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PHYSICAL PROPERTIES

Spin Dynamics in Conducting Poly(aniline)[1]

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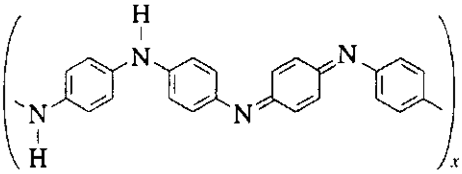
Abstract—Two types of paramagnetic centers in slightly and medium doped poly(aniline) were detected by 3-cm and 2-mm waveband EPR measurements. Spin–lattice and spin–spin relaxation times, as well as frequencies of the intra- and interchain motion of mobile centers were determined separately by a steady-state saturation technique in the temperature range 90–330 K. The charge transport in slightly doped poly(aniline) can be described within the framework of the Kivelson theory, while the process in moderately doped polymer proceeds predominantly by the mechanism of variable range hopping. It is shown that doping of the polymer leads to the formation of small polarons, which are the major paramagnetic charge carriers in metallike poly(aniline), and bipolarons. In the ultimately doped poly(aniline), the concentration of diamagnetic bipolarons may exceed the concentration of polarons.

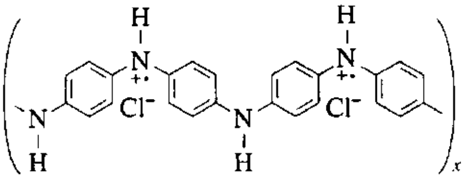
INTRODUCTION

In recent years, the structural and electrodynamic properties of conducting π-conjugated polymers have been extensively studied [1, 2]. However, the fundamental characteristics were reported only until recently for *trans*-poly(acetylene) and poly(*p*-phenylene). For example, it was established that even very slight doping of poly(acetylene) leads to changes in the polymer structure and soliton pinning in the polymer chain. As the doping level increases, the individual soliton levels merge to form a soliton band, which may eventually overlap with the valence and conduction bands [3], thus transforming the polymer into a metallic state. These phenomena are observed upon doping poly(*p*-phenylene) and the similar polymers capable of forming the nonlinear excitations of other types such as polarons and bipolarons [3]. The energetic and dynamic properties of these quasiparticles have also been rather extensively studied in recent years.

Poly(aniline) macromolecules contain nitrogen heteroatoms incorporated between phenylene rings of the polymer chain. It is this structural feature that accounts for the considerable difference between the properties of poly(aniline) and other conducting polymers. Depending on the degree of oxidation, poly(aniline) may exist in the form of either emeraldin base (EB)



or emeraldin salt (ES) [4]]



The protonation or oxidation of EB changes the conductivity of the polymer by more than 10 orders of magnitude. In addition, the polymer exhibits the Pauli magnetic susceptibility typical of classical metals [5, 6]. This behavior may be due to the appearance of completely protonated or oxidized conducting crystalline clusters within the nonconducting amorphous polymer phase. A dominating charge transfer mechanism in poly(aniline) with low degree of oxidation is the electron hopping between polarons and bipolarons. Similar to the other conjugated polymers, the polaron energy levels in doped poly(aniline) form a polaron lattice that accounts for the metallike band structure of the polymer [5, 7, 8]. The results of the experimental and theoretical investigations led to the conclusion [9] that the major charge carriers in poly(aniline) polarons move along the individual polymer chains.

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Nonlinear excitations in the conducting polymers are characterized by electron and nuclear spins. Therefore, magnetic-resonance methods are among the most efficient tools for the investigation of charge carrier dynamics in the conducting polymers, capable of probing samples within a few macromolecular chains or even a single macromolecule [10–12]. The unique feature of these methods is the possibility of determining the carrier velocity and the anisotropy of spin mobility, even in unoriented powdered samples. For example, the results of EPR and NMR measurements showed that dominating transport mechanism in ES consists in the spin hopping between polymer chains [13, 14]. Such experiments are typically performed at an EPR frequency not exceeding 10 GHz. However, insufficient spectral resolution in these wavebands hinders realization of the entire potential of EPR for obtaining a most exhaustive pattern of processes occurring in conducting organic polymers.

We have previously demonstrated that EPR measurements in the 2-mm waveband allow this method to be used with a markedly increased experimental efficiency for studying the nature and dynamics of charge carriers in various organic polymeric semiconductors [12, 15, 16].

This article presents the results of our first investigation into the dynamics of charge carriers in undoped and oxidized poly(aniline) samples described within the framework of a polaron–bipolaron formalism, which was performed for the most part by EPR measurements in the 2-mm waveband. It was established, in particular, that EB features the pinning of paramagnetic centers having different magnetic and dynamic parameters. In this polymer the major charge carriers are polarons, and the dominating charge transfer mechanism is the isoenergetic interchain tunneling as described within the framework of the Kivelson theory. In ES, the charge is transferred for the most part by bipolarons according to the Mott model of the variable range hopping. The poly(aniline) samples studied exhibited a tendency toward increasing dimensionality upon oxidation.

