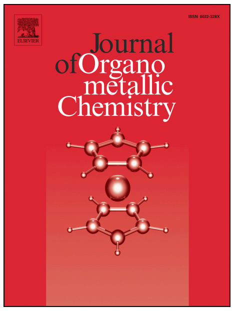

Water-soluble stable polymer nanocomposites with AuNPs based on the functional poly(1-vinyl-1,2,4-triazole-co-N-vinylpyrrolidone)

A.S. Pozdnyakov, A.A. Ivanova, A.I. Emel'yanov, Yu I. Bolgova, O.M. Trofimova, G.F. Prozorova

PII: S0022-328X(20)30254-0

DOI: https://doi.org/10.1016/j.jorganchem.2020.121352

Reference: JOM 121352

To appear in: *Journal of Organometallic Chemistry*

Received Date: 31 January 2020

Revised Date: 23 May 2020

Accepted Date: 23 May 2020

Please cite this article as: A.S. Pozdnyakov, A.A. Ivanova, A.I. Emel'yanov, Y.I. Bolgova, O.M. Trofimova, G.F. Prozorova, Water-soluble stable polymer nanocomposites with AuNPs based on the functional poly(1-vinyl-1,2,4-triazole-co-N-vinylpyrrolidone), *Journal of Organometallic Chemistry* (2020), doi: https://doi.org/10.1016/j.jorganchem.2020.121352.

Water-soluble stable polymer nanocomposites with AuNPs based on the functional poly(1-vinyl-1,2,4-triazole-co-N-vinylpyrrolidone)

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Abstract

New water-soluble polymer nanocomposites with gold nanoparticles (AuNPs) were synthesized using functional copolymer of 1-vinyl-1,2,4-triazole with N-vinylpyrrolidone (poly(VT-co-VP)) as a stabilizing matrix. The polymer AuNPs nanocomposites were studied by transmission electron microscopy, scanning electron microscopy, ultraviolet-visible spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, atomic absorption and thermogravimetric analysis. The gold content in nanocomposites ranged from 4.4 to 25.7%wt (the gold content depends on the ratio of poly(VT-co-VP):Au (III)). The obtained polymer nanocomposites consist of isolated gold nanoparticles with a diameter of 1 to 12 nm having a predominately spherical shape, which are uniformly distributed throughout the bulk of the polymer matrix. Nanocomposites contain AuNPs of various sizes, which is determined by the ability of the polymer matrix to stabilize the different metal contents. The resulting AuNPs nanocomposites are promising materials for the design of novel hydrophilic antiseptics and antimicrobial components for medical purposes.

Keywords: 1-vinyl-1,2,4-triazole, N-vinylpyrrolidone, polymer nanocomposites, gold nanoparticles.

1. Introduction

In the last decade, the research in new polymer composite materials, including hybrid nanocomposites with nanoparticles of different metals are gathering momentum. For example, gold nanoparticles are of interest due to their unique optical, electronic, catalytic [1,2] and biological properties [3–7], applicable in various fields of science.

Since the last century, gold and its compounds have been employed in medicine for the treatment of rheumatic and infectious diseases, including tuberculosis [8]. The development of modern technologies has allowed to obtain gold in a nanosized state, thereby increasing its activity in comparison with block metal. Therefore, gold was used in significantly lower concentrations, while its properties were preserved. This enables to expand the application scope of gold nanoparticles in the development of new biosensors and biophotonics [9–11] as well as antibacterial [12,13] and anticancer drugs [14].

The ability of nanoparticles to penetrate into a cell strongly depends on their size and shape [15]. The main problem is that gold nanoparticles are very unstable and prone to aggregation [16]. Therefore, search for routes to stabilization of these particles remains a challenge. Various high molecular compounds both natural (chitosan, cellulose, arabinogalactan, etc.) [17,18] and synthetic (polyvinylpyrrolidone, polyacrylamide, polyvinyl

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alcohol, etc.) origin [19–22] are used as effective stabilizers. Application of polymers as a stabilizing matrix not only contributes to the stabilization of nanoparticles giving them the necessary size and shape [23,24], but also to synthesize new compounds that exhibit synergism of the unique properties of polymers and metal nanoparticles.

Polymers of N-vinylpyrrolidone (VP) find widespread application as stabilizing matrices of metal nanoparticles [25,26]. Also, N-vinylpyrrolidone is widely used as a comonomer of various vinyl compounds, allowing the preparation of polymer compounds with different functionality. 1-Vinyl-1,2,4-triazole (VT) is the most interesting comonomer, since its polymers possess a number of valuable properties such as thermal stability and resistance to aggressive media, ability of complex formation and quaternization, biocompatibility and non-toxicity, etc [27–29].

Previously, we found that hydrophilic copolymers of 1-vinyl-1,2,4-triazole with N-vinylpyrrolidone (LD_{50} >5000 mg/kg) are effective non-toxic platform for stabilizing silver [30,31] and copper [32] nanoparticles. New polymer nanocomposites synthesized from functional poly(VT-co-VP) can extend the range of nontoxic hydrophilic polymer materials that opens up new prospects for their use in medicine.

