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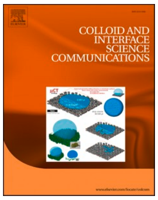

Rapid Communication

# The radiation-induced preparation of ultrasmall gold nanoparticles in Au(III) complexes with units of poly(1-vinyl-1,2,4-triazole) and poly(1-vinyl-1,2,4-triazole) – poly(acrylic acid)

Alexey A. Zharikov [a,*], Rodion A. Vinogradov [a], Elena A. Zezina [a], Alexander S. Pozdnyakov [b], Vladimir I. Feldman [a], Alexandr L. Vasiliev [c], Alexey A. Zezin [a,d]

[a] *Department of Chemistry, Lomonosov Moscow State University, Moscow 119991, Russia*
[b] *Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Favorskogo st., 1, Irkutsk 664033, Russia*
[c] *Moscow Institute of Physics and Technology (National Research University), Dolgoprudny, Moscow Region 141701, Russia*
[d] *Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, Profsoyuznaya st., 70, Moscow 117393, Russia*

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ABSTRACT

Gold nanoparticles (AuNPs) with average sizes of 1.5 nm and 3 nm and narrow size distribution have been prepared in the irradiated aqueous solutions and suspensions of Au(III)-complexes with units of poly(1-vinyl-1,2,4-triazole) (PVT) and poly(1-vinyl-1,2,4-triazole) – poly(acrylic acid) (PAA) respectively. The formation of AuNPs has been studied using UV-VIS spectroscopy and transmission electron microscopy. The effective stabilization of ultrasmall AuNPs is achieved due to the combination of both electrostatic interaction of polymer units and the specific adsorption of functional groups on the nanoparticle surface. The radiation-chemical approach makes it possible to obtain nanoparticles of a controlled size and containing no impurities of chemical reducing agents.

## 1. Introduction

Unique optical, electronic and catalytic properties of gold nanoparticles (AuNPs) are the reason for high attention in AuNPs-based materials [1–3]. Ultrasmall AuNPs ranging in size from one to several nanometers are considered to be of particular interest due to quantum-size effects, their extremely high specific surface area and catalytic ability [1–3]. Over the past three decades, there has been a focus on functional metal polymer nanocomposites combining the remarkable size-dependent properties of a nanodisperse component with benefits, which can be offered by a polymer matrix [4,5]. Such metal polymer hybrids may serve as excellent candidates for the development of advanced biosensor, drug delivery systems and components of theranostics [4–7]. In this regard, the greatest attention has been paid to biocompatible and chemically stable polymers [4,6,8,9]. Poly(1-vinyl-1,2,4-triazole) (PVT) and poly(acrylic acid) (PAA) employed in this work are biocompatible, non-toxic, hydrophilic, chemically stable polymers, moreover, the triazole units are strong ligands for transitional and noble metal ions, which ensures the effective stabilizing properties of PVT regarding to metal nanoparticles [10,11]. For example, a recent work [12] has shown high stability and effective antibacterial properties of PVT-based silver nanoparticles. Thus, PVT-based nanocomposites containing AuNPs might be promising materials for medical and pharmaceutical applications.

A number of approaches to the synthesis of AuNPs were developed within the past decades; meanwhile, reduction of metal ions in the presence of macromolecular stabilizers is probably the most common way [1,5,13]. Basically, the Au(III) ions can be easily reduced by various chemical agents [14]. However, in case one needs the high-purity nanocomposites with tunable size and distribution of NPs, the radiation-chemical reduction becomes a particularly attractive method [15–17], because the irradiation of aqueous solutions leads to the generation of powerful and “clean” reducing species, such as hydrated electrons. Radiation technologies, including irradiation with high energy electrons, gamma or X-rays, have been successfully employed to produce AuNPs [17–23]. In our research group the radiation-chemical method was previously applied for the preparation of various-type metal polymer nanocomposites from metal-polymer and metal-interpolyelectrolyte complexes in aqueous-organic media [24,25,28]. Generally speaking, both radiation parameters (such as the total

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[*] Corresponding author.
*E-mail address:* garikov-aleksey@mail.ru (A.A. Zharikov).