EXPERIMENTAL

The samples of conducting poly(aniline) in the powder form were synthesized by polymerization in the presence of $(NH_4)_2S_2O_8$ according to the procedure described in [17]. To obtain polymers with a preset doping level y (the number of dopant molecules per monomer unit), equal amounts (2 g) of the undoped polymer were exposed in a sulfuric acid solution with known pH in the range 0–14. The degree of polymer oxidation, as represented by the [S]/[N] ratio, was determined by methods of elemental analysis. The room-temperature direct-current (dc) conductivity of samples prepared in the form of pressed disks was measured by the two-point-probe method. The Pauli spin susceptibility was determined by the SQUID method.

The EPR measurements were performed on 3-cm (PS100X) and 2-mm (EPR-0.5 [18]) spectrometers operated at a 100 kHz modulation frequency of the polarizing magnetic field. The total spin concentration in the samples was determined by doubly integrating the 3-cm waveband EPR spectra using $CuSO_4 \cdot 5H_2O$ single crystal as a reference. The g values and the magnetic field scan range were calibrated in the 2-mm waveband using the EPR spectra of a MgO powder with an admixture of Mn^{2+} ions and adopting $g_{eff} = 2.00102$ and $a = 8.74$ mT. The imaginary χ' and real χ'' components of the complex paramagnetic susceptibility were measured in the 2-mm waveband in the temperature range 90–330 K. The spin–lattice (T_1) and spin–lattice (T_2) relaxation times for the paramagnetic centers in poly(aniline) were determined separately by 2-mm EPR measurements using the steady-state spin parcel saturation technique [19].

RESULTS AND DISCUSSION

Figure 1 shows the plots of the dc conductivity σ_{dc} and the Pauli spin susceptibility χ^P of poly(aniline) samples versus their doping level y. The monotonic variation of σ_{dc} with increasing y is similar to that described earlier [20]. An analysis of these results shows that samples with $y \geq 2$ contain metallike clusters with 3*D*-delocalized electrons [5, 9], which is in agreement with the data obtained previously by electron microscopy and X-ray diffraction [21].

Figure 2 presents the experimental EPR spectra of undoped poly(aniline) (spectra *e* and *f*) in comparison with superpositions of the calculated spectra (*a*, *c* and *b*, *d*). An analysis of these spectra showed that undoped poly(aniline) contains paramagnetic centers of at least two types. The first type is represented by the R_1 radicals (model spectra *a*, *b*) localized in the polymer chain and characterized by anisotropic magnetic parameters $g_x = 2.00535$, $g_y = 2.00415$, $g_z = 2.00238$, $A_x = A_y = 0.33$ mT, and $A_z = 2.3$ mT. The second type is represented by mobile R_2 radicals (model spectra *c*, *d*) with the magnetic parameters $g_\perp = 2.00351$ and $g_\parallel = 2.00212$.

The relative content n_1 of the R_1 radical varies between the samples with different doping levels and depends on the temperature as depicted in Fig. 3. The total concentration of the paramagnetic centers of both types in poly(aniline) samples with different y values are as follows (in units of 10^{19} spin/g):

y	0	0.01	0.02	0.06	0.22	0.31	0.42	0.53
n	1.0	1.2	3.2	4.7	22	54	92	196

These data and the results of the conductivity measurements presented in Fig. 1 show that a change in the concentration of the paramagnetic centers by approximately two orders of magnitude leads to a 7-order increase in the conductivity. This can be explained by a collapse of the paramagnetic polarons with the formation of diamagnetic bipolarons in samples with $y \geq 02$. The paramagnetic centers R_1 with asymmetric EPR spectrum can be identified with macroradicals $(-Ph-\dot{N}-Ph-)_n$ localized in the short segments of the polymer chain. The magnetic parameters of the R_1 radical differ only slightly from those of the $Ph-\dot{N}-Ph$ radical [22, 23], which is probably explained by a lower density of the unpaired electrons on the nitrogen nucleus ($\rho_N^\pi = 039$) and by a more planar configuration of the latter radical. According to calculations [24], the contribution of the CH groups of the $Ph-\dot{N}-Ph$ radical into the Δg_x value is comparatively small ($\sim 1.7 \times 10^{-5}$). The minimum energy of the excited state of a radical can be calculated by the following formula [24]:

$$\Delta E_{ij} = 2\lambda_N \rho_N^\pi / \Delta g. \qquad (1)$$

where λ_N is the spin–orbital coupling constant of the unpaired electron and the nitrogen nucleus and $\Delta g = g_{x,y} - g_z$. For the R_1 radical, these values are $\Delta E_{n\pi^*} = 3.8$ eV and $\Delta E_{\sigma\pi^*} = 6.5$ eV.