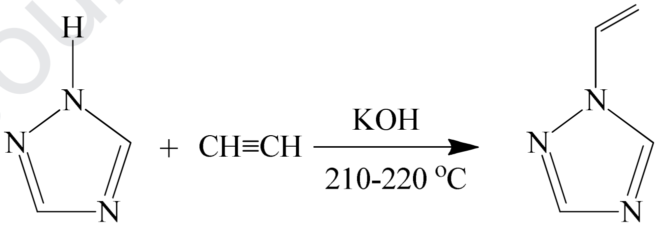
In the present work, we report on the synthesis and characterization of new water-soluble polymer nanocomposites based on non-toxic copolymer of 1-vinyl-1,2,4-triazole with N-vinylpyrrolidone with different AuNPs content.

Materials and Methods

2.1. Materials

The initial 1-vinyl-1,2,4-triazole (VT) (bp 43 °C/3 mmHg, n_D^{20} 1.5100) was synthesized by direct vinylation of 1,2,4-triazole with acetylene in dioxane at a pressure of 14 atm.

The reaction was carried out for 4 hours at a temperature of 220 °C in the presence of a catalyst - potassium hydroxide. The yield of VT was 78%.



N-Vinylpyrrolidone (99%, Sigma-Aldrich) (flash point 95 °C, n_D^{20} 1.512) was used as comonomer for the synthesis of functional copolymers. $HAuCl_4$ (99.9%, Sigma-Aldrich) and α,α′-azobisisobutyronitrile (AIBN) (99%, Aldrich) were used without any treatment as a precursor of nanoparticles and radical initiator, respectively. Hydrazine hydrate (99.99%, Sigma-Aldrich) was used as the reducing agent. Dimethylformamide (DMF), acetone and ethanol were distilled and purified according to the known procedures.

2.2. Synthesis of 1-vinyl-1,2,4-triazole and Acrylonitrile Copolymers (poly(VT-co-VP))

Poly(VT-co-VP) was synthesized by radical copolymerization of 1-vinyl-1,2,4-triazole and N-vinylpyrrolidone in DMF under the action of AIBN as initiator at 60 °C in argon atmosphere. 1-Vinyl-1,2,4-triazole (1.9 g, 20.0 mmol), N-vinylpyrrolidone (2.2 g, 20.0 mmol), DMF (1 mL), and AIBN ($2.0 \cdot 10^{-2}$ mol/L) were placed in ampoule. Then the mixture was stirred and kept in a thermostat at 60 °C for 1.5 h until the transparent block forms (completion of polymerization). The reaction mixture was dissolved in DMF, precipitated into acetone, and dried in vacuo over P_2O_5 at 50 °C to a constant weight. Then the product was filtered and dissolved in water. Then the reaction mixture purified by dialyzed for 48 h through a cellulose membrane with a pore size of 5 kDa (Cellu Sep H1, MFPI, Seguin, USA), and freeze-dried to give copolymer as a white powder. The product yield was above than 84% and the polymer was soluble in water and dipolar organic solvents (DMF and DMSO). Further, the obtained copolymer was used for the subsequent synthesis of the metal polymer nanocomposites.

2.3. Synthesis of Nanocomposite based on poly(VT-co-VP) with gold nanoparticles

Poly(VT-co-VP) (1.0 g, 9.6 mmol) in water (10 mL) was added to aqueous solution (10 mL) containing $HAuCl_4$ (0.28–11.1 g, 0.4–16.5 mmol). The reaction mixture was stirred intensively for 30 min at room temperature. Then, aqueous solution containing N_2H_4 (0.05–1.85 g, 0.2–6.0 mmol) was added dropwise over 5 min, and the mixture was stirred further for 6 h at room temperature. The resulting solution was precipitated into ethanol. The product was then filtered from ethanol, purified by dialysis against water through a cellulose membrane (Cellu Sep H1, MFPI, Seguin, USA), and freeze-dried to obtain nanocomposites as a dark-brown powder. The product yield was 79-85%. The resulting nanocomposite is soluble in water and dipolar organic solvents (DMF, DMSO and DMAA). The gold content in the nanocomposites was from 4.4% to 25.7%. The content of gold depends on the initial molar ratio of stabilizing copolymer and Au(III).

