR spectra measured at room temperature has shown that the addition of 0.2 iodine atoms per monomeric unit effects that in the time scale of 3 cm ESR the spectrum is to more than 90 % due to mobile  $R_2$  radicals and to less than 10 % due to localized radicals.

### 3.2. Results of ESE measurements

In the used equipment (Ref.20) only those paramagnetic centres contribute to the ESE detected ESR spectrum which has a phase memory time  $T_M > 250 \text{ ns}$ . From the radicals in PTFE discussed up to now, only the localized or trapped radicals  $R_1$  and  $R_2^T$  were detected. The ESE detected ESR spectra of the phenylene-bridged PTFE A3 are presented in Fig.4 (Ref. 16).

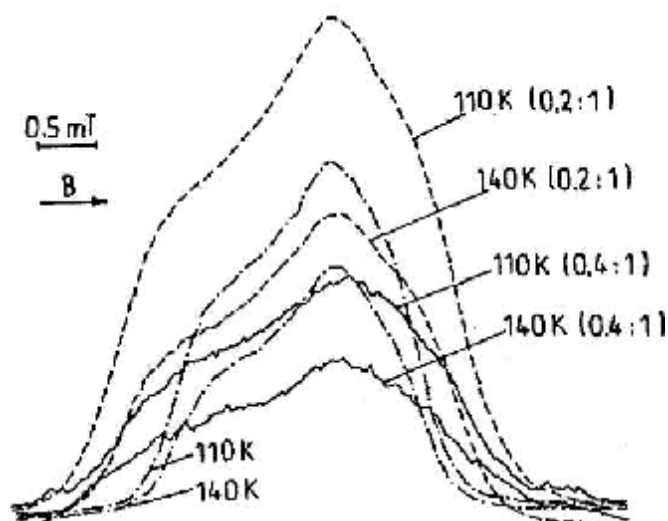


Fig.4: ESE detected ESR spectra of PTFE A.3 recorded in 3 cm wave band at 110 K and 140 K from an "undoped" sample ( ) and two iodine doped samples containing 0.2 and 0.4 iodine atoms per monomeric unit which corresponds to  $y = 0.06$  and  $0.12$ , respectively.



In the case of the not iodine doped or "undoped" sample the magnetic field distances between the singular points of this powder pattern agree well with those of the ESR spectrum of the immobile radicals  $R^i$  trapped by reaction or interaction with oxygen ( $R_1$ ,  $R_2^T/O_2^-$ ) which, predominantly determines the shape of the spectra A. 2 and A.3 in Fig.3 of the "undoped" PTF. However, there are significant differences in the g-value anisotropy detectable by ESE of the immobile radicals in the weakly doped samples of A.3 if the dopants are oxygen and iodine, respectively. Probably the anisotropic spectrum in iodine doped samples is due to localized radical  $R_2^T$  trapped by an interaction with the counter anion  $I_x^-$  ( $R_2^T/I_x^-$ ). Also from the chemical viewpoint it can be assumed the peroxy species cannot be present in the iodine doped samples because  $I_x^-$  is a reducing anion and would destroy  $R_1$ ,  $R_2^T/O_2^-$  (Refs. 16,17). The number of immobile radicals  $N_R$  decreases with rising temperature  $T$  according to

$$N_R = N_R^0 \exp[-E_A/(kT)]$$

with  $k$  - Boltzmann constant, and an activation energy  $E_A = 0.01$  eV, equal for both samples weakly doped with iodine.

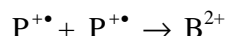
The basic idea of interpretation is that with increasing temperature the  $R_2^T/I_x^-$  lose their trapping state and become mobile cation radicals  $R_2^m$  (or polarons) with such a short relaxation time that they are undetectable by the ESE spectrometer applied or they form bipolarons thus losing their spin paramagnetism. The activation energy  $E_A$  for the decrease of localized radicals is of the same order of magnitude as the  $E_A$  of increasing electrical conductivity in this temperature region ( $E_A = 0.03$  eV). This points out that the radical conversion mentioned really contributes to the increase of conductivity measured in the low temperature range (Ref. 16).

