

Polymer–Magnet Nanosystems



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Abstract Macroscopic magnetism in organic materials is a very complex but promising scientific problem. The need to create an organic magnet is due to several expected advantages, such as lightness, transparency, flexibility, ability to switch under the influence of light (magneto-optics), sensitivity to external factors (sensors), absorption of radiation, etc. Studying the state of a spin glass, biomagnetism, and the mechanism of paramagnetic probe action in living tissues can help to understand the mechanism of human thinking and DNA functioning. This chapter is devoted to molecular magnetism in organic polymer–magnet nanosystems. The ways of synthesis and magnetic properties of materials based on conjugated polymers and their complexes with transition metals are considered. Particular attention is paid to the hybrid polymer–magnetic nanosystems formation and application. The study of magnetic properties of polymer–magnet nanosystems is helpful for understanding the nature of “organic magnetism” and identifying new approaches to the fabrication of functional hybrid nanomaterials.

1 Introduction

A new field of scientific research related to obtaining organic and molecular magnets is developing rapidly [1–20]. Physico-chemistry of molecular and organic magnetism is described in only a few reviews [1–5] but many pioneering works [6–14].

One of the main tasks of modern physical and chemical research is the development of scientific foundations and new approaches to the creation of polymer and composite materials with specified functional properties—electrical, optical, and magnetic, the ability to accumulate and transform charge, catalyze some reactions, sensors, etc. [6–14]. Research and development of highly dispersed composite materials based on polymers doped or filled with organic and inorganic components, in particular compounds of transition metals, is an urgent problem of science and

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technology. Due to the nanostructure of composites (the particle size ranges from a few units to tens of nm), they have unique magnetic, spectral, and electrochemical properties.

Providing macroscopic magnetism in organic materials is an arduous but promising scientific task. The need to create an organic magnet is due to several expected advantages, such as lightness, transparency, flexibility, the ability to switch under the influence of light (magneto-optics) or compounds (sensors), the creation of modern toners for digital printing, materials for chemical current sources, etc. [9–13]. Investigation of the spin glass state, biomagnetism, and the paramagnetic probe action in living tissues will help in understanding the mechanism of biological processes, in particular, human thinking and the functioning of DNA [14–19].

One of the ways to solve the problem of creating organic magnets is obtaining crystals of organometallic complexes—molecular magnets [1–3, 15], doping organic matrices with transition metal ions—polymeric organometallic magnets [7, 16–19], synthesis of high-spin macromolecules based on organic compounds [4, 8, 20], filling polymer matrices with colloidal metals and oxides of transition metals—magnetic dispersions [6, 11–14]. Studying the magnetic properties of new organometallic materials can help to understand the nature of “organic magnetism” and develop new approaches to organic magnet creation.

Forms of magnetism, namely diamagnetism, paramagnetism, ferro-, antiferro- and ferrimagnetism, and spin glasses, are ultimately related to the electron magnetic moment. The difference between the forms is the types of interaction of moments. Thus, molecular magnets based on materials in which unpaired electrons are associated with discrete molecules would provide possibilities for controlling the interaction of elementary moments. As well as achievements in the molecular synthesis make it possible to place a molecule in a defined position.

All known ferromagnets are built of metal atoms with unfilled *d*- or *f*-electron orbital, i.e., based on the spin magnetism of internal *d*- and *f*-electrons. The magnetic interaction is positive and arranges the electron spins of nearby atoms in parallel—ferromagnetically. In contrast, the interatomic/intermolecular interaction is negative for atoms with *s*- or *p*- electrons, and their spins orient antiparallel—antiferromagnetically.

Diamagnetic materials contain only spin-paired electrons, and the density of field lines decreases in a magnetic field. Paramagnetism is due to the unpaired electrons, and the magnetic field strength increases in material that kind. The magnetic susceptibility in the last case is described by the Curie law or the Curie–Weiss law:

$$\chi = C/(T - \Theta)$$

where *C*—Curie constant (temperature), Θ —Neel temperature.

Depending on the sign and value of the parameter Θ , the following types of magnetic interaction are distinguished:

$\Theta > 0$ is a ferromagnet; $\Theta < 0$ —antiferromagnet; $\Theta = 0$ —paramagnet.

Living systems mainly consist of diamagnets, and as a result, the magnetic susceptibility of the biomass of organic substances turns out to be negative. However, the degree of diamagnetism in different cells, organs, and tissues has not been comparatively studied. The known studies determine the value of the cells' magnetic susceptibility by the ratio of dia- and paramagnetic compounds, special magnetosomes, the electromagnetic field generated by the cell, the nature and intensity of energy exchange. It was noted that it is different in living and dead objects, reflects the degree of cell viability, and is a kind of barometer of dissociative shifts in bacteria when the geomagnetic field changes. Therefore, magnetic susceptibility is related to many vital functions of organisms. Perhaps, it even provides their ability to navigate in space and migrate along the lines of force of the geomagnetic field.

There are few natural magnetic materials, mainly transition metals and their oxides. The increase in the number of magnetic materials is achieved mainly due to the production of alloys, double oxides, and intermetallic compounds. Research in the design of molecular ferromagnets and polymer nanocomposites significantly expands the range of magnetically active compounds and magnetic materials. In addition, using conventional synthetic approaches, it is possible to create new magnetic materials by methods alternative to the known energy-intensive metallurgical technologies.

2 Basic Approaches to Creating “Organic Magnets”

An organic ferromagnet is a magnetic material built from organic paramagnetic molecules [3–5, 20]. This is a partial case of a molecular ferromagnet consisting of paramagnetic molecules that can contain metal atoms (e.g., organometallic molecules). The ferromagnetic properties of known metallic magnets are determined by the orderly arrangement of d- and f-electron spins in a definite “domain”. In contrast, research in molecular magnetism is related to obtaining substances whose solid phases are formed from individual molecules or ions that contain paramagnetic centers.

A classical ferromagnet is a macro-object, for example, a piece of iron, nickel, cobalt, or their alloys, but in no case is an individual molecule. By its nature, the magnetic phase transition to the ferromagnetic state is a cooperative phenomenon.

