

Optical Absorption of Composite Systems with Silver Nanoparticles Dispersed in Arabinogalactan and Arabinogalactan-G-Polypyrrole Block Copolymer Matrices

A. V. Zhmurova^{a, *}, L. E. Zelenkov^b, A. I. Illarionov^{c, d}, R. Yu. Shendrik^e, E. A. Radzhabov^e,
I. V. Klimenkov^f, A. N. Sapozhnikov^e, T. V. Ganenko^b, B. G. Sukhov^b, and B. A. Trofimov^b

^a*Irkutsk State University of Railways, Irkutsk, 664074 Russia*

^b*Favorsky Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, 664033 Russia*

^c*Irkutsk National Research Technical University, Irkutsk, 664074 Russia*

^d*Irkutsk Branch of the Institute of Laser Physics, Siberian Branch, Russian Academy of Sciences, Irkutsk, 664033 Russia*

^e*Vinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, 664033 Russia*

^f*Limnological Institute, Siberian Branch, Russian Academy of Sciences, Irkutsk, 664033 Russia*

*e-mail: 2zhannazh2@gmail.com

Abstract—The absorption of a nanocomposite of silver nanoparticles and arabinogalactan in the UV–Vis spectral range is due to the presence of end aldehyde groups in the arabinogalactan and plasmon vibrations in 0D nanosilver. The absorption spectrum of a fundamentally new nanocomposite of silver with arabinogalactan-g-polypyrrole block copolymer reveals additional long-wavelength overlapping absorption bands resulting from the longitudinal component of plasmon resonance in 1D nanosilver and polarons in polypyrrole.

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INTRODUCTION

Polypyrrole (PPy), one of the best known and most studied conducting organic polymers, continues to attract the attention of researchers [1–7]. Due to the availability of monomers, the relative ease of synthesis, low cost, and high conductivity of the structures based on PPy, this polymer is widely used in such fields as electronics, optoelectronics, electrical engineering, and medicine, and has considerable potential for more applications. From a technological point of view, however, the insolubility of PPy in almost any solvent is a great drawback. Based on the current literature and the results from our studies, one can solve this problem by obtaining copolymers of PPy and biopolymers, particularly polysaccharides [1, 8–11], of which arabinogalactan (AG) is one of the most promising [11–16].

Another actual line of work today is the synthesis of inorganic nanoparticles (e.g., metal nanoparticles) in polysaccharides and conductive organic polymers with advanced optical (including chiral-plasmonic), magnetic, electrically conductive, biologically active, and other properties [17–29]. The optical absorption of such structures depends on the nature of the nanometal, its shape, the degree of nanoparticle monodispersity, and the dielectric properties of the matrix. The

absorption bands of a nanocomposite can indicate the presence of nanoparticles of a specific metal in a specific shape. For example, the spectra of structures containing spherical silver nanoparticles show characteristic absorption bands for spherical particles at around 419 nm [30], and for rod particles at 419 nm, along with broadband absorption in the 600–900 nm range [31, 32].

Works on creating silver nanocomposites based on a copolymer matrix of polysaccharide and a conductive polymer are also promising, since polysaccharide in such structures reduces the technologically undesirable properties of polypyrrole. Due to their good conductivity, superior mechanical properties, biocompatibility, and antibacterial activity, silver nanocomposites based on copolymers of a specified type can be used in the important and rapidly growing field of biomedical applications, e.g., antibacterial materials, diagnostics, and drug delivery systems [33].

The aim of this work was to prepare and investigate the optical absorption of silver nanocomposites in the 250–800 nm range in a specially synthesized new matrix that is a grafted block copolymer of AG and PPy.

EXPERIMENTAL

In this work, we used industrial AG (Fig. 1) of Siberian larch manufactured by OOO Wood Chemistry (Irkutsk). The AG was additionally purified to remove impurities of polyphenols [34].

PPy was prepared via the oxidative polymerization of pyrrole with ferric iron cations in water, according to a standard method [35].

Silver nanocomposites with arabinogalactan matrix were synthesized by the means of a technique described in [36, 37].