As was demonstrated earlier [25], the magnetic parameters g_x and A_z of the nitroxyl radicals incorporated into polymers are most sensitive to changes in the radical microenvironment, including the polarity and dynamics. The data presented in Fig. 4 show that the g_x value of the R_1 radical is affected significantly by the doping level and temperature. Therefore, a shift of the x-component in the EPR spectrum of this radical toward higher fields with increasing doping level and/or temperature can be attributed not only to higher polarity of the radical microenvironment, but to growing intensity of the motion of radical itself in the yz plane of the molecular system of coordinates as well.

The average g values of the R_1 and R_2 radicals are approximately equal: $\langle g\rangle_1 = \frac{1}{3}(g_x + g_y + g_z) \approx \langle g\rangle_2 = \frac{1}{3}(g_\parallel + 2g_\perp)$. This implies that a less anisotropic spectrum of the R_2 radical can be assigned to a polaron diffusing at a minimum velocity along the polymer chain [26]:

$$v_{1D}^0 \geq \frac{(g_x - g_e)\mu_{BB}}{2\pi\hbar}. \qquad (2)$$

where μ_B is the Bohr magneton, B_0 is the strength of external magnetic field, and $\hbar$ is the Planck constant. Using the g_x value determined above for EB, we obtain an estimate $v_{1D}^0 \geq 5.7 \times 10^7$ s^{-1}.

As is seen from Fig. 5, the width of the perpendicular component in both 3-cm and 2-mm EPR spectra of the R_1 radical varies with y. This is evidence for the formation of regions with high spin density and fast exchange between spin parcels in the sample.

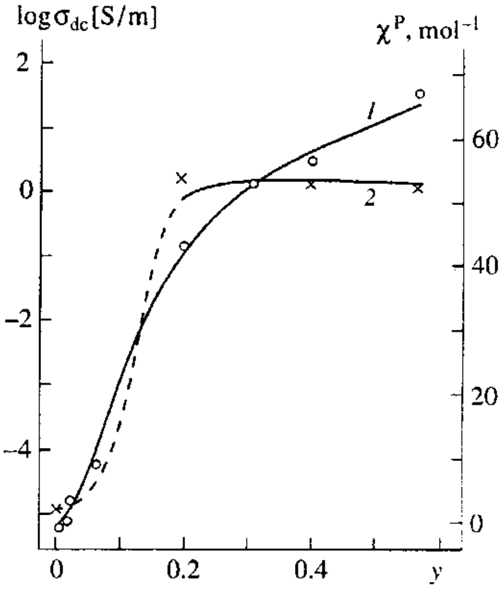

Fig. 1. The plots of (1) the dc conductivity σ_{dc} and (2) the Pauli spin susceptibility χ^P of poly(aniline) samples versus their doping level y. The measurements performed at 300 K.

The doping of poly(aniline) leads both to narrowing of the EPR signal of the R_2 radical and to a decrease in the g value. The latter effect can be due to a decrease in the spin density on the nitrogen nucleus according to equation (1) and a change in the polymer chain conformation. In particular, the angle –Ph–N–Ph– may change upon the doping of poly(aniline) by 22° [27]. However, calculation [12] shows that such a change in the angle may decrease the $g_\perp$ value only by a few percent. Therefore, the above-mentioned variation in the spectroscopic parameters is apparently due to a doping-induced decrease in the dihedral angle θ between planes of the neighboring phenyl rings in the Ph–N–Ph fragment. The transfer integral I_{C-H} between the p_z orbitals of nitrogen and carbon, occurring in the *para* position to the benzene rings of poly(aniline), depends on the dihedral angle as $I_{C-N} \sim \cos\theta$, which is typical of aromatic hydrocarbons [28]. Assuming $\theta = 56°$ for EB, we can calculate the effective dihedral angle ($\theta = 33°$) and the spin density on the nitrogen atom in ES with $y = 0.2$ ($\rho_N^\pi(0) = 0.42$). This decrease in the θ value leads to growth in the spin density on the benzene rings as a result of increase of the transfer integral I_{C-N}. Thus, the aforementioned variations in the magnetic parameters may be indicative of a more pronounced spin delocalization along the polymer chain and of a more planar chain conformation caused by doping.