### 3.3. Structure and temperature dependent polaron/bipolaron conversion

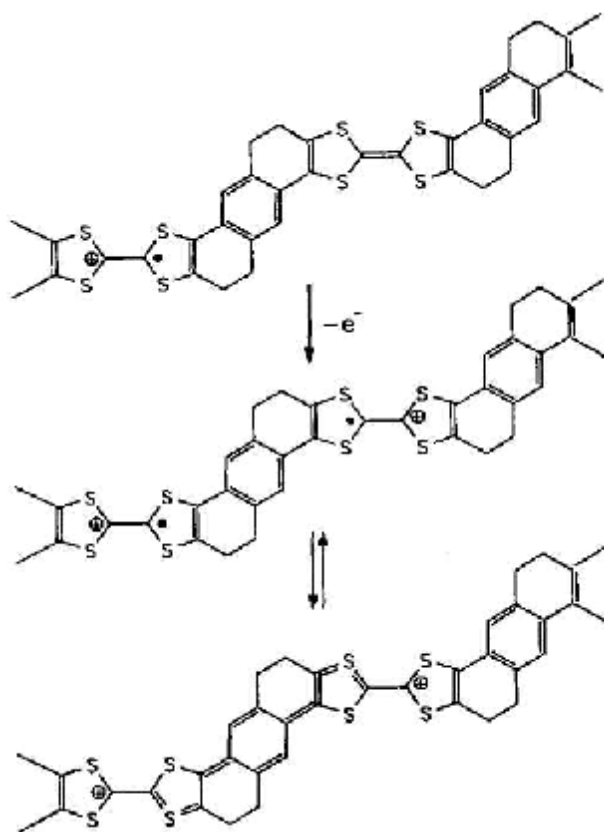
Both  $^{127}\text{I}$ -Mössbauer and Raman spectroscopies find that iodine intercalates in poly(tetrathiafulvalenes) in the form of polyiodine species, namely  $I_3^-$  and  $I_5^-$ . The relative  $I_3^-$  content decreased with rising doping level. Below 0.5 iodine per monomeric unit, iodine is present mainly as  $I_3^-$  molecules (Ref. 21). The  $I_3^-$  (and  $I_5^-$ ) anions are found to be more strongly bound in the PTF polymers than in polyacetylene. This behaviour is also reflected by their Raman frequencies. We can estimate the charge carrier density from the dopant concentration. If we assume the predominant formation of  $I_3^-$  as counterions, every third iodine atom takes an electron from the PTF generating a cation; in the samples there is a minimum of about  $10^{21}$  charge carriers per gram. The radical concentration amounts to max.  $10^{19}$  spins per gram. That means the spin density in the doped PTF is almost two orders

of magnitude lower than the charge density.

From these ESR measurements it follows that there are on average less mobile radicals  $R_2 = P^{+\bullet}$  in the sample than macromolecules. If a second polaron  $P^{+\bullet}$  is formed on a macromolecule two polarons can form a diamagnetic bipolaron  $B^{2+}$



This process takes place with a higher probability in molecules with plane structure where electron interaction is favoured between the monomeric units. This can be assumed because the samples A.1 and B. 1 with almost plane structure show a lower radical concentration than the polymers A.2 and A.3 (which are of a twisted molecular structure), but the samples A.1 and B.I have the highest conductivity. These results support the assumption that the bipolarons generated via polarons provide the main contribution to the conductivity of the doped PTF (Refs.16,17). The following formulas represent possible structures of polarons and bipolarons in the PTF samples B. 1.



The decrease in temperature from room temperature to 150 K leads to a slight decrease in the signal amplitude supposed because of the bipolaron formation. However, below 150 K an increase in the signal was observed in some PTF. The observed variation of radical concentration with decreasing temperature leads us to the assumption that there is a temperature-dependent equilibrium between polarons and bipolarons which tends to shift again more to the polaron-side in the low-temperature region below 150 K (Ref.16).