The basis of cooperative physicochemical phenomena characteristic of substances, such as electrical conductivity, magnetic susceptibility, and optical activity, is the interaction between electric and magnetic charges that make up the structure of substances. Quasiparticles of the soliton or polaron type (radical ions) with charge $q = 1$ and spin $s = \frac{1}{2}$ can be elementary charged particles in the case of conjugated polyarenes and their composites with organic and inorganic compounds [21–23]. The interaction of charges in a substance determines the electrical conductivity, magnetization, the ability to convert electric and light energy, absorption, and emission of light in the visible part of the spectrum, which ensures the connection between the electrical, magnetic, and optical properties of materials.

The word “molecular” reflects the methodology of the approach—individual molecules or ions form a spatial structure that contributes to the realization of a magnetic phase transition when a solid phase is formed. The problem can be solved by various chemical methods united by the term “chemical design of molecular ferromagnets”. The layered or framework structure formation in the solid phase is necessary for the magnetic phase transition into a ferromagnetic state. However, this condition is not sufficient. Paramagnetic centers in polymers must be connected by a definite chain of atoms, serving as an “exchange channel” so that the polymer can “magnetize” in a magnetic field [3–5].

The problem of the synthesis of a molecular ferromagnet can be solved by organizing paramagnetic molecules with a high density of oriented spins into a definite supramolecular structure, providing the necessary energy of intermolecular interaction and thus ferromagnetic ordering of spins [4, 24].

The class of organometallic polymers is based on multi-spin organometallic macromolecules in which spins belong to paramagnetic ions. There are poly-complexes of inorganic ions with organic ligands synthesized by inorganic chemistry methods. Methods of synthesis of ferromagnets based on organometallic polymers with paramagnetic metal atoms, covalently bound in the main polymer chain, are also being developed. It is necessary to ensure exchange interaction between metal atoms for turning such polymers into ferromagnets. In terms of dynamic properties, these high-temperature ferromagnets are rigid—magnetic susceptibility is close to unity, and the magnetic loss tangent is extremely small in the wave range of 0.8–30 cm. This direction in the chemical design of ferromagnets overlaps with the modern materials science of metal-filled polymer composites.

An attempt to obtain a purely organic magnet using high-spin molecules of electrically conductive polymers as a “building material” was made by us in cooperation with scientists from the Institute of Physics of the Polish Academy of Sciences [25–27]. The idea was to use supramolecular compounds as alloying agents to create “exchange channels” in polymer formations. The paramagnetic–antiferromagnetic phase transition is possible upon the formation of so-called polymer blends—molecular mixtures of conjugated high-spin molecules—and a dielectric polymer matrix [20, 28, 29]. In this case, for the first time, we established several interesting electrical and magnetic phenomena, the interpretation of which is quite complicated.

3 Organic Magnets Based on Polymer Nanosystems

The nature of magnetism in polymers, as in other substances, is determined by the total contribution of diamagnetic and paramagnetic components. The paramagnetic susceptibility of polymers is caused by the unpaired spins due to the breaking of chemical bonds, stable free radicals, macroradicals, ions with uncompensated spins, and temperature-independent spin paramagnetism of conduction electrons (Pauli paramagnetism).

Conducting polymers can be considered as “synthetic nanometals” with a particle diameter of 10–20 nm and unique electronic, optical, electrochemical, and catalytic properties, the ability to absorb radioactive rays [30]. Delocalization of p -electrons is due to conjugated double bonds in the polymer backbone. The conductivity of conjugated polymers can be very high in doped states (p -doping or n -doping). Charge transfer proceeds according to a hopping mechanism along the polymer chain with π -conjugated bonds [21–23].

The widely used conjugated polymer—polyaniline (PAn), and its copolymers with organic sulfonic amino acids were studied as a model object with a stable paramagnetic response.

Polymer films were obtained on the plane Pt electrode by electrochemical polymerization of 0.1 M aniline solution in 0.5 M sulfuric acid at current density $i = 0.1$ – 1.0 mA/cm². The structure of the film was investigated using transmission electron microscopy (UEMB-100K), scanning electron microscopy (ISI-DS-130), electronography (EG-100K), and X-ray diffraction analysis (DRON-2, FeK α -radiation). A statistical method of correlative functions, namely radial distribution of atomic density, was used to describe a polymer design in a thin layer [31]. The radial distribution of intensity (I) as a function of scattering vector $S = 4\pi \sin\theta/\lambda$ was obtained according to electronography at low angles of scattering and photometry of the electronograph.

It is found that polymer film thinner than 80 nm is amorphous with a close order in the disposition of structure elements (Fig. 1). Wide diffusion maximums at $S = 1.8 \text{ \AA}^{-1}$, 2.9 \AA^{-1} , and additional low angle maximum at $S = 1.35 \text{ \AA}^{-1}$ are observed at the scattering intensity distribution for thin polymer films (Fig. 1b).

Thin films up to 60–80 nm in thickness are formed from ordering islands (domains) with a diameter of 100–1000 nm (Fig. 1a). The domain is an ensemble of spherical globules (grains) with a diameter of 10–30 nm.

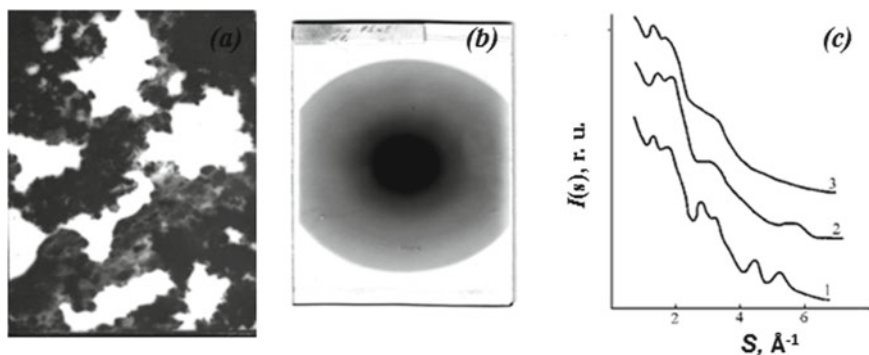


Fig. 1 a TEM image of PAn layer on Pt surface ($\times 10,000$), film thickness 60 nm; b electron diffraction pattern and c distribution of scattering intensity for PAn films obtained at current density: 0.5 (I); 0.7 (2); 1.0 mA/cm² (3), film thickness 60–80 nm

Based on the radial distribution of intensity as a function of scattering vector $S = 4\pi \sin\theta/\lambda$, parameters of polyaniline short-range ordered structure preserved the coplanar orientation of aromatic fragments have been calculated (Table 1).

