

## Spin Charge Carrier Dynamics in Poly(*bis*-alkylthioacetylene)

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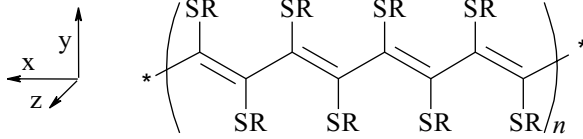
Received October 4, 2001; revised April 15, 2002

**Abstract.** Initial and laser-irradiated poly(*bis*-alkylthioacetylene) (PATAC) samples were investigated by electron paramagnetic resonance (EPR) at X-band (9.6 GHz), Q-band (37 GHz), and D-band (140 GHz) in a wide temperature range. Two types of paramagnetic centers were proved to exist in laser-modified polymer, namely, localized and mobile polarons with the concentration ratio and susceptibility depending on the irradiation dose and temperature. Superslow torsion motion of the polymer chains was studied by the saturation transfer method at D-band EPR. Additional information on the polymer chain segment dynamics was obtained by the spin probe method at X-band EPR. Spin-spin and spin-lattice relaxation times were measured separately by the steady-state saturation method at D-band EPR. Intrachain and interchain spin diffusion coefficients and conductivity arising from the polaron dynamics were calculated. It was shown that the polaron dynamics in laser-modified polymer is affected by the spin-spin interaction. The interchain charge transfer is stimulated by torsion motion of the polymer chains, whereas the total conductivity of irradiated PATAC is determined mainly by the dynamics of diamagnetic charge carriers. Magnetic, relaxation and dynamics parameters of PATAC were also shown to change during polymer storage.

### 1 Introduction

The magnetic and electronic properties of organic polymer semiconductors (OPS) with an extended  $\pi$ -conjugated system, e.g., *trans*-polyacetylene (*trans*-PA), poly(*p*-phenylene) (PPP), are widely studied in the last years [1–4] due to bright prospects on their utilization in molecular electronics [5–7]. Neutral undoped conjugated polymers are insulators. At doping by different ions their conductivity increases by more than 15 orders of magnitude reaching ca.  $10^5$  S/cm for *trans*-PA and  $10^1$ – $10^3$  S/cm for PPP-like OPS. It is well known that the charge is transferred by nonlinear excitations, solitons in *trans*-PA and polarons in other OPS. Such quasi-particles possess an unpaired electron with spin  $S = 1/2$  that allows studying OPS successfully with electron paramagnetic resonance (EPR) spectroscopy [8–12].

The *trans*-PA derivative, poly(*bis*-alkylthioacetylene)



(PATAc, here  $R \equiv$  methyl, ethyl, propyl,  $8 \leq n \leq 53$ ) is also an insulator in a neutral form. From the  $^{13}\text{C}$  nuclear magnetic resonance study [13] the conclusion was made that PATAc has an  $sp^2/sp^3$ -hybridized carbon atom ratio typical for polyacetylene, however, in the contrast with the latter, pristine polymer has a more twisted backbone. The direct current (dc) conductivity of PATAc at chemical doping increases from  $\sigma_{\text{dc}} \approx 10^{-14}$  S/cm up to  $\sigma_{\text{dc}} \approx 10^{-10}$ – $10^{-4}$  S/cm depending on the kind and/or concentration of an anion introduced into the polymer in a liquid or gas phase. The conductivity of PATAc irradiated by argon laser increases up to  $\sigma_{\text{dc}} \approx 10$ – $200$  S/cm depending on the absorbed dose [14]. Hall coefficient measurements of laser-modified PATAc [14] have shown that the charge carriers are of p-type and their mobility depends on the temperature as  $\mu \propto T^n$  with  $0.25 \leq n \leq 0.33$  at  $80 \leq T \leq 300$  K being close to  $0.1$ – $8$   $\text{cm}^2/(\text{V} \cdot \text{s})$  at room temperature (RT). The latter value is close to  $\mu = 2$   $\text{cm}^2/(\text{V} \cdot \text{s})$  obtained for *trans*-PA [15].

The X-band EPR study [14] has shown that  $\pi$ -like paramagnetic centers (PC) with different mobility exist in laser-modified PATAc, however, the conductivity of the polymer is mainly determined by the dynamics of diamagnetic bipolarons. It was proposed that as the temperature increases, the bipolaron mobility decreases and their concentration in laser-modified PATAc increases, so these processes should lead to the extremally low (close to  $10^{-3}$   $\text{K}^{-1}$ ) temperature coefficient of the PATAc dc conductivity. At the optimal polymer treatment by laser, the concentration,  $g$ -factor and peak-to-peak linewidth of PCs change at RT respectively from  $N \approx 2.7 \cdot 10^{14}$   $\text{cm}^{-3}$ ,  $g = 2.0056$ , and  $\Delta B_{\text{pp}} = 0.72$  mT to  $N \approx 4.7 \cdot 10^{17}$   $\text{cm}^{-3}$ ,  $g = 2.0039$ , and  $\Delta B_{\text{pp}} = 0.65$  mT.

Previously [9, 12], we have shown that the use of D-band EPR spectroscopy makes it possible to obtain new information on various organic conducting polymers. With the data obtained in this waveband, we can determine all components of the spin Hamiltonian as well as calculate the relaxation and dynamics parameters of different PCs and study the charge transfer process in such low-dimensional systems.

The present communication is devoted to a detailed EPR study at a wide range of wavebands of molecular and charge carrier dynamics of the initial and laser-converted PATAc samples with different irradiation doses and conductivity. X-band spin-probe EPR has been used additionally for the study of dynamics of the probe together with the nearest polymer chain segments in solid-state and dissolved unmodified polymer.

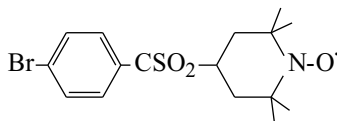
The preliminary results were published in refs. 14 and 16.