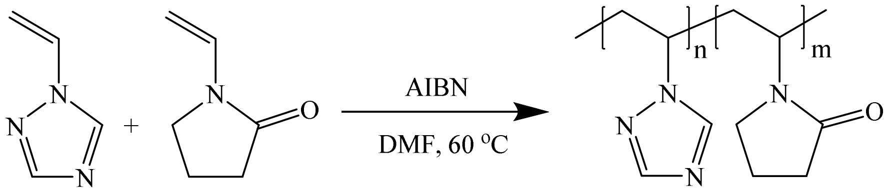
2.4. Characterization

The composition and structure of the synthesized copolymers are confirmed by elemental analysis, IR, NMR spectroscopy. Elemental analysis was performed with a Thermo Scientific Flash 2000 CHNS-Analyzer. FTIR spectra were recorded on a Vertex 70 FT-IR in KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (^1H, 400.13 MHz; ^{13}C, 100.62 MHz) in DMSO-d_6. The molecular weight of the copolymer was determined by gel permeation chromatography at 50 °C using Shimadzu LC-20 Prominence system fitted with a differential refractive index detector Shimadzu RID-20A and column Agilent PolyPore 7.5 x 300 mm (PL1113-6500). N,N-Dimethylformamide solution was used as the eluent at the flow rate of 1 mL/min. Dissolution of samples was performed at 50 °C for 24 h with stirring. Calibration was carried out using a series of polystyrene standards Polystyrene High EasiVials (PL2010-0201), consisting of 12 samples with molecular weights from 162 to 6570000 g/mol. Microphotographs were obtained on scanning electron microscope (TM 3000, HITACHI). The gold content in the studied nanocomposites was estimated by atomic absorption analysis using a Shimadzu AA-6200. X-ray diffraction patterns (XRDs) were obtained on a powder diffractometer (D8 Advance, Bruker Corporation, Cu radiation). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using STA 449 Jupiter (Netzsch, Germany) in air atmosphere at heating rate of 5 ºC per min, the weight of the samples was 7 mg. Microphotographs were obtained using a transmission electron microscope (Leo 906E, Zeiss, Germany). The water solution with 0.1 mg/mL nanocomposite concentration was used to determine the hydrodynamic particle radius of the synthesized samples by means of the dynamic light scattering (DLS) and electrophoretic light scattering with phase analysis (PALS) methods, respectively, using a Zetasiser Nano-ZS photon particle analyser (Malvern Instruments, UK). The measurements were carried out in thermostated cuvettes with operating temperature of 25 ºC and angle of detection of scattered light equal to 173º.

Results and Discussion

3.1. Copolymer of 1-vinyl-1,2,4-triazole and N-vinylpyrrolidone

The copolymerization reaction proceeds in accordance with Scheme1.



Scheme 1. Synthesis of poly(VT-co-VP).

The copolymer obtained (white powder) is well soluble in water and dipolar organic solvents. According to NMR data content of the triazole and pyrrolidone fragments in the copolymer was 49 and 51 mol%, respectively. The M_n and M_w of the polymer were measured to be 29541 and 57119 Da, respectively. The polydispersity index (M_w/M_n) of the copolymer was 1.9 (Fig. 1).

The ^{1}H NMR spectra of the obtained copolymers does not contain proton signals of the *N*-vinyl group, but show the signals of the methylene group protons in the region of δ_H 2.2–1.1 ppm and the signals of the polymer chain methine protons at δ_H 4.3–3.4 ppm. The broaden signals of the triazole ring protons are observed at δ_H 7.9–7.3 ppm, while the lactam ring protons resonate in the region of δ_H 3.2–2.6 ppm.

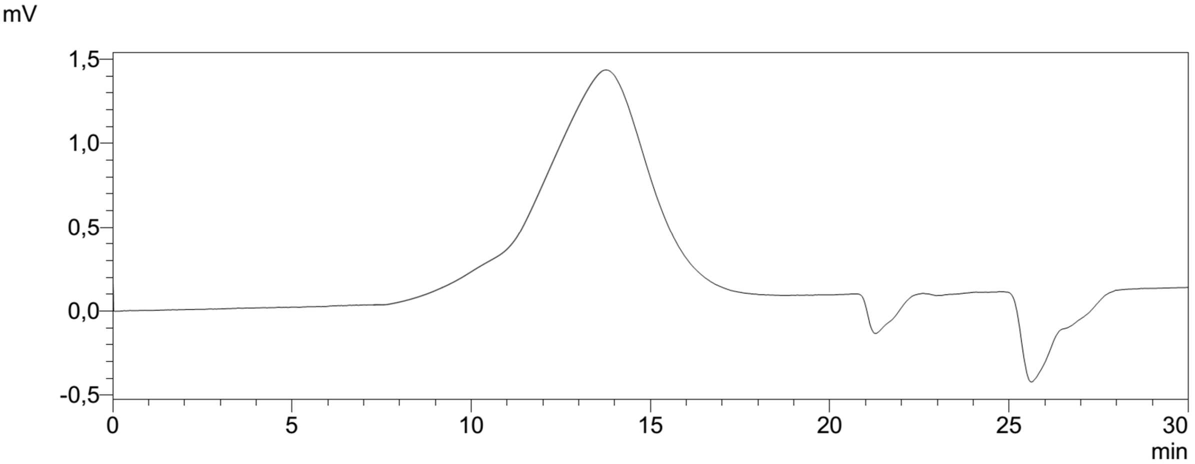


Fig. 1. GPC traces of poly(VT-co-VP).