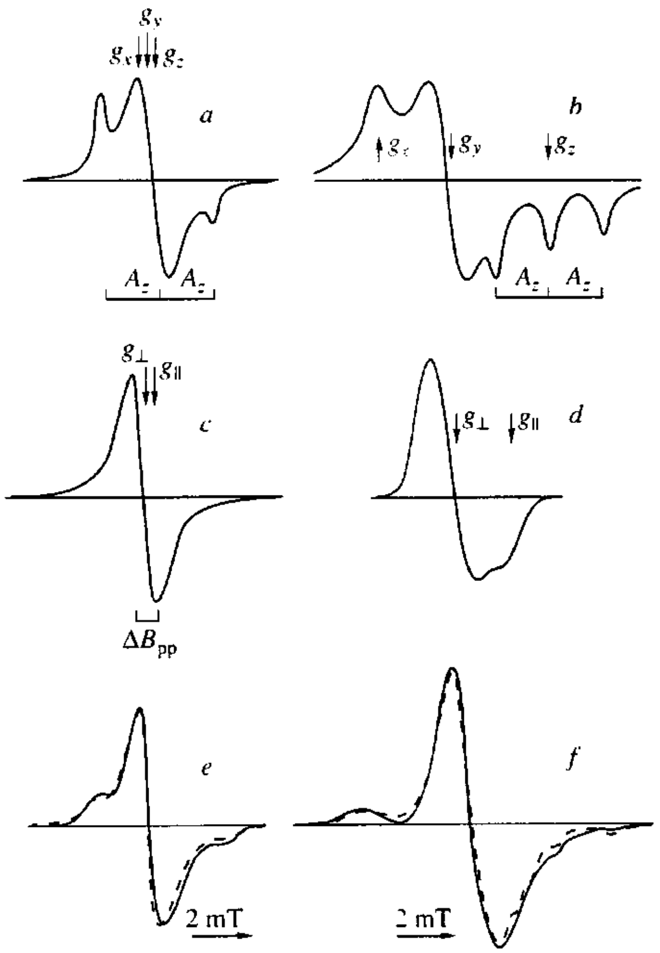

Fig. 2. EPR spectra of (*a*, *b*, *e*) R_1 and (*c*, *d*, *f*) R_2 radicals for (*a*, *c*, *e*) 3-cm and (*b*, *d*, *f*) 2-mm wavebands: (*a*–*d*) model spectra calculated for $g_x = 2.00535$, $g_y = 2.00415$, $g_z = 2.00238$, $A_x = A_y = 0.33$ mT, $A_z = 2.3$ mT, $g_\perp = 2.00351$, $g_\parallel = 2.00212$; (*e*, *f*) experimental spectra measured at 300 K (solid lines). Dashed lines in (*e*, *f*) show superpositions of the calculated spectra of radicals R_1 and R_2 taken with the relative contributions 1 : 4. Quantities g_i, A_z, and ΔB_{pp} represent measurable magnetic parameters.

The EPR spectra of ES with $y \geq 0.3$ show a low-intensity hyperfine structure resulting from the interaction of unpaired electron with protons of the benzene rings and with the nitrogen nucleus. The constant of hyperfine splitting varies in various samples within $a_H = 5.0$–9.6 μT, showing no such correlation with the *y* values. The spin density on protons ρ_H^π in these polymers, determined from the well-known McConnell relation $a_H = Q_H \rho_H^\pi$ using $Q_H = 2.25$ mT for the benzene anion [29], is $\rho_H^\pi = (2.2$–$4.3) \times 10^{-3}$. This estimate differs from the value $\rho_H^\pi = 1.5 \times 10^{-2}$ obtained for the EB solution in dioxane [30], where the unpaired electron was found to interact with two side benzene rings of poly(aniline). In this context, our experimental data confirm the assumption above concerning delocalization of the spin density along the chain and a more planar chain configuration in the ES samples studied.

The inphase and quadrature contributions to the 2-mm waveband dispersion signal of a neutral or low-doped poly(aniline) exhibit dome-shaped components with a Gaussian distribution of the spin parcels (Fig. 6, spectra *c* and *d*). Such components are usually observed for the rapid passage of paramagnetic centers, provided that the conditions of saturation ($\gamma_e B_1 \sqrt{T_1 T_2} > 1$) and adiabatic resonance passage ($dB/dt = B_m \omega_m < \gamma_e B_1^2$) are fulfilled (here, γ_e is the gyromagnetic ratio for electron; dB/dt is the velocity of resonance passage; B_m and ω_m are the modulation amplitude and frequency, respectively; and B_1 is the magnetic component of the polarizing SHF field). An analysis of the shapes and relative amplitudes of the components of the dispersion signal allows the times of spin–lattice and spin–spin relaxation of the paramagnetic center to be determined as described in [19].

Figure 7 shows the temperature variation of the effective spin– lattice and spin–spin relaxation times calculated for several poly(aniline) samples. As is seen, an increase in the polymer doping level leads to a decrease in the effective relaxation time of the paramagnetic centers studied. This can be explained by increasing spin interaction with the lattice and other spins pinned in the neighboring polymer chains of highly conducting clusters. It should be noted that electron relaxation processes in condensed media at high temperatures are determined primarily by the Raman interaction of electrons with the optical phonons of the lattice. The probability (i.e., the rate) of these processes depends on the concentration *n* of the paramagnetic centers localized, for example, in ionic crystals ($W_R \sim T_1^{-1} \sim n^2 T^7$) and π-conjugated polymers ($W_R \sim T_1^{-1} \sim nT^2$) [31].