## 2 Experimental

Initial PATAc was polymerized from *bis*-alkylthioacetylene in the presence of  $\text{Hal}_2\text{Ni}(\text{PPh}_3)_2$  catalyst ( $\text{Hal} \equiv \text{Cl}, \text{Br}, \text{I}$ ) according to the method described in ref. 17. The polymer obtained is easily soluble in halogenated hydrocarbons and aromatic solvents. An insulating sample 1 was obtained as a thin (with thickness of about 2  $\mu\text{m}$ ) film by spinning the polymer solution on a glass surface followed by its drying in the presence of air and visible light. Powderlike samples 2–4 were obtained by irradiation of the sample 1 with a medium-power argon ion laser ILA 120 at  $\lambda = 488 \text{ nm}$  with doses of 5, 20, and 80  $\text{J}/\text{cm}^3$ , respectively.

EPR investigations were carried out mainly in the 80–360 K temperature range on X-band (9.56 GHz) Bruker EMX10/12, Q-band (37.47 GHz) RE1308, and D-band (140.7 GHz) EPR5-01 [18] spectrometers. For the determination of the spin concentration at X-band EPR, a diphenylpicrylhydrazyl (DPPH) standard was used. The second standard,  $\text{Mn}^{2+}$  in  $\text{MgO}$ , was used for the determination of the  $g$ -factor at D-band EPR. The spectra were simulated with Microcal Origin V6.0 and WINEPR SimFonia V1.25 (Bruker) programs.

A stable nitroxide radical

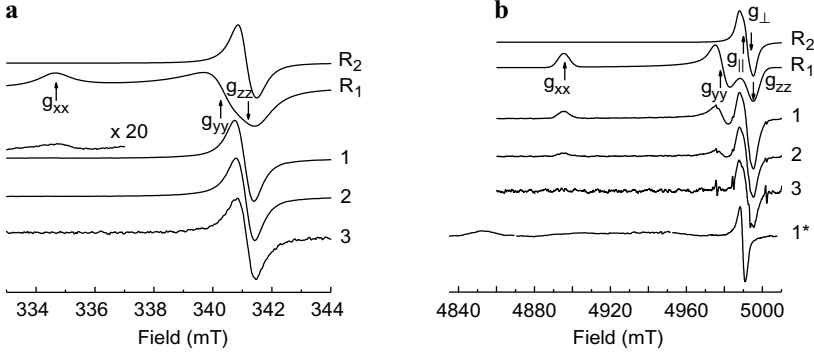


was used as a spin probe in the study of an unmodified sample.

## 3 Results and Discussion

### 3.1 Spin Composition and Susceptibility of PATAc Samples

At X-band the PC in, e.g., the PATAc sample 2 demonstrates a slightly asymmetric Lorentzian spectrum with a weak component at low fields (Fig. 1a). The intensity of the latter component decreases during the PATAc laser modification and/or as the temperature increases. The spectrum simulation has shown that this line asymmetry arises due to the  $g$ -factor anisotropy. This supposition was confirmed by a more detailed study of the samples at higher registration frequency. D-band EPR spectra of the samples 2–4 are presented in Fig. 1b. Higher spectral resolution and computer simulation have shown that two types of PCs exist in PATAc, namely, a polaron localized on the short  $\pi$ -conjugated polymer chain  $R_1$  with  $g_{xx} = 2.04331$ ,  $g_{yy} = 2.00902$ ,  $g_{zz} = 2.00243$ , and the linewidth  $\Delta B_{pp} = 6.1 \text{ mT}$  (D-band), and a polaron moving along the main  $\pi$ -conjugated polymer chain  $R_2$  with  $g_{xx} = 2.00551$ ,  $g_{yy} = 2.00380$ ,  $g_{zz} = 2.00232$ , ( $2g_{||} = g_{xx} + g_{yy}$ ,  $g_{\perp} = g_{zz}$ ) and  $\Delta B_{pp} = 2.7 \text{ mT}$  (D-band). Simulated spectra of PCs  $R_1$  and  $R_2$  are shown in



**Fig. 1.** X-band (a) and D-band (b) EPR absorption spectra of an as-modified (curve 1) and stored for two years (curve 1\*) sample 2, as well as of the samples 3 (curve 2) and 4 (curve 3) registered at 100 K. The spectra of radical  $R_1$  calculated with  $g_{xx} = 2.0433$ ,  $g_{yy} = 2.00902$ ,  $g_{zz} = 2.00243$ , and radical  $R_2$  calculated with  $g_{xx} = 2.00551$ ,  $g_{yy} = 2.00380$ ,  $g_{zz} = 2.00232$  are shown as well.

Fig. 1 as well. The principal  $x$ -axis is chosen parallel to the longest molecular  $c$ -axis, the  $y$ -axis lies in the C-C-C plane, and the  $z$ -axis is perpendicular to  $x$ - and  $y$ -axes.

Since the  $g$ -factor of the PATAc samples is considerably higher than that of most PPP-like conjugated polymers,  $g \cong 2.003$  [8, 10, 12, 19], one can conclude that the unpaired electron in PATAc interacts with sulfur atoms. It is typical for other sulfur-containing compounds, e.g., poly(tetrathiafulvalenes) (PTTF) [12, 19–21] and benzo-trithioles [22–24] in which sulfur atoms are involved into the conjugation. Taking into account that the overlapping integral  $I_{c-c}^p$  in such organic  $\pi$ -systems depends on the dihedral angle  $\theta$  (the angle between p-orbits of neighboring C-atoms) as  $I_{c-c}^p \propto \mu \cos \theta$  [25, 26], the shift of the  $g$ -factor from the  $g$ -factor for the free electron ( $g_e = 2.00232$ ) is expressed by a modified equation [27]:

$$g_{ii} - g_e = \frac{g_e \lambda_s \rho_s(0)}{\Delta E_{nj}} \frac{1 - \cos \theta}{1 + k_1 \cos \theta}, \quad (1)$$

where  $\rho_s(0)$  is the spin density on the sulfur nucleus,  $\lambda_s = 0.047$  eV [27] is the constant of the spin-orbit interaction of the electron spin with the sulfur nucleus,  $\Delta E_{nj}$  is the energy of the electron excitation from the ground orbit to nearest  $\pi^*$  and  $s^*$  orbitals (respectively  $\Delta E_{n\pi^*}$  and  $\Delta E_{ns^*}$ ), and  $k_1$  is a constant. The  $g$ -factor of PC in sulfur-containing solids in which electrons are localized mainly on the sulfur atom lies in the region of  $2.014 \leq g_{iso} \leq 2.020$  [22–24, 28]. In tetrathiafulvalene (TTF) derivatives an unpaired electron is delocalized on 12 or more carbon atoms and four sulfur atoms leading to the decrease of both  $\rho_s(0)$  and  $g_{iso}$  values [12]. An additional fast spin motion takes place in the PTTF [9, 12, 24] leading to a further decrease in the  $\rho_s(0)$  value, and therefore in the decrease of  $g_{iso}$  down to 2.007–2.014 depending on the structure and effective polarity in

PTTF samples [9, 12]. Due to the smaller  $g$ -factor in PATAc one can expect a higher spin delocalization in this polymer as compared with the above mentioned organic semiconducting solids.