#### 4. Studies on PTFE by high-field ESR in the 2 mm wave band

In Ref.14 both high spectral resolution and saturation effects in the 2 mm wave band ESR have been used for a more correct determination of the nature and dynamics of trapped and mobile paramagnetic centres (PC) in one slightly doped PTFE sample. With this investigation we demonstrated also the possibility of studying superslow anisotropic molecular reorientations in conjugated polymers using the 2 mm wave band saturation transfer ESR (ST-ESR) method (Ref.9).

##### 4.1. Determination of ESR parameters

ESR experiments were performed using a 3 cm (PS 100.X) wave band ESR spectrometer and a 2 mm (ESR 5-01) spectrometer with a superconductive magnet described in detail in Ref.22. The powder-like PTFE A.2 sample (with a doping level  $y = 0.12$  (or 0.4:1), total spin concentration of  $1\text{-}10^{18}$  spin/cm<sup>3</sup> and d.c. conductivity of  $10^5$  S cm<sup>-1</sup>) has been investigated (Ref.14).

In the 3 cm wave band the PTFE sample shows a nearly symmetrical signal which seems to be not influenced by immobilized PCs (Fig. 5a). Individual components of immobilized PCs are manifest more evidently in the 2 mm ESR spectrum. In fact, the 2 mm wave band ESR absorption spectra of the sample are more informative (Fig. 5b). They allow a correct determination of all major components of the anisotropic g-tensor and the separation of the lines of different shapes.

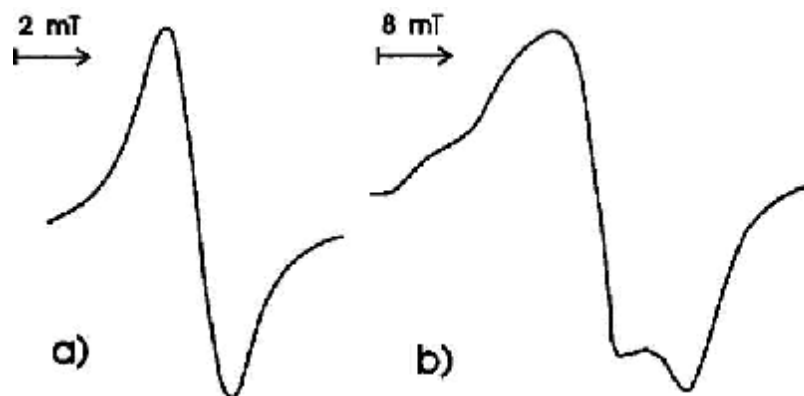


Fig.5: ESR spectra of the PTFE sample A.3 doped with 0.4 iodine atoms per monomeric unit measured at 110 K; a) in the 3 cm wave band, b) in the 2 mm wave band.

Computer simulation shows that the signal is a superposition of a strongly asymmetric spectrum with temperature independent magnetic parameters of  $g_x = 2.01424$ ,  $g_y = 2.00651$ ,  $g_z = 2.00235$  and a symmetric one with  $g_p = 2.00706$ . As measured in the time scale of 140

GHz or 2 mm ESR at low temperatures the two types of PCs are present in the sample with a concentration ratio of 1:1.8, or  $n_1 = 3.8 \times 10^{-5}$  and  $n_2 = 6.9 \times 10^{-5}$  spin per monomeric unit, respectively.

The  $g$ -factor  $g_p$  of the symmetric part of the spectrum is close to the average  $g$ -factor of the immobile PCs determined as  $\langle g \rangle = 1/3 (g_x + g_y + g_z) = 2.00770$ . It is known (Refs.7,9,23) that the principal components of the  $g$ -tensor of PCs in some conjugated polymers could be averaged if the PCs are moving with a rate  $v_{ID}^0 \geq (g_x - g_z)\beta B_0/h$ .