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absorbed dose, dose rate and radiation type [17]) and polymer metal surface interactions are important in this case. Here we report the first application of this approach to the preparation of ultra-small AuNPs with controlled size based on PVT and PVT- PAA matrix, which combines the properties of a typical polyelectrolyte and a nonionic polymer. It has been shown previously, that double interpolymer complexes based on PAA [26–29] can ensure the effective stabilization of metal nanoparticles due to the formation of ternary complexes "Polymer I (PAA) - Metal nanoparticle - Polymer II". The main focus of this work is studying the effects of interactions between macromolecules and nanoparticles on the size distribution of the resulting AuNPs.

## 2. Experimental

### 2.1. Materials

The following reagents were used: poly(1-vinyl-1,2,4-triazole) ($M_w$ = 80 kDa), synthesized at Favorsky Irkutsk Institute of Chemistry, Irkutsk, Russia, aqueous solution (35 wt%) of polyacrylic acid ($M_w$ = 100 kDa, Sigma-Aldrich, USA), hydrogen tetrachloroaurate(III) trihydrate (Sigma-Aldrich, USA), ethanol (the analytical grade) and NaOH (0.5 M standard titre solution). Distilled water was used as the solvent.

### 2.2. Preparation and irradiation of metal-polymer complexes

PVT-Au(III) and PAA-Au(III) complexes were prepared as follows: an aqueous solution of $HAuCl_4$ was added to an equal volume of 0.3 wt% PVT or 0.23 wt% PAA. To prepare ternary PVT-PAA-Au(III) suspension, $HAuCl_4$ was added to a double volume of a solution containing PAA (0.1 wt%) and PVT (0.1 wt%). The total molar ratio of polymer units to Au (III) ions was 25:1 (see Table 1).

The samples of double and ternary complexes were irradiated by X-rays using a 5-BKhV-6 W tube with tungsten anode (applied voltage was 45 kVp, anode current ca. 80 mA) at 293 K in polymer Eppendorf test tubes of 8 mm thick. Such conditions ensured essentially uniform generation of radiolysis products in the volume. Before irradiation ethanol (10 vol%) was added to the solutions as a scavenger of hydroxyl radicals. To remove air oxygen dissolved in a water-ethanol medium the samples were bubbled with argon (extra pure grade). The dose rate of 23 Gy/s was measured using a ferrosulfate dosimeter irradiated in the same geometry as the samples studied. For metal-polymer complexes the actual dose rate was calculated taking into account the mass absorption coefficients [30] for X-rays with an effective energy of 20 keV, which provides reasonable representation of the actual X-ray spectrum.

### 2.3. Characterization

The spectra of irradiated samples and turbidimetric data were obtained using a Perkin Elmer Lambda 9 spectrophotometer with an optical range of 200–900 nm in quartz optical cells (optical path 1 mm). The structure of AuNPs nanocomposites was examined in a Leo-912 AB OMEGA (Karl Zeiss, Germany, resolution 0.3 nm) transmission electron microscope (TEM), operating at 120 kV. The FTIR spectra of the metal-polymer nanocomposites preliminarily deposited on germanium plates and dried were recorded in the 4000–500 $cm^{-1}$ range using a Bruker Tensor II spectrometer equipped with a cooled MCT detector.

**Table 1**
Concentrations of Au(III) ions and polymer units for suspensions.

| | C(Au(III)), mol/l | C(PVT-units), mol/l | C(PAA-units), mol/l |
|---|---|---|---|
| PVT-Au | **$6{,}4\cdot10^{-4}$** | **$1{,}6\cdot10^{-2}$** | – |
| PAA-Au | **$6{,}4\cdot10^{-4}$** | – | **$1{,}6\cdot10^{-2}$** |
| PVT-PAA-Au | **$6{,}4\cdot10^{-4}$** | $7\cdot10^{-3}$ | $9\cdot10^{-3}$ |