These data allow us to conclude that relaxation of the paramagnetic centers in poly(aniline) samples with $y \leq 0.02$ is characterized by the law $T_1^{-1} \sim nT^{-k}$, where $k = 3$–4, whereas, the polymer with $y = 0.2$ exhibits a less steep dependence with an inverse temperature variation $T_1^{-1} \sim nT^{0.3}$ (Fig. 7). This fact suggests that the doping of poly(aniline) results in the appearance of an additional channel for the energy transfer from the spin ensemble to lattice similar to what takes place in classical metals.

The relaxation times of the electron and proton spins in poly(aniline) depend on the frequency ν_e as described by the formula $T_{1,2} \sim n^{-1} \nu_e^{1/2}$ [13, 14]. Therefore, the experimental data can be interpreted assuming

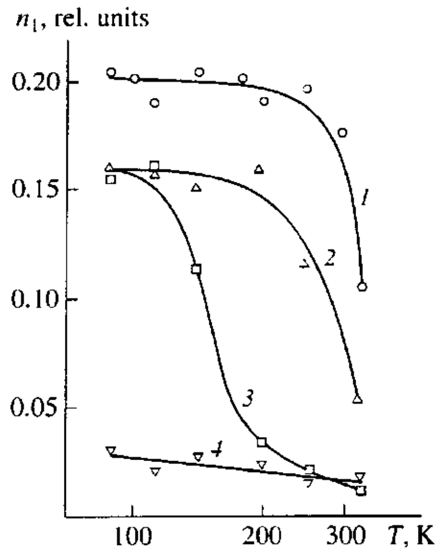

Fig. 3. Temperature dependence of the relative concentration of R_1 radicals localized in the chain of poly(aniline) with various doping levels $y = 0$ (*1*); 0.01 (*2*); 0.02 (*3*); and 0.2 (*4*).

that the electron relaxation is modulated by the 1*D* diffusion of radicals R_2 along the polymer chain and their 3*D* hopping between the chains with the rates ν_{1D} and ν_{3D}, respectively. In this case, the spectral density function for the spin mobility in a 1*D* system is [32]

$$J(\nu) = n\phi(\nu)\Sigma_{ij}, \tag{3}$$

where $n = (n_1 + n_2)/\sqrt{2}$ is the effective concentration of localized (n_1) and delocalized (n_2) paramagnetic centers per monomer unit of poly(aniline) and Σ_{ij} is the lattice sum for the powder sample.

$$J_{1D}(\omega) = \frac{1}{\sqrt{4\pi\nu'_{1D}\nu_{3D}}}\sqrt{\frac{1+\sqrt{1+(\omega/\nu_{3D})^2}}{1+(\omega/\nu_{3D})^2}}$$

$$= \begin{cases} (2\nu'_{1D}\omega)^{-1/2} & \text{for } \nu'_{1D} \gg \omega \gg \nu_{3D}, \\ (4\pi\nu'_{1D}\nu_{3D})^{-1/2} & \text{for } \omega \ll \nu_{3D} \end{cases}$$

where $\nu'_{1D} = 4\nu_{1D}/N^2$, N is the spin delocalization length expressed in monomer units, and $\omega = 2\pi\nu_e$ is the EPR frequency.

Taking into account that electron relaxation is determined primarily by the dipole–dipole interaction between localized and delocalized spins, we obtain the following equations for the electron relaxation rates [33]:

$$T_1^{-1} = \langle\omega^2\rangle[2J(\omega) + 8J(2\omega)] \tag{4a}$$

$$T_2^{-1} = \langle\omega^2\rangle[3J(0) + 5J(\omega) + 2J(2\omega)], \tag{4b}$$

where $\langle\omega^2\rangle = 0.1(\mu_0/4\pi)^2\gamma_e^4\hbar^2S(S+1)n\Sigma_{ij}$ is the averaged constant of spin dipole interaction for the powder.

Figure 8 shows the temperature variation of the dynamic parameters ν_{1D} and ν_{3D} for the R_1 radicals in some poly(aniline) samples calculated using the data of Fig. 7 and equations (7) and (6) for $N \approx 5$ [34]. It is quite evident and reasonable that the result of the anisotropy of the spin dynamics is at the maximum in the initial EB sample and decreases with increasing *y*. At a sufficiently high doping level ($y \geq 0.2$), the electron relaxation times become comparable. Moreover, the dynamic parameters at these values of *y* are weakly dependent on the temperature because of a strong spin–spin coupling in the metallike clusters and an increase

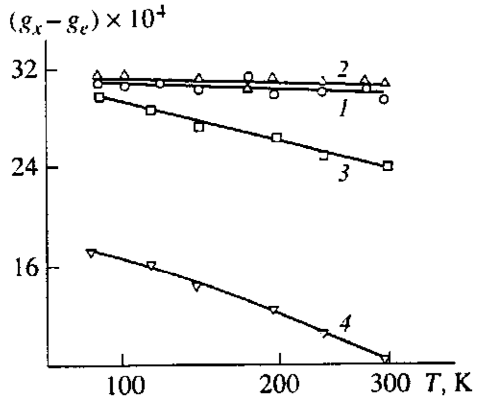

Fig. 4. Temperature variation of the shift of g_x value (relative to the free-electron value $g_e = 2.00232$) for R_1 radicals localized in the chain of poly(aniline) with various doping levels $y = 0$ (*1*); 0.01 (*2*); 0.02 (*3*); and 0.2 (*4*).