In PTFE there exist two types of PCs with approximately equal magnetic parameters, they are polarons moving along the polymer chain (X-axis) with the rate of  $v_{ID}^0 \geq 5 \cdot 10^9 \text{ s}^{-1}$  and polarons pinned on short polymer chain segments. The part of mobile polarons increases with rising dopant concentration (Refs. 16,17).

The measurements of Krinichnyi et al. (Ref.14) have shown that the linewidth of ESR spectral components of immobilized polarons,  $\Delta B_{pp}$ , is temperature-independent and may vary within 0.28 - 0.38 and then to 3.9 mT while the operation microwave frequency  $\nu_e$  increases from 9.5 to 37 and then to 140 GHz, respectively. The line width of mobile polarons,  $\Delta B_{pp}$ , in this case increases at 270 K from 1.0 to 1.12 and then to 17.5 mT, respectively. The line width of both types of PCs in PTFE increases quadratically only in the  $37 \text{ GHz} \leq \nu_e \leq 140 \text{ GHz}$  frequency region. This fact is discussed in terms of the non-interacting spin-packets in Ref.14. In this paper the fact that the mobile PCs have a broader line than the immobile ones is explained by the strong interaction with dopants. So the mobile PCs have probably a stronger interaction with the dopants than the immobile PCs. This is another interpretation than given in Refs. 16,17.

The decrease in the spectrum line width of the mobile polarons by 2.2 mT together with the 2-fold temperature decrease indicates that the ID-mobility of polarons becomes more intensive as the temperature falls and the so-called motional narrowing of the line takes place. Such a change in  $\Delta B_{pp}$  is very similar to the temperature dependence of the line width in metals.

#### 4.2. Spin-dynamics in PTFE

Spin-packets in paramagnetic systems are characterized by spin-lattice and spin-spin relaxation times  $T_1$  and  $T_2$ , resonance frequencies  $\omega_i$  and exchange frequency  $\nu_{ex}$ . In a reasonably strong magnetic field the inequality  $\nu_{ex} < \Delta\omega_{ij}$  can be satisfied, so that the line broadens inhomogeneously with the total width of  $\Delta B_{pp} = 1/(\gamma_e T_2) + \Delta\omega_{ii}^2/8\gamma_e \nu_{ex}$  (Ref.24) and is described by the Gaussian distribution function of separate non-interacting spin-packets. The passage effects are observed in the ESR spectrum under the condition of microwave saturation of spin-packets:

$$\gamma_e B_1 \sqrt{T_1 T_2} > 1 \quad (1)$$

and the well-known conditions of adiabatic resonance passage

$$dB/dt = B_m \omega_m < \gamma_e B_1^2 \quad (2a)$$

$$\gamma_e B_m \ll \Delta\omega_G \quad (2b)$$

$$\omega_m T_1 \leq 1 \quad (2c)$$

where  $\gamma_e$  is the gyromagnetic ratio for electron,  $dB/dt$  is the rate of resonance passage,  $B_m$  and  $\omega_m$  are the a.c. modulation amplitude and angular frequency, respectively, and  $\Delta\omega_G$  is the width of the Gaussian function of spin-packet distribution. In this case the precession period of the magnetization vector  $\mathbf{M}$  of PCs around the vector  $B_1$  becomes smaller than the effective electron relaxation time  $T_{\text{eff}} = \sqrt{T_1 T_2}$  as a result the relaxation processes within the resonance conditions do not produce a strong effect on the behaviour of  $\mathbf{M}$  rotation.

