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POLYTHIOPHENE AND POLYACETYLENE CONDUCTORS IN THE 3-cm AND 2-mm ESR BANDS

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Highly conducting organic compounds consisting of radical-ion salts and charge-transfer complexes containing oligomer and high-molecular-weight components, in particular, polyacetylene [1] and polythiophene, have attracted recent attention.

Radiospectroscopic methods are commonly used in studying such organic conductors [2]. However, there are definite difficulties in clarifying the nature of the paramagnetism of different compounds and the interrelationship of the form and intensity of the ESR signal with the electrical characteristics of these compounds such as conductivity. The ESR spectra of these systems in the 3-cm ESR band, as a rule, display singlets which provide little information. The magnetic resonance parameters of these lines are almost identical [3]. The information provided by ESR spectroscopy, as shown in our previous work [4], may sometimes be enhanced by going to the 2-mm band.

In the present work, we compared the magnetic resonance data in the 3-cm and 2-mm ESR bands with the electrical indices of compounds containing polythiophene (PT) and polyacetylene (PA).

The PT samples were combined with BF_4^-, ClO_4^-, I^-, $FeCl_4^-$, and MnO_4^- ions, while the PA sample were combined with I^- anions. These polymers are insoluble in the usual organic solvents and in sulfuric and hydrochloric acids and have good adhesion.

The data obtained are given in Table 1. ESR signals were not found for PT combined with $FeCl_4^-$ and MnO_4^- anions. In the series of compounds with BF_4^-, ClO_4^-, and I^- anions (I), almost symmetrical singlets are observed in the 3-cm band at 20°C. The width of these bands increases in the series of compounds with anions $BF_4^- < ClO_4^- < I^-$. A tendency toward increasing g factor and a weak drop in the paramagnetic center concentration are noted in the same series. Such behavior indicates that the anion properties affect the structure and properties of the paramagnetic centers and PT. It is interesting that a regular change in electrical conductivity σ measured by the two-contact method is not seen in this series of (I).

The ESR spectra in the 2-mm range for these systems have greater variation in line form (Fig. 1a,b,c). A characteristic feature of the ESR spectra in this band is axial anisotropy of the g tensor, which is not seen in the ESR spectra of the 3-cm band.

Tokumoto et al. [2] have reported a significant increase in sample conductivity leads to a decrease in the thickness of the skin layer. When the skin layer thickness and characteristic sample dimensions are comparable, the ESR spectrum shows the asymmetry, which increases with further increase in the electrical conductivity without marked change in the signal intensity (Dyson line [5]). Similar asymmetry was detected in the perpendicular component of the ESR signal of $PT(BF_4^-)$ and the ESR signal of $PA(I^-)$ (see Fig. 1a,c). The asymmetry of these signals increased with a further reduction in temperature and markedly diminished with grinding of the samples. This permitted the assignment of the line shape of their spectra to a Dyson line. Knowing the characteristic particle dimensions, we may estimate the specific electrical conductivity of organic conductors at the temperature, at which signal asymmetry begins to appear. For $PT(BF_4^-)$ and $PA(I^-)$ with 0.03-0.07 mm

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TABLE 1. Magnetic Resonance and Electrical Parameters of Organic Conductors

Parameters	Polythiophene			Polyacetylene
	BF_4^-	ClO_4^-	I^-	I^-
$[R]$, spin/g	$8 \cdot 10^{19}$	$5 \cdot 10^{19}$	$2 \cdot 10^{19}$	$3 \cdot 10^{19}$
σ, $\Omega^{-1} \cdot cm^{-1}$	$1{,}2 \cdot 10^{-5}$	$1{,}6 \cdot 10^{-4}$	$5{,}1 \cdot 10^{-6}$	$6 \cdot 10^{-3}$
λ 2 mm, 300 K				
$\Delta H_{\perp}$, Oe	15,1	26	65	12
ΔH_{anis}, Oe	37	24		
$g_{\parallel}$	2,00412	2,00230		
$g_{\perp}$	2,00266	2,00329		
$\langle g \rangle$	2,00314	2,00296	2,00381	2,00325
λ 3 cm, 77 K, 300 K				
$\Delta H^{300\ K}$, Oe	2,3	4,6	7,5	7,7
$\Delta H^{77\ K}$, Oe	3,4	5,2	8,0	
g	2,0026	2,0028	2,0036	

Note: The errors in the g factors in the 3-cm and 2-mm uhf bands are $2 \cdot 10^{-4}$ and $7 \cdot 10^{-5}$, respectively. The errors in the determination of ΔH in the 3-cm and 2-mm uhf bands are 0.1 and 1 Oe, respectively. The values for σ determined by the two-contact method did not exceed 100%.