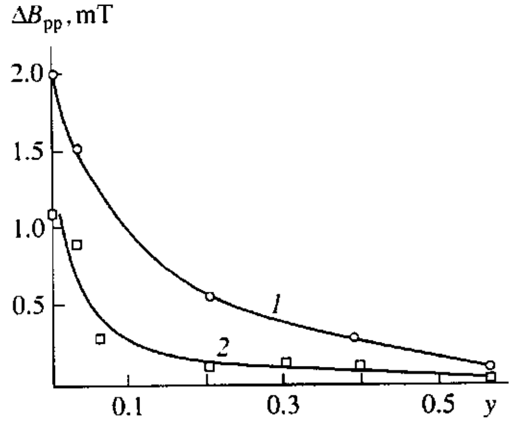

Fig. 5. Effect of the poly(aniline) doping level *y* on the linewidth ΔB_{pp} of the (*1*) 2-mm and (*2*) 3-cm room-temperature EPR spectra of R_2 radicals.

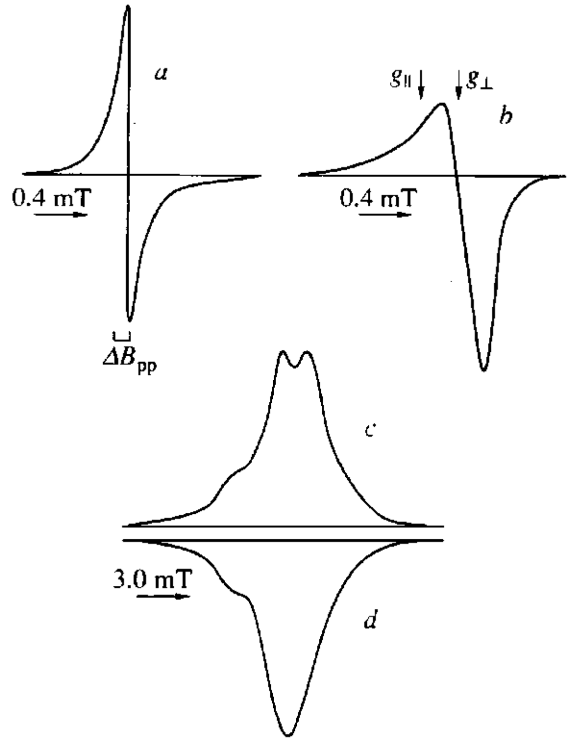

Fig. 6. Room-temperature (*a*) 3-cm and (*b*) 2-mm waveband absorption spectra of the emeraldin salt with $y = 0.50$ and the (*c*) inphase and (*d*) quadrature components of the 2-mm waveband dispersion signal of poly(aniline) with $y = 0.02$. Quantities ΔB_{pp}, $g_{\parallel}$, $g_{\perp}$ represent the measurable parameters.

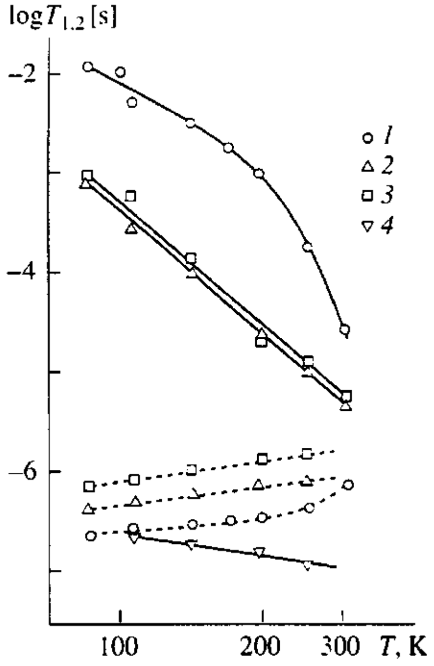

Fig. 7. Temperature dependence of the effective spin-lattice T_1 (solid lines) and spin–spin T_2 (dashed lines) relaxation times of poly(aniline) with various doping levels $y = 0$ (*1*); 0.01 (*2*); 0.02 (*3*); and 0.2 (*4*).

in the effective dimensionality of the system. Under these conditions, the sensitivity of the steady-state saturation method becomes less sensitive to changes in the relaxation and dynamics of paramagnetic centers. However, the rate of spin diffusion can be estimated from equations (4) assuming $T_1 \approx T_2$. For ES with $y = 0.2$ this estimate yields $\nu_{iso} \approx 2.0 \times 10^{11}$ s^{-1}.