3.2. Nanocomposites with gold nanoparticles

Nanocomposites with gold nanoparticles were synthesized by chemical reduction of gold(III) ions. The reaction was carried out in two main stages, the molar ratio of poly(VT-co-VP):Au(III) ranging from 40:1 to 5:1 (Table 1). In the first stage, a metal-polymer complex was obtained as a finely dispersed yellow residue by mixing the aqueous solutions of copolymer and hydrogen tetrachloroaurate (III) ($HAuCl_4$). The transparent solutions of the copolymers turn yellow after addition acidic solution to them and the viscosity of the solutions increases significantly. In the second stage, the metal ionic form was reduced to metallic state using hydrazine hydrate, with a gradual change of the solution color to dark-red. The reaction mixture was stirred for 6 hours. The finely dispersed suspension of the polymer complex gradually disappears and a colored solution of the polymer nanocomposite was formed. It should be noted that the coordination interaction of gold ions with functional triazole and lactam groups of the copolymer macromolecules creates a favorable microenvironment that contributes to the effective stabilization of nanoparticles in the early stages of their formation.

Table 1

The synthesis conditions and characteristics of the nanocomposites with AuNPs.

Nanocomposite	Copolymer:Au(III), mol	Au content, %wt	Yield, %	λ_{max}, nm	Nanoparticle size, nm	Hydrodynamic radius, nm
1	40:1	4.4	83	511	1–6	135.9
2	20:1	8.3	81	522	1–9	210.2
3	10:1	16.2	83	534	2–12	358.3
4	5:1	25.7	79	554	2–20	482.8

Elemental analysis and atomic absorption spectroscopy showed that the gold content in the nanocomposites ranged from 4.4% to 25.7% (Table 1). The gold content depends on the initial molar ratio of stabilizing copolymer and Au(III). Increase in the gold content relative to copolymer leads to a decrease in the stabilizing ability of the polymer matrix relative to a large number of formed nanoparticles, which inevitably leads to a partial coagulation and the formation of nanoparticles with a large size. In addition, increase in the gold content to higher than 16–17 wt.% leads to a partial loss of solubility of nanocomposite (for the molar ratio copolymer: gold equal to 5:1).

Analysis of the changes in the absorption bands in IR spectra (Fig. 2) on going from the initial poly(VT-co-VP) to the polymer complexes with gold ions and nanocomposites with gold nanoparticles shows that the bands at 1658 (C=O), 1503 (C=N), 1274 (N=N), assigned the vibration frequencies of the triazole and lactam cycles, are shifted by 3-13 cm^{-1}. This indicates the coordination of the copolymer functional groups with both the ionic form of gold and with metal nanoparticles [33–35].

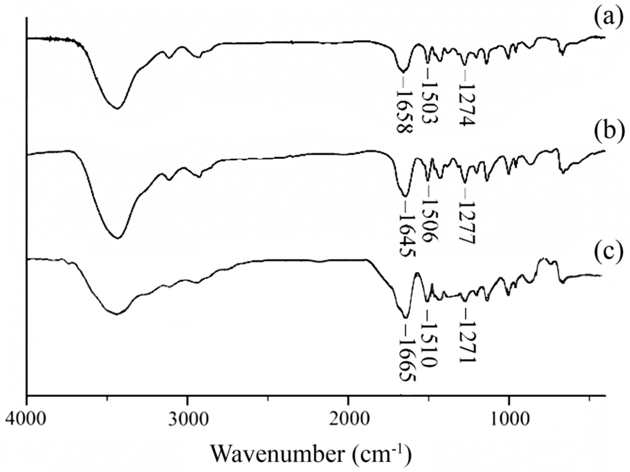


Fig. 2. FTIR-spectra of poly(VT-co-VP) (a), polymer complex with gold ions (b) and nanocomposites №2 with AuNPs (c)

The optical absorption spectrum of nanocomposite in aqueous solution, unlike that of the initial poly(VT-co-VP) and $HAuCl_4$ aqueous solutions, shows a characteristic plasmon resonance absorption band of conductivity electrons from the metallic AuNPs in the region of

511–554 nm (Fig. 3).

The stabilizing matrix contains functional triazole and lactam cycles capable of forming coordination bonds that ensures effective stabilization of gold nanoparticles, which prevents their aggregation for a long time. The aqueous solutions of the nanocomposites were centrifuged at 10,000 rpm for 15 min. A small amount of bulky residue was formed at the bottom of the tube, which was completely dissolved after shaking. The bands of the plasmon absorption of gold nanoparticles were identical before and after centrifugation, which evidences a high stabilizing ability of the polymer matrix.

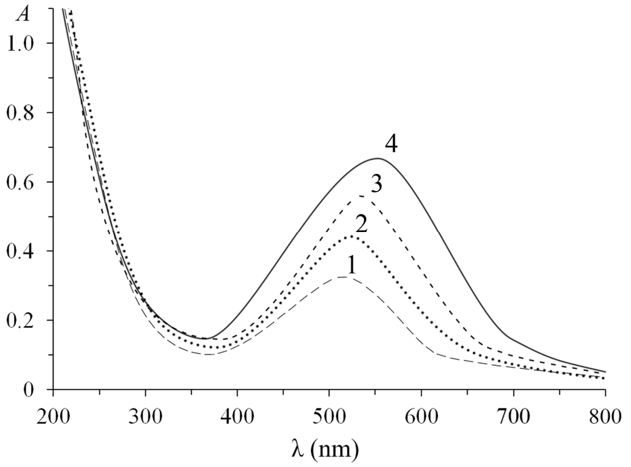


Fig. 3. Electronic absorption spectra of aqueous solutions of polymer nanocomposites with AuNPs. The number of the curve corresponds to the polymer nanocomposite number (Table 1).