Due to X-ray diffraction spectra (Fig. 2a), crystallinity level of PAn increases from 25% to 41–44% because of acid doping. Size of crystallites increases in the range of 15–30 Å. The degree of crystallinity decreases for the iodine-doped polymers (Table 2). The estimated parameters of short-ordered structure and the localization radius of electronic states in metallic grains are grain sized and the scaled of repetitive polymer units.

Table 1 Parameters of short-range ordered structure for polyaniline

Period of identity, d , Å	Length of conjugation, Å	Number of monomer links
4.6	25–30	5–6

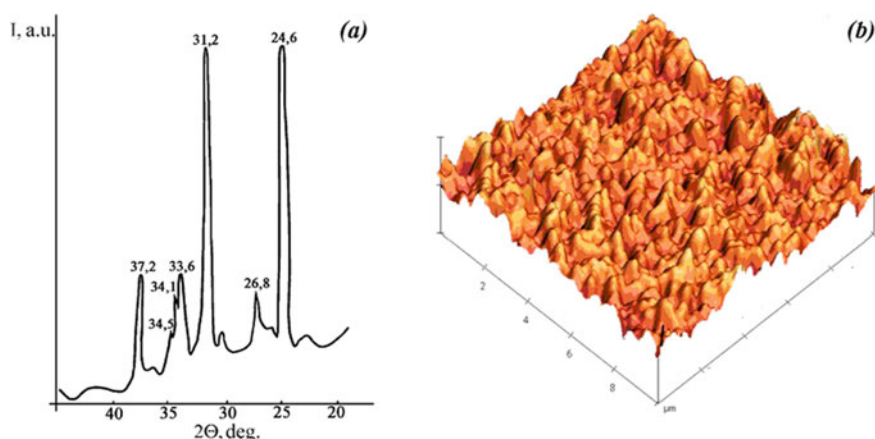


Fig. 2 **a** X-ray diffraction spectrum of polyaniline doped with sulfate acid; **b** AFM image of polyaniline film. Size of grains 10–30 nm

Table 2 Effect of doping on the parameters of X-ray diffraction, size of crystallites and degree of the crystallinity of polyaniline

Polymer	Doping agent	Interplane distance, d , Å	Crystallite dimension, $l \pm 10\%$, Å	Level of crystallinity, $I \pm 2\%$
Polyaniline	–	4.47; 4.23; 3.58	15–20	25
	H ₂ SO ₄	4.55; 4.37; 3.49	25–30	41
	HCl	4.66; 4.31; 3.57	20–30	43
	I ₂	4.46; 4.27; 3.54	15–25	18

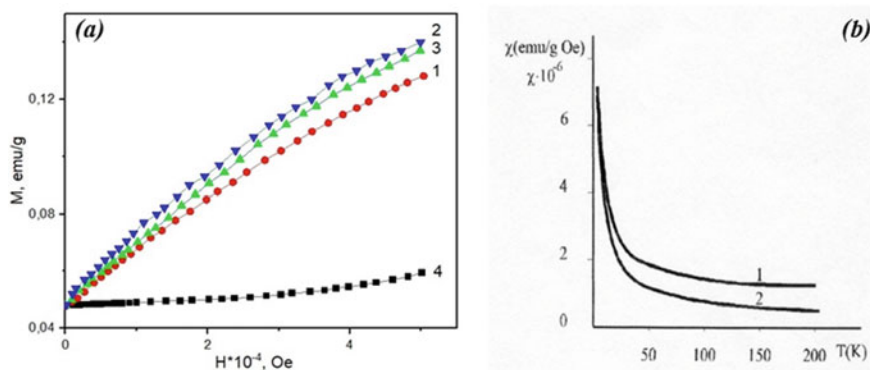


Fig. 3 **a** Field dependence of magnetization at $T = 5$ K for PAn (1), PAn-I₂ (2), PAn-H₂SO₄ (3), and PAn at $T = 300$ K (4); **b** Temperature dependence of magnetic susceptibility of PAn doped with I₂ in the field of 0.1 T (1) and 5 T (2)

The magnetization of undoped PAn and doped with sulfuric acid (50 mol %) or iodine (2.6 mol %) was studied in the temperature range 5–300 K. It was found that the diamagnetic contribution predominates at room temperature, while the paramagnetic—at lower temperatures. The “degree” of paramagnetism depends on the type of doping agent (Fig. 3).

It was found that the magnetic susceptibility of polymers in weak fields can be described by an equation that includes a temperature-independent component (χ_o) and a temperature-dependent component according to the Curie–Weiss law

$$\chi = \chi_o + C(T - \Theta)$$

Due to this dependence and the minimum of the root-mean-square deviation of the experimental susceptibility data at $H = 5$ T, the values of the paramagnetic Weiss constant (Θ), the Curie constant (C), and the parameter χ_o were obtained (Table 3). The concentration of unpaired spins N_s was calculated from the found values of C [25].

It was established that the magnetic susceptibility is almost independent of the temperature at $T > 200$ K [25, 29]. Pauli paramagnetism ($\chi_o > 0$) was found for PAn doped with iodine. For acid-doped PAn $\chi_o > \chi_{\text{diam}}$ indicates the presence of a paramagnetic contribution. Thus, there is a superposition of diamagnetic and paramagnetic

Table 3 Parameters of magnetic susceptibility of polyaniline $\chi = \chi_o + C(T - \Theta)$

Polymer	$C \times 10^5, \text{ K/gE}$	$\chi_o \times 10^7, \text{ 1/gOe}$	$\Theta, \text{ K}$	$N_s \times 10^{-19}, \text{ 1/g}$
PAn base undoped	2.9	– 3.5	– 0.89	4.7
PAn-H ₂ SO ₄	3.4	– 0.7	– 0.94	5.5
PAn-I ₂	3.9	+ 1.3	– 1.19	6.2

Table 4 Results of X-ray studies of composites Fe₃O₄-polymer

Sample	Magnetite content, mass %	Lattice parameter, <i>a</i> , Å	Average grain size, Å	Average maximum stress, %
Fe ₃ O ₄	100	8.3479 (17)	75.5 (± 7.3)	13.1 (± 8.3)
Fe ₃ O ₄ -polymer	10	8.345 (2)	102.0 (± 9.5)	10.0 (± 6.7)
	12.4	8.3491 (12)	111.1 (± 1.8)	8.8 (± 2.8)
	13.3	8.351 (3)	98.7 (± 2.8)	9.9 (± 3.1)

components in the magnetization of PAN. In strong magnetic fields, the diamagnetic contribution (M_{diam}) is well approximated by the dependence:

$$M_{\text{diam}} = M_0 + \chi_{\text{diam}} \cdot H$$

where χ_{diam} —the diamagnetic susceptibility of the polymer matrix, H —the magnetic field strength, M_0 —a constant associated with hardware corrections. The values found at $T = 300$ K are shown in Table 3. To estimate the real diamagnetic contribution with correction for paramagnetism, the obtained values of χ_{diam} must be supplemented with the paramagnetic contribution C/T at $T = 300$ K, where C —the Curie constant.

