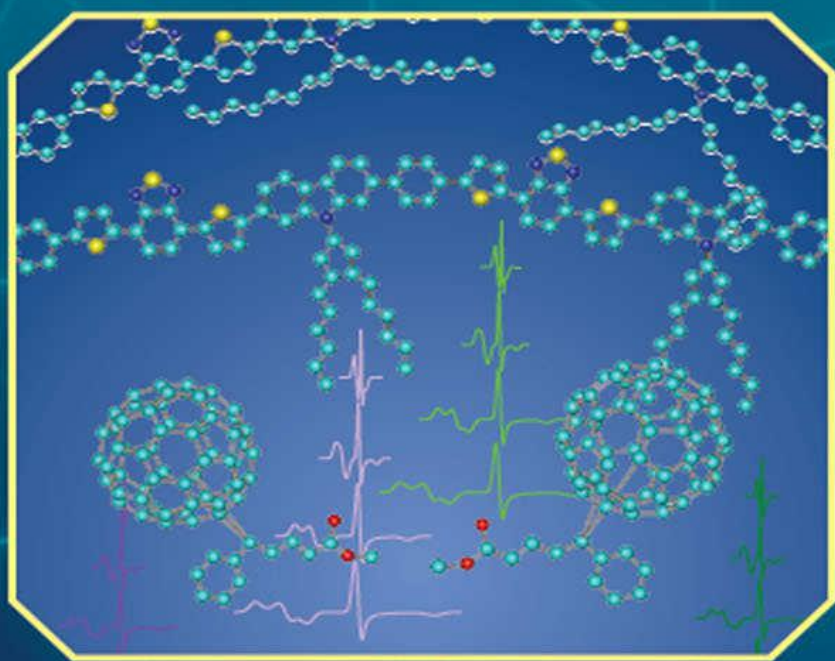


# Multi Frequency EPR Spectroscopy of Conjugated Polymers and Their Nanocomposites



**Victor I. Krinichnyi**



**CRC Press**  
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EPR Spectroscopy of  
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**Victor I. Krinichnyi**

Russian Academy of Sciences  
Moscow, Russia



**CRC Press**

Taylor & Francis Group

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*This book is dedicated to my wife, Tatiana Krinichnaia. Without her understanding and support, I would never have completed this project.*



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## List of Symbols

<b>A</b>	Tensor of hyperfine interaction
$A$	Anisotropic hyperfine interaction constant (mT)
$A$	Orientation degree of chains
$A_{fr}$	Friction force
$A_{ii}$	Principal values of the hyperfine interaction tensor (mT)
$A/B$	Asymmetry factor of spectrum
$a = \frac{1}{3} \sum_3 A_{ii}$	Averaged (isotropic) hyperfine interaction constant (mT)
$a$	Lattice constant (nm)
$A/B$	Asymmetry factor of EPR spectrum
$b$	Lattice constant (nm)
$\mathbf{B}_0$	External magnetic field vector
$B_0$	External magnetic field modulus (1 T = $10^4$ Oe, G)
$B_1$	Amplitude of magnetic term of microwave polarizing field
$B_{hf}$	Magnetic field due to spin hyperfine interaction
$B_m$	Amplitude of Zeeman magnetic modulation
$B_{loc}$	Local magnetic field strength
$c$	Light velocity ( $c = 2.99792458 \times 10^8$ m/s)
$c$	Lattice constant (nm)
$D$	Diffusion coefficient ( $\text{m}^2/\text{s}$ )
$D_{1D,3D}$	Intra- and interchain diffusion coefficients, respectively (rad/s)
$d$	Dimensionality of a disordered system (1–3)
$d_{1D,3D}$	Intra- and interchain lattice constants (nm)
$E$	Energy (1 eV = $1.60217733 \times 10^{-19}$ J = $8.06557982 \times 10^3$ cm $^{-1}$ = $2.41800 \times 10^{14}$ Hz)
$E_0$	Energy distribution width (eV)
$E_a$	Activation energy (eV)
$E_d$	Potential of induced electric field
$E_g$	Energy gap (eV)
$E_h$	Hopping energy (eV)
$E_p$	Formation energy of polaron (eV)
$E_{ph}$	Energy of lattice phonons (eV)
$E_r$	Inner- and outer-sphere reorganization energy (eV)
$E_t$	Trap depth (eV)
$e$	Elementary charge ( $e = 1.60217733 \times 10^{-19}$ Coul)
$G(\tau)$	Autocorrelation function
$g$	Splitting tensor
$g$	Landé splitting factor ( $g_e = 2.00231930436153$ for free electron)