Assuming  $\Delta E_{n\pi} \approx 2.6$  eV, typical for benzo-trithioles and PTTF [23, 28], the  $g$ -factor components of the initial PATAc yield by Eq. (1)  $\rho_s(0) \approx 1.1$  and  $\Delta E_{n\sigma} = 15.6$  eV for the PC in unmodified PATAc. This means that in the initial polymer the spin is localized within one monomer unit.

Figure 1b shows also the D-band EPR spectrum of the PATAc sample 2 stored for two years. From the analysis of the spectrum one can conclude the increase of  $g_{xx}$  and  $g_{yy}$  values of  $R_1$  respectively up to 2.0451 and 2.00982. The RT linewidth of this PC increases up to  $\Delta B_{pp} = 12.9$  mT as well. This means the increase of spin localization on the sulfur nucleus due to the shortness of polymer chains in amorphous regions during the PATAc storage. On the other hand, such destruction does not lead to the change in the magnetic parameters and concentration of mobile polarons.

The treatment of various OPS leads to the polaron formation and to the spin delocalization onto approximately five polymer units [29]. If one supposes that the analogous process occurs during the laser treatment of PATAc, then the  $\rho_s(0)$  value determined above should decrease down to 0.22. This fits very well the  $g$ -factor measured for the sample 2. Further spin delocalization during laser modification of the polymer with higher laser irradiation dose can be accompanied by the decrease of the  $\theta$  value. This should lead to an additional acceleration of spin diffusion along the polymer chains. The decrease of  $\rho_s(0)$  and  $\theta$  values calculated from Eq. (1) for PC on polaron in sample 4 are approximately equal to 0.032 and  $21.3^\circ$ , respectively. The latter value is close to that ( $\Delta\theta = 22\text{--}23^\circ$ ) realized, e.g., at the transition from the benzoid to the quinoid form in PPP [30], at the transition from the emeraldine-base to the emeraldine-salt form of polyaniline [31], and at the transition from PTTF with phenyl bridges to PTTF with tetrahydroanthracene ones [12]. This change in the  $g$ -factor supports the assumption made by Roth et al. [14] that laser irradiation leads to a more planar structure of the polymer chains and therefore to a higher spin delocalization and to a higher conductivity of PATAc.

The concentration ratio  $[R_2]/[R_1]$  of ca. 1:2 for the insulating sample 1 increases during the laser modification of PATAc up to 2:1, 4:1, and 10:1, respectively, for the samples 2–4. This means that the laser treatment leads to the increase of the concentration of mobile polarons in conducting PATAc. The total spin concentration increases by the maximum factor of 30 at the PATAc treatment. On the other hand, the concentration of charge carriers was determined from Hall and dc conductivity studies to change by more than 15 orders of magnitude reaching  $N \sim 10^{19}$  cm $^{-3}$  in the relatively strongly laser-irradiated polymer [14]. This means that the charge, as in the case of some other conducting polymers, is predominantly transferred by paramagnetic polarons in an initial and slightly modified PATAc. In highly irradiated more planar polymer the most of polarons collapse into diamagnetic bipolarons which are the dominant charge carriers in the polymer.

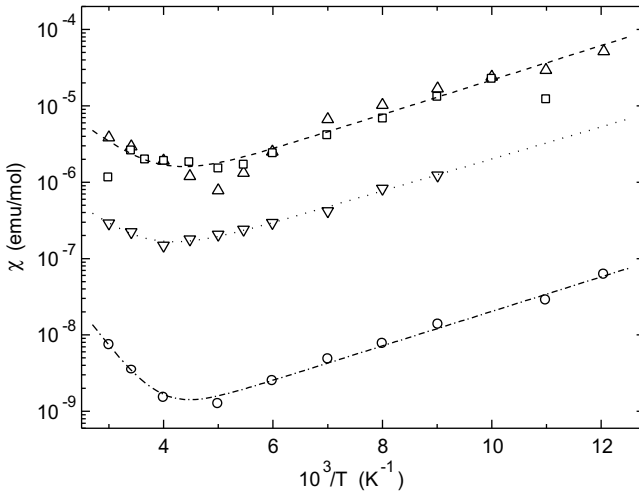
Spin susceptibility  $\chi$  of PATAc depends not only on the laser irradiation dose absorbed but also on the temperature. Figure 2 presents the temperature dependences for the  $\chi$  value of the samples 1–4. The  $\chi$  value decreases as the temperature decreases from maximum down to a critical temperature  $T_c \approx 220$ – $250$  K and then increases at lower temperatures. The observed increase of the magnetic susceptibility at temperatures lower than  $T_c$  can result from the formation of clusters with collective magnetism like spin glasses or of microphases with ferri- or ferromagnetic behavior. As in the case of the polyaniline perchlorates [32], the spin susceptibility of PATAc seems to include a thermally activated term  $\chi_A$  and a contribution due to a singlet-triplet spin equilibrium  $\chi_{ST}$ , so the total observed spin susceptibility should follow the equation [33]:

$$\chi(T) = \chi_A \exp(-E_a/kT) + \chi_{ST} \frac{\exp(-J/kT)}{1 + 3 \exp(-J/kT)}, \quad (2)$$

where  $E_a$  is the activation energy,  $k$  is the Boltzmann constant, and  $J$  is the spin-spin interaction energy.

Figure 2 shows that  $\chi(T)$  dependences of the PATAc samples are fitted well by Eq. (2) with  $E_a \cong 0.045$  eV and  $J \cong 0.12$ – $0.19$  eV.

It is obvious that the above processes are accompanied by a reversible collapse of polarons into bipolarons and dissociation of bipolarons into polarons. However, Stafström et al. [34, 35] have shown that the bipolaron state is not the favorable state in main conducting polymers.