## 3. Results and discussion

The complexation of Au(III) ions with macromolecules was examined using UV-VIS spectroscopy and turbidimetry. Upon adding $HAuCl_4$, PVT-Au(III) and PAA-Au(III) remain in the form of transparent solutions, while the mixtures of Au(III) ions, PVT and PAA yield dispersions. Mixing of PVT and $HAuCl_4$ solutions leads to the disappearance of the band at 310 nm (Fig. 1, A), corresponding to electronic transitions from occupied $Cl^-$ ligand orbitals to unoccupied metal orbitals [31]. This result demonstrates the replacement of chlorine ions in the chloride complex by the PVT-units. The pH-dependence of the turbidity of the unirradiated samples is shown in Fig. 1 B. The formation of PVT-PAA-Au (III) dispersions (Fig. 1 B, curve 1) indicates intermolecular crosslinking of polymer chains, whereas intramolecular complexes are predominantly obtained in binary systems (curves 3 and 4). The schematic representations of the proposed structures of the complexes are shown in Fig. 1 C. Depending on pH, L could be either a low molecular weight ligand $Cl^-$, $OH^-$ [31] or another one polymer unit. Although PVT and PAA can yield turbid interpolymer complexes stabilized by the H-bonding without Au (III) ions (Fig. 1 B, curve 2 and Fig. 1 C, structure 2), these ones are formed only at low pH values and completely dissolve at pH above 4.5. In contrast, the ternary metal-polymer complexes are stable in the pH range of 3.5 to 7, the maximum turbidity being observed at pH 5–6. This fact clearly indicates that the crosslinking of PVT and PAA is due to the coordination of Au (III) ions. Thereby, the radiation-induced formation of AuNPs for both binary and ternary systems was studied at pH 5.5, since this value corresponds to the maximum turbidity of the PVT-PAA-Au (III) dispersions. In this case, the PVT units are not protonated (degree of protonation 5%) [12], and the carboxyl groups of PAA are partially dissociated (degree of dissociation 35%) [25].

Irradiation of the PVT-Au(III) solutions leads to a red coloration, which qualitatively indicates the formation of gold colloids [3,17]. The UV-VIS spectra of irradiated samples are shown in Fig. 2A. The broad absorption bands at ca. 520 nm corresponding to the surface plasmon resonance of AuNPs [3,17,32] rise when increasing the dose due to gradual conversion of Au (III) ions into AuNPs. The intensity of the plasmon bands increases up to the absorbed doses of 10–14 kGy, which indicates the completion of the reduction of gold ions in solution. For TEM study, the sample irradiated at 14 kGy was used. The bright field (BF) TEM image together with the selected area electron diffraction pattern (SAEDP) is presented in Fig 2C and D respectively. The SAEDP unambiguously proves that the nanoparticles obtained are Au with *fcc*-crystal structure. The rings corresponding to the interplanar distances 2.35 Å, 2.03, 1.44 Å and 1.23 Å (Fig. 2D) fit perfectly to expected gold crystals [33]. The size distribution of AuNPs stabilized by PVT is given in Fig. 2B ($D_n$ = 2.9 nm, $D_w$ = 3.8, $D_w/D_n$ = 1.31, where $D_n$ is a number-average diameter and $D_w$ a weight-average diameter).

In contrast, irradiation of PAA-Au solutions results in the purple coloration, which is usually associated with large nanoparticles [3]. In addition to the band at 520 nm, the UV-VIS spectra (Fig. 3A) exhibit an increased absorbance in the range from 600 to 900 nm corresponding to non-isotropic nanostructures and aggregates [3]. For TEM study the solution irradiated at 7 kGy was used, since further irradiation leads to a decrease in the intensity of the peak at 520 nm and aggregation of the NPs. The BF TEM- image (Fig. 3B) demonstrates the formation of both spherical and non-spherical nanoparticles exceeding 10 nm in size. The SAEDP (Fig. 3C) shows the combination of the ring pattern arises from relatively large (See SAEDP in Fig. 2D) gold crystals.

The UV-VIS spectra of irradiated suspensions of PVT-PAA-Au (III) are shown in the Fig. 4A. Upon irradiation, the turbidity of the samples gradually decreased to the absorbed doses up to 8 kGy, after which an increase in absorbance was observed in the range of 450–600 nm due to the formation of AuNPs. The low intensity and width of the plasmon bands, as well as characteristic brown colour of dispersions (Fig. 4B) indicate the formation of ultrasmall AuNPs [3,34,35]. The TEM and electron diffraction data (Fig. 5A and 5B, correspondingly) are