The EPR measurements at frequencies in the range 5–450 MHz [13, 14] showed that anisotropy of the spin dynamics in ES doped with hydrochloric acid molecules is retained at a sufficiently high level up to $y = 0.6$, even at room temperature. However, our data indicate that a high anisotropy of the motion of charge carriers is observed only in the neutral sample and in polymers doped with sulfuric acid to $y < 0.2$. This discrepancy may be explained by the fact that the effective dimensionality of our samples modified by sulfuric acid to $y \geq 0.2$ exceeds the dimensionality of poly(aniline) doped with HCl. An increase in the system dimensionality leads to a decrease in the number of electron traps and, hence, in the probability of electron scattering on the lattice phonons. This results in a virtually isotropic spin motion and a relatively weak temperature dependence of the rates of electron relaxation and the diffusion of paramagnetic centers in doped poly(aniline), similar to what is observed in amorphous inorganic semiconductors [35, 36].

The components of conductivity due to the mobility of spin charge carriers can be determined using the well-known relation

$$\sigma_{1,3D}(T) = \frac{Ne^2 D_{1,3D} c_{1,3D}^2}{k_B T}, \qquad (5)$$

where $c_{1D} = 0.95$ nm and $c_{3D} = 0.7$ nm are the lattice constants of ES [27] and k_B is the Boltzmann constant. The room- temperature conductivity along the chain for $0 \leq y \leq 0.02$ is $\sigma_{1D} = 10$ S/m. Under the same conditions, the σ_{3D} component increases from 1×10^{-3} to 0.5 S/m. These estimates provide additional evidence for the decreasing anisotropy of the spin motion and agree with the earlier conclusions [37].

As noted above, the EPR method allows the spin dynamics and conductivity to be studied on the level of a few polymer chains. In principle, the macroscopic σ_{dc} and microscopic (alternating-current) σ_{ac} conductivities may be correlated, but are expected to differ significantly in a doped polymer containing a sufficiently large amount of bipolarons. Therefore, the above values (obtained by different methods) can be compared only qualitatively. If the diffusion coefficients of the spin and spinless charge carriers are close, the contribution of bipolarons to the total conductivity must compare to or even exceed the conductivity due to the spin carriers in poly(aniline) doped to $y > 0.2$.

Data on the spin dynamics can be interpreted within the framework of various models available for the charge transfer in low-dimensional systems. Previously, we demonstrated [21] that the dynamic processes in ES with $y \geq 0.2$ can be described using the model of variable range interchain hopping of the charge carriers [36]. According to this model, the σ_{dc} value must exhibit an approximately quadratic temperature dependence, while the function $\sigma_{ac}(T)$ has to be linear. Steeper temperature variation of the conductivity in ES samples with lower doping levels can be interpreted using the model of activated charge transfer between polymer chains [36], according to which the total conductivity components are as follows:

$$\sigma_{dc}(T) = \sigma_{dc}^{0}\exp\left(-\frac{E_a}{k_B T}\right) \qquad (6a)$$

$$\sigma_{ac}(T) = \sigma_{ac}^{0}\nu_e^{0.8}T\exp\left(-\frac{E_a}{k_B T}\right), \qquad (6b.)$$

where E_a is the activation energy for the electron transfer between polymer chains.

Indeed, the experimental variation of $\nu_{3D}(T)$ is sufficiently well approximated for the initial sample by a function of the type (6b) with $\sigma_{ac}^{0} = 3.2 \times 10^{-18}$ S m^{-1} s$^{0.8}$ K^{-1}, $E_a = 0.06$ eV for $T \leq 240$ K and with $\sigma_{ac}^{0} = 9.1$ S m^{-1} s$^{0.8}$ K^{-1}, $E_a = 0.9$ eV for $T \geq 240$ K. The data for the samples doped to $y = 0.01$ and 0.02 are described well by the function with $\sigma_{ac}^{0} = 1.4 \times 10^{-11}$ S m^{-1} s$^{0.8}$ K^{-1}, $E_a = 0.13$ eV. A comparison of the quantities $\nu_{3D}(T)$ and $\sigma_{ac}(T)$ shows that the latter function approximates the experimental curve well. For the activated charge transfer between polymer chains, the σ_{dc} value must be a linear function of the temperature. However, the temperature dependence observed for the ES samples is essentially nonlinear. and we have to propose an alternative charge transfer mechanism in this polymer.

As noted above, the spin–lattice relaxation time in poly(aniline) depends strongly on the temperature. This fact implies that, according to the law of energy conservation, the electron hopping must be accompanied by the absorption or emission of a minimum number of lattice phonons of the polymer studied. The strong spin–lattice interaction renders multiphonon processes dominating in a neutral or slightly doped poly(aniline), after which the electron-dynamic processes in the polymer can be treated within the framework of the Kivelson formalism [38] based on the notion of the isoenergetic electron transfer between the polymer chains. According to these notions. The conductivity components can be expressed as follows:

$$\sigma_{dc}(T) = \sigma_{dc}^{0}T^{n} \qquad (7a)$$

$$\sigma_{ac}(T) = \sigma_{ac}^{0}T^{-1}\nu_e\left[\ln\frac{k_1\nu_e}{T^{m+1}}\right]^{4}, \qquad (7b)$$

where k_1 is a constant, and $m = 10$. Using the method described in [39], we may estimate the ratio σ_{ac}/σ_{dc} in the limit $\omega/2\pi = \nu_e \longrightarrow \infty$. For poly(aniline) this estimate proves to be $\sigma_{ac}/\sigma_{dc} \sim 130$.