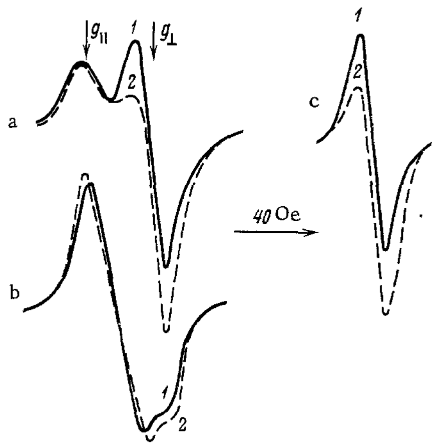

Fig. 1. ESR spectra of polythiophenes $PT(BF_4^-)$ (a), $PT(ClO_4^-)$ (b) and polyacetylene $PA(I^-)$ (c) in the 2-mm uhf band at 1) 300 and 2) 200°K.

characteristic particle dimensions, line asymmetry appeared beginning at 200°K. This permitted us to evaluate the specific electrical conductivity of these samples at 200°K (2-5 $\Omega^{-1} \cdot cm^{-1}$) using the equation given by Tokumoto et al. [2].

Thus, the dependence of the spectroscopic parameters of the paramagnetic centers on the anion has been established. Use of the 2-mm ESR band permitted us to evaluate the conductivity in these systems and measure the anisotropic g-tensors. These values may be used for constructing theoretical models of the paramagnetic centers in organic conductors. We should note that comparison of the magnetic resonance parameters in the 3-cm and 2-mm ESR bands and the electrical indices of PT and PA and, specifically, the lack of correlation of the σ values measured by the two-contact method with the magnetic resonance parameters of the samples indicated that the current carriers and paramagnetic centers are apparently not the identical species.

EXPERIMENTAL

The addition of anions to PT was carried out by an electrochemical method [6]. The reaction was carried out in an electrochemical cell equipped with a platinum anode and cathode in 0.05-0.1 M electrolyte salt solutions (anhydrous Et_4NBF_4, Bu_4NClO_4, Ph_4PMnO_4, and the complex $[Fe(AH)_6][FeCl_4]_2$) in acetonitrile purified by consecutive distillation over CaH_2 and then twice over P_2O_5 at 0.1-2.0 mA/cm^2 anodic current density. The chemical composition of modified PT depends on the reaction conditions. A typical composition is a nonstoichiometric composition such as $(C_4H_{2.5}S)(BF_4)_{0.6}$. Neutral PT was obtained by catalytic polymerization of the Grignard reagent obtained from a 1:1 mixture of 2,5-dibromothiophene and magnesium [7]. In order to obtain PT(I^-), neutral PT was treated with iodine vapor for several hours at 50°C.

The conductivity of PT and PA for direct current was measured by the two-contact method at about 20°C.

The ESR spectra in the 3-cm band were recorded on an ÉPR-V spectrometer produced at the Institute of Chemical Physics of the Academy of Sciences of the USSR. A spectrometer with H_{011} bulk cylindrical probe was used to record the ESR spectra in the 2-mm band [8]. Regulation of the phases of the microwave and high-frequency fields was monitored relative to the signal of an external standard ($(BF)_3PlBr_2$ microcrystallite, where BF is benzofulvalene). MgO powder with trace Mn^{2+} ions (whose g factor was calibrated relative to the g factor of an aqueous solution of Fermi salt [g = 2.00550]) was used to measure the g factor in the 2-mm band, while a solution of the 2,2,6,6-tetramethylpiperidin-1-oxyl nitroxyl radical in CCl_4 (g = 2.00608 [9]) was used to measure in the g factor in the 3-cm band.

CONCLUSIONS

1. A dependence of the magnetic resonance parameters on the nature of the anion was established for organic polythiophene conductors with various anions.

2. The major values of the anisotropic g-tensor were measured by 2-mm band ESR spectroscopy and the conductivity of polythiophene (BF_4^-) and polyacetylene(I^-) was evaluated at 200°K.

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