The polymer matrix diamagnetism does not depend on temperature, so all the obtained dependences were corrected. Polyaniline doped by iodine demonstrates a paramagnetism without magnetic metal ions (Table 3). The study of injection of the doping magnetic ions on the magnetic behavior of the conjugated polymers caused growing interest.

4 Magnetic Properties of Polymers Doped with Magnetic Ions. Temperature Dynamics of EPR Magnetic Centers in Polymer-Magnetic Nanosystems

The influence of doping on the magnetic properties of polyaniline (PAN) and poly-paraphenylene (PPP) was studied. As noted earlier, the undoped matrix of polyaniline and PAN doped with sulfuric acid have mainly diamagnetic properties [25]. Doping with HCl or iodine causes paramagnetic behavior, which can be described by the Curie-Weiss law at $T < 120$ K. All investigated samples of PAN, its derivatives, and copolymers give a time-stable EPR signal already at room temperature with a g -factor of 2.0003–2.0027 [26, 29]. However, the effect of doping with magnetic ions on the polymer paramagnetic properties is unstudied, and the influence of the polymer matrix on the magnetic center's closest surroundings on the magnetic behavior of

polymer composites too. To solve this problem, we studied the temperature dependence of EPR for polyaniline composite matrices doped with the complex compound $K_3[Fe(CN)_6]$.

The samples were synthesized by oxidative polymerization followed by treatment with an ammonia solution to remove inorganic impurities and obtain a polymer in the form of an emeraldine base. The dedoped sample was kept for 24 h in a 0.02 M potassium hexacyanoferrate in 0.05 M sulfuric acid to obtain the hybrid material based on PAN by the ion exchange method. After washing and drying, the samples were stored in quartz ampoules. The content of doping impurities, determined by X-ray microanalysis, was 0.3% $K_3[Fe(CN)_6]$.

The spectrum of the obtained doped polymer is a superposition of the EPR spectrum of free radicals of the PAN polymer matrix and Fe(III) ions. The EPR spectrum of pure PAN in the temperature range $T = 4.2\text{--}295$ K has one resonance line with $g = 2.000 \pm 0.001$, the width of which (ΔH_{pp}) decreases with increasing temperature [26].

The value of the g -factor does not depend on the temperature. The resonance line observed in undoped PAN is caused by the radicals stabilized by the π -conjugation system [22, 32].

The EPR spectrum of the sample doped with $K_3[Fe(CN)_6]$ consists of 3 resonance lines (Fig. 4a). The first and second lines, probably due to Fe(III) ions, appear after doping. The third resonance line, according to the value of the g -factor and the nature of the temperature behavior, refers to the free radicals of the PAN.

The value of the g -factor of line 1 at 4.2 K is equal to $g_1 = 4.22 \pm 0.03$ and is almost independent of temperature. For line 2 $g_2 = 2.13 \pm 0.05$ at $T = 295$ K. While the temperature decreases, the intensity of line 1 decreases until it completely disappears at $T = 290$ K (Fig. 4). At the same time, the width of the line increases by no more than 30% (Fig. 4b). In contrast, width decreases with increasing temperature for undoped PAN (Fig. 4c).

The revealed features of EPR spectra should appear in other disordered polymer systems doped with magnetic ions. Therefore, polyparaphenylene (PPP) matrices obtained by chemical synthesis and characterized by structural and spectral methods [33] were studied.

A dispersed fine-crystalline sample was kept for 24 h in a solution of anhydrous ferric chloride in nitromethane to introduce magnetic ions into the PPP matrix, washed with a solvent, and dried. According to the spectral analysis, the Fe content in this material was 2.3% by mass.

One (300 K) or two (4.2–100 K) resonance lines can be observed in the EPR spectrum of PPP doped with ferric chloride, depending on the temperature. Low-intensity line with $g_1 = 4.21 \pm 0.05$ and a high-intensity line with $g \approx 2$ appears at low temperatures. The second one is a superposition of two lines, one of which refers to the impurity ion Fe^{3+} (Fig. 5). The EPR line for undoped PPP at $T = 4.2$ K has the value $g = 2.12 \pm 0.03$ and the width $\Delta H_{pp} = 0.38$ kE, while for resonance line 2 the width $\Delta H_{pp} = 0, 65$ kE and the g -factor $g_2 = 2.00 \pm 0.09$. The contribution of the PPP to the total intensity of line 2 is 4% due to the computer simulation method.