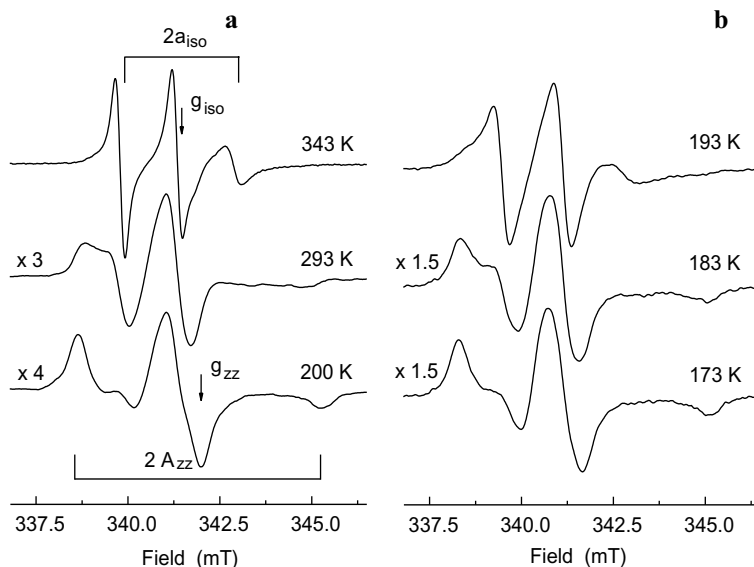


**Fig. 2.** Arrhenius dependences of spin susceptibility of the PATAc samples 1 (○), 2 (△), 3 (□), and 4 (▽). The dependences calculated with Eq. (2) with  $\chi_A = 1.2 \cdot 10^{-7}$ ,  $E_a = 0.045$  eV,  $\chi_{ST} = 2.2 \cdot 10^{-4}$ ,  $J = 0.12$  eV (dashed line),  $\chi_A = 1.6 \cdot 10^{-8}$ ,  $E_a = 0.042$  eV,  $\chi_{ST} = 2.1 \cdot 10^{-5}$ ,  $J = 0.12$  eV (dotted line), and  $\chi_A = 1.1 \cdot 10^{-10}$ ,  $E_a = 0.045$  eV,  $\chi_{ST} = 5.0 \cdot 10^{-6}$ ,  $J = 0.19$  eV (dash-dotted line) are shown as well.

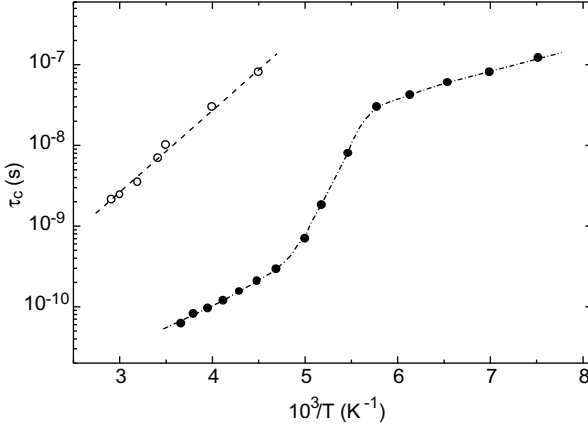
### 3.2 Packing Order and Dynamics in Unmodified PATAc

In order to verify if the observed minimum of the spin susceptibility reflects a structural phase transition in the polymer matrix at  $T_c$ , the molecular dynamics in this system should be studied. Because the intrinsic spin concentration in the as-prepared sample 1 is too low, the spin-probe EPR seems more suitable for such investigation of this PATAc sample and its solution in chloroform. Other PATAc samples are not solvable in organic solvents, so they cannot be studied by this method.

Figure 3 shows X-band EPR spectra of the stable nitroxide radical introduced into the PATAc sample 1 and, for comparison, in its solution in chloroform as a spin probe and registered at different temperatures. The nitroxide radical in PATAc is characterized by the isotropic and anisotropic constants of the spin-orbit interaction,  $a_{\text{iso}} = 1.52$  mT and  $A_{zz} = 3.25$  mT, respectively. In its solution these magnetic parameters of the spin probe appear to increase up to  $a_{\text{iso}} = 1.59$  mT and  $A_{zz} = 3.54$  mT due to the increase of polarity of the radical microenvironment [36]. The shape of the spectra evidences that an active fragment of the spin probe rotates with a relatively high frequency. This means that the average size of the pockets where the probes are situated is considerably large if compared with an effective diameter of the nitroxide radical. So we can conclude that the packing order of polymer is relatively low. The analysis of spectra of the nitroxide spin probe made according to the method described in refs. 37 and 38 has shown that the spin probe rotates in PATAc and its solution in frame of



**Fig. 3.** X-band EPR spectra of the nitroxide spin probe in the solid-state unmodified PATAc sample 1 (a) and in its solution in chloroform (b) registered at different temperatures. The measured magnetic parameters are shown.



**Fig. 4.** Arrhenius dependences, evaluated from X-band EPR spectra of the nitroxide spin probe in the solid-state unmodified PATAC sample 1 (O) and in solution of this polymer in chloroform (●) in the framework of the model of the nitroxide radical hopping on arbitrary angles. The dependences calculated from Eq. (3) with  $\tau_c^0 = 3.44 \cdot 10^{-12} \text{ s}^{-1}$  and  $E_a = 0.192 \text{ eV}$  (dashed line),  $\tau_c^0 = 3.18 \cdot 10^{-13} \text{ s}^{-1}$  and  $E_a = 0.124 \text{ eV}$  (high-temperature region),  $\tau_c^0 = 4.03 \cdot 10^{-10} \text{ s}^{-1}$  and  $E_a = 0.065 \text{ eV}$  (low-temperature region) (dash-dotted line) are shown as well.