$g_{ii}$	Principal values of the splitting tensor
$g_{\text{iso}}$	Isotropic (averaged) $g$ -factor equal to $1/3(g_{xx} + g_{yy} + g_{zz})$ or $1/3(2g_{\perp} + g_{\parallel})$
$g(\omega)$	Factor of line shape
$\mathbf{H}$	Hamiltonian of magnetic interaction
$h = 2\pi\hbar$	Planck quantum constant ( $h = 6.6260755 \times 10^{-34}$ J·s)
$I$	Nuclear spin
$I$	Inertia moment
$\mathbf{I}_i$	$i$ th term of nuclear spin operator
$I_i$	Intensity of $i$ th spectral component
$J$	Total electron angular momentum
$J_{\text{af}}$	Antiferromagnetic exchange coupling constant
$J_{\text{c}}$	Exchange coupling coefficient
$J_{\text{ex}}$	Spin exchange interaction constant
$J(\omega)$	Spectral density function
$k_{\text{B}}$	Boltzmann constant ( $k_{\text{B}} = 1.380658 \times 10^{-23}$ J/K)
$L$	Total electron orbital momentum
$L$	Spin/charge wave localization function
$l_i$	Mean free path of spin/charge
$M_0$	Equilibrium magnetization of spin ensemble
$\mathbf{M}$	Total magnetization of spin ensemble
$M_2$	Second moment of a spectrum
$M_{\text{d}}$	Disturbing force
$m$	Orientation magnetic number
$m_{\text{c}}$	Mass of charge carrier
$m_{\text{e}}$	Mass of electron ( $m_{\text{e}} = 9.10938356 \times 10^{-31}$ kg)
$m_{\text{s}}^*$	Effective mass of soliton
$m_{\text{u}}$	Number of monomers in a polymer chain
$N$	Spin concentration ( $\text{cm}^{-3}$ )
$N_{\text{A}}$	Avogadro's number ( $6.02214129 \times 10^{23}$ mol $^{-1}$ )
$N_{\text{s}}$	Soliton width in polyacetylene
$n$	Spin/charge concentration per monomer unit
$n(\varepsilon_{\text{F}})$	Density of states at the Fermi level $\varepsilon_{\text{F}}$
$p_{\text{cr}}$	Probability of spin cross-relaxation
$p_{\text{ff}}$	Spin flip-flop probability
$P(r, r_0, t)$	Translating spin motion propagator
$Q$	McConnell proportionality constant ( $Q = 2.3$ mT)
$R$	Spin/charge hopping distance
$\mathbf{r}$	Radius vector between dipoles
$r_i$	Separation between impurities
$r_{\text{NO}}$	Distance between N and O atoms in nitroxide radical
$r_{\text{ss}}$	Distance between spins (cm)
$\mathbf{S}$	Electron spin operator
$S$	Total electron spin of molecule

$S$	Single spin configuration
$s$	Saturation factor
$T$	Absolute temperature (K)
$T_{+,0,-}$	Triple spin configuration
$T_0$	Percolation constant of disordered system (K)
$T_1$	Electron longitudinal (spin-lattice) relaxation time
$T_{1p}$	Proton longitudinal (spin-lattice) relaxation time
$T_2$	Electron transverse (spin-spin) relaxation time
$T_c$	Characteristic temperature
$T_g$	Glass transition temperature (K)
$t$	Time (s)
$t_C$	Coulombic integral
$t_{cc}$	Resonant overlapping integral of C=C bond
$t_h$	Hopping integral (eV)
$t_r$	Intrachain transfer integral (eV)
$t_{  }$	Intrachain–interchain coupling integral (eV)
$t_{\perp}$	Interchain coupling integral (eV)
$\bar{U}(\omega t)$	Dispersion signal term
$g(\omega)\sin(\omega t - \varphi)$	In-phase ( $\varphi = 0$ ), out-of-phase ( $\varphi = -\pi$ ), and $\pi/2$ -out-of-phase ( $\varphi = \pm\pi/2$ ) (in phase quadrature) dispersion signal terms registered at $\varphi$ shift in phase detector with respect to applied modulation
$u_i$	Amplitude of $i$ th dispersion signal
$V$	Sample volume
$v$	Spin motion rate (cm/s)
$v_F$	Velocity of spin diffusion near the Fermi level (cm/s)
$W$	Spin/charge hopping energy (eV)
$x, y, z$	Axes of molecular coordinate system
$y$	Doping level
$\alpha$	Constant of electron–phonon interaction
$\alpha, \beta$	Spin levels
$\beta$	Medium <i>reactive</i> dispersion parameter
$\gamma$	Transition rate
$\gamma_e$	Gyromagnetic ratio for electron ( $\gamma_e = 1.760859708_{39} \times 10^{11} \text{ T}^{-1}\text{s}^{-1}$ )
$\gamma_p$	Gyromagnetic ratio for proton ( $\gamma_p = 2.675221900 \times 10^8 \text{ T}^{-1}\text{s}^{-1}$ )
$\Delta_0$	Half-bandgap
$\Delta B_{pp}$	Linewidth from peak to peak
$\Delta B_{pp}^L$	Lorentzian peak-to-peak linewidth
$\Delta B_{pp}^G$	Gaussian peak-to-peak linewidth
$\Delta E_{\alpha\beta}$	Difference in electron $\alpha$ and $\beta$ energy levels
$\Delta E_{ij}$	Energy barrier between $i$ and $j$ sites
$\Delta g$	Shift of $g$ -factor