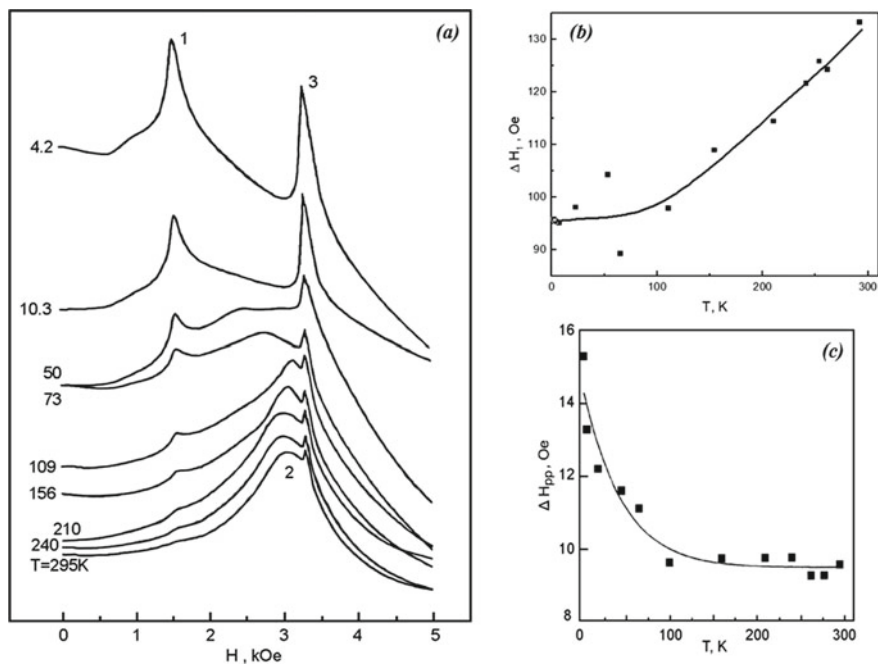
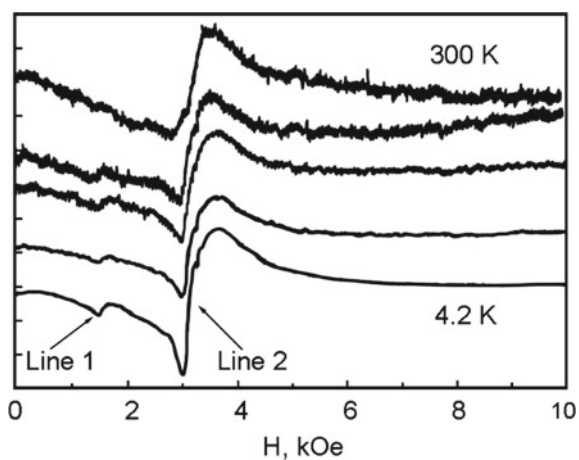


Fig. 4 **a** Temperature-induced changes in the resulting absorption line in the EPR spectrum of polyaniline doped with $K_3[Fe(CN)_6]$; **b** temperature dependence of the width of the first resonance line ΔH_1 ; **c** temperature dependence of the resonance linewidth ΔH_{pp} for pure polyaniline

Fig. 5 EPR spectrum of polyparaphenylene doped with $FeCl_3$ at $T = 4.2, 25, 49, 100,$ and 300 K



Therefore, in some organic magnets—complexes of iron with nitrosonaphthol [27], disordered polymer matrices—polyaniline [7, 26], polyparaphenylene [33], polymethoxyaniline [29, 34], polyaminothiazole [29, 35, 36], doped with FeCl_3 or $\text{K}_3[\text{Fe}(\text{CN})_6]$, interesting temperature dependence of the EPR spectra was revealed. In these substances, the EPR spectrum is a superposition of several lines, two of which refer to the magnetic center—Fe(III). When the temperature decreases, the intensity of one-line increases, and the other contra. So, the first line has the maximum intensity at low (helium) temperatures and the other at room temperatures. The first line is the low-temperature component of the EPR spectrum, and the second is the high-temperature component. A change in temperature leads to a redistribution of absorption intensity between its. The EPR spectrum indicates the unusual dynamics of the molecules surrounding the Fe^{3+} ion. These dynamics can significantly influence various properties of substances. Based on the temperature dependence of EPR spectra and the crystal field theory [32, 37], it can be assumed that the temperature changes of the EPR spectrum are not caused by movements of Fe^{3+} ions from one non-equivalent position to another but rather the transition of the magnetic center from one state to another [29, 34].

Therefore, the Fe^{3+} ion can act as a paramagnetic probe in the polymer complexes revealing temperature dynamics different from the polymer matrix. The magnetic center dynamic depends on the iron ion external molecular (ligand) environment and the structural non-equivalence of its positions in conjugated polymer matrices. This phenomenon can be used in biology and medicine to monitor and predict the behavior of nerve cells and other biological objects [37–41].

5 Micro- and Nanocomposites Polymer–Magnetite

Nowadays, with intensive studies of molecular polymer magnets [3–5, 8], much attention is paid to hybrid polymer–magnetic composites [6, 9–14, 42]. Most of the studies are devoted to the methods for obtaining systems, their structure, morphology, and some physical properties, namely electrical conductivity, magnetization, and thermal stability. At the same time, the chain structure of polymer matrix macromolecules and the fluctuation network determine the mechanical properties of polymer composites depending on the action of external factors—temperature, pressure, and load. The relative value of elastic deformation in polymers tends to be tens of percent, so composites of polymers with magnetic particles will likely exhibit useful properties, primarily as plastic magnetic materials of small specific gravity, as well as toner materials for digital printing [13].

The enhanced functionality of hybrid nanocomposites is achieved by adding various functions—magnetic, conductive, fluorescent, etc. [9, 43–47]. Functionalized magnetic polymer capsules are promising for this aim [9]. Marking capsules with fluorescent substances, such as semiconductor nanocrystals, makes it possible to trace their way into the tissues and capillaries. Loading capsules with magnetic nanoparticles simultaneously allows controlling their movement by changing the

gradient of the external magnetic field. An intermediate polymer layer between the magnetic particles and fluorescent labels is necessary to reduce the adverse effects of quenching the nanocrystal luminescence. It is achieved by the polymer shell encapsulation of magnetic particles [9]. According to magnetometry and Mossbauer spectroscopy, encapsulated magnetite particles preserve superparamagnetic properties [44].

Improvement of the properties of the composites is also possible by providing electrical functions using conducting polymers [6]. Such modification allows controlling the nanoparticle movement by both electric and magnetic fields and tracking it in different mediums [9, 43]. Conducting polymer–magnetic composites provide magneto-switchable charge transport and bioelectrocatalysis [43, 48]. However, there were reported only a few attempts to obtain hybrid magnetic composites with both luminescence and conductivity. In addition, despite intensive research on hybrid systems, the influence of the polymer matrix on the properties of fluorescent substances remains to be fully elucidated [49, 50].

We have studied the conditions of preparation, structure, luminescence, and electrical properties of composites based on magnetite nanoparticles encapsulated with polymer shells and modified by barium zirconate and polyaniline [14, 51].

Highly dispersed magnetite Fe_3O_4 was synthesized by alkaline hydrolysis of iron II and iron III salts with sodium oleate as a stabilizer. For better compatibility of the magnetic part with the epoxy matrix, the magnetite nanoparticles were modified with a polystyrene (PS) shell [42]. Spherical particles (granules) of dispersed magnetite with a size of about 1–2 μm were separated from the suspension by magnetic decanting.

