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# Light-scattering study of silver nanocomposites based on hydrophilic nitrogen-containing heterocyclic copolymers

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***Abstract:*** *A light scattering study was performed on new silver-containing polymer nanocomposites based on water-soluble copolymers of 1-vinyl-1,2,4-triazole having sodium salt of vinylsulphonic acid of various compositions. The formation of nanocomposites was carried out using chemical reduction of silver ions by sodium borohydride in a copolymer- containing aqueous medium. According to the dynamic light scattering data, a decrease in the average sizes of metal-polymer coils in water-salt solutions of nanocomposites is explained in terms of an increase in the content of sulphonate groups in the stabilising polymer matrix. The electrophoretic light scattering with phase analysis of synthesised nanocomposites reveals the zeta potential (ζ) to vary from -35.0 to -75.3 mV with an increased sulphonate unit proportion in the stabilising polymer matrix, indicating an increase in the stability of the colloidal system. The functional composition of the stabilising polymer matrix is established to provide a significant effect on the hydrodynamic dimensions of polymer nanocomposites in an aqueous medium.*

***Keywords:*** *polymer nanocomposites, silver nanoparticles, 1-vinyl-1,2,4-triazole, vinylsulphonic acid sodium salt*

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# Исследование нанокомпозитов серебра на основе гидрофильных азотсодержащих гетероциклических сополимеров методами светорассеяния

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***Резюме:*** *Методами светорассеяния исследованы новые полимерные серебросодержащие нанокомпозиты на основе водорастворимых сополимеров 1-винил-1,2,4-триазола с натриевой солью винилсульфоновой кислоты различного состава. Формирование нанокомпозитов осуществляли методом химического восстановления ионов серебра боргидридом натрия в водной среде в присутствии сополимеров. По данным динамического светорассеяния с увеличением содержания сульфонатных групп в стабилизирующей полимерной матрице наблюдается уменьшение средних размеров металло-полимерных клубков-вводно-солевых растворах нанокомпозитов. Исследования синтезированных нанокомпозитов методом-электрофоретического светорассеяния с анализом фаз показывают, что с увеличением доли сульфо-*

*натных звеньев в составе стабилизирующей полимерной матрицы величина дзета-потенциала (ζ) изменяется от -35,0 до -75,3 мВ, что указывает на повышение стабильности коллоидной системы. Установлено, что функциональный состав стабилизирующей полимерной матрицы оказывает существенное влияние на гидродинамические размеры полимерных нанокомпозитов в водной среде.*

***Ключевые слова:*** *полимерные нанокомпозиты, наночастицы серебра, 1-винил-1,2,4-триазол, натриевая соль винилсульфоновой кислоты*

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## INTRODUCTION

Obtaining organic-inorganic nanocomposites based on functional polymers appears to be a promising direction. In the processes of nanoparticle formation, a stabilising matrix is necessary, since the presence of various functional groups allows further modification [1–3], opening up promising new avenues for utilising target composites [4–6].

Due to the possibility of using different approaches to stabilise nanoparticles [7–9], accounting for the ability of the stabilising polymer matrix to interact with nanoparticles in order to avoid their agglomeration is of a great importance [10]. The copolymers of 1-vinyl-1,2,4-triazole are acknowledged to be effective stabilisers of metal nanoparticles [11–20].

This paper presents the results of the synthesis and property study of new silver-containing nanocomposites based on copolymers of 1-vinyl-1,2,4-triazole (VT) with the sodium salt of vinylsulphonic acid (Na-VSA).

## EXPERIMENTAL PART

The silver content was determined using an AA-6200 atomic absorption spectrometer (Shimadzu, Japan) in flame atomisation mode. The solution of 0.1 M $NaNO_3$ with 0.1 mg/mL nanocomposite concentration was applied to determine the hydrodynamic particle radius and zeta potential (ζ) of the studied 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 an of 25 °C and an angle of detection of scattered light operating temperature equal to 173°.

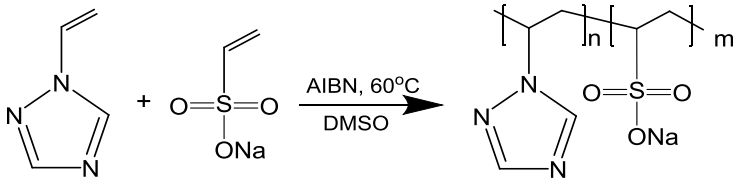
The initial reagents for the synthesis of nanocomposites consisted of CP grade substances of $NH_4OH$, $AgNO_3$ and $NaBH_4$, as well as copolymers of VT with Na-VSA of various compositions, obtained under conditions of radical initiation of azobisisobutyronitrile (AIBN) at a temperature of 60 °C in DMSO [21].