To graft PPy blocks to arabinogalactan macromolecules (Fig. 2a), the polypyrrole was first functionalized by anchoring tetrahydroindole groups containing one pyrrole fragment [38, 39].

Polypyrrole branches were then grown on these pyrrole anchor centers via the oxidative polymerization of pyrrole by silver cations (Fig. 2b). Silver was reduced to zero-valence metal nanoparticles implanted into new macromolecules of grafted arabinogalactan-polypyrrole block copolymer [38, 39]. The weight content of silver in the nanocomposite was 8.9 wt %.

All samples of the polymers and the silver nanocomposites based on them were studied via spectroscopy, optical absorption, X-ray diffraction, and transmission electron microscopy (TEM). Optical absorption spectra were recorded on a Perkin Elmer LAMBDA 950 spectrophotometer (United States) with an integrating sphere (150 mm). The instrument error was 0.08 nm. For each measurement, the samples were placed at the center of the integrating sphere in a quartz cylindrical cuvette with an inner diameter of 2.5 mm and a wall thickness of 0.25 mm. X-ray phase analysis was performed using a Bruker D8 ADVANCE diffractometer (Germany). The size and shape of the silver nanoparticles were determined from photomicrographs obtained with a LEO 906E transmission electron microscope (Carl Zeiss, Germany) at an accelerating voltage of 80 kV. Photomicrographs were taken with a MegaView II camera.

RESULTS AND DISCUSSION

The optical absorption spectra of our AG and PPy polymers, the silver nanoparticles in the AG, and in its block copolymer with PPy (AG-PPy) were measured in the 250–800 nm range.

The spectrum of the AG powder exhibited an absorption band at 282 nm (Fig. 3a).

It is known that the absorption in the 300 nm region was associated with a forbidden $n \rightarrow \pi^*$ transition in the terminal aldehyde groups [40] present in the structure of this polysaccharide (Fig. 1).

The spectrum of the PPy powder exhibits an absorption band at 600 nm (Fig. 3a, curve 2). According to the literature data, PPy exhibits absorption maxima at 446 [41, 42], 468 [43], 294 and 420 nm

[44], 360 and 600 nm [45], and 381 and 572 nm [46]. Mahore et al. attributed the absorption maxima at 294 and 420 nm to transitions from the valence band to the polaron and bipolaron states of the oxidized form of PPy [44]. According to Jayamurugan et al. [45], the maxima at 360 and 600 nm were due to $\pi-\pi^*$ transitions in the benzoid rings and the transition of electrons to the polaron and bipolaron states. Munusamy et al. reported that the absorption maxima at 381 and 572 nm correspond to transitions from the valence band to the polarons and bipolarons of the oxidized form of PPy nanoparticles [46].

We measured the optical absorption spectra of powder composites of nanosilver in AG (AG-Ag) with different silver contents (8 and 17.5 wt %) (Fig. 3b). We can see that the absorption spectra of AG-Ag have maxima at 282 nm and around 440 nm. The maximum at 282 nm shows no shift in absorption spectra of AG-Ag nanocomposites with different silver content. This maximum corresponds to an absorption band of AG. In other words, assuming that the absorption spectra of AG and AG-Ag overlap, we can see that the absorption band of AG at 282 nm does not shift after the formation of AG-Ag nanocomposite (Fig. 3c). As is seen from Fig. 3b, the plasmon maximum of silver nanoparticles at 450 nm in the spectrum of the nanocomposite with a high content of metal is shifted to the red by 20 nm, compared to its position (430 nm) in the spectrum of a nanocomposite with a lower silver content. The half-widths of the spectral line of the AG-Ag nanocomposites with Ag contents of 17.5 and 8 wt % are 226 and 166 nm, respectively. The maximum of plasmon resonance for the aqueous solutions of AG-Ag nanocomposites lies at 410 nm for the sample with an average nanoparticle size of 5.6 nm (9.7 wt % silver, 8.8×10^{-3} mol L⁻¹ AgNO₃, 0.08% AG) [37] and at 420 nm for the nanosilver with an average size of 10.0 nm (9.7 wt % silver, 0.36×10^{-4} mol L⁻¹ AgNO₃, 0.08% AG) [47].

