

## Study of doped polypyrrole by the spin probe method at 3 cm and 2 mm waveband EPR

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### Abstract

The possibility of applying the spin probe and label method to the investigation of semiconductive polymer materials at 2 mm waveband EPR has been shown. Advantages of this method in the study of polymer structural, conformational and electrodynamic characteristics have been exemplified by polypyrrole modified by nitroxide radicals as a probe. The distance between nitroxide radical and spinless charge carriers on polymer chain, effective dipole momentum and size of spinless charge carriers as well as the bipolaronic charge transfer mechanism in doped polypyrrole have been determined. The use of the spin probe and label method with a high spectral resolution EPR technique has permitted a detailed analysis of mobility, nature and size of charge carriers in polymer semiconductors.

### Introduction

The spin probe and label method is widely used to investigate the structure and dynamic properties of organic and biological polymers [1, 2]. This method is based on introducing a spin probe or label into the system studied to report its molecular dynamics and structure as well as effective polarity of its microenvironment.

Nitroxide radicals (NR) of a different structure are generally used as spin probes or labels for this purpose. NR with an irregular distribution of unpaired electron between N and O cores are characterized by anisotropy of the  $g$  factor and hyperfine interaction (HFI) of electron with the nitrogen nucleus. The radical microenvironment affects this electron distribution. The EPR spectra of such modified systems therefore depend on the above properties. At present, approaches have been developed to study various properties of spin-modified systems of high viscosity based on analysis of their EPR spectra [1, 2].

Such investigations are usually carried out at 3 cm and rarely at 8 mm waveband EPR. However, the EPR spectra of organic free radicals in these bands are registered in a narrow range of the magnetic field. This leads to a weak spectral resolution of complicated EPR spectra, overlapping of its components and makes it difficult and sometimes impossible to apply such a method to the study of condensed-phase systems. For example, spectra

taken at 3 cm and 8 mm wavebands do not always enable correct interpretation of the cause of relaxation changes in the spectrum (e.g., slow anisotropic movements of the radical as a whole or fast rotation of the N—O fragment within the cone) as well as determination of micropolarity in real polymers. Thus, the study of polymer and other condensed matrices by the spin probe and label method faces a considerable limitation at a low operation frequency.

The millimetric waveband EPR has proved to be a more efficient and precise technique to study model [3] and real biological polymer [4] systems of high viscosity using spin probes and labels. At this waveband the absolute sensitivity and spectral resolution increase considerably for polyoriented paramagnetic centres (PC). That is why it becomes possible to determine all components of the  $g$  and  $A$  tensors as well as to use them for a more correct investigation of structure and dynamic processes in modified high viscosity matrices.

Particular interest in semiconductive polymers has arisen because of their possible application in molecular electronics [5]. They are usually paramagnetic. In low magnetic fields, however, the EPR spectra of such compounds are featureless [6] and therefore unsuitable for the study of semiconductive polymers. The spin probe and label method is therefore likely to be more effective for this purpose. Only a few papers have been devoted to the study of conductive polymers using spin probes [7, 8] and labels [9]. However, the low spectral resolution at 3 cm waveband EPR did not allow the registration of all components of the  $g$  and  $A$  tensors and thus the separate determination of the magnetic susceptibility of both labels and PC localized on the polymer chain, as well as the measurement of the dipole—dipole broadening via interaction of PC of a different nature. Polypyrrole (PP) modified during electrochemical synthesis by nitroxide doping anions as probes [8] or labels covalently joined to the pyrrole cycle [9] has been studied. However, in spite of a large number of nitroxide radicals introduced into PP, its spectrum did not contain label or probe lines.

We have shown earlier [10, 11] that the study of some semiconductive polymers was more efficient when the 2 mm waveband EPR was used. This paper demonstrates the possibility of studying doped PP by the spin probe method at 3 cm and 2 mm waveband EPR.