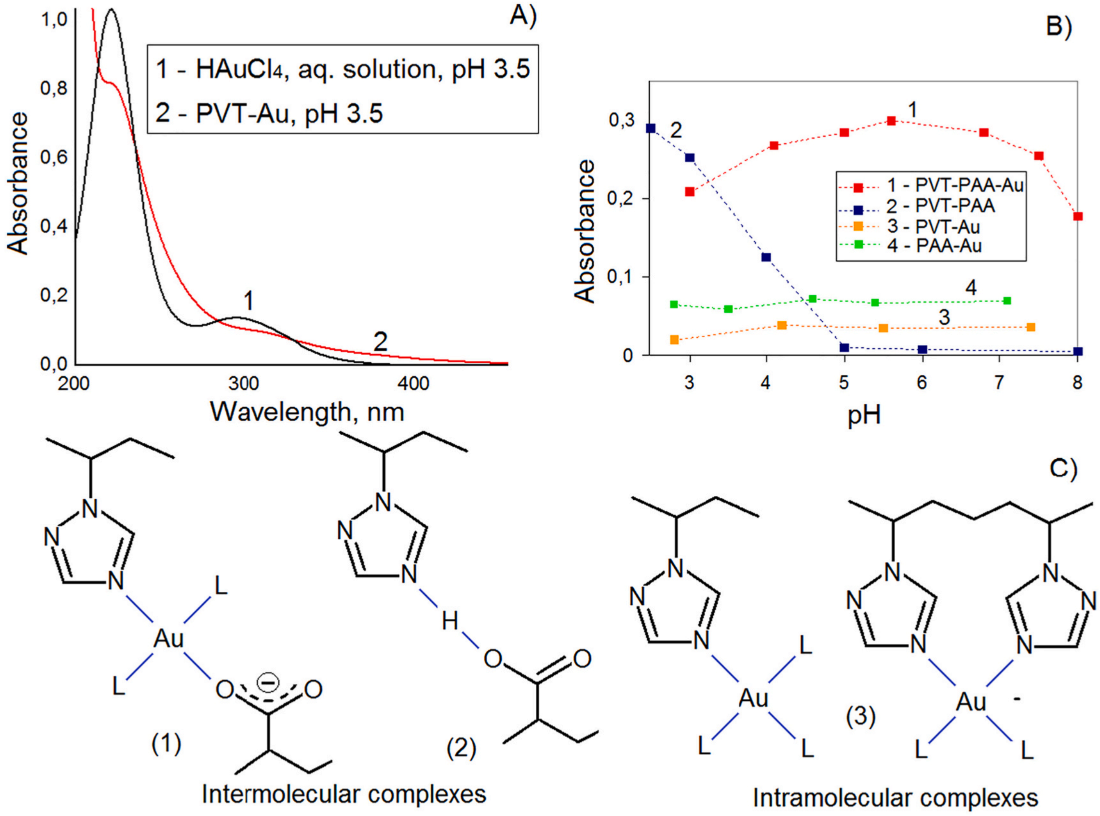

**Fig. 1.** The spectra of $HAuCl_4$ and PVT-Au (A), the turbidimetric data (the dependence of the optical density at $\lambda = 400$ nm on pH) of the unirradiated PVT-PAA-Au, PVT-Au, PAA-Au suspensions and PVT-PAA aqueous mixture (B), the structures of complexes (C).

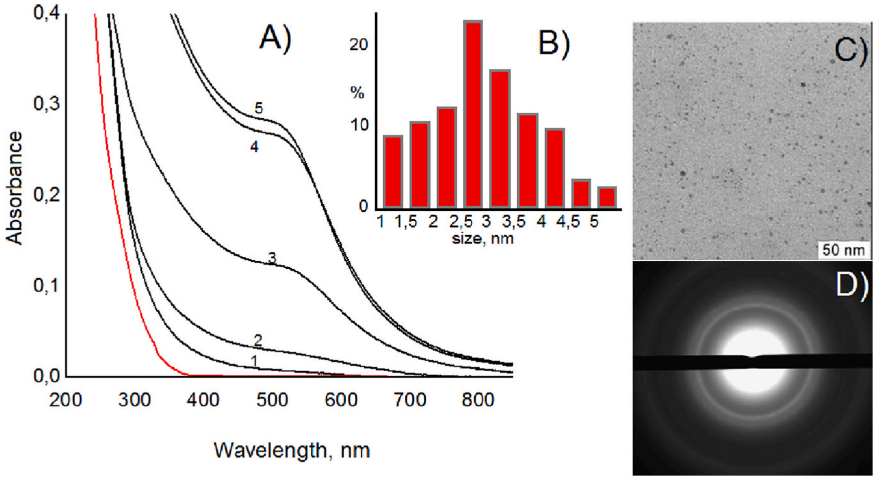

**Fig. 2.** The UV-VIS spectra of PVT-Au suspensions irradiated up to a dose of 0 (red curve), 1.5 (1), 3 (2), 5 (3), 7 (4), 14 (5) kGy (A); the AuNPs size distribution (B), BF TEM image (C) and SAEDP (D) of the irradiated (dose 14 kGy) PVT-Au solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

consistent with the UV-VIS data. The two wide diffuse rings corresponding to the interplanar distances of ca. 2.30 and 1.20 Å (an intermediate position relative to the pairs of *fcc*-gold lattice) demonstrate only a short-range order of Au atoms, which indicates that the gold lattice is not formed under such conditions (Fig. 5B). The sizes of nanoparticles (Fig. 4C and 5A) generated in irradiated PVT-PAA-Au suspensions do not exceed 3 nm ($D_n = 1.4$ nm, $D_w = 1.8$, $D_w/D_n = 1.29$).

