

Research Article

Synthesis and Characterization of Silver-Containing Nanocomposites Based on 1-Vinyl-1,2,4-triazole and Acrylonitrile Copolymer

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Insoluble silver-containing nanocomposites based on 1-vinyl-1,2,4-triazole and acrylonitrile copolymer was synthesized and characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, atomic absorption, X-ray diffraction, and thermogravimetric data analysis. The silver content of the nanocomposites varied from 8.0 to 23.5% (the silver content depends on the ratio of the copolymer-silver salt). Synthesis of silver nanocomposites was carried out by thermal treatment of a polymer complex of copolymer-silver salt without the use of an additional reducing agent. X-ray diffraction was used to control the formation of silver nanoparticles at different temperatures (210°C, 220°C, and 250°C). Synthesis of nanocomposites shows a developed porous structure with a channel diameter in most cases of 1-4 microns. The EPR monitoring of the nanoparticle germination and growth reveals that the generation of the nanocomposites proceeds via a stage of complex formation between the polymeric matrix and silver ions. The synthesized nanocomposites possess paramagnetic properties and show a narrow EPR symmetric signal with the concentration of unpaired electrons of 10^{20} spin/g, a g-factor 2.0050, and signal width 5-6 Gs. Thermal stability of silver-containing nanocomposites is up to 270-320°C.

1. Introduction

Creation of new polyfunctional polymeric materials with multifaceted valuable properties is a hot research topic due to ever-increasing demand for the development of innovation technologies. Among the most prospective classes of polymeric compounds are the polymers containing nitrogen heterocyclic fragments, which ensure a variety of valuable properties such as a high lyophilicity, ability of complex formation and quaternization, chemical and thermal stability, and biocompatibility [1-3]. Polymers of such a type are of a particular interest for the development of biologically active and hi-tech materials.

Acrylonitrile-derived polymers possess excellent performance characteristics and gain widespread acceptance in industry. Fibers on their basis show high strength, thermal stability upon long temperature heating, light resistance, and low heat conductivity that allows employing in mechanical engineering, textile, aerospace, and pharmaceutical industries [4, 5].

Polymeric nanocomposites containing silver nanoparticles are promising building blocks for medicine and optoelectronic materials, owing to unique properties of silver in a nanosized state and polyfunctional nature of the polymeric matrix [6-12].

Synthesis of the copolymers incorporating vinyltriazole and acrylonitrile motifs in the macromolecule allows

synergism of their valuable properties to be reached. This refers, in particular, to the thermal stability and ability to form complexes with metal ions caused by the presence of electronegative nitrogen atoms.

Earlier we have reported on the synthesis and properties of nanocomposites with silver nanoparticles in a matrix of 1-vinyl-1,2,4-triazole homo- and copolymers, possessing plasmon absorption, water solubility, and antimicrobial activity [13–16].

The present work is aimed at the synthesis of new silver containing nanocomposites based on 1-vinyl-1,2,4-triazole and acrylonitrile copolymer as well as at the study of their chemical and physical properties.

2. Materials and Methods

2.1. Materials. The starting 1-vinyl-1,2,4-triazole (VT) (boiling temperature 43°C/3 mmHg, n_D^{20} 1.5100) was synthesized and purified according to the previously developed technique [17]. Acrylonitrile (AN) (99%, Aldrich) (boiling temperature 77°C, n_D^{20} 1.3911), α,α' -azobisisobutyronitrile (AIBN) (99%, Aldrich), and AgNO_3 (99.9%, Sigma-Aldrich) were used without any treatment as an initiator and a precursor, respectively. Dimethylformamide (DMF) (Aldrich) and chemically pure nitric acid of 37% concentration were used as solvents.