## Experimental

Pyrrole electropolymerization in water solutions using salts of organic acids as electrolyte was earlier utilized [12]. If  $pK_a$  of the acid is above 3.4, thin nonconductive and electrically inactive films are formed. Nevertheless, nitroxide radicals can be oxidized into cations at 0.6 V [9]. We have therefore attempted either to electropolymerize pyrrole using the usual electrolyte with suitable nitroxide radicals (or its Na salt) or to obtain a composite with PP after immobilizing the radical in the polychlorovinyl film. The multicomponent spectrum of nitroxide radicals, however, was not registered in this case. So, we have used an aqueous radical solution as electrolyte to polymerize pyrrole

in the region of electrolyte discharge assuming that the possible degradation product of the radical does not exert sufficient influence on the EPR spectra of the synthesized PP.

The 2,2,6,6-tetramethyl-1-oxypiperid-4-ylacetic acid was used as a radical probe and counterion. The synthesis was carried out on a platinum electrode (approximately 10 cm<sup>2</sup>) in an aqueous solution of 0.2 M pyrrole and 2x10<sup>-2</sup> M radical using a PI-50-1 potentiostat either under constant potential conditions (1.3 V versus Ag/AgCl) or with a scanning potential at -0.1-1.3 V with a scan rate of 50 mV s<sup>-1</sup>. The PP was a thin black film with high adhesion to Pt. After synthesis the PP film was washed off by water, alcohol and acetone, and then dried.

The spectra of the nitroxide radicals introduced to the PP and its frozen solution in toluene (10<sup>-3</sup> M) were recorded using 3 cm (EPR-V) and 2 mm [13] waveband EPR spectrometers. In the latter case the PP sample of 5x10<sup>-2</sup> mm<sup>3</sup> volume was placed in the centre of a thin (0.6 mm diameter) quartz capillary filled with argon. The *g* factor and magnetic field scanning calibration was performed using the Mn<sup>2+</sup> standard with magnetic parameters of  $g_{\text{eff}} = 2.001\ 02$ ,  $a = 87.4$  G and the second-order correction to the effective resonant field that does not exceed 0.65 G at 2 mm waveband EPR [4].

## Results and discussion

The probe spectra in PP at room temperature and those in a frozen unpolar model system taken at 3 cm and 2 mm waveband EPR are shown in Fig. 1. One can see that in the PP spectrum with the probe at 3 cm waveband EPR the lines of nitroxide radicals with the rotating correlation time of  $\tau \geq 10^{-7}$  s overlap with the singlet of PC (*R*) localized on the PP chains. Such overlapping via low spectral resolution hinders separate determination of the magnetic parameters of the probe and *R* radical in PP as well as dipole—dipole broadening of its spectral components.

Indeed, the spectra of both model and modified polymer systems are expected to be more informative at 2 mm waveband EPR (Fig. 1(b)). In this case, all the canonic components of the EPR spectra of the probe in PP and toluene are completely resolved, and values of anisotropic *g* and *A* tensors can consequently be directly measured. Nevertheless, the asymmetrical spectrum of *R* radicals with magnetic parameters of  $g_{\parallel}^{\text{R}} = 2.003\ 80$ ,  $g_{\perp}^{\text{R}} = 2.002\ 35$  and the linewidth of 5.7 G were registered in the Z-component region of the probe spectrum. The difference  $\Delta g = g_{\parallel}^{\text{R}} - g_{\perp}^{\text{R}} = 1.45 \times 10^{-3}$  corresponds to an excited electron configuration in *R* with  $\Delta E = 2\lambda/\Delta g = 4.7$  eV ( $\lambda$  is the constant of the spin—orbital interaction of an unpaired electron with a carbon nucleus). The shape of the *R* spectrum indicates the localization of *R* radicals on the polymer chain and charge transport in PP by spinless carriers, possibly bipolarons [5] as it was proposed in the case of poly(*p*-phenylene)BF<sub>4</sub><sup>-</sup> [14].