$\Delta m_e$	Difference in orientation magnetic number for electron
$\Delta m_1$	Difference in orientation magnetic number for nuclear
$\Delta\omega$	Anisotropy of magnetic interaction
$\Delta\omega_{ij}$	Distance between spin packets (rad/s)
$\langle\Delta\omega^2\rangle$	Averaged constant of dipole spin interaction in a powder sample
$\delta$	Gamma function
$\delta$	Skin layer thickness
$\delta(\Delta B_{pp})$	Spectral line broadening
$\delta B$	Spectral diffusion distance
$\delta B(t)$	Time line shift
$\epsilon$	Dielectric constant
$\epsilon_0$	Dielectric constant for vacuum
$\epsilon$	Parameter of medium nonlinearity
$\epsilon_F$	Fermi energy level (eV)
$\xi$	Decay length for charge carries
$\eta$	Coefficient of dynamic viscosity
$\theta$	Angle between spin vectors
$\theta$	Torsion (dihedral) angle
$\vartheta$	Angle between main radical axis and external magnetic field
$\kappa$	Dimensionality constant
$\kappa$	Medium dissipation parameter
$\lambda$	Spin-orbit coupling constant (eV)
$\mu_{eff}$	Effective magneton
$\mu_B$	Bohr magneton ( $\mu_B = 9.27400968_{20} \times 10^{-24}$ J/T)
$\mu_0$	Permeability for vacuum ( $\mu_0 = 4\pi \times 10^{-7}$ V·s/A m)
$\mu$	Dipole moment of spin-modified molecule
$\mu$	Spin/charge mobility ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )
$\nu$	Charge diffusion rate
$\nu_e$	Resonance frequency of free electron ( $\nu_e = \omega_e/\pi$ )
$\nu_{ph}$	Photon frequency
$\nu_{ex}$	Frequency of spin-packets exchange
$\rho(r)$	Density of unpaired electron at distance $r$ from nucleus
$\Sigma_{ij}$	Lattice sum for powder
$\sigma$	Intrinsic conductivity
$\sigma_{ac}$	Alternating current electric conductivity (S/m)
$\sigma_{dc}$	Direct current electric conductivity (S/m)
$\tau$	Effective relaxation time
$\tau_0$	Spin separation in radical pair
$\tau_c$	Correlation time of radical rotation
$\tau_m$	Mechanical relaxation time
$\tau(R)$	Recombination time of spins separated by distance $R$
$\varphi$	Spin macroprobe orientation angle

$\chi$	Static magnetic susceptibility of spin ensemble
$\chi'$	Dispersion term of magnetic susceptibility
$\chi''$	Absorption term of magnetic susceptibility
$\chi_C$	Curie magnetic susceptibility
$\chi_P$	Pauli magnetic susceptibility
$\Psi(r)$	Wave function for electron localization ( $\Psi^2(r) = \rho(r)$ )
$\psi$	Angle between external magnetic field and polymer chain
$\omega_e$	Angular resonance frequency of electron transition between $\alpha$ and $\beta$ levels
$\omega_{ex}$	Exchange frequency between spin packets (rad/s)
$\omega_{hop}$	Angular frequency of spin diffusion
$\omega_0$	Hopping attempt frequency
$\omega_l$	Angular libration frequency (rad/s)
$\omega_m$	Angular frequency of Zeeman magnetic modulation (rad/s)
$\omega_p$	Angular precession frequency of proton (rad/s)