X-ray diffraction patterns of nanocomposites clearly show the amorphous halo of the polymer component and intense reflections of metallic gold nanoparticles, identified by comparing the values of interplanar distances and relative intensities with the reference ones (Fig. 4). The crystalline phase is a zero-valent gold, the crystallite size is 105–115 Å, the degree of crystallinity is 16%. The pattern of the sample matched well with the standard patterns of gold (JCPDS file No. 01-1174). All of the peaks of the patterns of the samples can be readily indexed to face-centered cubic gold. No peaks from other phases were detected, indicating high purity of the products.

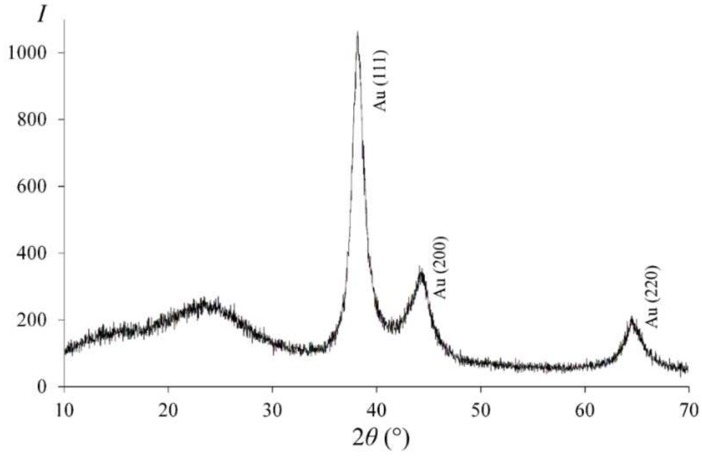
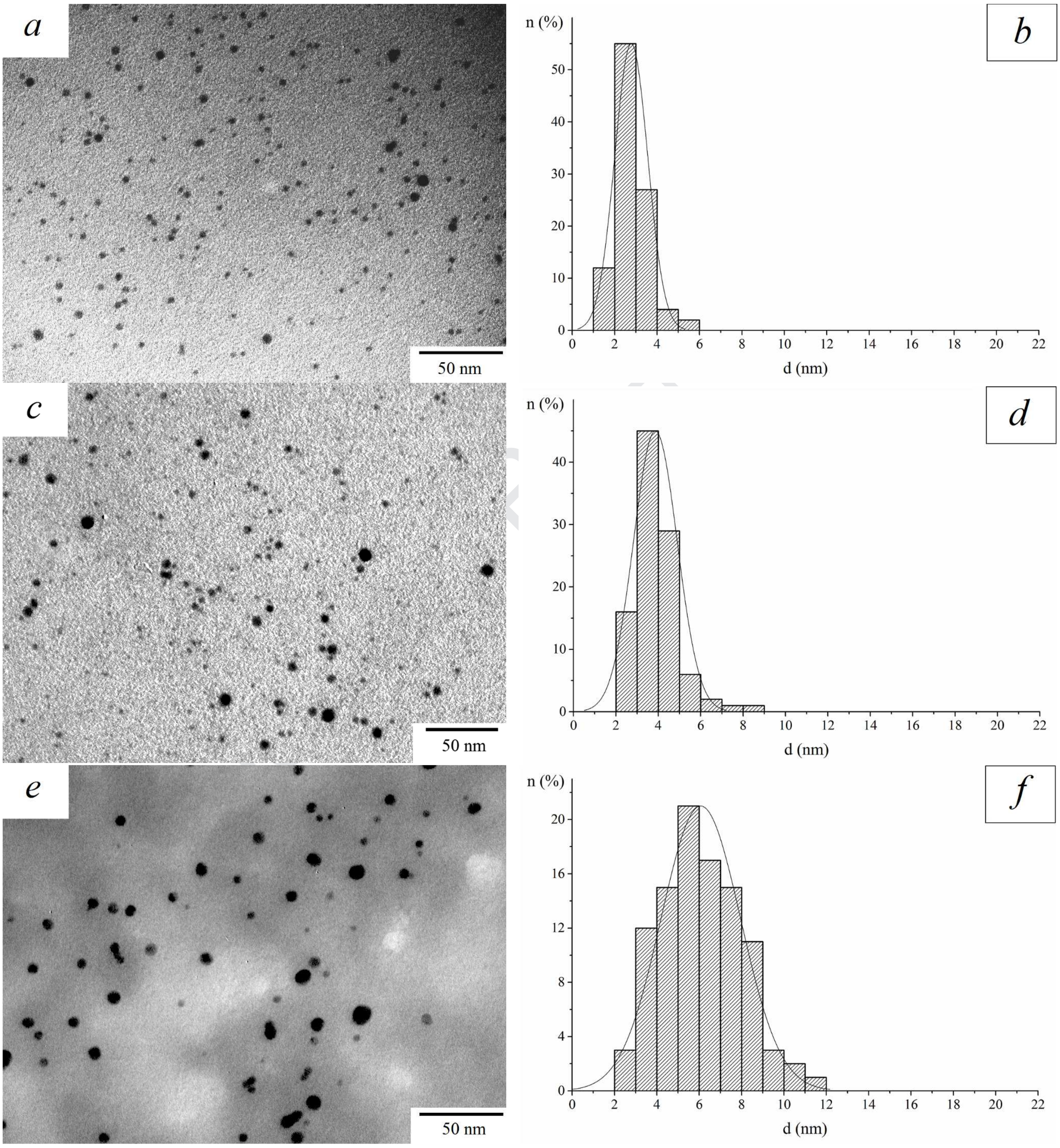