In order to rationalize the observations described above, we should first consider the basic scheme of the processes leading to preparation and stabilization of AuNPs. The radiation-induced synthesis of AuNPs is ensured by active species generated during radiolysis of water (items in parentheses stand for the radiation-chemical yields in species per 100 eV of absorbed energy) [15–17]:

$$H_2O^{\sim\sim\sim} > \dot{H}(0,6), H_2\ (0,45), H_2O_2\ (0,75), e^{-}(aq)\ (2,8),\ {}^{\cdot}OH\ (2,8) \tag{1}$$

The hydrated electrons are extremely strong reducing agents, while the OH radicals act as oxidizing agents for metal atoms and clusters [15–17]. The efficiency of reduction is enhanced by adding of alcohols, which acts as a scavenger of OH radicals, forming alcohol radicals with moderate reducing properties (H atoms are also effectively scavenged by

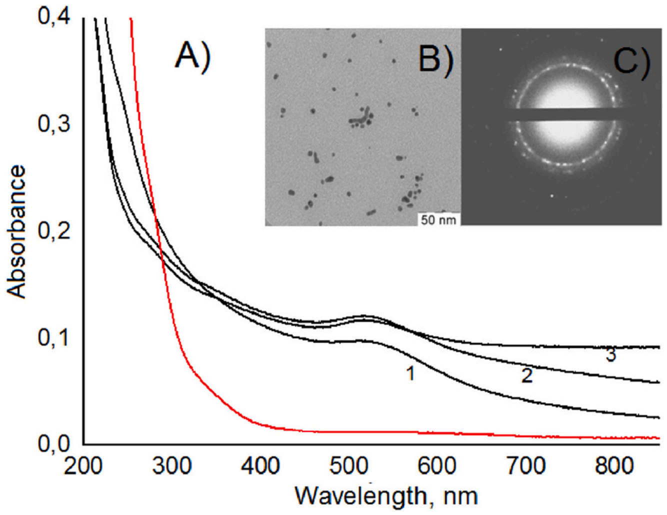

**Fig. 3.** The UV-VIS spectra of PAA-Au suspensions irradiated up to a dose of 0 (red curve), 0.7 (1), 1.5 (2), 7 (3) kGy (A); The BF TEM image (B) and SAEDP (C) of the irradiated (dose 7 kGy) PAA-Au solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

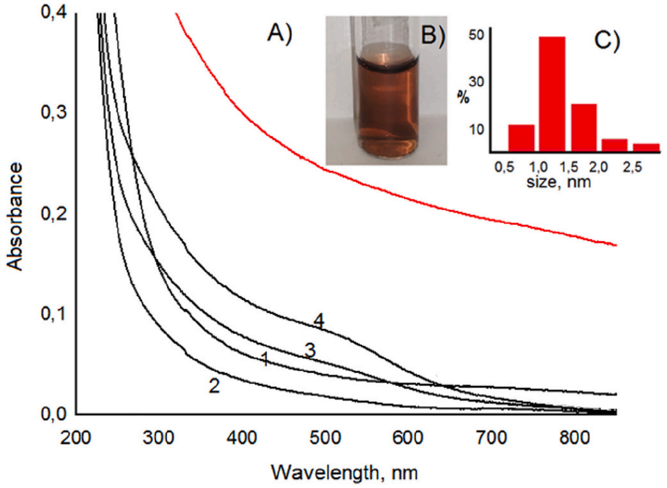

**Fig. 4.** The UV-VIS spectra of PVT-PAA-Au suspensions irradiated up to a dose of 0 (red curve), 1.5 (1), 7 (2), 10 (3), 14 (4) kGy (A); the image of PVT-PAA-AuNPs colloids (B) and the size distribution of AuNPs (dose 14 kGy) (C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

