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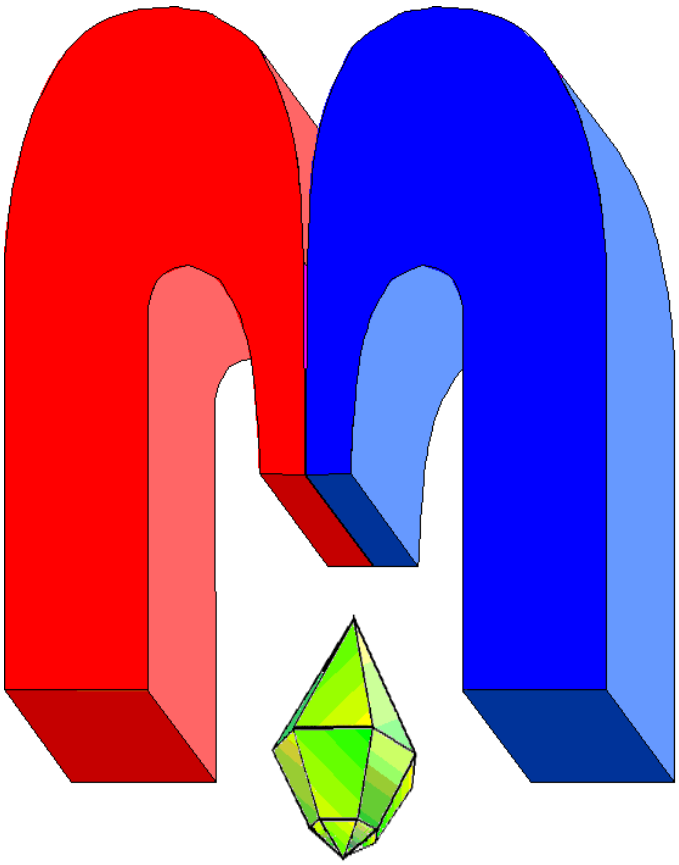

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

EPR investigation of nanosized silver particles in polymer composites

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In this work new paramagnetic composite materials based on (co)polymers of 1-vinyl-1,2,4-triazole containing silver nanoparticles were investigated and characterized. It was found that form and width of electron paramagnetic resonance (EPR) signals for silver particles of nanocomposites obtained depend on microwave power. Also the effect of temperature on intensity, *g*-factor and width of signal silver clusters was determined.

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Keywords: continuous wave EPR, pulse EPR, *g*-factor, Ag, nanosized particles, relaxation characteristics, polymers.

1. Introduction

In the recent years, nanocomposite materials containing metal particles and possessing complex properties relevant for up-to-date catalysts, drugs, etc. have received a wide recognition. This trend is closely connected with the problem of nanoparticles' stabilization within the matrix.

This paper is devoted to new nanocomposites on the basis of 1-vinyl-1,2,4-triazole (VT) polymer and its copolymers with acrylonitrile (VT-AN). The nanocomposites containing nanosized silver particles have been obtained and characterized. All the compounds have proved to be paramagnetic and they have been studied by the EPR method. It is noteworthy that powder microcrystalline samples, unlike monocrystals, show weaker anisotropic properties. Thus, as a rule, only averaged *g*-factor values can be measured for them. However, in the materials on the basis of transition metals, nanosized magnetic particles are often formed. These particles are able to be combined into so called clusters where, due to a certain magnetic order, unpaired electrons are strongly correlated. The substances containing such ordered regions (domains) acquire ferromagnetic properties essentially affecting the EPR spectra.

In this paper, we present the detailed investigation of paramagnetic polymer materials containing nanosized silver particles.

2. Experiment and discussion

The starting homo- and copolymers of 1-vinyl-1,2,4-triazole, which are high-resistance organic semiconductors in the form of white powders, are diamagnetic. The combination of VT and AN units in the copolymers' macromolecules provides their high coordination ability towards the metal, due to the presence of heterocycle nitrogen atoms and, in particular, cyano-groups of acrylonitrile, and decreases the nanoparticles' agglomeration. Nanocomposites on the basis of VT-AN copolymer (silver mass content, yield, 41-42%) have been obtained by Ag^+ thermal reduction from $AgNO_3$ in the presence of (co)polymer in solid phase, by analogy with [1]. They represent fine-dispersed black powders insoluble in water. According to X-ray data silver nanoparticles have sizes 17-20 nm in the composites.