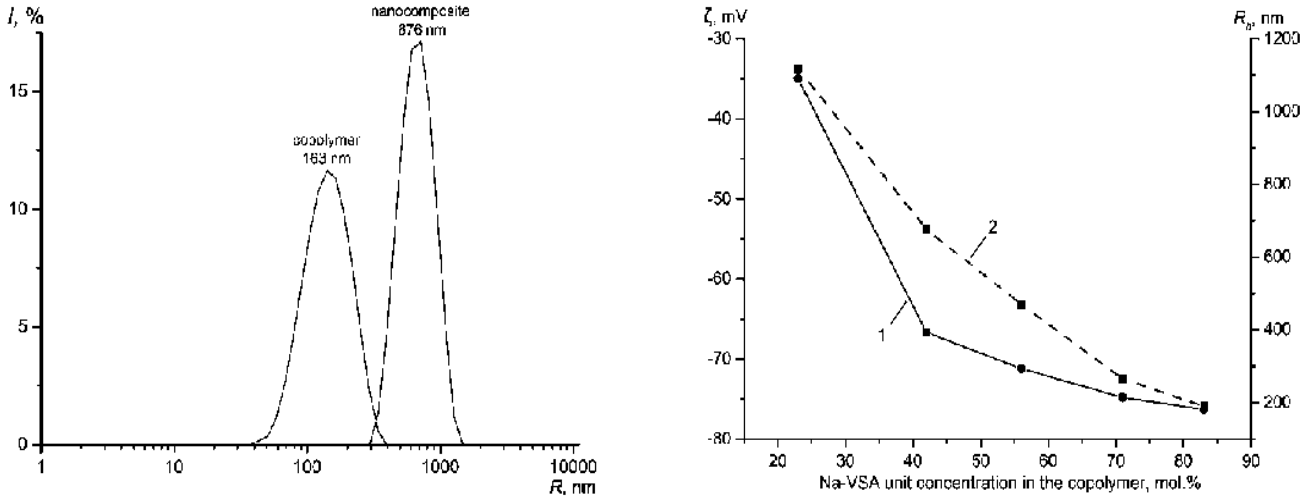
*Synthesis of copolymers.* The radical copolymerisation of VT and Na-VSA proceeded in DMSO at various initial monomer ratios under the influence of AIBN in argon-containing sealed ampoules at 60 °C for 8 hours. Further, the reaction mixture was dialysed against distilled water for 72 hours through a 5 KDa membrane (MFPI, Cellu Sep H1). Subsequently, the composite was isolated by lyophilisation. As the result, white nanocomposite powders were obtained with a yield of 82–89 %.

*Synthesis of nanocomposites*. A solution of 0.5 mmol $AgNO_3$ in 1 mL of 25% $NH_4OH$ was added to 1.0 g (10 mmol) of a copolymer dissolved in 15 mL of double-distilled water followed by intensively stirring for 30 min at 20 °C. Then, 1 mmol of $NaBH_4$ was gradually added with the stirring continued for 8 hours. Then the reaction mixture was dialysed for 48 hours. Subsequently, the composite was isolated by lyophilisation. The synthesis resulted in dark-brown powders of nanocomposites with a yield of 65–70 %.

## RESULTS AND DISCUSSION

The reaction of VT and Na-VSA radical copolymerisation proceeded in accordance with the scheme [21]






***a*** ***b***

***Hydrodynamic radii $R_h$ distribution of the scattering particles for the nanocomposite and the initial copolymer (a); Relationship between zeta-potential (1) and the hydrodynamic radii $R_h$ of scattering particles (2) of nanocomposites and content of Na-VSA in the original copolymer (b)***

***Гистограмма распределения по гидродинамическим радиусам $R_h$ рассеивающих частиц для нанокомпозита и исходного сополимера (a); Зависимость дзета-потенциала (1) и гидродинамических радиусов $R_h$ рассеивающих частиц (2) нанокомпозитов от содержания Na-ВСК в исходном сополимере (b)***

The histograms provided in the figure are characterised by a monomodal particle size distribution with a maximum corresponding to the effective hydrodynamic radius of the scattering particles. A noticeable increase is indicated in the hydrodynamic radius of complex nanocomposite particles presented by an ensemble of silver nanoparticles in a coil of copolymer macromolecules, as compared to the initial copolymer macromolecules (from 163 nm in the initial copolymer to 676 nm in the based nanocomposite). This is possibly due to the formation of coordinated cross-linked complex particles under the action of multiple cooperative forces of intermolecular interaction, with metallic silver nanoparticles acting as coordinating cross-linking agent. As a result of this interaction, relatively large macromolecular coils are formed.

With an increase in the proportion of Na-VSA in the stabilising copolymer, a decrease in the average sizes of metal-polymer coils is observed, indicating the formation of more compact structures. The functional composition effect of the stabilising matrix on the hydrodynamic dimensions of polymer nanocomposites is associated with the action of salt groups: sulphonate fragments in the ionised state cause the appearance of a negative charge on polymer macromolecules further immobilised on the positively charged surface of silver metal nanoparticles, leading to a denser coagulation of macromolecular coils.

Studies of synthesised nanocomposites by electrophoretic light scattering with phase analysis identified the zeta potential (ζ) ranging from -35.0 to -75.3 mV with an increase in the proportion of sulphonate units in the stabilising polymer matrix, indicating an increase in the stability of the colloidal system.

## CONCLUSION

A light scattering study was carried out on new stable polymer nanocomposites with silver nanoparticles based on 1-vinyl-1,2,4-triazole and the sodium salt of vinylsulphonic acid copolymers. The functional composition of the stabilising polymer matrix was established to cause a significant effect on the hydrodynamic dimensions of polymer nanocomposites in an aqueous medium.

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### *Contribution*

Anastasiya A. Ivanova carried out the experimental work, on the basis of the resuits summarized the material and wrote the manuscript. Anastasiya A. Ivanova has exclusive author's rights and bears responsibility for plagiarism.

### *Критерии авторства*

Иванова А.А. выполнила экспериментальную работу, на основании полученных результатов провела обобщение и написала рукопись. Иванова А.А. имеет на статью эксклюзивные авторские права и несет ответственность за плагиат.

### *Conflict of interests*

The authors declare no conflict of interests regarding the publication of this article.

*The final manuscript has been read and approved by all the co-authors*.

### *Конфликт интересов*

Автор заявляет об отсутствии конфликта интересов.

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