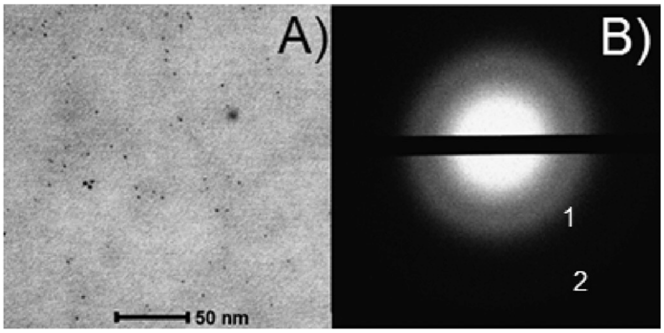

**Fig. 5.** The BF TEM image (A) and SAEDP (B) of the irradiated (dose 14 kGy) PVT-PAA-Au suspension.

alcohols) [15–17]:

$$CH_3CH_2OH + {}^{\cdot}OH\ ({}^{\cdot}H) \rightarrow CH_3C^{\cdot}HOH + H_2O\ (H_2) \tag{2}$$

The initial stage of the radiation-induced formation of AuNPs includes stepwise reduction of complex Au (III) ions (L is PVT or PAA units, $Cl^-$, $OH^-$) to neutral isolated atoms (3–5) [17,32,36]:

$$(\mathrm{Au\ (III)})_L + \bar{e}(aq)\ (CH_3C^{\cdot}HOH) \rightarrow (\mathrm{Au\ (II)})_L \tag{3}$$

$$(\mathrm{Au\ (II)})_L \rightarrow (\mathrm{Au\ (I)})_L + (\mathrm{Au\ (III)})_L \tag{4}$$

$$(\mathrm{Au\ (I)})_L + \bar{e}(aq)\ (CH_3C^{\cdot}HOH) \rightarrow (\mathrm{Au}^0)_L \tag{5}$$

The next steps involve coalescence of small charged clusters (6–8) [32]:

$$(\mathrm{Au}^0)_L + (\mathrm{Au\ (I)})_L \rightarrow (\mathrm{Au_2}^+)_L \tag{6}$$

$$2(\mathrm{Au_2}^+)_L \rightarrow (\mathrm{Au_4}^{2+})_L \tag{7}$$

$$\mathrm{Au}_k{}^{a+} + \mathrm{Au}_m{}^{b+} \rightarrow \mathrm{Au}_n{}^{c+} \tag{8}$$

Owing to reduction of Au(III) ions into atoms and small clusters and changes in the character of interactions in ternary complexes, the turbidity of PVT-PAA-Au samples decrease at low doses (Fig. 4A). Further reactions of reduction and aggregation of clusters lead to quasi-metal particles followed by AuNPs.

Now we turn to the deeper insight into the role of polymer matrix. Polymers can directly influence the processes of nucleation and growth, and thus the resulting NPs features [13,34,37]. The stabilizing efficiency of a polymer matrix is determined by the nature of the interaction between macromolecules and NPs. In the case of polyelectrolytes, which bear charged functional groups, the electrostatic interactions of metal surface and macromolecules play a dominating role [13,34]. Thereby, polycations are believed to be strong stabilizing agents for NPs with negatively charged surface, whereas polyanions are suitable for stabilizing positively charged colloids [34]. Besides polyelectrolytes, non-ionogenic amphiphilic polymers, such as polyvinylpyrrolidone (PVP), are also known as effective stabilizers for metal NPs [1,13,37]. Non-ionogenic functional groups, which are strong ligands for metal ions, can adsorb on metal surface on and thus ensure steric stabilization [37]. Notwithstanding, polyelectrolytes have an important advantage, namely, they can combine both steric and electrostatic effects due to charged functional groups [13].

AuNPs obtained by reduction of the chloride complex is known to acquire a negative charged due to the adsorption of chloride ions from the precursor. Therefore, polycations are widely applied as effective stabilizing agents regarding to ultrasmall AuNPs. For example, AuNPs with sizes 1–4 nm were successfully obtained in the presence of poly (diallyldimethyl ammonium chloride) [34].