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## List of Abbreviations

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<i>ac</i>	Alternating current
AFNP	2-(Azahomo[60]fullereno)-5-nitropyrimidine
AMPSA	2-Acrylamido-2-methylpropane sulfonic acid
BDPA	1,3- <i>bis</i> -Diphenylene-2-phenyl allyl
BHJ	Bulk heterojunctions
BKdV	Burgers–Korteweg–de Vries (theory)
CB	Conjugated band
<i>cis</i> -PA	<i>cis</i> -Polyacetylene
CSA	Camphorsulfonic acid
CW	Continuous wave
DBSA	Dodecylbenzenesulphonic acid
DBTTF	Dibenzotetrathiafulvalene
<i>dc</i>	Direct current
DPPH	2,2-Diphenyl-1-picrylhydrazyl
ENDOR	Electron nuclear double resonance
EPR	Electron paramagnetic resonance
FIR	Far infrared band/irradiation with photon energy of 0.00124–0.0827 eV and wavelength of $1.5 \times 10^4$ – $1.0 \times 10^5$ nm
HFI	Hyperfine interaction
HFS	Hyperfine structure
HCA	Hydrochloric acid
HOMO	Highest occupied molecular orbital level
IR	Infrared band/irradiation with photon energy of 1.2–1.8 eV and wavelength of 700–1000 nm
LEPR	Light-induced electron paramagnetic resonance
LUMO	Lowest unoccupied molecular orbital level
MW	Microwave (frequency)
NIR	Near infrared band/irradiation with photon energy of 0.89–1.6 eV and wavelength of 770–1400 nm
NMR	Nuclear magnetic resonance
P3AT	Poly(3-alkylthiophene)
P3DDT	Poly(3-dodecylthiophene)
P3HT	Poly(3-hexylthiophene)
P3MT	Poly(3-methylthiophene)
P3OT	Poly(3-octylthiophene)
PA	Polyacetylene
PANI	Polyaniline
PANI-EB	Emeraldine base form of polyaniline
PANI-ES	Emeraldine salt form of polyaniline



PANI-LE	Leucoemeraldine form of polyaniline
PANI-PN	Pernigraniline form of polyaniline
PATAC	Poly( <i>bis</i> -alkylthioacetylene)
PC	Paramagnetic centers
PC <sub>x1</sub> BM	[6,6]-Phenyl-C <sub>x1</sub> -butanoic acid methyl ester
PCDTBT	poly[ <i>N</i> -9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]
PdT	Polydithiophene
PMA	Poly(ortho-methoxyaniline)
PMNA	Poly( <i>m</i> -nitroaniline)
PP	Polyphenylene
ppm	Percents per a million cell units
PPP	Poly( <i>p</i> -phenylene)
PPS	Poly( <i>p</i> -phenylene sulphide)
PT	Polythiophene
PTTF	Polytetrathiafulvalene
QxD	Quasi- <i>x</i> -dimensionality
RT	Room temperature
SA	Sulfuric acid
SSH	Su-Schrieffer-Heeger (theory)
ST-EPR	Saturation transfer electron paramagnetic resonance
TCNQ	Tetracyano- <i>p</i> -quinodimethane
THA	Tetrahydroanthracene
TSA	<i>para</i> -Toluenesulfonic acid
TTF	Tetrathiafulvalene
<i>trans</i> -(CD) <sub>x</sub>	<i>trans</i> -Polyacetylene deuterated
<i>trans</i> -PA	<i>trans</i> -Polyacetylene
UV	Ultraviolet band/irradiation with photon energy of 3–120 eV and wavelength of 10–400 nm
VB	Valence band
Vis	Visible band/irradiation with photon energy of 1.8–3.2 eV and wavelength of 390–700 nm
VRH	Variable range hopping
X-, K-, W-, D-bands	30 mm, 8 mm, 3 mm, and 2 mm wavebands EPR when a spin $S = \frac{1}{2}$ with $g_{\text{iso}} = 2$ and precession frequency $\omega_e/2\pi = 9.7, 24, 85$ and 140 GHz is registered at resonant magnetic field $B_0 = 0.34, 0.86, 3.3,$ and 4.9 T, respectively
X-ray	Röntgen radiation with photon energy of 0.1–100 keV and wavelength of 0.01–10 nm

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## *Preface*

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The past two decades have seen extraordinary progress in the synthesis and study of organic conjugated polymers and their nanocomposites. This was mainly due to the widespread utilization of such systems in molecular electronics and spintronics. One of the main scientific goals is to reinforce the human brain with computer ability. However, a convenient modern computer technology is based on three-dimensional silicon crystals, whereas the human organism consists of lower-dimensional biological systems. Therefore, the combination of a future computer based on organic conducting polymers of low dimensions with biopolymers is expected to considerably increase the power of human apprehension. This is why understanding the major factors determining specific spin charge-transfer processes in conjugated polymers is now a hot topic in organic molecular science.