the model of thermally spin activation hopping on small arbitrary angles with the correlation time

$$\tau_c = \tau_c^0 \exp(E_a/kT). \quad (3)$$

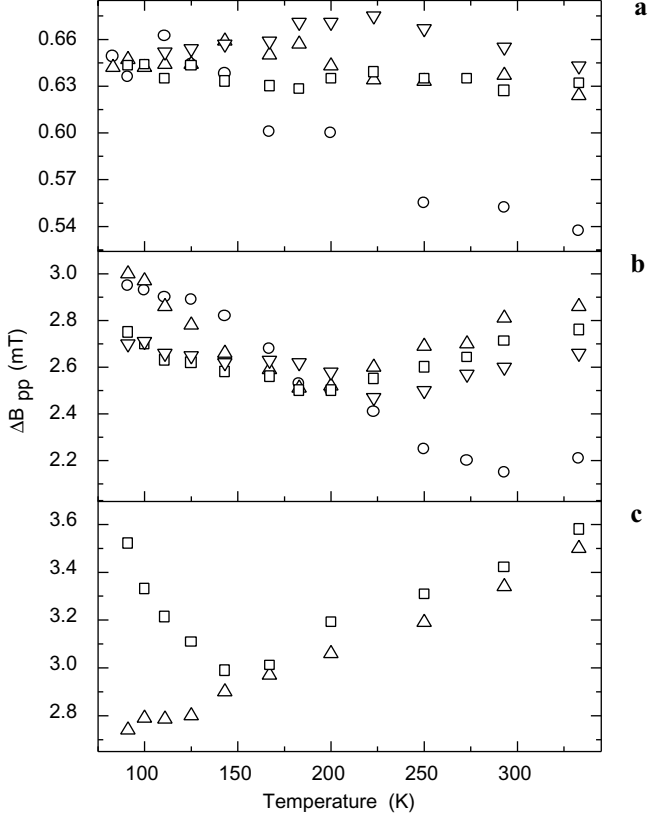
Figure 4 shows Arrhenius dependences for the correlation times of the spin probe rotation in both the powderlike PATAC sample 1 and in its solution in chloroform. From these dependences the activation energies of the probe rotation were calculated to be 0.19 eV for the powderlike sample 1 and 0.12 eV (high temperatures) and 0.065 eV (low temperatures) for the soluted polymer. In the last case the change in the activation energy was attributed to the phase transition in the system at  $T \approx 180 \text{ K}$ .

Because the unsoluted as-prepared PATAC sample 1 shows no effect in the correlation time due to a phase transition, the results of spin-probe studies allow one to conclude that the nonlinear temperature dependence of the spin susceptibility of PATAC samples cannot be explained by a structural phase transition but by a strong ferri- or ferromagnetic interaction in the polymer matrix.

### 3.3 Spin Dynamics in Laser-Modified PATAC Samples

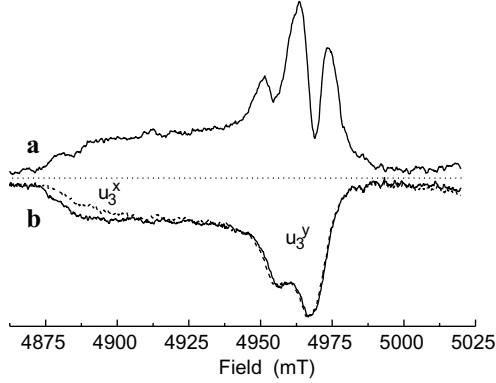
For the study of the spin dynamics in the laser-modified PATAC samples the temperature dependences of the linewidth  $\Delta B_{pp}$  of mobile polarons  $R_2$  in these samples can be analyzed. These dependences measured at X- and D-bands are shown in Fig. 5. It is seen from Fig. 5 that the linewidth measured at X-band EPR is weakly de-





**Fig. 5.** Temperature dependences of the linewidth of mobile polarons  $R_2$  in the PATAC samples 1 ( $\circ$ ), 2 ( $\Delta$ ), 3 ( $\square$ ), and 4 ( $\nabla$ ) determined from their X-band (a) and D-band (b) EPR spectra. The D-band linewidth of the PATAC samples 2 ( $\Delta$ ) and 3 ( $\square$ ) stored for two years is also shown in c as a function of temperature.

pendent on temperature. However, this value becomes more temperature-sensitive at the increase of the registration frequency due to the decrease of an interaction between spin packets. The D-band linewidth of the sample 1 increases with the temperature decrease. At the same time, this value of laser-modified samples 2–4 demonstrates the extremal temperature dependence with the critical temperature  $T_c$  close to 200–220 K. These functions are similar to  $\chi(T)$  presented in Fig. 2, therefore, such behavior can be associated with the polaron-bipolaron transition at  $T_c$  and probably cannot reflect the change of the mobility of charge carriers in the laser-treated samples. At the storage, the linewidth of the sample 2 becomes linearly dependent on the temperature, whereas  $T_c$  of the sample 3 shifts to a lower temperature region. (Fig. 5c). The RT linewidth of the samples 2–4 was measured at Q-band EPR to be 1.45, 1.34, and 1.31 mT, respectively. So, the linewidth of PC  $R_2$  at the transition from the X-band to the D-band increases by approximately four times mainly due to the dependence of its spin-spin relaxation on the registration frequency.

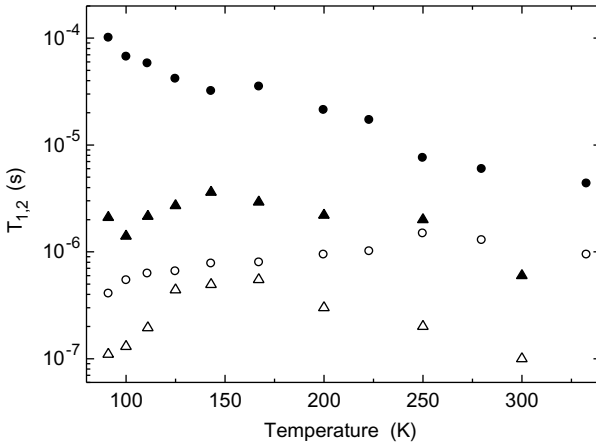


**Fig. 6.** D-band in-phase (a) and  $\pi/2$ -out-of-phase (b) dispersion spectra of the PATAC sample 2 registered at 280 K (solid lines) and 143 K (dashed line).