We have measured the relaxation times  $T_1$  and  $T_2$  of both types of PCs in the PTFE sample as function of temperature, determined from the 2 mm ESR spectra registered under the conditions (1) and (2). Thus  $T_1$  proves to change with temperature like  $T^{-\alpha}$ , where  $\alpha = 3.3$  and  $3.7$  for localized and mobile polarons, respectively. The exponent  $\alpha$  determined from the 2 mm wave band ESR is larger than that measured for immobile radicals using the 3 cm ESE technique (Ref. 16,17). This deviation may be explained by the circumstance, that in the 2 mm wave band many radicals appear immobile PCs which in the 3 cm wave band are counted to the mobile ones (because of the lower measuring frequency). For that reason also the absolute values of relaxation times are shorter in the 2 mm wave band compared with that measured for the immobile radicals in the 3 cm wave band (Ref. 16). The small difference between  $T_1^{\text{mob}}$  and  $T_1^{\text{imm}}$  may be a hint of a strong interaction and energy exchange between mobile and immobile PCs (Ref. 14).

The motion of chains in conjugated polymers, similar to the ordinary ones, is *a priori* strongly anisotropic with the correlation time  $\tau_c \geq 10^{-7}$  s. According to the saturation transfer (ST) ESR approach, if conditions (1) and (2) hold, the chain reorientation causes that spins pass through the resonance condition because of the anisotropy of the magnetic interaction. If a slow molecular motion around, e.g., the X-axis occurs, the inequality (1) may be not satisfied for radicals oriented by their Y or Z axis parallel to the direction of the external magnetic field (Ref. 14).

As shown in Ref. 12 the sensitivity of the ST-ESR method to a very slow molecular motion increased at the 2 mm wave band, and allows to study the relaxation and anisotropic motion

processes separately. In this case the PCs trapped in PTTF are sensors of a polymer chain segment motion. Because the sensitivity of the ST-ESR method to molecular motion is enhanced quadratically with the magnitude of the anisotropy of the magnetic interaction, the 2 mm wave band ST ESR method is particularly efficient for the investigation of PTTF by means of the immobilized PCs with a strongly anisotropic g-tensor. In Ref. 14 is reported on the detection of a very slow anisotropic librational reorientation of the immobilized PCs together with the polymer chains. The correlation time of such libration is temperature-dependent according to  $\tau_c = 9.8 \cdot 10^{-6} \exp[-0.02 \text{ eV}/(kT)]$ .

#### 4.3. Diffusive intrachain polaron motion and interchain polaron hopping, on-chain and interchain conductivities

It should be noted that the activation energy for such librations is comparable with that of d.c. conductivity in the low temperature region of a weakly doped PTTF sample (Ref.15), which indicates the interaction of immobilized and mobile polarons in PTTF. In comparison of our experimental results with the polaron theory, we assume the on-chain quasi-one-dimensional (1D) diffusive motion of mobile PCs in conjugated chain segments of PTTF with the rate of  $v_{1D}$  and their expansion by three-dimensional (3D) hopping between the chains with the frequency of  $\nu_{1D}$ .

The temperature dependences of  $v_{1D}$  and  $\nu_{3D}$  determined in Ref.14 are plotted in Fig.6. The extrapolation to room temperature displays that the maximum value of  $v_{1D}$  of the PTTF sample does not exceed  $5 \cdot 10^9 \text{ s}^{-1}$ . Taking into account the fact that the spin delocalization of a polaron in conjugated polymers occupies approximately three to five monomeric units (Ref.25), then  $v_{1D} \leq 2 \cdot 10^{10} \text{ s}^{-1}$  would be correct. This value is lower than that determined for polarons in polypyrrole (Ref.26) and polyaniline (Refs.1,27).

The spin dynamic behaviour can be related to the charge transport properties. At the equal diffusion coefficients for both spin and charge carriers, the PTTFs on-chain and interchain conductivities can be estimated from  $v_{1D}$  and  $\nu_{3D}$  using the Einstein relation

$$\sigma_{1D,3D} = n_2 e^2 v_{1D,3D} d^2 / (kT) \quad (3)$$

where  $d$  is the lattice constant and  $k$  is the Boltzmann constant. With  $n_2 = 6.9 \cdot 10^{-5}$ , one obtains the values of  $\sigma_{1D} \approx 1 \cdot 10^{-3}$  and  $\sigma_{3D} \approx 4 \cdot 10^{-5} \text{ S cm}^{-1}$  for the intrinsic on- and interchain conductivities, respectively, in the room temperature region (Ref.14). The behaviour of  $\sigma_{1D}(T)$  (and of  $\Delta B_{pp}^{mob}(T)$ ) dependences suggest a metallic state for PTTF, but this is only valid for the intrachain conductivity. Only the  $\sigma_{3D}$ -value is in agreement with  $\sigma_{dc} \approx 10^{-5} \text{ S cm}^{-1}$  as measured by electrical methods for PTTF. That means  $\sigma_{dc}$  is determined by interchain spin hopping.