In toluene the probe is characterized by the following magnetic parameters:  $g_{\text{xx}} = 2.009\ 87$ ,  $g_{\text{yy}} = 2.006\ 37$ ,  $g_{\text{zz}} = 2.002\ 33$ ;  $A_{\text{X}} = A_{\text{Y}} = 6$  G,  $A_{\text{Z}} = 33.1$  G. In

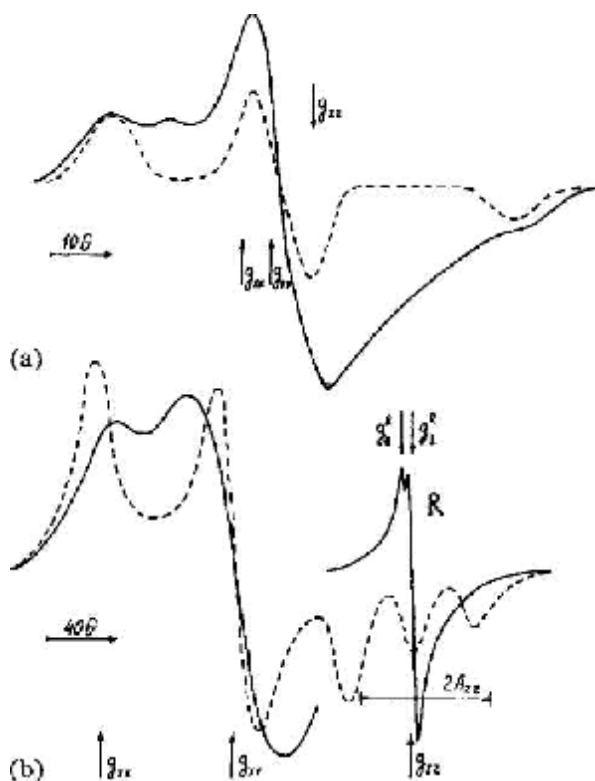


Fig. 1. Nitroxide probe EPR spectra in frozen (120 K) toluene (dotted lines) and probe-modified polypyrrole spectra at room temperature (solid lines) taken at 3 cm (a) and 2 mm (b) waveband EPR. The measured magnetic parameters are shown. The anisotropic spectrum of localized paramagnetic centres marked by the symbol  $R$  and taken at smaller amplification is also shown on the lower Figure.

PP the  $g_{xx}$  value of the probe decreases down to 2.009 06 and its  $X$ - and  $Y$ -components are broadened by 40 G (Fig. 1(b)). In addition, the shape of the probe spectrum in the latter case shows the absence of molecular motion in PP with correlation time  $\tau_c \leq 10^{-7}$  s at room temperature [3, 4] and the size of the pocket where the probe is localized does not exceed 1 nm.

The  $g_{xx}$  and  $A_z$  values, as was earlier shown [4], are more sensitive to changes in the radical microenvironment in biopolymers. As long as fragments with a considerable electric dipole momentum are a priori absent, the above change in the probe magnetic parameters may be caused by Coulomb interaction of the probe with the spinless charge carriers, bipolarons, formed at the PP film on doping. The effective electric dipole momentum of bipolarons nearest to the probe has been determined from the shift of  $g_{xx}$  value as described in ref. 4 and is equal to  $\mu_V = 2.3$  D. The electrostatic perturbation of both the Hückel molecular orbit and the Coulomb integral are the reason for changes in the main values of the  $A$  tensor [15]. Using the correlation

$\Delta g_{xx} = 3 \times 10^{-4} A_Z$  calculated for six-member nitroxide radicals in ref. 4, the expected shift of  $g_{xx}$  may be calculated within the frames of dipole—dipole interaction of the bipolaron with probe as

$$\Delta g_{xx} = 6 \times 10^{-3} e r_{NO} \beta^{-1} E_d \quad (1)$$

where  $e$  is the electron charge,  $r_{NO}$  is the distance between O and N nuclei of the probe,  $\beta$  is the overlapping resonant integral of the C=C bond and  $E_d$  is the potential of the electric field of the bipolaron in the probe location. The  $E_d$  value can be calculated from the following equation