Fig. 4. X-ray diffraction pattern of the nanocomposite with AuNPs based on poly(VT-co-VP) (Table 1 № 2).

According to transmission electron microscopy, nanoparticles size data and their distribution in the copolymer matrix were obtained (Fig. 5). The synthesized polymer nanocomposites consist of isolated electron-contrast gold nanoparticles of predominantly spherical shape, which are uniformly distributed in the polymer matrix. Size dispersion of the nanoparticles depends on gold content in the nanocomposites. A decrease in the gold content leads to the formation of a nanocomposite with the smallest distribution of nanoparticles in sizes. In this case, the narrowest distribution of the nanoparticles with predominant sizes up to 6 nm is observed (Fig. 5b). Increase in the gold content relative to the copolymer limits ability of the polymer matrix to stabilize large amounts of nanoparticles which is inevitably accompanied by coagulation processes to produce larger nanoparticles.



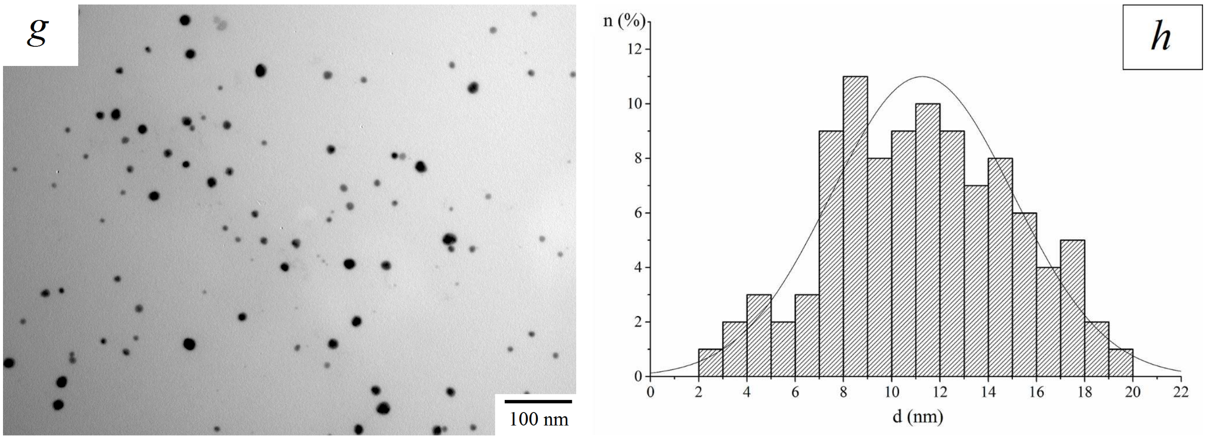


Fig. 5. Electron microphotographs (*a*, *c*, *e*, *g*) and diagrams of AuNPs size distribution (*b*, *d*, *f*, *h*) of polymer nanocomposites 1 (*a*, *b*), 2 (*c*, *d*), 3 (*e*, *f*) and 4 (*g*, *h*).

The nanoparticle size data was used to calculate weight average (D_w), number average (D_n) nanoparticle diameters and polydispersity index (PDI) (Table 2). The values were calculated using the following equations [36]:

$$D_n = \frac{\sum_i n_i D_i}{\sum_i n_i}$$

$$D_n = \frac{\sum_i n_i D_i^4}{\sum_i n_i D_i^3}$$

$$PDI = D_w / D_n$$

where n_i is the number of particles of size D_i.

The results show that gold nanoparticles have a narrow dispersion in size. The narrowest polydispersity (PDI = 1.28) is observed for nanocomposite **1**. The sizes of nanoparticles vary from 1 to 6 nm (Fig. 5b). With increase in the gold content in the stabilizing matrix, the polydispersity increases to 1.31.

Table 2

Average sizes and polydispersity of nanoparticles in nanocomposites calculated by transmission electron microscopy.

Nanocomposite	D_n, nm	D_w, nm	PDI
1	2.93	3.75	1.279
2	3.49	4.47	1.281
3	6.10	7.90	1.295
4	10.95	14.39	1.314

The dynamic light scattering method was used to measure the hydrodynamic radius of macroballs (R_h) of synthesized nanocomposites and the initial copolymer in aqueous solutions (Fig. 6).