Earlier we have shown [9, 12, 19] that spin dynamics in conducting polymers can be studied in detail by using steady-state saturation method at D-band EPR. In general, the equation for the first derivative of the dispersion signal  $U$  can be written as [39]:

$$U = u_1 \sin(\omega_m t) + u_2 \sin(\omega_m t - \pi) + u_3 \sin(\omega_m t \pm \pi/2), \quad (4)$$

where  $\omega_m$  is the angular frequency of the modulation magnetic field. For the modified PATAC samples the inequality  $\omega_m T_1 > 1$  is realized, therefore their in-phase and  $\pi/2$ -out-of-phase components of the dispersion signal (Fig. 6) are determined mainly by the two last terms of Eq. (4). Figure 7 presents the tempera-



**Fig. 7.** Temperature dependence of the effective spin-lattice  $T_1$  (filled symbols) and spin-spin  $T_2$  (open symbols) relaxation times for as-modified (circles) and stored for two years (triangles) PATAC sample 2.

ture dependence of effective spin-lattice and spin-spin relaxation times,  $T_1$  and  $T_2$ , respectively of, e.g., the as-modified sample 2 determined separately from the analysis of its dispersion spectral components  $u_2$  and  $u_3$  according to the method described earlier [40]. Relaxation parameters calculated for this sample stored for two years are presented in Fig. 7 as well. It is seen from Fig. 7 that both relaxation times of the sample decrease considerably during the storage. Besides, this process leads to the extremal temperature dependence with  $T_c \approx 160$  K at which the semiconductor-metal transition take place. The analogous phenomena were registered in the study of polyaniline [31, 41], poly(phenylenevinylene) [42], poly(3,4-ethylenedioxythiophene) [43], and other OPS [44].

It is well known that relatively slow macromolecular dynamics modulates the interchain charge transfer in conducting polymers [12]. It was shown that the correlation time of such reorientations of a localized spin with anisotropic magnetic parameters near, e.g., the polymer  $x$ -axis can be determined by the saturation transfer (ST-EPR) method [45] analyzing the shape of the D-band  $\pi/2$ -out-of-phase dispersion signal, i.e., the  $u_3^x/u_3^y$  ratio (see Fig. 6) from the equation [12, 19]

$$\tau_c^x = \tau_0(u_3^x/u_3^y)^{-m}, \quad (5)$$

where  $m$  is the constant depending on the  $g$ -factor anisotropy.

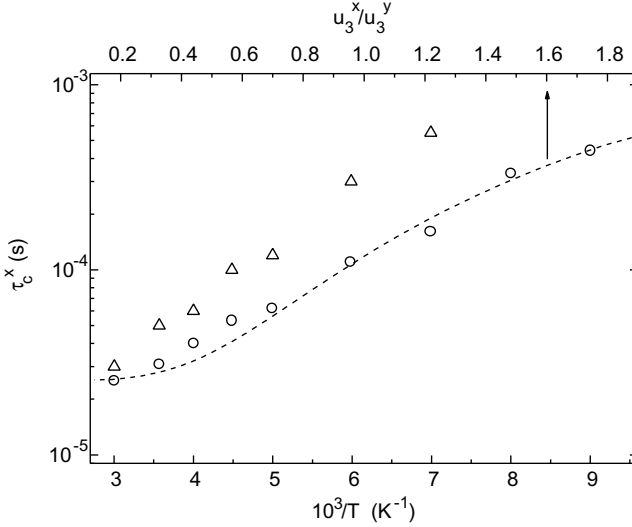
Indeed, the heating of the modified PATAC sample leads to the growth of the  $u_3^x/u_3^y$  ratio. As in the case of other polymers [12, 19], such a change in the spectrum shape is a result of anisotropic torsion (libration) reorientations of the pinned polarons near the main  $x$ -axis of the polymer chains.

Figure 8 presents the correlation times of such macromolecular librations in PATAC samples 2 and 3 determined from their ST-EPR spectra with Eq. (5) in the framework of the activation motion. These parameters were determined for the sample 2 to be  $\tau_c^x = 6.3 \cdot 10^{-6} \cdot \exp(0.043 \text{ eV}/kT)$  and for the sample 3 to be  $\tau_c^x = 3.1 \cdot 10^{-6} \cdot \exp(0.062 \text{ eV}/kT)$  s. The increase in the activation energy of the polymer chain librations evidences the strong dependence of the superslow macromolecular dynamics of both the pinned spins and polymer segments on the polymer treatment level. The higher the laser irradiation doses, the more rigid the polymer matrix becomes and the higher energy for the polymer chain motion is required (Fig. 8).

The involvement of spectral components into the motional exchange and therefore their shift to the spectrum center at the laser modification of PATAC apparently indicates the appearance of polarons moving along the polymer chains with the rate [46]

$$\nu_{1-D} \geq \sum_2 (g_{xx,yy} - g_e) \mu_B B_0 / h, \quad (6)$$

where  $\mu_B$  is the Bohr magneton,  $B_0$  is the strength of an external magnetic field, and  $h = 2\pi\hbar$  is the Planck constant. This value was determined from RT D-band EPR spectra for mobile polarons in laser-modified PATAC sample 2 as  $\nu_{1-D} \geq 3.2 \cdot 10^9 \text{ s}^{-1}$ .



**Fig. 8.** Arrhenius dependences for correlation times of superslow librations near the polymer main  $x$ -axis of polarons  $R_1$  localized on polymer chain segments in the PATAC samples 2 (○) and 3 (△) evaluated from their saturation transfer EPR spectra. The dependence calculated from Eq. (5) is shown by dashed line.

Except for the one-dimensional (1-D) diffusion along the polymer chain with the rate  $\nu_{1-D}$ , the spin 3-D hops between the chains with the frequency  $\nu_{3-D}$ . Such motion induces an additional magnetic field in the place of the localization of other spins that should accelerate spin relaxation and lead to  $T_{1,2} \propto \omega_e^{1/2}$  dependences [47], where  $\omega_e = 2\pi\nu_e$  is the angular spin precession frequency. As in the case of other conducting polymers with heteroatoms [21, 31, 48],  $\Delta B_{pp} \propto T_2^{-1} \propto \omega_e^{1/2}$  relation is realized for modified PATAC samples (see Fig. 5), thus the spin-charge dynamics in PATAC can be considered in terms of the above mentioned approach.