$$E_d = k T \mu_U^{-1} [x \coth(x) - 1] \quad (2)$$

where  $x = 2 \mu_U \mu_V (4 \pi \epsilon \epsilon_0 k T r^3)^{-1}$ ,  $\mu_U$  and  $\mu_V$  are electrical dipolar momenta of the radical and its microenvironment, respectively,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\epsilon$  and  $\epsilon_0$  are the dielectric constants of PP and vacuum, respectively, and  $r$  is the distance between the bipolarons and O nucleus of the probe. Substituting eqn. (2) into eqn. (1), one may write the equation for the shift of the  $g_{xx}$  value as

$$\Delta g_{xx} = 6 \times 10^{-3} e r_{NO} \beta^{-1} k T \mu_U^{-1} [x \coth(x) - 1] \quad (3)$$

Using  $\mu_V = 2.3$  D,  $\mu_U = 2.7$  D [15],  $r_{NO} = 0.13$  nm [16], the value of  $r = 0.92$  nm is obtained.

The spin-spin relaxation rate which determines the radical linewidth may be written as  $T_2^{-1} = T_{2(D)}^{-1} + T_{2(D)}^{-1}$ , where  $T_{2(D)}^{-1}$  is the relaxation rate of a radical noninteracting with the environment and  $T_{2(D)}^{-1}$  is the growth in the relaxation rate via electrostatic dipole—dipole interaction. Thus, the characteristic time,  $\tau_c$ , of such a dipole—dipole interaction between the probe and the bipolarons may be calculated [17] from the spectrum broadening,  $\delta \Delta H_{X,Y}$ , as

$$T_{2(D)}^{-1} = \gamma_e \delta \Delta H_{X,Y} = \frac{3}{20} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma_e^4 \mathbf{h}^2 r^{-6} \left[ 3\tau_c + \frac{5\tau_c}{1 + \omega_e^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_e^2 \tau_c^2} \right] \quad (4)$$

where  $\mu_0$  is the magnetic susceptibility for vacuum,  $\gamma_e$  is the gyromagnetic ratio for an electron,  $\mathbf{h}$  is the Planck constant,  $\omega_e$  is the angular operating frequency and  $r$  is the distance between the dipoles. The inequality  $\omega_e \tau_c \gg 1$  is valid in the case of a condensed matrix with high viscosity. Thus, the latter equation may be simplified as

$$T_{2(D)}^{-1} = \gamma_e \delta \Delta H_{X,Y} = \frac{9}{20} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma_e^4 \mathbf{h}^2 r^{-6} \tau_c \quad (5)$$

Using  $\gamma_e \delta \Delta H_{X,Y} = 7.0 \times 10^8$  s<sup>-1</sup> and  $r = 0.92$  nm determined from eqn. (3), the value of  $\tau_c = 5.5 \times 10^{-10}$  s is obtained.

The average delay between the translative jumps of the charge carriers is determined by the diffusive coefficient  $D$  and by the average jump distance equal to part of the polymer chain occupied by the carrier,  $\langle d \rangle$ , as  $\tau_c = 6 \langle d^2 \rangle D^{-1}$  [17]. Using  $D \approx 10^{-8}$  m<sup>2</sup> s<sup>-1</sup>, typical value for a spinless charge carrier, the average carrier size  $\langle d \rangle = 2.35$  nm equal to six pyrrole cycles is also determined.

## Conclusions

The interaction between spinless charge carriers with an active fragment of the probe thus results in redistribution of the spin cloud between the N and O nuclei in the probe and therefore in a change of its magnetic parameters. This makes it possible to determine the distance between the radical and the conductive chain as well as a typical bipolaron length in doped PP and possibly in other semiconductive compounds. The shape of the probe spectrum displays a very slow molecular motion and a high density of the polymer matrix.

The high spectral resolution EPR technique combined with the spin probe method has been shown to be effective for a detailed investigation of organic semiconductive compounds; in particular, the distribution of charge carriers by local electric weighing, determination of electric momentum and intermolecular distances of a small part of an extensive polymer sample as well as a verification of theoretical models of charge transport in PP and other semiconductive polymers.

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