The poly-1-vinyl-1,2,4-triazole shows high activity towards silver atoms by forming charge transfer complexes. Their EPR spectra depend on the orientation of a sample in the magnetic field. As a result, we have ascertained the anisotropy and the presence of several individual signals referring to

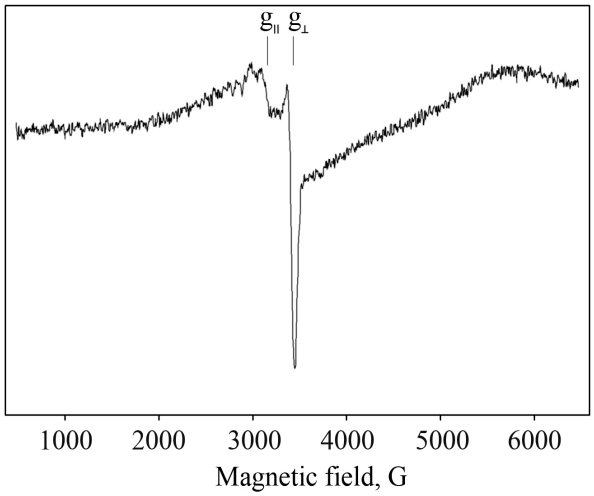

Figure 1. EPR spectrum measured at room temperature for the polymeric complex of the VT-AN copolymer with $AgNO_3$, where $g_{\|} = 2.2623(2)$, $g_{\perp} = 2.0762(2)$.

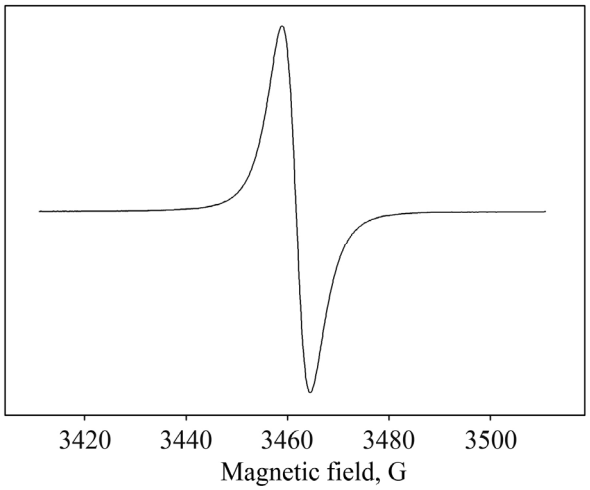

Figure 2. EPR spectrum measured at room temperature for colloidal silver nanoparticles containing VT-AN nanocomposite.

different types of paramagnetic centres (PC). The wide signals in the range of $g = 2.2$ belong to the polymeric complexes of divalent metal before thermal reduction (Fig. 1). Silver complexes were described in references [2, 3]. Signal observed in the range of $g = 2.00$ belong to the conduction electrons of reduced silver Ag(0) forming nanoclusters stabilized by polymeric matrix, it is conformed to row publications [4-6].

Nanocomposite materials on the basis of VT-AN matrix possess electroconductivity (7.8×10^{-12} S/cm) and paramagnetism (10^{19}-10^{20} spin/g). In their EPR spectra, narrow symmetric singlets of *g*-factor of 2.005 and of width of 5-6 G are observed, presented in Fig. 2. The studies upon the EPR signals' temperature dependencies and observations of their shapes and widths in conditions of microwave saturation have proved that these signals refer to zero-valence silver forming clusters stabilized by copolymer matrix. However, the complicated dependencies of the signals' intensities and widths on microwave power can be explained by the size variations of the nanoclusters (from one to several nanoparticles) and by some other factors [7]. The relaxation characteristics of these nanocomposites have been estimated by the pulsed EPR method at 113 K (T_1' = 6.874(±0.628) mks and T_1'' = 38.573(±1.559) mks, T_2' = 0.009(±0.004) mks and T_2'' = 0.192(±0.003) mks have been determined by pulse patterns of π-T-π/2-τ-π for T_1, π/2-τ-π for T_2, where $\pi/2 = 0.020$ mks, $\tau = 0.200$ mks and $T = 1.000$ mks (cw and pulse EPR spectra were recoded with an X-band Bruker ELEXSYS E-580 spectrometer)).

Since the EPR signals of zero-valence metals are registered in the range close to *g*-factor of free electron and they are similar to signals of polyconjugated polymers (triple C ≡ N-bond of acrylonitrile can polymerize under certain conditions forming double-chain conjugate polymers [8, 9]), it has been necessary to exclude or single out the contributions of the latter into the nanocomposites' narrow signals. Control samples of the starting copolymer, after heating at 210-250°C, have shown weak narrow singlets ($N = 1.6 \times 10^{16}$ spin/g, $g = 2.0050$, $\Delta H = 5.3$ G, $A/B = 1.0$), thus, the spectra observed can be regarded as a superposition of two signals (one of polymer matrix and one of zero-valence metal). For this purpose, we have studied the dependency of EPR signals' characteristics on microwave power (so called saturation effect) which is presented in Fig. 3. The signals of the silver containing samples represent complicated curves (dependences are shown in Fig. 4). There is an inflection point on the dependencies of line widths at microwave power of 0.2 mW implying that the signal is a superposition of two signals of similar *g*-factors and widths, but belonging to different PC.