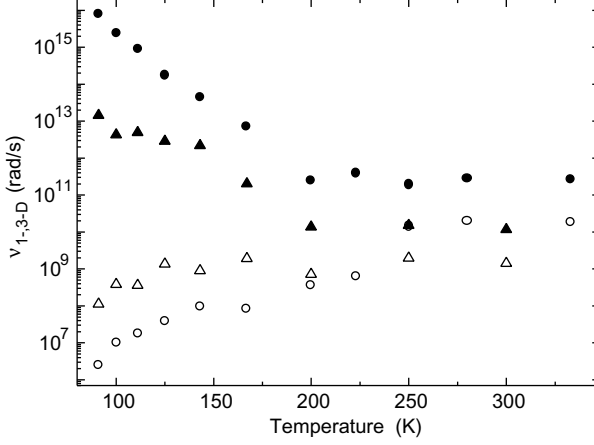
Spin relaxation rates are determined mainly by the dipole interaction of polarons, thus they depend on the spin diffusion and precession rates as [27]

$$T_1^{-1} = 0.1(\mu_0/4\pi)^2 \gamma_e^4 \hbar^2 S(S+1) n \sum_{ij} r_{ij}^{-6} [J_1(\omega_e) + J_2(2\omega_e)], \quad (7a)$$

$$T_2^{-1} = 0.1(\mu_0/4\pi)^2 \gamma_e^4 \hbar^2 S(S+1) n \sum_{ij} r_{ij}^{-6} [3J_0(0) + 5J_1(\omega_e) + 2J_2(2\omega_e)], \quad (7b)$$

where  $\mu_0$  is the permeability for vacuum, and  $n = n_1 + n_2/\sqrt{2}$  is the number of localized  $n_1$  and mobile  $n_2$  polarons per each polymer unit,  $J(\omega_e) = (\nu_{1-D}\omega_e)^{-1/2}$  at  $\nu_{3-D} \leq \omega_e \leq \nu_{1-D}$  and  $J(\omega_e) = (\nu_{1-D}\nu_{3-D})^{-1/2}$  at  $\omega_e \leq \nu_{3-D}$  [47].

Assuming for simplicity that the spins are situated near the points of the cubic lattice with the constant  $r_0 = (8/3N_c)^{-1/3}$  (here  $N_c$  is the concentration of the monomer units in the sample) and with the relation  $\sum_{ij} r_{ij}^{-6} = 6.8r_0^{-6}$  [49] and the data presented in Fig. 7 at the  $\nu_{3-D} \leq \omega_e \leq \nu_{1-D}$  limit, one can determine from



**Fig. 9.** Temperature dependences of the intrachain diffusion  $\nu_{1-D}$  (filled symbols) and interchain hopping  $\nu_{3-D}$  (open symbols) rates of mobile paramagnetic centers in as-modified (circles) and stored for two years (triangles) PATAC sample 2 determined with Eqs. (7).

Eqs. (7) separately the rates  $\nu_{1-D}$  and  $\nu_{3-D}$  of the spin motion in the PATAC samples. Figure 9 shows these values calculated for as-modified and stored for two years PATAC sample 2 as a function of temperature. It is seen from Fig. 9 that the rate of the spin intrachain diffusion in the samples remains invariable as the temperature decreases down to  $T_c \cong 200$  K due probably to the compensation effect of the  $T_1$  increase and the  $n$  decrease and starts to increase as the temperature decreases further. At the same time,  $\nu_{3-D}$  decreases monotonically with the temperature decrease of the as-modified sample 2. With sample storage this value has a weak fall in temperature (Fig. 9).

The conductivity coming from the intra- and interchain motion of polarons can be calculated as

$$\sigma_{1-,3-D}(T) = Ne\mu_{1-,3-D} = Ne^2\nu_{1-,3-D}c_{1-,3-D}^2/kT, \quad (8)$$

where  $N$  is the number of mobile polarons with the mobility  $\mu_{1-,3-D}$  and the elemental charge  $e$  and  $\nu_{1-,3-D}$  is the frequency of this charge carrier hopping between polymer sites separated by the distance of  $c_{1-,3-D}$ .

Figure 10 shows the contribution of both 1-D and 3-D polaron motions into the  $ac$  (140 GHz) conductivity of the as-modified and stored sample 2 determined from Eq. (8) with  $c_{1-D} = 0.251$  nm for *trans*-PA [50] and  $c_{3-D} \approx r_0 = 0.357$  nm.

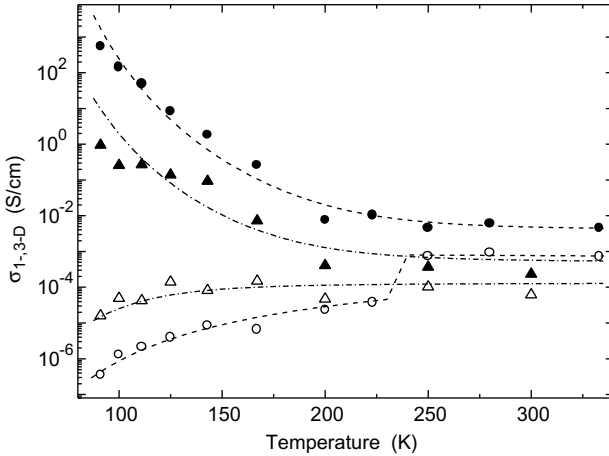
Analogously, in the case of spin 1-D diffusion rates,  $\sigma_{1-D}$  of these polymers consists of the temperature-independent part at  $T \geq T_c$  and the temperature-dependent part at  $T \leq T_c$ . The latter term can be interpreted according to the model of the charge carrier scattering on the lattice optical phonons proposed for metal-like clusters in conjugated polymers [51, 52]. In the framework of this model the total conductivity of the polymers can be expressed in the form

$$\begin{aligned}\sigma_{1-D}(T) &= \sigma_{1_0} + \frac{Ne^2c_{1-D}^2Mt_0^2kT}{8\pi\hbar^3\alpha^2}[\sinh(h\omega_{ph}/kT) - 1] \\ &= \sigma_{1_0} + \sigma_{2_0}T[\sinh(h\omega_{ph}/kT) - 1],\end{aligned}\quad (9)$$

where  $M$  is the mass of the polymer unit,  $t_0$  is the transfer integral, for the  $\pi$ -electron equal approximately to 2.5–3 eV,  $\omega_{ph}$  is the angular frequency of the optical phonon, and  $\alpha$  is the constant of electron-phonon interaction, for *trans*-PA equal to  $4.1 \cdot 10^8$  eV/cm [52].

As can be seen in Fig. 10, the  $\sigma_{1-D}(T)$  dependence for the PATAc sample 2 is fairly well fitted by Eq. (9) with  $h\omega_{ph} = 0.18$  eV. This value is close to that (0.13 eV) obtained for polyaniline doped by hydrochloric acid [53] but exceeds by a factor of 3–4 the activation energy of macromolecular librations in PATAc samples determined from their ST-EPR spectra (see Fig. 8). The 1-D conductivity of the stored sample 2 is also fitted by Eq. (9) with  $h\omega_{ph} = 0.15$  eV. From the  $\sigma_{0_2}$  values obtained,  $N = 4.2 \cdot 10^{18}$  cm<sup>-3</sup> and  $c_{1-D} = 0.251$  nm for *trans*-PA [50], we get  $\alpha = 7.7 \cdot 10^9$  eV/cm and  $\alpha = 4.1 \cdot 10^9$  eV/cm for these samples, respectively. The latter values lie close to  $\alpha = (4-20) \cdot 10^9$  eV/cm determined for highly doped polyaniline [53], however, they are higher than that calculated for *trans*-PA.

As in the case of the 1-D conductivity, the 3-D conductivity of PATAc samples in the high-temperature region weakly depends on temperature (Fig. 10). At low



**Fig. 10.** Temperature dependences of ac (140 GHz) conductivities  $\sigma_{1-D}$  (filled symbols) and  $\sigma_{3-D}$  (open symbols) calculated for the as-modified (circles) and stored for two years (triangles) PATAc sample 2 from Eq. (8) with  $N = 4.2 \cdot 10^{18}$  spin/cm<sup>3</sup>,  $c_{1-D} = 0.251$  nm [50] and  $c_{3-D} = 0.359$  nm. The dependences calculated from Eq. (9) with  $\sigma_{0_1} = 4.1 \cdot 10^{-3}$  S/cm,  $\sigma_{0_2} = 2.9 \cdot 10^{-9}$  S/(cm · K) and  $h\omega_{ph} = 0.18$  eV (dashed line) and with  $\sigma_{0_1} = 5.3 \cdot 10^{-4}$  S/cm,  $\sigma_{0_2} = 8.3 \cdot 10^{-10}$  S/(cm · K) and  $h\omega_{ph} = 0.15$  eV (dash-dotted line) are shown. The dependences calculated from Eq. (10) with  $\sigma_{0_1} = 1.2 \cdot 10^{-4}$  S/cm,  $\sigma_{0_2} = 1.7 \cdot 10^{-4}$  S/(cm · K) and  $E_a = 0.051$  eV (dash-dotted line) and with  $\sigma_{0_1} = 5.2 \cdot 10^{-5}$  S/cm and  $\sigma_{0_2} = 1.2 \cdot 10^{-5}$  (cm · K) ( $T \leq 230$  K),  $\sigma_{0_2} = 9.8 \cdot 10^{-4}$  S/cm<sup>-1</sup> and  $\sigma_{0_1} = 1.9 \cdot 10^{-4}$  S/(cm · K) ( $T \geq 230$  K) and  $E_a = 0.061$  eV (dashed line) are shown as well.

temperatures the conductivity due to the interchain spin diffusion can be interpreted in the framework of the activation of spin charge carriers to the extended states [54]. Therefore, the total conductivity is determined by two parallel processes

$$\sigma_{3-D}(T) = [\sigma_{0_1}^{-1} + \sigma_{0_2}^{-1} T^{-1} \exp(E_a/kT)]^{-1}, \quad (10)$$

where  $E_a$  is the activation energy.

Figure 10 shows that  $\sigma_{3-D}$  experimental data of the as-modified and stored sample 2 are fitted well by Eq. (10) with  $E_a = 0.061$  eV and  $E_a = 0.051$  eV, respectively. These values are close to the typical activation energy of the interchain spin hopping in some other compounds of low dimensionality. The decrease in  $E_a$  evidences the decrease of crystallinity during PATAc storage. The break in the  $\sigma_{3-D}(T)$  curve could be attributed to a change in the conformation of the system at  $T_c$  as it occurs in other conducting polymers [9, 12, 19]. The activation energy necessary for the charge carrier hopping between polymer chains is close to those obtained above from the PATAc paramagnetic susceptibility data and polymer chain librations. This fact leads to the conclusion about the interference of these processes in the polymer.

From the average RT mobility  $\mu \cong 0.5$  cm<sup>2</sup>/(V · s) obtained by the Hall study for charge carriers in highly irradiated polymer [14] one can evaluate an intrinsic conductivity to be close to 0.34 S/cm. However,  $\sigma_{1-D} = 4.8 \cdot 10^{-3}$  S/cm and  $\sigma_{3-D} = 8.5 \cdot 10^{-4}$  S/cm obtained from EPR data are much lower. This means that the intrinsic conductivity in highly conducting PATAc is determined mainly by dynamics of spinless bipolarons with concentration exceeding the number of mobile polarons by approximately two orders of magnitude.

#### 4 Conclusions

Multifrequency EPR spectroscopy allowed us to postulate the existence of two types of paramagnetic centers in laser-modified PATAc – polarons moving along polymer chains in crystalline domains and polarons localized on polymer chains in amorphous regions. Assuming that the polaron is covered by electron and excited phonon clouds, one can propose that both spin relaxation and charge transfer should be accompanied by the phonon dispersion. The mobility of the polarons depends strongly on their interaction with other PCs and with the lattice phonons. The charge transfer integral and therefore the intrinsic conductivity of the sample is modulated by macromolecular dynamics and this dynamics reflects the effective crystallinity of PATAc with metal like domains. The strong spin-spin interaction at high temperatures leads to the decomposition of bipolarons into polaron pairs. The number of bipolarons exceeds the number of polarons at least by two orders of magnitude, so the total conductivity of PATAc is determined mainly by dynamics of diamagnetic charge carriers. Magnetic resonance, relaxation and dynamics parameters of PATAc are shown to change during its storage that can be explained by degradation of the polymer.

## Acknowledgements

We thank Prof. Dr. E. Fanghänel for providing us with an initial sample and M. R. Zhdanov for assistance at the EPR experiment. This study was supported in part by the Thuringian Ministry of Sciences and Research and by the Russian Foundation for Basic Research, grant 01-03-33255.

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