In contrast, the polyanion based matrices are usually not considered as protective media for AuNPs. Nevertheless, the anionic polymers modified with various functional groups are also used in the synthesis of gold colloids [13]. For example, AuNPs with diameters smaller than 5 nm were obtained using thioether- and thiol-functionalized PAA and poly(methacrylic acid) [35]. Another example is PAA hydrophobically modified with various degrees of grafting of butylamine introduced randomly along the chain ensures the stabilization of relatively large AuNPs with an average size of 18 to 38 nm, depending on the polymer matrix [38]. Finally, PAA without any modification also provides the formation AuNPs of about 20 nm with the various shape [38]. In this work we have shown that radiation-chemical reduction of gold ions in the presence of PAA also leads to the formation of both spherical and nanocoral [3] particles. This fact indicates the key role of electrostatic repulsion between the negatively charged metal surface and polyanions, which hinders the effective stabilization of small AuNPs. Nevertheless, somewhat stabilization is achieved for large nanoparticles. In this case, a significant contribution can be made by hydrophobic interactions between polymer chains and the metal surface.

The stabilizing properties of PVT with regard to AuNPs are ensured by the specific adsorption of functional groups on the Au surface. Polymer units, which are strong ligands, partially replace chloride ions layer on the gold surface, providing effective stabilization. This leads to the formation of small AuNPs with a narrow size distribution. It should be noted that PVT has an amphiphilic character and hydrophobic interactions of backbones also can contribute to the stabilizing effect.

Since the AuNPs formed in the PVT-PAA-Au suspensions are much smaller than in the PAA-Au solutions, it should be concluded that the stabilization of colloids in ternary systems is mainly ensured by interactions between the triazole groups of PVT and the Au-surface. However, the average size of AuNPs in PVT-PAA-Au systems is also smaller than that in PVT-Au ones. Although PAA, unlike PVT, is not a good protective matrix for small AuNPs, it facilitates the stabilization of nanoparticles in the presence of both polymers. The FTIR data show that the infrared absorption bands of the triazole ring vibrations of the PVT-PAA-AuNPs metal-polymer nanocomposite (see Fig. 6) are shifted relative to the positions of the corresponding vibrations of the both PVT and PVT-AuNPs. This indicates the formation of precisely the ternary nanocomposite, in which the PVT and PAA molecules form macromolecular complex. A reasonable explanation of the stabilization effect of PAA macromolecules is concerned with the donor-acceptor interactions between PAA and PVT, where the carboxylate group of PAA acts as an electron donor, while the triazole group exhibits the properties of $\pi$-electron acceptor [39] (see Fig. 7). These interactions can increase the adsorption energy of the triazole groups on the metal surface due to increasing the $\pi$-electron density at the triazole rings. Note that such an indirect involvement of PAA is not associated with the strong effect of electrostatic repulsion between carboxylates and the Au-surface (Fig. 7); meanwhile, combination of both electrostatic interaction of polymer units and the specific adsorption of functional groups on the nanoparticle surface ensures additional stabilization of colloids.

The thermodynamical aspects of the AuNPs formation under conditions of strong interaction of polymer macromolecules with the surface of nanoparticles can be described within the framework of the theory of pseudo-matrix processes based on the idea of cooperative noncovalent interactions of NPs with macromolecule leading to the formation of “particle-polymer” complexes [40,41]. In outline, an increase in the energy interactions of macromolecules with the metal surfaces results in the stabilization of smaller particles [40,41]. The pseudo-matrix theory gives good semi-quantitative predictions for nanoparticles with the sizes of 1–10 nm and makes it possible to estimate the energy gain $\Delta G$ in the formation of “particle-polymer” complexes. According to the theory [40,41]

$$\Delta G = \frac{kTlnc}{\pi D^2} \tag{9}$$

where $\pi D^2$ is the surface area of a spherical particle ($D$ is the maximum of the numerical function of particle size distribution), $c$ is the initial polymer units molar fraction, $T$ is the temperature and $k$ is the Boltzmann constant. For AuNPs stabilized by PVT only $\Delta G = -1.3\cdot10^{-3}$ J/m$^2$ and for those stabilized by both PVT and PAA $\Delta G = -6.0\cdot10^{-3}$ J/m$^2$. These values are relatively small (less than 1% of specific surface energy values of the bulk metals [40,41]); nevertheless, such a small difference in the values of the energy of polymer-particle interactions in the two systems is sufficient to lead to a difference in AuNPs average sizes of more than 1 nm.