According to the diffractogram of the magnetite (Fig. 6), the peaks denoted with hkl indicate the cubic phase Fe_3O_4 with spinel structure and cell parameter $a = 8.3490(3)$ Å. The average size of the Fe_3O_4 granules, determined by microstructure studies, is $75.5 (\pm 7.3)$ Å. The amorphous halo, observed for magnetite with polymer shells, refers to polystyrene and diffraction reflections to magnetite (Fig. 6b). At the same time, diffraction peaks of cubic Fe_3O_4 phase with low intensity for powder diffraction are almost vanishing.

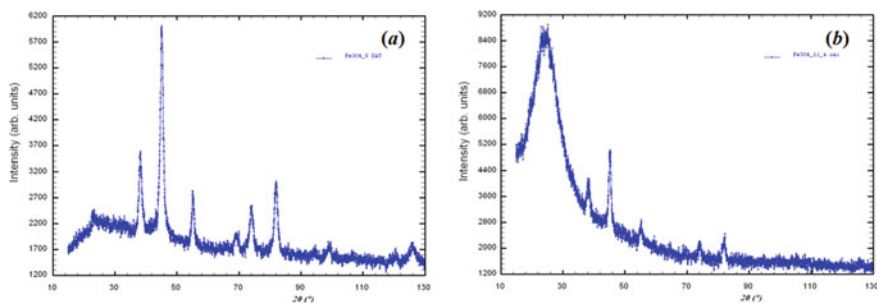


Fig. 6 X-ray diffractogram of Fe_3O_4 (a) and polymer/magnetite composite (b)

The cell parameter a is almost the same for both samples within standard deviation. But it is a bit larger $a = 8.3491$ (12) Å for the composite. It is important to note that the average size of the composite granules exceeds one for Fe_3O_4 without polymer (Table 4). It confirms the formation of a polymer shell around magnetite particles.

The oxidative polymerization of aniline in the aqueous dispersion of polymer–magnetite capsules leads to additional microsphere encapsulation by conducting polyaniline shells. The adsorption of luminescent nanocrystals BaZrO_3 (BZO) was used for surface modification of polymer–magnet microcapsules.

EDX analysis confirmed the adsorption of BZO nanocrystals on the surface of polystyrene capsulated magnetite. According to the elements distribution profile on the surface of the composite, the intensive peaks from Zr, Ba, and Fe are observed (Fig. 7). The number of adsorbed nanocrystals grows with the increase of BaZrO_3 content in the initial reaction mixture from 1 to 20%. Experimental diffraction patterns (Fig. 8) indicate an amorphous halo from polymer (PS), semi-amorphous reflections of magnetite [42, 52], and formed peaks from BaZrO_3 [53].

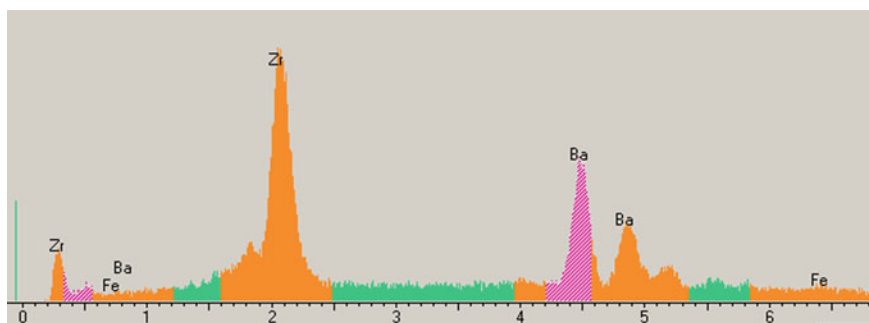
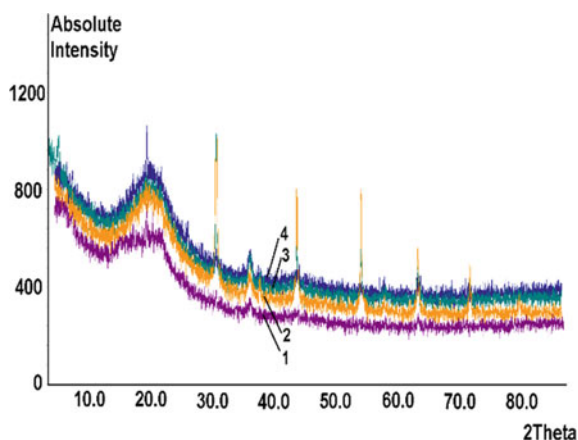


Fig. 7 Profile of distribution of elements on the surface of polymer–magnetite composite, modified by nanocrystals at BaZrO_3 at its 10% content in initial dispersion

Fig. 8 XPD pattern of Mt-PS-BZO-PAn composites obtained at 1 (1), 5 (2), 10 (3) and 20% (4) content of BZO in the initial dispersion



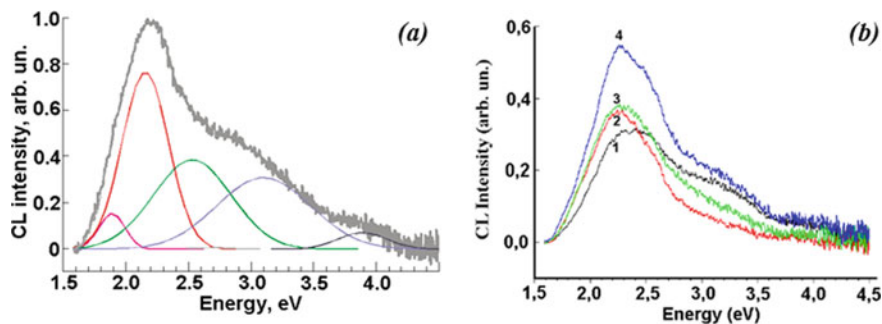


Fig. 9 **a** CL spectrum of BZO-PS composites at BZO content 5%; **b** CL spectrum of Mt-PS-BZO-PAn hybrid composites. Content of BZO, %: 1—1; 2—5; 3—10; 4—20

Light radiation of polymer-magnetite nanocapsules was studied by cathode luminescence (CL) spectra of the pellet samples. Adsorption of BZO nanocrystals on the surface of polymer-magnetite grains causes significant changes in the CL spectrum [49, 50]. According to the Gaussian decomposition of CL curves, the additional lowest and the highest energy bands appear at a significant reduction of the CL intensity. New bands at $E = 1.9, 2.15, 2.45, 3.0,$ and 3.96 eV were observed in the PS-BZO composites spectra (Fig. 9a).