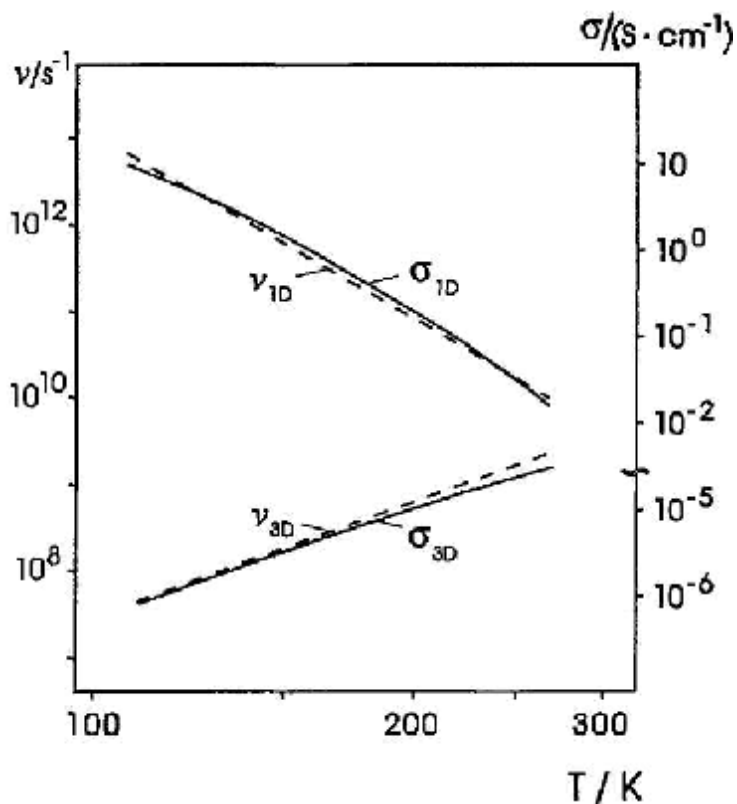


Fig.6: Frequencies  $\nu_{1D}$  and  $\nu_{3D}$  of diffusive on-chain polaron motion and of interchain polaron hopping, respectively. Quasi-1D-intrachain conductivity  $\sigma_{1D}$  and 3D-interchain conductivity  $\sigma_{3D}$  as estimated by ESR.

Because the  $E_A$  value of the dc-conductivity in the low temperature region corresponds to the above determined activation energy for PTF chains libration,  $E_a = 0.02$  eV, we conclude that the conductivity of PTF is determined mainly by a phonon-assisted interchain hopping of polarons. It is stimulated by multiphonon processes and it is supported by the libration of polymer chains due to the strong electron-lattice coupling (Ref.14).

## 5. Conclusions

The discussed investigation examples have shown that ESR spectroscopy is a valuable tool for getting deeper insight in the interesting electronic and magnetic properties of conducting polymers.

The study of spin dynamics by ESR in the 2 mm wave band allows a separate investigation of the quasi-1D-intrachain polaron diffusion and of the 3D-interchain polaron hopping. In PTF, as in many other semiconducting polymers, a large anisotropy of the electron or polaron

motion is to be observed in the whole temperature region and at all doping levels, whereas in highly doped PANI, near room temperature, the anisotropy of polaron motion disappears. That means  $v_{1D} \approx v_{3D}$  which supports the assumption of metallic islands in PANI.

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