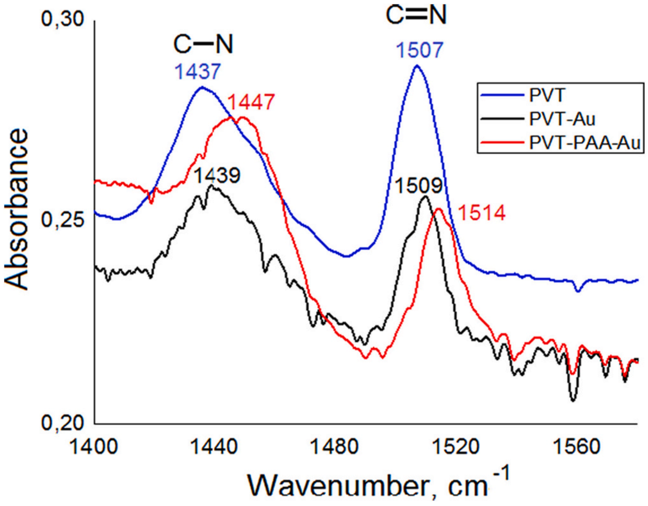

**Fig. 6.** FTIR spectra of PVT-PAA-AuNPs and PVT-AuNPs metal-polymer nanocomposites and PVT (the corresponding bond vibrations of the triazole ring are indicated above the absorption bands).

## 4. Conclusions

The results obtained exhibit the great potential of using the metal-polymer complexes based on PVT as a precursor for the synthesis of size-controlled AuNPs. The pronounced ability of triazole-units to bind Au (III) ions predetermines the high specific adsorption of PVT macromolecules on the Au surface and, consequently, the high efficiency of PVT as a stabilizing matrix for AuNPs. The irradiation of ternary PVT-PAA-Au(III) metal-polymer complexes has been shown to lead to the formation of AuNPs which are smaller than those obtained in double PVT-Au(III) complexes. According to the theory of pseudo-matrix processes, this indicates the substantial increasing the energy gain in the formation of “particle-polymer” complexes. Such result seems to be intriguing, considering that PAA itself is not a suitable protective media for AuNPs duo to polyanionic character. However, this fact can be reasonable explained by the contribution of PAA to the stabilization of AuNPs realized by the donor-acceptor interactions between PAA and PVT. Thereby, due to the combination of specific adsorption and electrostatic interactions, the effectiveness of the PVT-PAA interpolymer complex for stabilizing ultrasmall AuNPs turns out to be comparable to that of cationic polymer matrices or covalent binding molecules. No less interesting fact is the change in the morphology of AuNPs synthesized in ternary complexes. Whereas AuNPs obtained in double systems demonstrate the formed gold crystal lattice, nanoparticles stabilized in PVT-PAA suspensions show only a short-range order of Au atoms.

Finally, it worth to mention, that the radiation-induced method ensures the high purity of the nanocomposites, which is important for biotechnological, medical and catalytic applications.

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## CRediT authorship contribution statement

**Alexey A. Zharikov:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Rodion A. Vinogradov:** Validation, Investigation. **Elena A. Zezina:** Methodology, Validation, Investigation. **Alexander S. Pozdnyakov:** Project administration, Resources. **Vladimir I. Feldman:** Project administration, Writing – original draft. **Alexandr L. Vasiliev:** Methodology, Formal analysis, Resources. **Alexey A. Zezin:** Conceptualization, Project administration, Writing – review & editing.

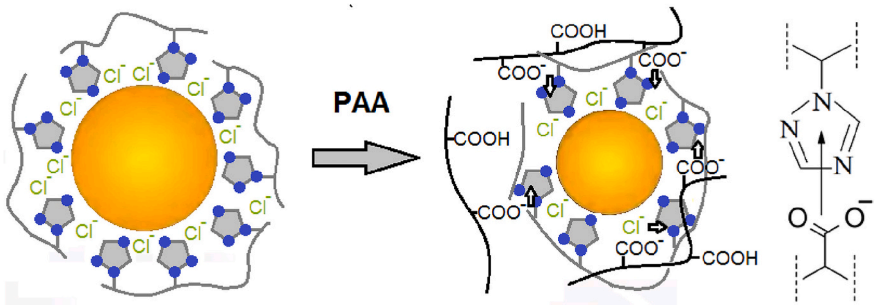

**Fig. 7.** The illustration of a possible way of additional stabilization of gold nanoparticles in the presence of PAA. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## Declaration of Competing Interest

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The authors Alexey A. Zharikov, Rodion A. Vinogradov, Elena A. Zezina, Alexander S. Pozdnyakov, Vladimir I. Feldman, Alexandr L. Vasiliev, Alexey A. Zezin declare no any conflicts of interest.

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