The composites with polyaniline preserve the ability of radiation. The CL intensity increases with the increase of the BZO content in the composite (Fig. 9b). The polyaniline modification of nanocapsules causes a decrease in the specific volume resistance ρ ($T = 293$) from 4×10^8 $\text{Om} \cdot \text{m}$ to 18.2 ± 0.5 $\text{Om} \cdot \text{m}$.

For the first time, the hybrid composites with magnetic, luminescent, and conductive functions were obtained by surface modification of the magnetite-polymer nanoparticles by BaZrO_3 and polyaniline [14, 51]. The influence of the polymer matrix on the cathodoluminescence spectrum of BaZrO_3 was found. CL spectra modification in composites is probably due to the change in the nanocrystal substructure caused by the PS matrix. The lattice parameter decreases from 4.19083 (6) for nano-BZO to 4.1879 (2) Å in BZO-PS composite. Interaction between the PS matrix and BZO was confirmed by FTIR spectra [14]. The proposed method of surface modification may be used in sensors and medical diagnostics [54, 55].

Composite materials containing dielectric or semiconductor nanoparticles of a particular shape or micro- and nanostructures capable of spatial redistribution of scattered electromagnetic radiation in desired directions are perspectives as anti-radar screens. Iron oxides, magnetite, or Fe_3O_4 are especially interesting due to their ability to absorb electromagnetic waves of near IR and microwave ranges [56]. Carbon threads or nanotube inclusions in magnetite-based composites may provide a synergetic effect, i.e., enhance electromagnetic energy absorption and improve anti-corrosive properties on the metal surface [57, 58]. We suggest filling the composite with magnetite particles with a diameter commensurate with the microwave's length that may provide an effective reflection and radiation scattering [59]. The hybrid composites with stabilized by a polymer shell magnetite microparticles were prepared

as described above. Instead of expensive and scarce nanotubes, we use conducting polymer polyaniline as an organic additive [60]. Variation in the size of Fe_3O_4 –PS particles does not affect the period of the magnetite elementary cell. In contrast, it influences the magnetite–polymer composite magnetic susceptibility and microhardness (Table 5). Partial aggregation of magnetite grains and formation of polymer shell on their surface results in the appearance of spherical core–shell particles with an average size of 1.5–2 μm .

The granules Fe_3O_4 –PS of $\approx 2 \mu\text{m}$ size were used as magnetic fillers to obtain thermosetting polymer composites with antiradar and protective functions [59]. We propose to use polyaniline doped with TSA as a component with intrinsic electron conductivity. The polymer has high specific conductivity of $(3.0 \pm 0.3)10^{-2} \text{ S/cm}$. So, the formation of conducting channels inside the composite structure is possible. It is necessary to enhance the absorption and scattering of electromagnetic radiation [56, 57].

Magnetic and electric properties of hybrid nanocomposite materials depend on the nature of the initial components, the amount of ferromagnetic and conductive fillers, polyaniline dopants, and the preparation procedure. Composite films with conducting polymer prepared in the presence of ferromagnetic nanoparticles can be alternatives to metal-containing systems due to improved properties and lower prices.

The polymer composite was spilled onto a flat Teflon substrate and peeled off the surface after film formation. Thus, a free polymer composite film of 0.2 mm thickness was obtained. Details of synthesis can be found in [59].

It is worth noting that the encapsulation of magnetite into a polymer shell weakly affects the magnetic susceptibility of magnetic filler [51]. Thus, composites can absorb IR and microwave electromagnetic radiation effectively [58].

The microstructures of the composite polymer coatings of the thermosetting mixtures based on epoxy resin, amine hardener, and different fillers are noticeably different (Fig. 10a, b). The uniform microstructure is observed for the composite containing a mixture of fillers of 10% and a weight ratio of 1:1 (Fig. 10b). In this case, there is a better interaction of components inside of composite, probably due to the compatibility of magnetite microgranules surrounded by polystyrene shell and PAn doped with TSA (plasticizer) with hydrophobic epoxy matrix.

Table 5 Physical properties of magnetite–polystyrene granules

Granule size of Fe_3O_4 –PS composite, μm	Magnetic susceptibility, $\chi \times 10^{-6}$, cm^3/g	Period of the elementary cell, \AA	Microhardness, $F_\infty \times 10^{-8}$, N/m^2
1.5–1.7	1797	8.36 (2)	2.45
1.7–2.0	1969	8.357 (9)	2.47
2.0–2.5	2822	8.333 (9)	3.03
2.2–2.5	2589	8.35 (2)	3.89
2.5–3.0	2123	8.36 (2)	2.78

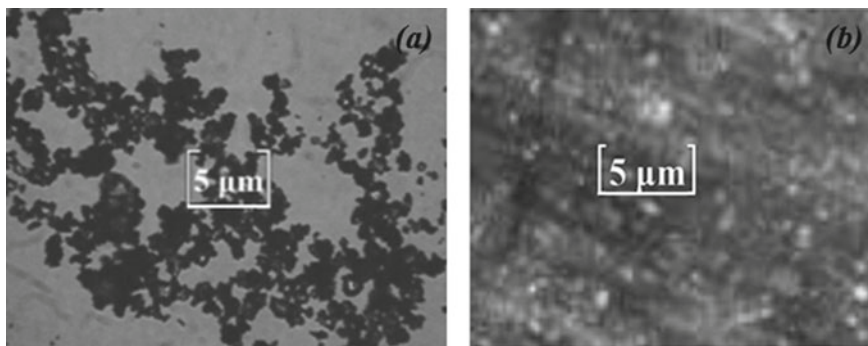


Fig. 10 Micrograph of magnetite Fe_3O_4 particles encapsulated into polystyrene shell (a); micrograph of the composite (5% magnetite + 5% PAN/TSA powder) taken by “Olympus” optical microscope (b). A long-focus lens with a magnification of $50\times$ was used

The interaction leads to a significant increase in the microhardness F_∞ of the filled composites—up to $18.7 \times 10^9 \text{ N/m}^2$ compared to the unfilled epoxy composite with $F_\infty = 1.25 \times 10^9 \text{ N/m}^2$ [59].