2.2. Synthesis of 1-Vinyl-1,2,4-triazole and Acrylonitrile Copolymers (Poly(VT-co-AN)). The copolymers, poly(VT-co-AN), were synthesized by free radical copolymerization of 1-vinyl-1,2,4-triazole with acrylonitrile in an equimolar ratio, in the presence of AIBN (0.5 wt%) in DMF under an argon atmosphere at 80°C for 0.5 h. The viscous copolymerization product was diluted by DMF, precipitated in the distilled water, washed several times with ethyl alcohol, and dried in a vacuum at 50°C up to the constant weight. Yield of the copolymer was 2.13 g (71%). The ratio of the VT and AN links in the copolymer is 51 : 49 mol%. The composition of the copolymer was determined by quantitative ^{13}C NMR analysis (found: C, 59.28%; H, 6.01%; N, 34.71%). The GPC traces for poly(VT-co-AN) were obtained using polystyrene standards. The M_n and M_w of the polymer were measured to be 38632 and 88625 Da, respectively. The polydispersity index (M_w/M_n) of the copolymer was 2.3.

2.3. Synthesis of Nanocomposite Based on Poly(VT-co-AN) with Silver Nanoparticles. A solution of poly(VT-co-AN) copolymer (0.15 g, 1.01 mol) in nitric acid (5 mL) was added a solution of AgNO_3 (0.08 g, 0.5 mol) in nitric acid (4 mL). The reaction mixture was allowed to stand at 25°C for 5 h until complete dissolution of the salt. Nitric acid was evaporated to obtain a metal-polymer complex as yellow solid color, which was washed with water, dried up in a vacuum oven, and thermally treated at 210°C for 1 h. Consequently, the nanocomposite with silver nanoparticles (AgNPs) was prepared as fine dark brown powder, silver content being 23.5 mas%. Nanocomposites with various contents of silver (8–23.5%) were synthesized by varying a ratio of copolymer and a metal precursor.

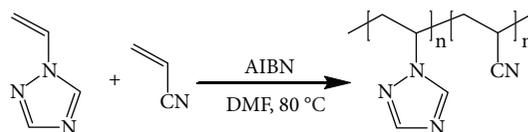


FIGURE 1: Synthesis of 1-vinyl-1,2,4-triazole and acrylonitrile copolymer.

2.4. Characterization. The composition and structure of the copolymer were established by the data of elemental analysis, IR, ^1H , and ^{13}C NMR spectroscopy. The elemental analysis was performed on a Flash EA 1112 analyzer of CHNS series. IR spectra were recorded on a Vertex 70 FTIR instrument in KBr pellets. ^1H and ^{13}C NMR spectra were run on a Bruker DPX-400 spectrometer (400.13 and 100.62 MHz, respectively) in $\text{DMSO}-d_6$. GPC measurements were carried out using a PL-GPC 220 (RI) detector (Agilent High Temperature Chromatograph). Dissolution of samples was performed at 80°C for 12 h using a system for sample preparation Varian PL-SP 260VS, combining functions controlled by heating and stirring. DMFA solution was used as an eluent with a flow rate of 1 ml/min. Calibration was carried out using a series of polystyrene standards. Microphotographs were obtained using a scanning electron microscope (TM 3000, Hitachi). The silver content in the studied nanocomposites was evaluated by atomic absorption analysis using a Shimadzu AA-6200. X-ray diffraction (XRD) patterns were obtained on a powder diffractometer (D8 Advance, Bruker Corporation, Cu radiation). Thermogravimetric analysis (TGA) was performed using an STA 449 Jupiter derivatograph (NETZSCH, Selb, Germany) under an atmosphere of air at a rate of 10°C per min; the weight of the samples was 5 mg. EPR spectra was recorded with the FT X-band Bruker ELEXSYS E-580 spectrometer (X-wave range 9.7 GHz). The EPR monitoring was carried out at 210°C. The concentration of paramagnetic centers was calculated by the known method [18] with the use of diphenylpicrylhydrazyl as a standard.

3. Results and Discussion

3.1. Copolymer of 1-Vinyl-1,2,4-triazole and Acrylonitrile. Radical copolymerization of 1-vinyl-1,2,4-triazole with acrylonitrile was carried out in DMF solution in the presence of an initiator (AIBN) at 80°C for 0.5 h, molar ratio of the starting monomers being 50 : 50 (Figure 1).

The copolymer obtained (white powder) is well soluble in dipolar organic solvents (DMF, DMSO). Composition and structure of the copolymer were established by FTIR, ^1H , ^{13}C NMR technique, and elemental analysis data. Content of the triazole and acrylonitrile fragments in the copolymer was 51 and 49 mol%, respectively.

FTIR spectroscopy has been used to study the interactions between the polymeric matrix and the AgNPs. Figure 2 depicts the FTIR spectra of the starting poly(VT-co-AN) copolymer and nanocomposite. The stretching and deformation vibrations of the initial polymer are observed for the triazole rings at 3116 (C-H), 1506 (C=N), 1436 (C-N), 1277 (N-N), 1005 (C-H), and 663 (C-N) cm^{-1} and for the acrylonitrile fragments 2934 (CH_2) and 2242 ($\text{C}\equiv\text{N}$)

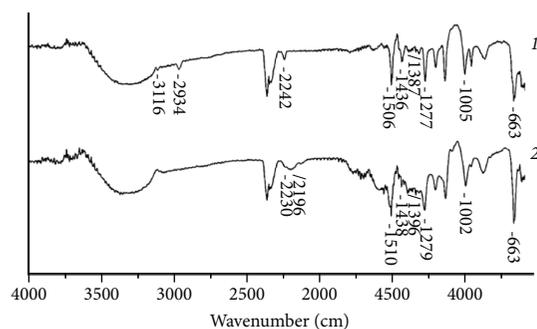


FIGURE 2: FTIR-spectra of 1-vinyl-1,2,4-triazole and acrylonitrile copolymer (1) and nanocomposites with silver nanoparticles (2).

cm^{-1} . The FTIR spectrum of the nanocomposite is similar to that of the initial copolymer. The bands corresponding to the vibrations of the triazole rings are shifted by 2.9 cm^{-1} , which indicates the coordination interactions of the N atoms with AgNP. The vibration band of the nitrile unit at $2196\text{--}2230\text{ cm}^{-1}$ turned out to be much broader than the initial copolymer (2242 cm^{-1}), possibly due to the dehydrogenation of the acrylonitrile units.

The ^1H NMR spectra of the copolymer show broaden signals of the CH protons of the main polymeric chain of VT and AN links AN ($\delta_{\text{H}}=2.0\text{ ppm}$), CH of VT protons ($\delta_{\text{H}}=4.7\text{ ppm}$), protons of the VT triazole ring ($\delta_{\text{H}}=7.9\text{--}8.7\text{ ppm}$), and CH of AN links ($\delta_{\text{H}}=3.1\text{ ppm}$).

In the ^{13}C NMR of the copolymer, there are signals of carbon atoms (ppm) of the triazole rings in the region $152.7\text{--}150.7$, $143.5\text{--}142.8$ (C-H), cyano groups in the range of $120.5\text{--}118.5$ (CN), methine fragments at $56.0\text{--}52.0$ and $28.2\text{--}24.0$ (CH), and methylene groups at $37.2\text{--}34.5$ and $33.5\text{--}32.0$ (CH) of the VT and AN units, respectively.

According to data of the thermogravimetric analysis, under oxidative conditions, intensive thermodestruction of the copolymer starts at 330°C (Figure 3).

It is found that at $190\text{--}220^\circ\text{C}$, loss of the sample mass is 2.7% and formation of low-molecular compounds with $m/z = 2, 13, 15, 16$ is observed, which correspond to the abstraction of hydrogen and the methyl radical from the polymer. Also, a small amount of the nitrile fragment is released ($m/z = 26, 27$). Intensive thermal destruction occurs at $330\text{--}450^\circ\text{C}$ with 34.3% loss of the sample mass, accompanied by the exothermic effect at 350°C . At this stage, triazole and nitrile fragments of the polymer are abstracted ($m/z = 67, 68, 26, 27$) followed by oxidation to H_2O , CH_4 , NH_3 , NO , CO_2 , and NO_2 ($m/z = 16, 17, 18, 30, 44, 46$). At $450\text{--}760^\circ\text{C}$, the intensive exothermic effect, accompanied by 60.4% loss of the sample mass, is observed.

3.2. Nanocomposites with Silver Nanoparticles. The presence of acrylonitrile links in the structure of the synthesized copolymers enables to prepare on their basis polymeric nanocomposites without the use of an additional reducing agent. Indeed, it is a common knowledge that such copolymers (in case of polyacrylonitrile) are capable of isomerization to afford a ladder polymer with the fused dihydropyridine cycles, which upon further oxidation are easily dehydrogenated to the pyridine cycles. It should be noted that the

formed hydrogen can act as an effective reducing agent of ionic silver to the metal state.

An important property of the synthesized poly(VT-co-AN) is their high thermal stability. Owing to this feature, these copolymers have been used as the stabilizing matrix for the formation of nanocomposites with silver nanoparticles by thermal treatment of the copolymer-silver salt complex. As a precursor of metal silver, silver nitrate was used. It was added to a solution of the copolymer dissolved in nitric acid to furnish light-yellow polymeric complex, [poly-(1-vinyl-1,2,4-triazole-acrylonitrile)- Ag^+]. The latter was isolated by evaporation to a solid state. Further, the complex was subjected to thermal treatment at 210°C for 1 h to deliver silver-containing polymeric nanocomposites as fine dark brown powder, insoluble in all available solvents.

It should be emphasized that due to the coordination binding of silver ions with functional groups of the copolymer macromolecules, a favorable microenvironment for their reduction is formed. The silver nanoparticles are incorporated in the copolymer macromolecules and are retained in them mainly by numerous specific bonds between functional triazole and nitrile groups and silver atoms on the nanoparticle surface.

According to the data of atomic absorption analysis, the content of silver in the obtained nanocomposites ranges $8\text{--}23.5\%$ (the content of silver depends on a ratio of silver-copolymer salt).

X-ray diffraction patterns clearly show the intense halo of the polymeric component from 10 to 30° and intense reflections of the metal silver nanoparticles identified by comparison of the interplanar distance values and relative intensities with references for metal silver (Figure 4). The average size of metal silver nanocrystallites (average coherent dispersion region), calculated by broadening of X-ray diffraction lines using the Debye-Scherrer formula, is 17.2 nm (8% silver content). The pattern of the sample matched well with the standard patterns of silver (JCPDS file no. 04-0783). All of the peaks of the patterns of the samples can be readily indexed to face-centered-cubic silver (JCPDS file no. 04-0783), where the diffraction peaks at 2θ values of 38.24 , 44.42 , and 64.44° can be ascribed to the reflection of (111), (200), and (220) planes of the face-centered cubic silver, respectively. No peaks from other phases were detected, indicating high purity of the products.

For monitoring the formation of silver nanoparticles at different temperatures, X-ray diffraction was used. Nanocomposites with 23.5% silver nanoparticles were synthesized at different times from 2 to 90 minutes and heat treatment at a temperature of 210 , 230 , and 250°C (Table 1).

At 210°C for 5 and 15 minutes, no formation of the crystalline phase is observed. Silver nanoparticles begin to form after 30 minutes after the start of heating. Increasing the reaction time from 30 to 90 minutes leads to a change of the degree of crystallinity from 11.5 to 38.9% , while the average sizes of silver nanoparticles increase from 46.2 to 80.1 nm . After 90 minutes, the degree of crystallinity reaches 38.9% , which is 15.4% more than the initial content of silver in the ionic state. Since the degree of crystallinity is due to the phase of the metal and the mass loss of the nanocomposite is

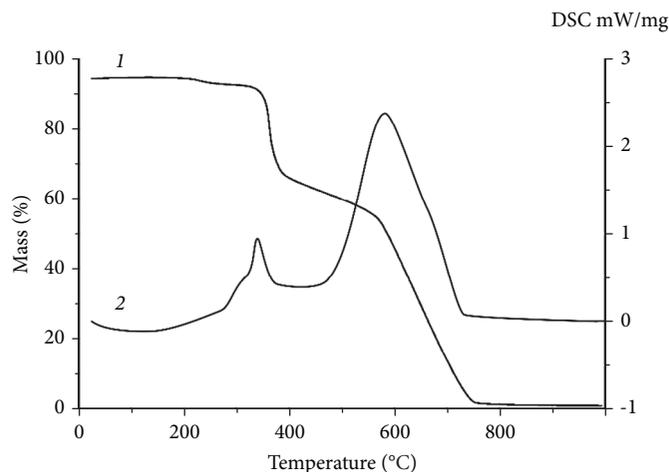


FIGURE 3: Thermogravimetric (1) and DSC (2) curves of 1-vinyl-1,2,4-triazole and acrylonitrile copolymer.

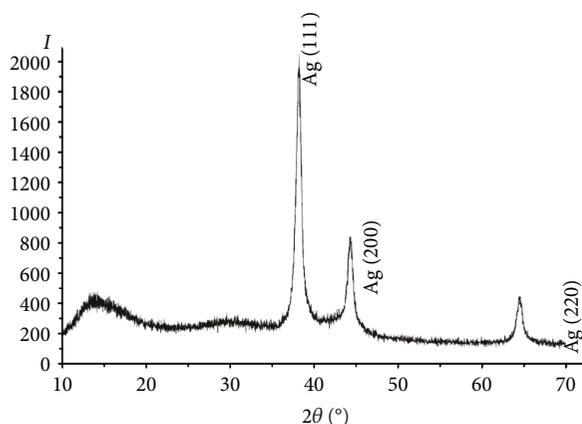


FIGURE 4: X-ray diffraction pattern of the nanocomposite with silver nanoparticles (8% silver content) based on 1-vinyl-1,2,4-triazole and acrylonitrile copolymer.

provided only by the polymer component as a result of the temperature treatment, it can be stated that at a given time, the reduction of the ionic silver to the metal state occurs.

At 230°C, a crystalline phase appears after 15 minutes. Dimensions of silver nanoparticles increase from 55.1 to 75.6 nm at 15 and 30 minutes, respectively. At 250°C, the crystalline phase appears even faster after just 5 minutes. Increasing the degree of crystallinity from 46 to 73% and the average size of silver nanoparticles from 90.0 to 125.6 nm is observed with an increase in duration from 5 to 30 minutes.

With the increase of the synthesis temperature of nanocomposites from 210 to 250°C at heating time 30 min, the dimensions of the crystalline phase increase from 46.2 to 125 Å.

Thus, an increased duration of the reaction at all investigated temperatures leads to an increase in the degree of crystallinity of nanocomposites and the formation of a crystalline phase of silver nanoparticles with large average dimensions. Analysis of diffractograms indicates structural changes in the polymer matrix with an increased temperature from 210°C to 250°C with a heating time of 15 minutes; the intensity

TABLE 1: Conditions of the synthesis of nanocomposites with 23.5% silver at a temperature of 210, 230, and 250°C.

No.	Time (min)	Crystalline phase	Degree of crystallinity (%)	The average size of crystallites (Å)	Weight loss (%)
210°C					
1	5	—	—	—	—
2	15	—	—	—	—
3	30	Ag	11.5	46.2	2.7
4	45	Ag	16.3	58.4	3.6
5	60	Ag	23.2	68.9	5.2
6	90	Ag	38.9	80.1	14.7
230°C					
7	5	—	—	—	—
8	15	Ag	33.9	55.1	10.2
9	30	Ag	58.0	75.6	34.3
250°C					
10	2	—	—	—	—
11	5	Ag	46.0	90.0	22.1
12	15	Ag	63.8	114.8	40.7
13	30	Ag	73.0	125.6	48.8

of the amorphous halo organic component in the range 10 to 30 θ gradually decreases and is practically not observed at 250°C, which is consistent with an increase in the degree of crystallinity to 63.8% (Figure 5).

The completion of the formation of the metallic phase of silver nanoparticles is accompanied by a decrease in the proportion of the polymer component to various degrees: at 210°C, the loss of the organic component is 14.7%, at 230°C—34.3%, and at 250°C—already 48.8%. This behavior is associated with a greater thermooxidative degradation of the BT-AN copolymer at higher temperatures. Moreover, the forming silver nanoparticles probably catalyze the process of thermooxidative degradation, reducing the activation energy of destruction and oxidation of the polymer matrix.

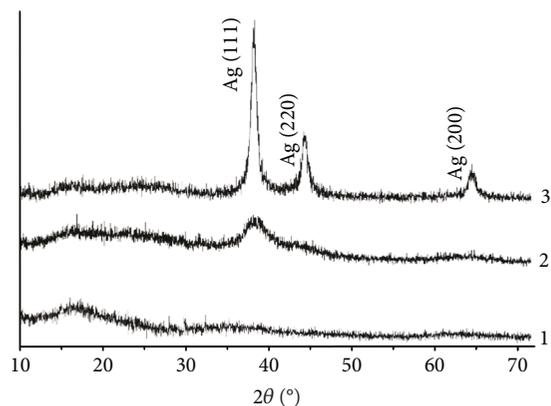


FIGURE 5: X-ray diffraction patterns of the nanocomposites with silver nanoparticles (23.5% silver content, heating time: 15 min) based on 1-vinyl-1,2,4-triazole and acrylonitrile copolymer at (1) 210°C, (2) 230°C, and (3) 250°C.

According to X-ray phase analysis, the average size of the crystalline phase of silver nanoparticles depends significantly on the metal content. Carrying out the reaction for 60 minutes at 210°C for nanocomposites with a silver content of 8 to 23.5 wt% leads to the formation of a crystalline phase with average sizes from 17.2 to 68.9 nm, respectively.

Nanocomposite with the smallest silver content (8% by weight) is characterized by an average size of 17.2 nm (Figure 3). With increasing silver content up to 16.1%, nanocomposites with dimensions of 43.8 nm are formed; with a silver content of 23.5%, the dimensions become already 68.9 nm. Probably, this dependence is a consequence of the fact that a larger number of nanoparticles are formed with increasing silver content, which are less effectively incorporated into the macromolecular matrix.

Thus, an increase in the metal content with respect to the copolymer leads to a limitation of the polymer matrix's ability to stabilize a relatively large number of nanoparticles formed, which inevitably is accompanied by coagulation processes and leads to the formation of larger nanoparticles.

The synthesized nanocomposites are paramagnetic and characterized by a narrow symmetric EPR signal with the concentration of unpaired electrons 10^{20} spin/g, g-factor 2.0050, and line width 5-6 Gs. Character and parameters of the signal confirm the formation of zero-valent metal silver clusters in a matrix of VT-AN copolymer (Figure 6(a)).

The EPR signals of a complex of VT-AN copolymer with AgNO_3 are different ($g_{\parallel} = 2.2623$ and $g_{\perp} = 2.0762$) that testify their sophisticated nature [19] with electronic configuration $4d^9$ for silver (Figure 6(b)). Formation of silver-containing nanocomposites, namely, the process of the nanoparticle generation and growth, has been monitored directly in the resonator of the EPR spectrometer. During 1 h, a gradual lowering of the signal intensity for the polymeric complex and increasing of the narrow singlet intensity for the nanocomposite (up to complete disappearance of the complex broad signal [20]) were observed. This indicates the formation of zero-valent silver nanoparticles (1-30 nm in size) in the polymeric matrix [21, 22].

According to the SEM data, the initial poly(VT-co-AN) has loose volume surface structure (Figure 7(a)).

The surface morphology of the metal-containing nanocomposites is essentially different. It shows a developed porous structure, resembling a sponge with numerous channels, with a diameter in most cases of 1-4 μm (Figure 7(b)). This can be very important for the application of the synthesized nanocomposites as the catalysts ensuring the reagent transport.

The obtained nanocomposites are thermally stable (up to 270-320°C), depending on the content of silver. The increase of the silver content in the polymeric nanocomposite leads to the decrease of the thermal stability threshold. The character of the nanocomposites thermal decomposition differs from the destruction of the VT-AN initial copolymer (Figure 8).

It is found that at 90-150°C physically adsorbed water (weight loss from the sample is 2.1%) is released from the sample volume without its destruction and this is accompanied by an endothermic effect in the differential scanning calorimetry curve. This is evidenced from a signal of the quadrupole mass spectrometer relative to the corresponding mass number ($m/z = 18$).

The first stage of thermal destruction of the polymeric component is observed at 290-430°C as evidenced from the presence of one exothermic effect (weight loss from the sample is 27.7%). According to MS data related to the released gases, the main products are low molecular compounds with $m/z = 17, 18, 30, 44, 46$, which correspond to NH_3 , H_2O , NO , CO_2 , and NO_2 . The nitrile and triazole fragments of the polymer ($m/z = 26, 27, 67, 68$) are not observed that indicates their rapid oxidation to the low molecular compounds. The stage of thermal destruction of the copolymer is observed at 450-760°C, while those of the nanocomposite is manifested at 430-670°C (loss of the sample mass is 58.5%). This is evidenced from the presence of two overlapping exothermic effects at 533°C and 589°C and corresponding to burning of the carbon skeleton, to yield mainly CO_2 (mass number 44).

Thus, the observed changes in thermal destruction of silver-containing nanocomposites (comparison with the VT-AN initial copolymer) are probably caused by catalytic properties of the metal nanoparticles which, like in the case of other polymeric nanocomposites, are manifested in the decrease of thermodestruction activation energy and in the oxidation of the polymeric matrix.

This approach to the synthesis of polymeric nanocomposites via thermal treatment of the polymeric complex leads to the formation of the metal phase in nanosized state without the application of an additional reducing agent. This, certainly, facilitates both the synthesis (no reducing agents are required) and purification of the polymeric silver-containing nanocomposites. This favorably distinguishes this approach from other widely known methods for chemical reduction using various reducing agents of ionic metal (sodium borohydride, glucose, formaldehyde, etc.). The application of such reducing agents, on one hand, can negatively affect the purity of the nanoparticles (precipitation of elemental boron on a surface of the nanoparticles) and, on the other hand, requires careful purification of the polymeric nanocomposites.

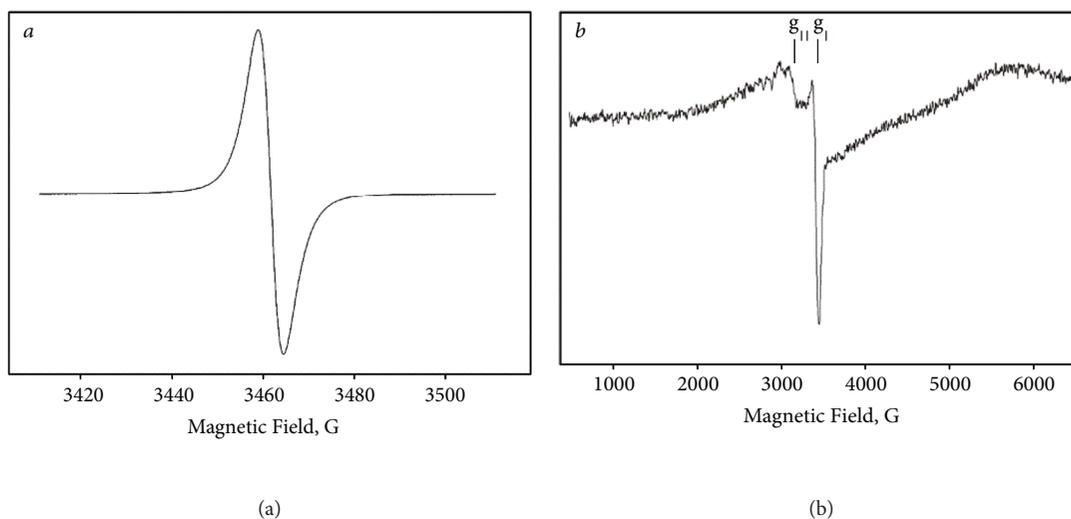


FIGURE 6: EPR spectra of complex of 1-vinyl-1,2,4-triazole and acrylonitrile copolymer with AgNO_3 (a) and nanocomposite with silver nanoparticles based on it (8% silver content) (b).

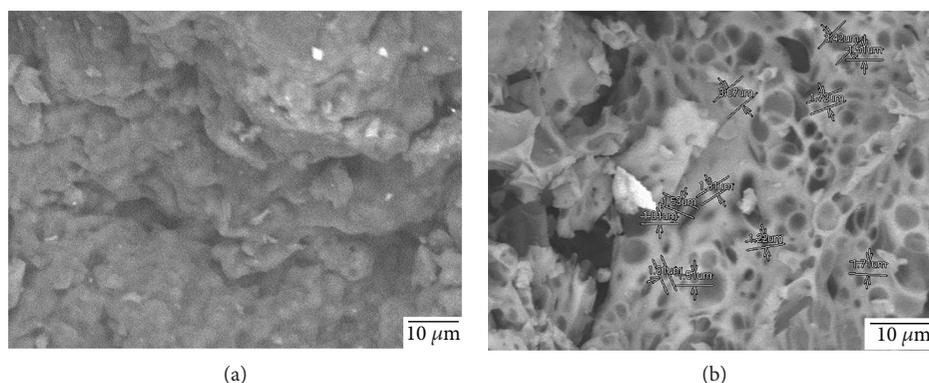


FIGURE 7: SEM images of 1-vinyl-1,2,4-triazole and acrylonitrile copolymer (a) and nanocomposite with silver nanoparticles based on it (8% silver content) (b).

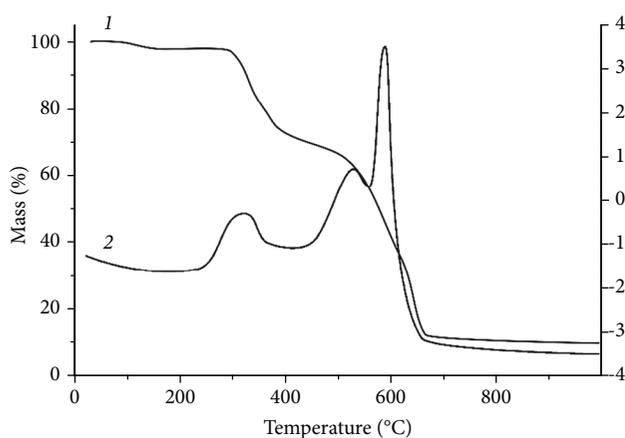


FIGURE 8: Thermogravimetric (1) and DSC (2) curves of 1-vinyl-1,2,4-triazole and acrylonitrile nanocomposite with silver nanoparticles (8% silver content).

Owing to high thermal stability and the developed porous structure, the synthesized polymeric silver-containing nanocomposites represent promising materials as catalysts of

different chemical processes, ensuring the wide temperature range of application and effective transport of reagents.

4. Conclusion

New functional insoluble silver-containing nanocomposites based on 1-vinyl-1,2,4-triazole and acrylonitrile copolymer were synthesized and characterized. The obtained nanocomposites possess the developed porous structure and high thermal stability (up to 270-320°C). According to the X-ray diffraction analysis, the average size of the silver nanoparticles is 17-125 nm. The synthesized nanocomposites display paramagnetic properties and are characterized by a narrow symmetric EPR signal with the concentration of unpaired electrons of 10^{20} spin/g. The synthesized nanocomposites represent promising compounds for the development of advanced catalytic materials.

Data Availability

The data used to support the findings of this study are included within the article.

Additional Points

The main results were obtained using the equipment of Baikal Analytical Center for collective use of SB RAS. The research was completed in the framework of the scientific project V.44.5.4 of the program of fundamental research of SB RAS.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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