The charge in such systems is transferred by topological excitations, solitons, and polarons characterized by spin and high mobility along polymer chains. This stipulated the use of electron paramagnetic resonance (EPR) spectroscopy as a unique direct tool for more efficient study and monitoring of reorganization, relaxation, and dynamic processes carried out in polymer systems. Twenty years have passed since the publication of the first book [122] in which the basic methodological approaches of millimeter waveband EPR spectroscopy in the study of various model, biological, and polymer systems were described. It was demonstrated that the study of such objects at higher registration frequencies allows increasing sufficiently the efficiency of the method to obtain qualitative new information on organic solids and to solve various scientific problems. During this time, the variety of EPR techniques was expanded. For example, the Bruker Corporation developed and started supplying scientific centers with EPR spectrometers operating at wide (1–263 GHz) wavebands. Besides, home-made millimeter waveband EPR spectrometers were constructed and widely used in different scientific centers.

This book's focus is on the use of the technique in conjunction with spin label and probe, steady-state saturation, saturation transfer, and conductometric methods in the study of initial and nanomodified conjugated polymers. Chapter 1 of this book discusses the fundamental properties of conjugated polymers in which a charge is transferred by topological distortions, solitons, polarons, and bipolarons. The theoretical background of magnetic resonance, relaxation, and dynamic parameters of such charge carriers in conjugated polymers is briefly explicated in Chapter 2. It could be a valuable introduction to students interested in EPR, particularly of conjugated

polymers. The instrumentation and experimental details are described briefly in Chapter 3. Chapter 4 is devoted to the original data obtained by an X-band to D-band (30–2 mm, 9.7–140 GHz) EPR study of the nature, relaxation, and dynamics of paramagnetic centers delocalized on nonlinear charge carriers as well as the mechanisms of charge transfer in some conjugated polymers differently modified with nanoadducts. The use of some conjugated polymers as electron donors in organic composites is described in Chapter 5. Chapter 6 reveals the possibility to handle charge transport in some multispin polymer composites by using spin–spin exchange. Chapter 7 presents concluding remarks, including the prospects of the study of organic polymer systems for the further construction of novel elements of molecular electronics. Therefore, this book documents both background knowledge and the results of latest research in the field. Unique features include comparisons of data obtained at different microwave frequencies and magnetic fields. Coherent treatment of the subject by the leading Chernogolovka high-field EPR laboratory covers the theoretical background as well as state-of-the-art research both in terms of instrumentation and application to conjugated polymer systems.

The author hopes that the multifrequency EPR spectroscopy and related approaches will be of interest to students and scientists and will encourage them to apply EPR methods more widely to polymeric materials. This book covers a wide range of specific approaches suitable for analyzing processes carried out in polymer systems with paramagnetic adducts providing readers with knowledge of the underlying theory, fundamentals, and applications. These, no doubt, help bridge the gap between the chemistry and physics communities and stimulate research in this fascinating and important field. The goal of this book is not to make the reader an expert in the field, but rather to provide enough information about the EPR spectroscopic method for the reader to determine how the available approaches can be used to solve a particular polymer problem. This book reviews in detail the main experimental methodological approaches developed by our team for the study of various organic condensed systems. It provides an outlook for future developments and references for further reading. This information is essential for postdoctoral scientists, professionals, academics, and graduate students working in this field as well as analytical chemists and chemical engineers designing and studying novel molecular electronic objects. Besides, the author would feel well rewarded if this book helps resolve some of the problems of finding useful information on properties of conjugated polymers and their composites in the ever-growing scientific literature.