Figure 8 shows the temperature dependence of σ_{ac} calculated by equation (7b) for $m = 12.9$, $\sigma_{ac}^{0} = 2.8 \times 10^{-12}$ S m^{-1} s K for EB and for $m = 12.6$, $\sigma_{ac}^{0} = 8.8 \times 10^{-14}$ Sm m^{-1} s K for the samples with $0 \leq y < 0.02$ and $k_1 = 1 \times 10^{24}$ s K^{m+1}. As is seen from this figure, the experimental plots of $\nu_{1D}(T)$ are satisfactorily approximated by the theoretical functions $\sigma_{ac}(T) \equiv \sigma_{1D}(T)$. Taking into account the law $\sigma_{dc}(T) \sim T^{m}$, which is also valid for poly(aniline) with $0 \leq y < 0.02$, we may conclude

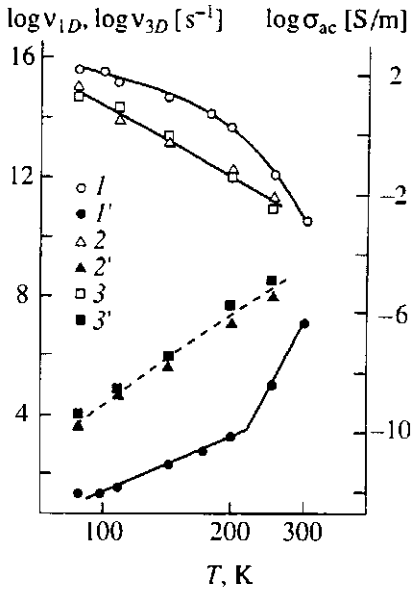

Fig. 8. Temperature dependence of the rates of (*1–3*) polaron diffusion along the chain and (*1'–3'*) polaron hopping between the chains of poly(aniline) with various doping levels $y = 0$ (*1*, *1'*); 0.01 (*2*, *2'*); and 0.02 (*3*, *3'*). Solid lines show the function $\sigma_{1D}(T) \equiv \sigma_{ac}(T)$, calculated using equation (7b) for (*1*) $m = 12.9$, $\sigma_{ac}^{0} = 2.8 \times 10^{-12}$ S m^{-1} s K and (*2*, *3*) $m = 12.6$, $\sigma_{ac}^{0} = 8.8 \times 10^{-14}$ S m^{-1} s K; $k_1 = 1 \times 10^{24}$ s K^{m+1}. Dashed lines show the function $\sigma_{3D}(T) \equiv \sigma_{ac}(T)$ calculated using equation (6b) for (*1'*) $\sigma_{ac}^{0} = 3.2 \times 10^{-18}$ S m^{-1} s$^{0.8}$ K^{-1}, $E_a = 0.06$ eV ($T \leq 240$ K) and $\sigma_{ac}^{0} = 9.1$ S m^{-1} s$^{0.8}$ K^{-1}, $E_a = 0.9$ eV ($T \geq 240$ K) and (*2'*, *3'*) $\sigma_{ac}^{0} = 1.4 \times 10^{-11}$ S m^{-1} s$^{0.8}$ K^{-1}, $E_a = 0.13$ eV.

that the proposed mechanism of charge transfer is applicable to these samples.

CONCLUSION

Doping of EB leads to the growth in the number and size of highly conducting clusters with charge carriers having different mobilities, which gives rise to the Raman relaxation processes and accounts for the increase in the conductivity, as well as the Pauli spin susceptibility in the samples with $y \geq 0.02$. This modification leads to an increase in the sample dimensionality and changes the mechanism of charge transport from isoenergetic interchain tunneling to variable range interchain hopping.

The concentration of diamagnetic charge carriers in poly(aniline) with $0.2 \leq y < 0.5$ is approximately equal to the number of spins or may even exceed this number. This implies that the charge transfer in these samples is performed by small polarons and in the ultimately doped ES samples by diamagnetic polarons. Our data generally agree with the concept of stabilized metallike clusters in poly(aniline) comprising strongly interacting polymer chains with 3*D*-delocalized conduction electrons [5, 6], but do not completely confirm this model.

The data presented in this paper demonstrate the advantages offered by EPR measurements in the 2-mm waveband for determination of the composition of paramagnetic centers and investigation of the spin dynamics and charge transfer mechanism in poly(aniline) samples with $0 \leq y < 0.2$ in a broad temperature interval. This method can be applied as well for studying the spin and electron-transport properties of other organic polymeric semiconductors.

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