The spectrum of the silver nanocomposite with the block copolymer matrix exhibits absorption bands at 294, 426, and 585 nm (Fig. 3a). The first maximum is associated with the presence of AG in the grafted block copolymer matrix of the nanocomposite. In the absorption spectrum of this nanocomposite, the AG absorption band at 282 nm shifts by 12 nm to the long wavelength region; this can be explained by the formation of free radicals [48], particularly the acyl radicals that form in the polymer matrix from aldehyde groups during the redox synthesis of the nanocomposite.

The second absorption peak (426 nm) of the silver nanocomposite and grafted block copolymer could be a consequence of the surface plasmon resonance of spherical silver nanoparticles and the transverse components of plasmon absorption of ellipsoid-rod silver nanoparticles, which might have been present in the system [49].

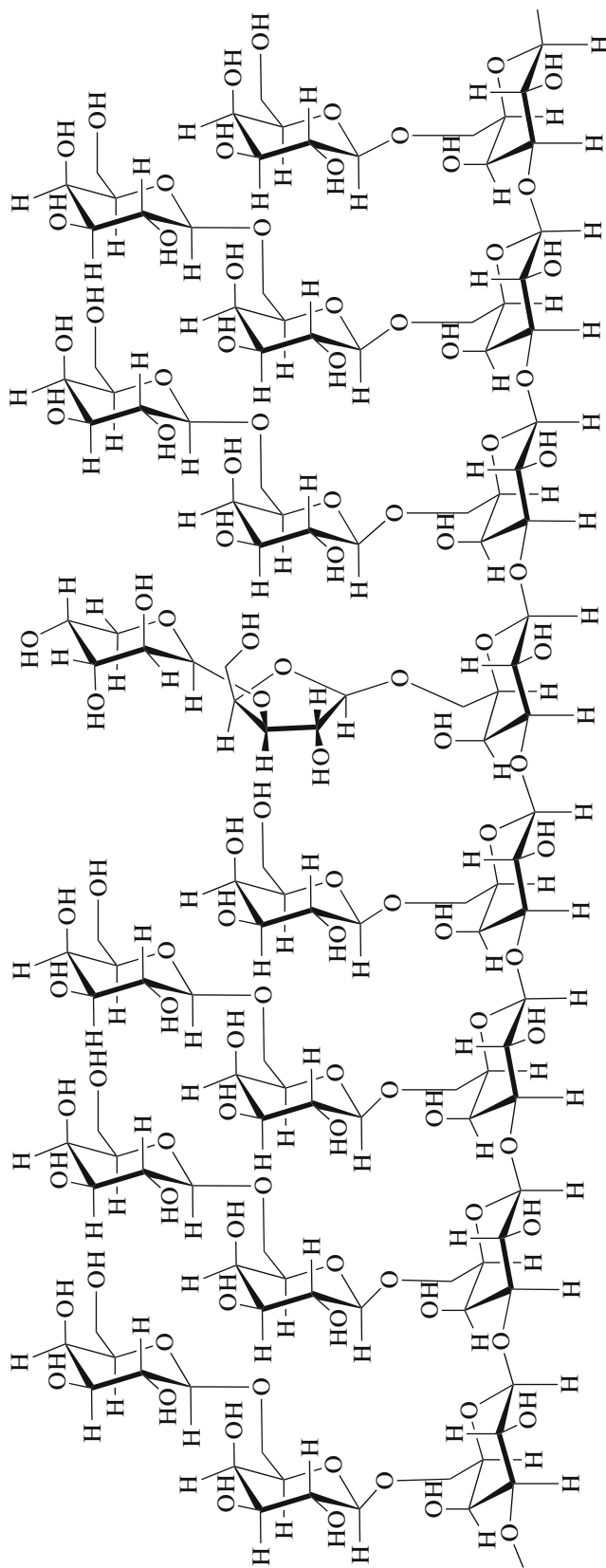


Fig. 1. Fragment of the structural formula of arabinogalactan.