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## *Acknowledgments*

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The author is very grateful to Professors Yakov S. Lebedev and Gertz I. Likhtenshtein, who introduced him to the field of EPR, and also to Professor Dr. Hans-Klaus Roth for introducing him to the field of conducting polymers and for the many discussions. Their early influence and mentoring are deeply appreciated. He sincerely thanks all his coworkers and graduate students for their excellent contributions to this book. He expresses sincere gratitude to the outstanding designer Grigory T. Rudenko, a veteran of World War II, for his inestimable contribution to the implementation of the present work. A constructive collaboration with Professor Oleg Y. Grinberg and Drs. Evgenija I. Yudanova and Nikolai N. Denisov is gratefully acknowledged. The author especially expresses sincere gratitude to his father and mother for their rare kindness and to his family for their love, as well as to relatives and friends for their help and support.



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## *Author*

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**Victor I. Krinichnyi** received his higher education at Kazan State University, Kazan, Russia, the birthplace of electron paramagnetic resonance (EPR), after completion of a diploma in 1975 in “Microwave study of mechanism of molecular dynamics in liquids” at the Institute of Chemical Physics at the Russian Academy of Science (RAS) under the supervision of Professor L.A. Blumenfeld. Since then he was employed as an engineer, a principal engineer, and a young scientific researcher at the Institute of Chemical Physics in Chernogolovka, RAS. During this period, Dr. Krinichnyi, in Prof. Y.S. Lebedev’s laboratory (the Institute of Chemical Physics RAS) participated in the pioneering joint collaboration and creation of the first multifunctional X-band (140 GHz, 5 T) EPR spectrometer with superconducting magnet. The first exemplificative D-band EPR studies of different organic and biological systems showed great efficiency of this method and allowed to obtain qualitative new information on these objects and solve various practical problems in physics, chemistry, molecular biology, and interdisciplinary sciences. The basic methodological approaches developed at this waveband EPR were then implemented in the first commercial 3 mm waveband Bruker ELEXSYS E680 spectrometer.

Dr. Krinichnyi’s PhD (physics and mathematics) work, “2-mm Waveband EPR spectroscopy as a method of the study of paramagnetic centers in biological and organic polymers,” was carried out under partial supervision of Professor Y.S. Lebedev and was successfully defended in 1986 at the Institute of Chemical Physics in Chernogolovka RAS. He was employed as a scientific researcher and a senior scientific researcher at the institute (formerly the Institute of Problems of Chemical Physics RAS). His SciD (physics and mathematics) thesis (habilitation) titled “High-resolution 2-mm wave band EPR spectroscopy in the study of biological and conducting polymers” was also successfully defended in 1992 at the same institute, where he works today as a leading scientific researcher and heads the High-Frequency EPR Group.

Research interests of Dr. Krinichnyi resulting from the practical application of multifrequency EPR spectroscopy are concerned with relaxation and dynamics of nonlinear charge carriers, solitons, and polarons in conjugated polymers and their nanocomposites, mechanism of charge transport in molecular crystals, spin phenomena in condensed systems, and organic molecular electronics, photonics, and spintronics. Since 1992, he is member of the International EPR (ESR) Society. Thirteen Russian and International scientific projects were carried out under his direct guidance as principal

investigator. The original theoretical and experimental results obtained through these projects were reported at international summits, invited lectures at different European scientific centers, and described in more than a hundred scientific publications, including a monograph, 5 invited contributions in edited books, and 11 reviews.



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The past two decades have seen extraordinary progress in synthesis and study of organic conjugated polymers and their nanocomposites. Utilization of such systems in molecular electronics and spintronics to empower the human brain with computer capabilities is eagerly anticipated. Modern computer technology is based on three-dimensional silicon crystals, whereas human organisms consist of lower-dimensional biological systems, so the combination of a future computer based on organic conducting polymers of low dimensionality with biopolymers is expected to considerably increase the power of human comprehension. Thus understanding the major factors determining specific spin charge transfer processes in conjugated polymers is now a hot topic in organic molecular science.

Multi Frequency EPR Spectroscopy of Conjugated Polymers and Their Nanocomposites reviews the main experimental methodological approaches in detail for the study of various organic condensed systems and provides an outlook on future developments and references for further reading. Covering a wide range of specific approaches the author provides readers with knowledge of the underlying theory, fundamentals, and applications and bridges the gap between the chemistry and physics communities.

The goal of the book is not to make the reader an expert in the field, but rather to provide enough information about the EPR spectroscopic method that the reader can determine how the available approaches can be used to solve a particular polymer problem. The book is essential reading for postdoctoral scientists, professionals, academics and graduate students working in this field as well as analytical chemists and chemical engineers designing and studying novel molecular electronic objects.