Synthesized magnetite microgranules with polystyrene shells and TSA-doped polyaniline were used to form composite coatings with antiradar functions. The highest microhardness and corrosion resistance of coatings are observed for the composite with 10% filler. It is achieved by combining magnetic and conducting components due to the synergistic effect.

The composite, containing magnetic microparticles and polyaniline doped with toluene sulfonic acid at a 1:1 ratio, reveals the strongest IR absorption coefficient $A = 35.2 \text{ cm}^{-1}$ and low reflectivity $R = 0.022$ (Table 6). At the same time, this composite has excellent anti-corrosive properties and high microhardness.

The composite containing only the conductive PAN-TSA component has a low level of both reflectivity and absorption (Table 6). The composites doped with 10% of magnetite reveal high absorption and reflectivity undesired for protective coatings. Doping with both PAN and magnetite fillers leads to the expected properties—high absorption and low reflectivity of composite.

Table 6 The influence of fillers on IR absorption and reflectivity

Magnetite, w.%	PAN-TSA, w.%	Reflectivity, R (at $\lambda = 1200 \text{ nm}$)	Absorption coefficient, A , cm^{-1}
0	0	0.082	3.5
5	5	0.022	35.2
10	0	0.056	31.7
0	10	0.014	14.8

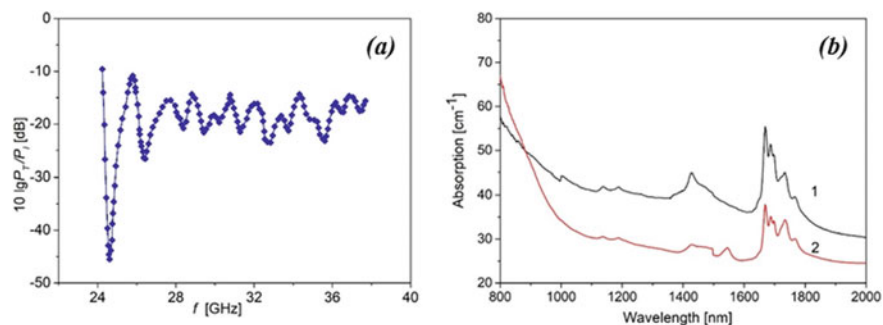


Fig. 11 **a** RF radiation power absorption spectrum measured by HP 8722C spectrum analyzer for ED20/PEPA composites with 10% content of fillers (5% Fe_3O_4 + 5% PAn/TSA). Film thickness 0.2 μm ; **b** IR absorption spectra of film samples of epoxy composition with different content of fillers: 1—5% magnetite + 5% PAn/TSA; 2—10% magnetite. Film thickness 0.2 μm

The microwave absorption of the composite was studied with HP 8722C spectrum analyzer. The sample of 0.2 mm thickness was placed across the waveguide perpendicularly to the direction of electromagnetic radiation (EMR) propagation. The composite film was cut to fit the internal cavity of the waveguide. The composite reveals high attenuation of EMR in K band (18–26.5 GHz) and Ka-band (26.5–40 GHz) at the level of -25 dB with a peak value of -47 dB at 23 GHz (Fig. 11a). That makes the material perspective for electromagnetic radiation shielding and anti-radar purposes [60]. Shielding properties of similar composite materials based on epoxy resins with graphene nanoplates in the microwave frequency range show only 10 dB at 27 GHz [61].

The film samples of different compositions were prepared to study the absorption of the composites in the near IR range. The IR absorption spectra were recorded using an MDR-23 monochromator with a halogen lamp as a light source. The absorption spectra in the near IR (NIR) range of samples with different filler content are shown in Fig. 11b.

The composite containing magnetic microparticles and TSA-doped polyaniline at a 1:1 ratio reveals stronger IR absorption than the composite filled only with magnetite (Fig. 11b).

In conclusion, we have synthesized composite material with high absorption of electromagnetic radiation in microwave and NIR spectral ranges. The composite comprises polyaniline doped with TSA and magnetite microparticles stabilized by polystyrene shells. This coating may find dual military and common-purpose applications. It can be used for electromagnetic shielding, anti-radar, and light harvesting in solar thermal energy applications.

6 Conclusion

We have studied the magnetic properties and structure of polymer–magnet nanosystems based on conjugated polymers and magnetic nanoparticles in a wide range of temperatures and magnetic fields. Charge transport in macromolecular chains occurs along a conjugated system of π -electron bonds, which is the source of charge carriers and paramagnetic centers. The parameters of the short-range ordered structure of polyaniline, preserved the coplanar orientation of aromatic fragments, were calculated. The size of repetitive fragments is 0.46 nm, and the conjugation length is 2.5–3.0 nm. It was found that the magnetic properties of conjugated polymers are the superposition of dia- and paramagnetic contributions depending on the type of doping and temperature. The interesting new phenomena in the temperature dynamic of paramagnetic centers in a series of conjugated polymers doped with magnetic ions were revealed by EPR spectroscopy. Ion Fe^{3+} in the formed polymer complexes can act as a paramagnetic probe demonstrating its own temperature dynamic, different from the polymer matrix. The peculiarities of the behavior of paramagnetic “probe”—the dynamics of magnetic centers depend on the external molecular (ligand) environment of the Fe atom and the presence of structural non-equivalence of its positions in conjugated polymer matrices. This phenomenon can be used in biology and medicine to monitor and predict the behavior of nerve cells and other biological objects.

Particular attention is given to hybrid polymer–magnetic micro- and nanocomposites from the point of view of their practical use as materials sensitive to magnetic and electric fields, modern absorbers of radiation, etc.

For the first time, we obtained hybrid composites with magnetic, luminescent, and conductive functions simultaneously by surface modification of the magnetite-polymer nanoparticles with luminescent BaZrO_3 nanocrystals and polyaniline as conducting substance. The proposed surface modification method may be used to develop sensors and functional materials for medical diagnostics.

Also, we have synthesized a composite material with high absorption of electromagnetic radiation in microwave and NIR spectral ranges. This coating can have military and common purposes—for electromagnetic shielding and antiradar, as well as solar thermal energy applications. Composite films of conducting polymer with ferromagnetic nanoparticles can be alternatives to metal-containing systems due to improved properties and lower prices.

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