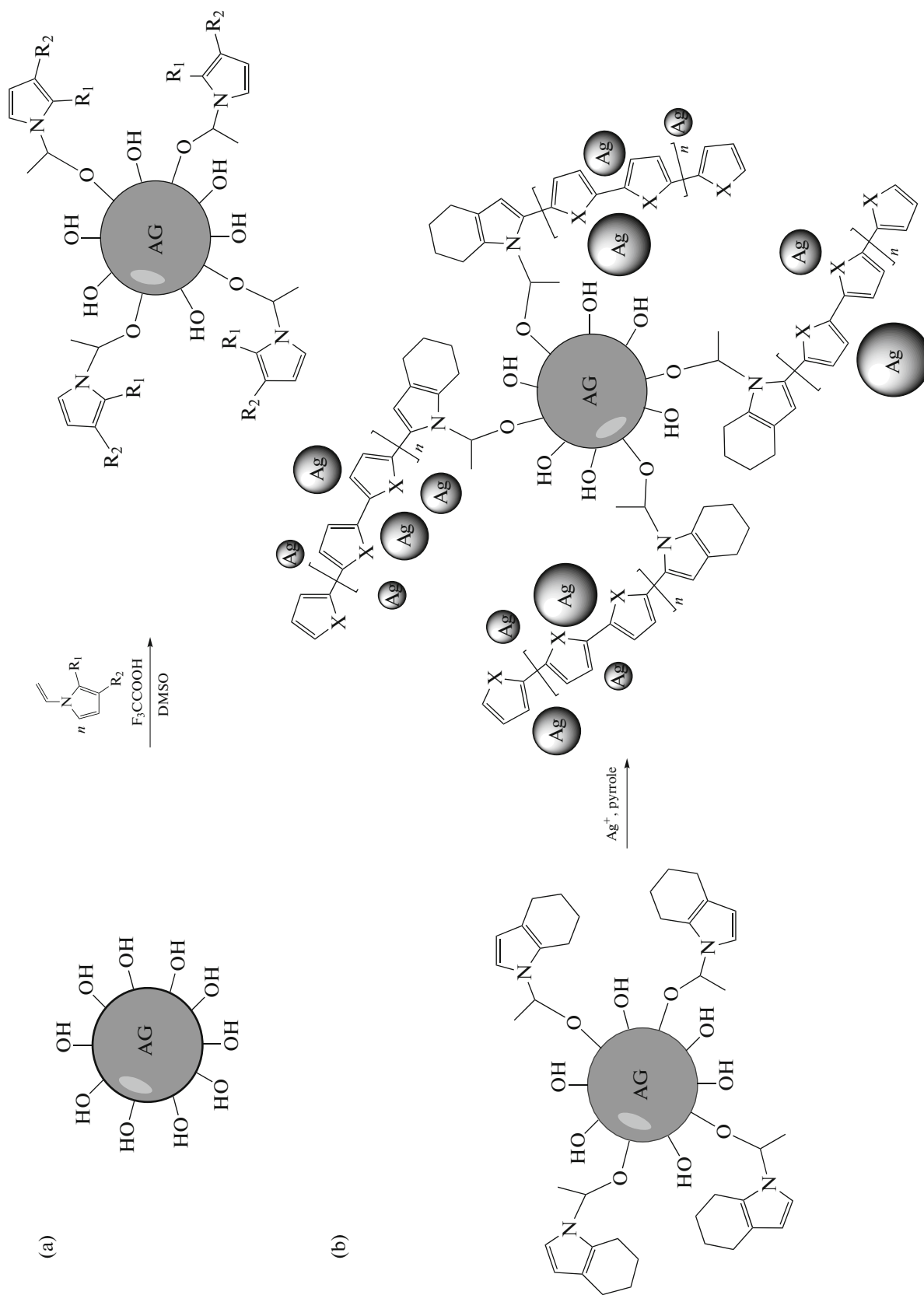


Fig. 2. Schemes for the chemical synthesis of silver nanocomposite in the matrix of grafted block copolymer arabinogalactan-polypyrrole: (a) synthesis of arabinogalactan functionalized by anchor tetrahydroindole groups (containing one pyrrole fragment); (b) synthesis of the nanocomposite of grafted block copolymer arabinogalactan-polypyrrole with silver nanoparticles dispersed in it. In the schemes, $R_1 = -(\text{CH}_2)_2-$, and AG denotes an arabinogalactan macromolecule.