The histograms are characterized by a monomodal particle size distribution; with increase in the gold content in the nanocomposite, the average R_h value increases. It should be noted that the hydrodynamic radius of gold nanocomposite particles in a coil of copolymer macromolecules significantly increases by more than 4–15 times in comparison with the initial copolymer (R_h = 31.5 nm). This can be explained by the formation of coordinated complex particles under the action of multiple cooperative forces of intermolecular interaction, as a result of which large macromolecular tangles are formed.

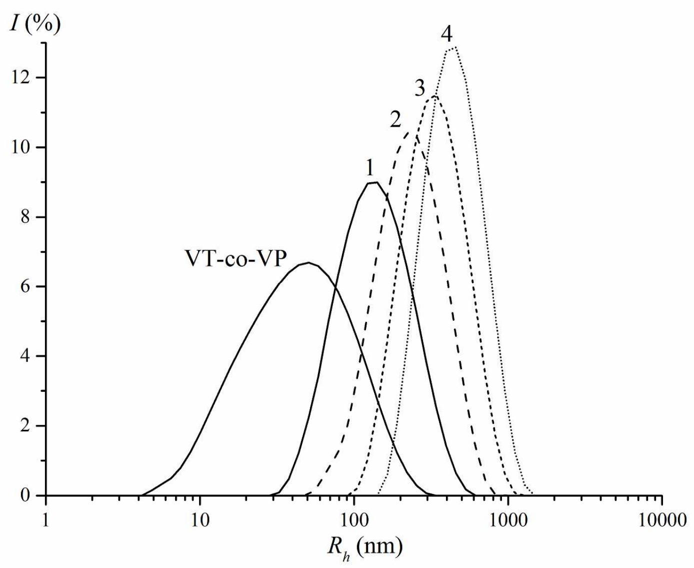


Fig. 6. Histogram of the distribution over the hydrodynamic radii R_h of the scattering particles for the nanocomposite and the initial copolymer (table 1).

The presence of poly(VT-co-VP) in the reaction mixture promotes coordinated interaction (at the reduction stage) between AuNPs and coordination rings (triazole and lactam) in the copolymer. This prevents their further agglomeration and ensures their homogeneous distribution throughout the copolymer matrix. The aqueous solutions containing AuNPs nanocomposite were left in the air for a long time at room temperature, and no signs of sedimentation were observed even after 4 months of storage. This indicates that the AuNPs synthesized in this polymer matrix are stable and the hydrophilic poly(VT-co-VP) has highly stabilizing ability.

The results of thermogravimetric analysis and differential scanning calorimetry show that the initial poly(VT-co-VP) has thermal stability up to 320 °C. The obtained nanocomposites are thermally stable (up to 270-320 °C), depending on the content of gold. The increase of gold content in the polymer nanocomposite leads to the decrease of the thermal stability threshold. The character of the nanocomposites thermal decomposition differs from destruction of the initial copolymer (Fig. 7).

For nanocomposite, it was found that at 60-150 °C physically adsorbed water (weight loss from the sample is 7.2%) is released from the sample volume without its destruction and this is accompanied by endothermic effect in the differential scanning calorimetry curve. This is evidenced from a signal of quadrupole mass spectrometer relative to the corresponding mass number (m/z = 18).

The first and second stages of thermal destruction of the polymer component are observed at 270–405 °C which is confirmed by presence of two exothermic effects (sample weight loss is 44.8%). This is accompanied by abstraction of the triazole and lactam fragment from the macromolecular chain with subsequent oxidation to H_2O, CO_2 and NO_2 that is confirmed by appearance of signals in the mass spectrum at the corresponding mass numbers (18, 44 and 46). At 425–600 °C, sample weight loss reaches 38.7% and intensive exothermic effect at a maximum at 570.1 °C takes place, corresponding to burning of the carbon skeleton, to yield mainly CO_2 (mass number 44). On the differential scanning calorimetry curve, the endothermic effect responsible for melting of metallic gold is detected at 1070.1 °C.

The decreased thermal stability of the nanocomposites is caused by the catalytic peculiarities of AuNPs, which decrease the activation energy of thermal destruction and oxidation of the polymer matrix. The weight loss or difference in decomposition between the copolymer and gold nanocomposite is found to be 7.9% thus indicating the presence of AuNPs (weight loss) in the poly (VT-co-VP).