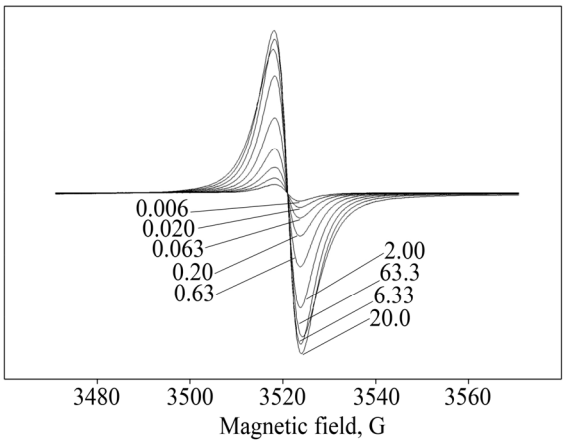

Figure 3. EPR spectra measured at room temperature for the nanocomposite of silver and VT-AN copolymer at various microwave powers (mW).

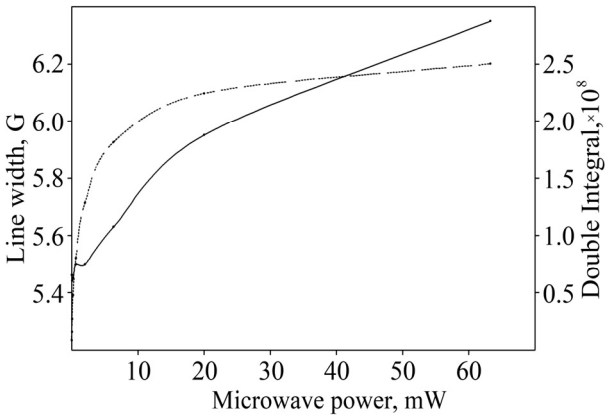

Figure 4. Dependency of signal width (solid line) and double integral (broken line) on microwave power for colloidal silver nanoparticles containing VT-AN nanocomposite.

In accordance with this is the fact that, at a higher power, this dependency for silver containing nanocomposite has two linear intervals with inflection point at 15 mW (Fig. 4). As for the dependency of the signals' intensities on microwave power, the saturation curve plateau starts already at 20 and continues till 65 mW. This means that the samples obtained contain both free electrons of zero-valence metals and organic radicals referring to polymeric matrix (the mentioned above polyconjugated polymer) due to the formation of double-chain structures by C ≡ N bond. During the saturation process, *g*-factor remains unchanged and the signal is symmetric. The lineshape is almost Lorentzian and at saturation it becomes absolutely Lorentzian, which points to the increase of metal nanoclusters' sizes, it is discussed in review by Shabatina [10]. As the temperature decreases, the EPR signal intensity, *g*-factor and signal width increase (data is given in Tab. 1, Fig. 5).

Note that, in Ag(0)-containing nanocomposite spectrum, weak doublet lines which are satellites of ^{107}Ag and ^{109}Ag isotopes with constants of 670 and 770 G, respectively [10-13], have been registered at 113 K at high and low fields. The ratio between the constants is 1.15 which coincides with one of magnetic moments of the silver isotopes and, thus, confirms the lines' references.

Table 1. Experimental EPR-characteristics for the nanocomposite of silver and VT-AN copolymer.

T, K	Intensity, r.u.	*g*-factor	Δ*H*, G
293	–	2.00500	5.30
223	3.817	2.00520	5.55
203	4.197	2.00525	5.57
183	4.907	2.00530	5.60
163	5.415	2.00540	5.64
143	5.898	2.00543	5.68
123	6.768	2.00553	5.70
113	7.893	2.00561	5.72

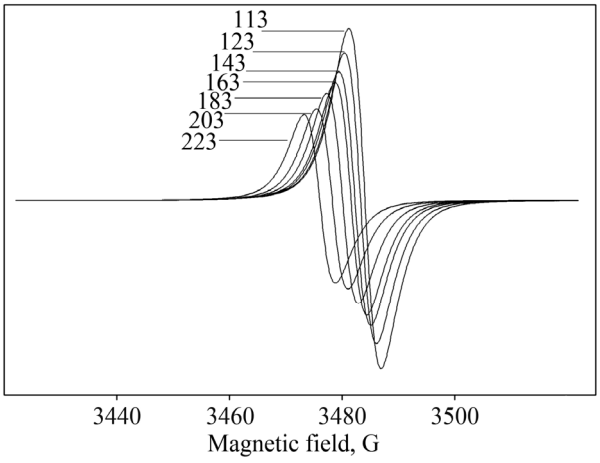

Figure 5. Temperature dependency (K) EPR spectra of the nanocomposite of silver and VT-AN copolymer.

3. Summary

In this paper it was demonstrated that thermal reduction of $AgNO_3$ in the system of copolymer VT-AN leads to new paramagnetic composite materials containing silver nanoparticles stabilized by polymeric matrix. It was shown that weak intramolecular polycyclization in the course of nanocomposites formation occurrs, which results in impossibility to study the only signal of silver clusters. Nevertheless exploration of completely reduced salt in polymer matrix VT allowed to register and analyse EPR signal of silver nanoclusters.

Acknowledgments

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