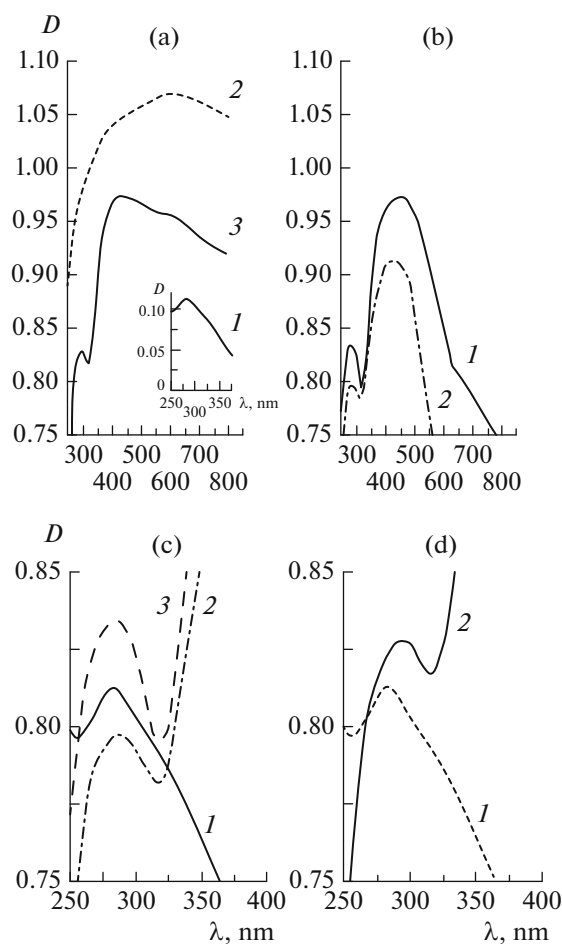


Fig. 3. (a) Spectra of optical absorption (D): (1) arabinogalactan, (2) polypyrrole, and (3) nanocomposite of silver in the matrix of grafted block copolymer arabinogalactan-polypyrrole. (b) Absorption spectra of nanocomposites of silver in the arabinogalactan matrix with metal content of (1) 17.5 and (2) 8 wt %. (c) Overlap of absorption spectra: (1) arabinogalactan and (2, 3) nanocomposites of silver in arabinogalactan matrices with metal percentages of 17.5 and 8%. (d) Overlap of optical absorption spectra: (1) arabinogalactan and (2) nanocomposite of silver in the matrix of grafted block copolymer arabinogalactan-polypyrrole.

The band at 585 nm can be also explained by the longitudinal plasmon component of ellipsoid-rod silver nanoparticles, along with the optical absorption of the polarons of PPY chains.

TEM images obtained via transmission electron microscopy showed that approximately 73% of the total number of nanoparticles in the nanocomposite were spherical, while the rest were actually 1D nanoparticles (Fig. 4).

The average size of the spherical silver nanoparticles in the composite with the grafted block copolymer matrix was 21.3 nm; the average length and width of the ellipsoid-rod nanoparticles was 28.7 and 20.9 nm, respectively. According to x-ray analysis, the average

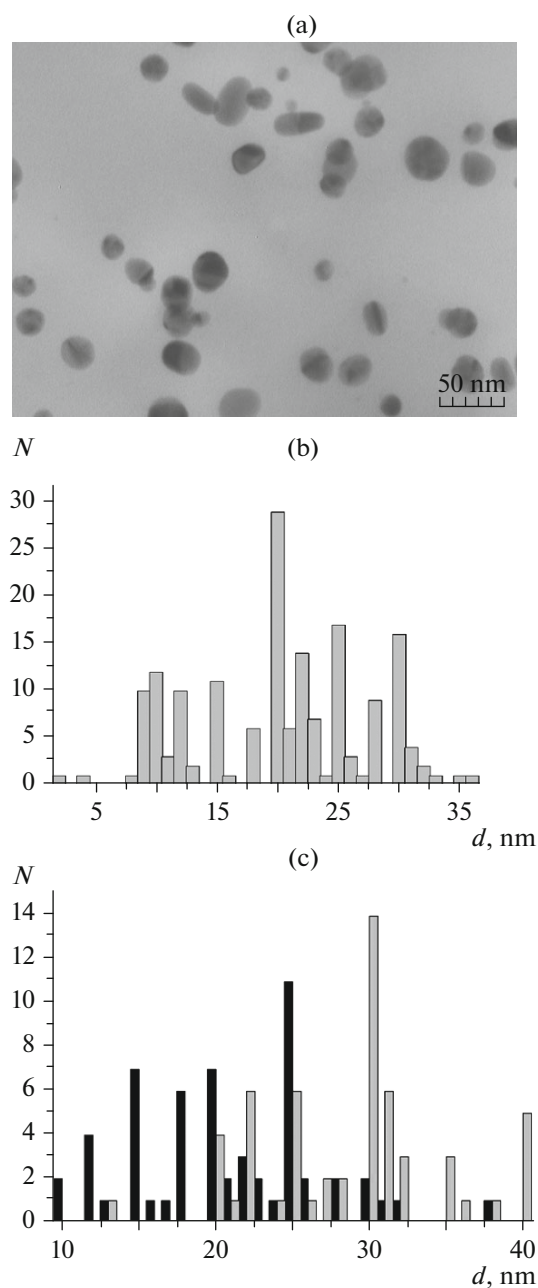


Fig. 4. Results from our TEM study of the dimensional characteristics of silver nanoparticles in a matrix of grafted block copolymer arabinogalactan-polypyrrole: (a) TEM image of the nanocomposite; (b) histogram of the size distribution of spherical nanoparticles (N is the number of nanoparticles; d is diameter); (c) histogram of the distribution of 1D nanoparticles, according to their longitudinal (light) and transverse (dark) dimensions.

diameter of the nanoparticles was 17 nm, which correlates fairly well with the TEM data.

CONCLUSIONS

Silver-containing nanocomposites of arabinogalactan and its block copolymer with polypyrrole and

different silver contents were synthesized. The latter nanocomposite was obtained for the first time.

The absorption of the nanocomposite of silver and arabinogalactan in the short wavelength region (a maximum at 282 nm) was due to the terminal aldehyde groups of arabinogalactan. The absorption with a maximum at 430–450 nm was due to plasmon oscillations in the spherical silver nanoparticles.

The absorption of the terminal aldehyde groups in the new composite of arabinogalactan-polypyrrole block copolymer with nanosilver was shifted by 12 nm to the long wavelength range; this can be attributed to one-electron oxidation of these groups with the formation of acyl radicals.

Compared to the plasmon resonance in the nanocomposite of silver and arabinogalactan, the maximum of plasmon resonance in the new nanocomposite was shifted only slightly to shorter wavelengths (the band with a maximum at 426 nm); this can be explained by the plasmon resonance of the initially available spherical silver nanoparticles, along with the transverse component of the plasmon absorption by the emergent new ellipsoid-rod silver nanoparticles.

The new long wavelength band with a maximum at 585 nm (for the nanocomposite of silver and grafted arabinogalactan-polypyrrole block copolymer) can be attributed to overlapping signals from the longitudinal components of the plasmon resonance of ellipsoid-rod silver nanoparticles, along with the signal from the polarons of polypyrrole blocks grafted to arabinogalactan.

In the future, we plan to investigate the evolution of optical absorption in the obtained structures with the aim of synthesizing stable nanocomposites.

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