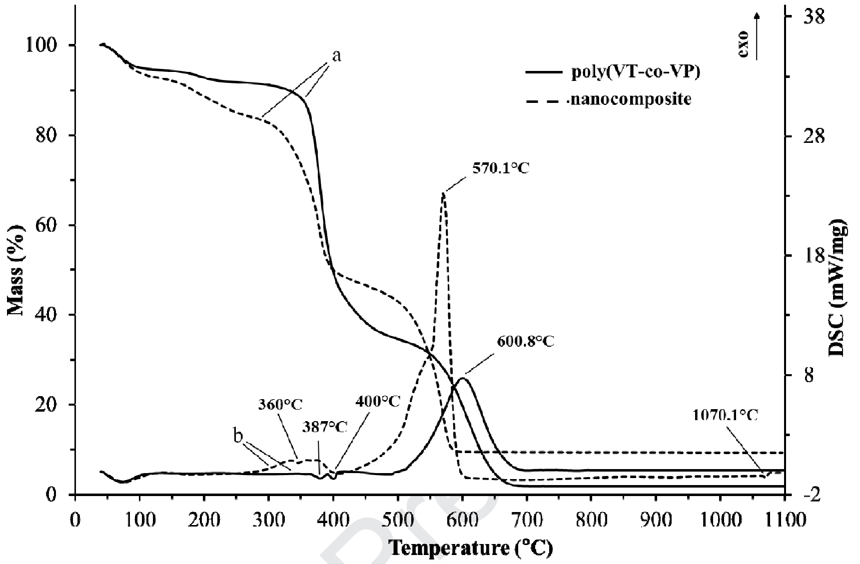


Fig. 7. TGA (a) and DSC (b) curves for the starting poly(VT-co-VP) and nanocomposite with AuNPs (Table 1, nanocomposite № 2).

The SEM images of poly(VT-co-VP)copolymer and nanocomposite with AuNPs confirm their different surface morphology. It has been shown that the initial copolymer has highly porous sponge-like surface with numerous channels of 2–6 μm in diameter (Fig. 8a). In the case of AuNPs nanocomposite, the surface morphology becomes denser, and porous structure is still observed on SEM image (Fig. 8b).

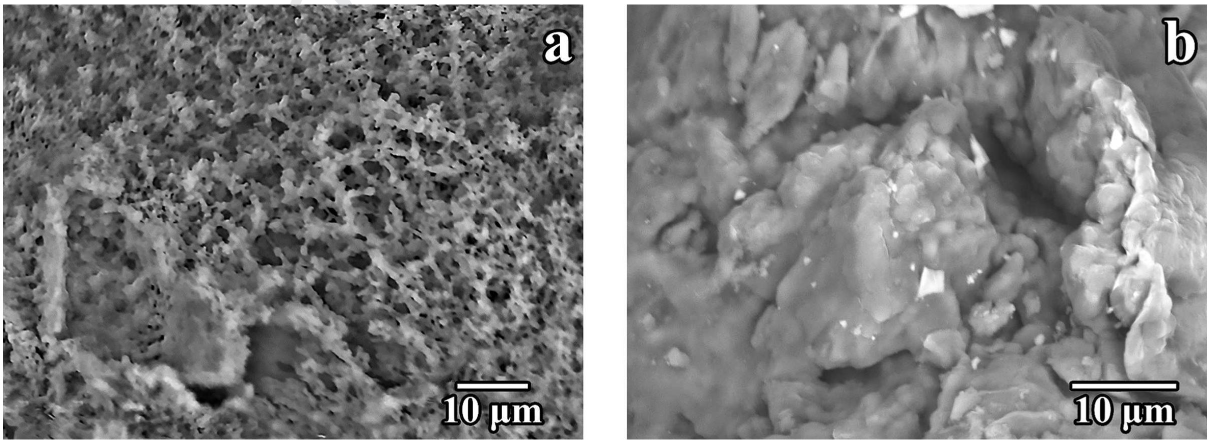


Fig. 8. SEM microphotograph of poly(VT-co-VP) copolymer (*a*) and AuNPs nanocomposite (*b*).

The synthesized nanocomposites exhibit properties of organic high-resistance semiconductors: they possess electrical conductivity of 10^{-9}–10^{-10} S/cm. Electrical conductivity of the synthesized polymer nanocomposites increases on the average by 4–5 orders of magnitude in comparison with the initial copolymer ($4.5 \cdot 10^{-14}$ S/cm), which is probably due to the contribution of individual local currents induced between electroconductive metal nanoparticles closely located in the dielectric polymer matrix.

Conclusions

Novel gold-containing water-soluble stable nanocomposites based on copolymer of 1-vinyl-1,2,4-triazole and N-vinylpyrrolidone was synthesized. The copolymer poly(VT-co-VP) was synthesized by free radical-initiated polymerization in DMFA solution under argon atmosphere. The reduction of gold ions in the presence of copolymer containing triazole and lactam groups, as the stabilizing matrix, leads to effective stabilization of metal gold nanoparticles. The effect of the polymer matrix on size of nanoparticles during their stabilization at gold content from 4.4% to 25.7% is established. The obtained AuNPs nanocomposites are thermally stable up to 270 °C. AuNPs don’t precipitate and don’t change size after storage in aqueous solutions for 4 months. New water-soluble AuNPs nanocomposites in a poly(VT-co-VP) matrix are promising materials for the design of novel nontoxic hydrophilic antiseptics and antimicrobial components for medical purposes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

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

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Nanocomposites based on copolymer of 1-vinyl-1,2,4-triazole and N-vinylpyrrolidone

Nanocomposites contain AuNPs of various sizes.

Gold content up to 25.7%.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: