

## Polyelectrolytes with tetrazole pendant groups useful in the stabilization of Au and Ag nanoparticles

M. Caldera-Villalobos,<sup>1</sup> Ana M. Herrera-González,<sup>2</sup> J. García-Serrano,<sup>2</sup> M. A. Martins-Alho,<sup>3</sup>  
M. I. Montalvo-Sierra<sup>1</sup>

<sup>1</sup>Doctorado en Ciencias de los Materiales, Universidad Autónoma del Estado de Hidalgo, México

<sup>2</sup>Universidad Autónoma del Estado de Hidalgo, Instituto de Ciencias Básicas e Ingeniería, Área Académica de Ciencias de la Tierra y Materiales, Laboratorio de Polímeros. Carretera Pachuca-Tulancingo Km. 4.5 Colonia Carboneras, Mineral de la Reforma, Hidalgo, México

<sup>3</sup>Cátedra de Química Orgánica, Departamento de Química, Facultad de Ingeniería, Universidad de Buenos Aires, Buenos Aires, Argentina

Correspondence to: A. M. Herrera-González (E-mail: anamhg\_1@hotmail.com)

**ABSTRACT:** Stabilization of metallic nanoparticles is a challenge of enormous dimensions because the nanosize nanoparticles are not stable by themselves and therefore they tend to coalesce, forming large agglomerates causing the loss of the properties of individual nanoparticles. In this work, we report the synthesis of polyelectrolytes with tetrazole groups useful as stabilizing agents of Au and Ag nanoparticles. The polyelectrolytes with tetrazole groups were synthesized from the appropriate starting materials with nitrile groups, which were successfully converted to the corresponding 1*H*-tetrazole rings using 1,3-dipolar cycloaddition with ammonium azide. These new materials were characterized by NMR and FT-IR techniques and they were used for the stabilization of Au and Ag colloidal nanoparticles at room temperature, using sodium borohydride as reducing agent. Formation and stabilization processes of the nanoparticles were monitored by UV-vis spectroscopy. Shape and size of nanoparticles were studied by TEM. The polyelectrolytes with tetrazole pendant group are suitable materials for synthesis and stabilization of gold nanoparticles, obtaining average sizes lower than 10 nm. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43773.

**KEYWORDS:** nanoparticles; nanowires and nanocrystals; polyelectrolytes; spectroscopy

Received 10 January 2016; accepted 10 April 2016

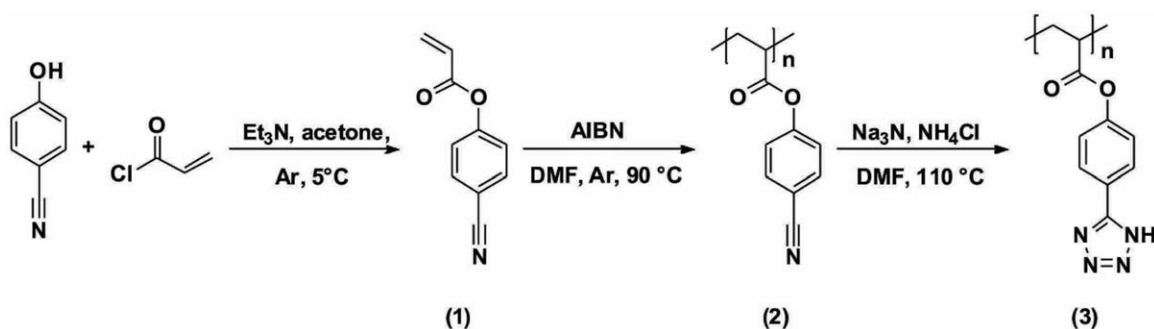
DOI: 10.1002/app.43773

### INTRODUCTION

The stabilization of nanomaterials to avoid coalescence or agglomeration is a crucial aspect to consider during their synthesis. The interaction between metallic nanoparticles and the ligands, surfactants or polymers employed as stabilizing agents is based in the coordination chemistry. The most important characteristic of a stabilizing agent is to have at least one atom with free electron pairs.<sup>1</sup> Some polymers with heterocyclic groups containing nitrogen have showed to be excellent stabilizing agents during the synthesis of metallic nanoparticles in colloidal solutions. For example, polyvinylpyrrolidone (PVP) is a polymer with nitrogen heterocycles typically employed in the synthesis of metallic nanoparticles with controlled size.<sup>2,3</sup> The excellent performance of PVP as stabilizing agent of metallic nanoparticles is attributed to its high ability of coordination.<sup>4</sup> Thereby, PVP has been employed as stabilizing agent of nanoparticles of different metals like Au,<sup>5</sup> Ag,<sup>6,7</sup> Pt,<sup>8</sup> Pd,<sup>9,10</sup> Cu,<sup>11</sup> Ru,<sup>12</sup> Ir,<sup>10</sup> and Co.<sup>13</sup> Meanwhile, nitrogen

rich heterocycles such triazole and tetrazole and their derivatives are compounds with high donor character in the formation of metallic complexes and they are an important family of ligand compounds.<sup>14</sup>

Particularly, tetrazole compounds have shown its utility in the formation of Au, Ag, Cu, Pd, Pt, and Rh complexes<sup>15–17</sup> and in the synthesis and stabilization of Au nanoparticles. For example, 1-*R* thiotetrazoles have allowed to obtain spherical gold nanoparticles with size of 2.8–4.7 nm, employing sodium borohydride as reducing agent.<sup>18</sup> Also, these compounds have shown to be good stabilizing agents for the synthesis of Pd and Pt nanoparticles.<sup>19</sup> The synthesis of Au and Ag nanoparticles has been performed employing ionic liquids with the cation tetrazolium as stabilizing agent. The obtained nanoparticles have a size smaller than 20 nm and spherical shape.<sup>20</sup> A theoretical study about interaction between Ag nanoparticles and 5-aminotetrazol indicated that a nitrogen atom of tetrazole ring is linked with the surface of the nanoparticle.<sup>21</sup>



**Scheme 1.** Synthetic route to obtain the poly[4-(1*H*-tetrazol-5-yl) phenyl acrylate] (3).

Recently there has been an increase in the use of polyelectrolytes as stabilizers of metallic nanoparticles. An advantage of the polyelectrolytes as stabilizing agents is that stabilization is carried out by steric and electrostatic effects simultaneously.<sup>22</sup> *N*-unsubstituted tetrazole compounds are moderately strong acids with  $pK_a$  values between  $-0.8$  and  $6$  depending on the electronic properties of the substituent at position 5 of the tetrazole ring.<sup>23</sup> The acidity properties of tetrazole ring make it a structural group useful on the design and synthesis of polyelectrolytes. In our previous work, we reported the synthesis of polyelectrolytes containing the arsonic acid  $[-AsO(OH)_2]$ <sup>24</sup> and sulfonic acid  $[-SO_2(OH)]$ <sup>25</sup> groups, both of them able of reduce gold and silver ions and stabilize Au and Ag nanoparticles. Therefore, in this work we report the design, synthesis and characterization of novel acid polyelectrolytes with tetrazole rings useful for the stabilization of Au and Ag nanoparticles in colloidal solution.

## EXPERIMENTAL

### Materials and Instruments

All reagents used for the synthesis of polyelectrolytes and metallic nanoparticles are commercially available from Sigma-Aldrich. Acryloyl chloride was distilled in the presence of hydroquinone to remove the phenothiazine. Triethylamine and *N,N*-dimethylformamide were dried by distillation on potassium hydroxide before their use. Tetrahydrofuran (THF) was dried over metallic sodium under inert atmosphere. Ammonium azide was generated in situ from sodium azide and ammonium chloride. The acetone, ethyl acetate, methanol, and ethanol solvents were previously distilled in presence of a convenient drying agent. The other reagents were used as received.

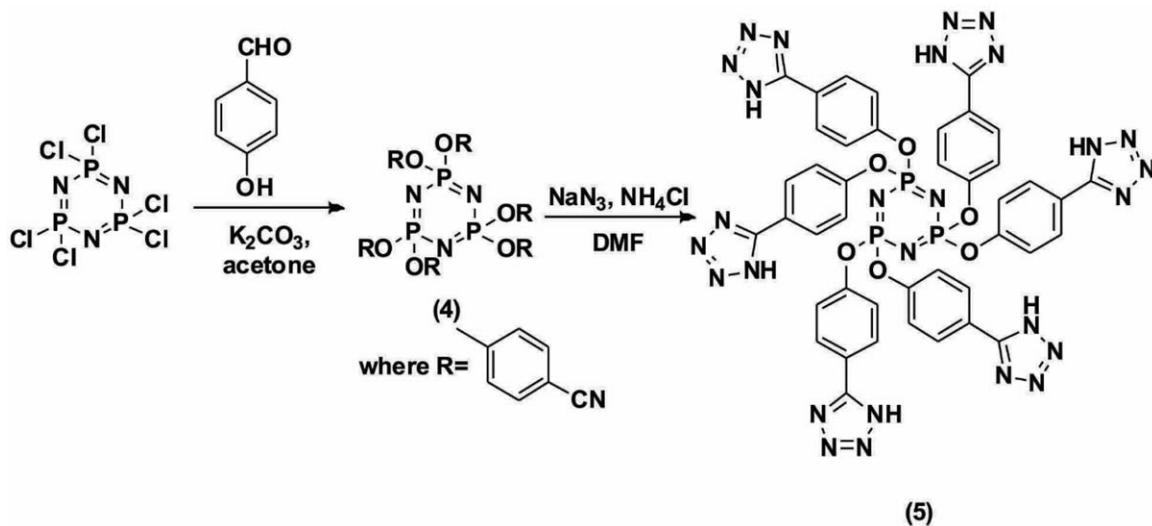
Melting points were measured in an Electrothermal MELT-TEM using the Celsius scale. Infrared absorption spectra were recorded with a Perkin-Elmer spectrophotometer Frontier with a spectral resolution of  $4\text{ cm}^{-1}$ . The samples were prepared using anhydrous KBr. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Varian Nuclear Magnetic Resonance 400 (400 MHz/100 MHz) spectrometer. The samples were prepared using deuterated chloroform ( $CDCl_3$ ), deuterated dimethylsulfoxide ( $DMSO-d_6$ ) or deuterium oxide ( $D_2O$ ) as solvent. For the UV-vis measurements an UV-vis spectrophotometer Perkin-Elmer (model Lambda 2S) was used. The samples were placed in quartz cuvettes ( $1\text{ cm} \times 1\text{ cm} \times 3\text{ cm}$ ) at room temperature, the spectra were obtained in the range of 200–800 nm. The size and shape of the

nanoparticles were analyzed by transmission electron microscopy (TEM). The TEM images were taken with a JEOL (model JEM 2100) transmission electron microscope operating at 200 kV. The samples for TEM were made by depositing the colloidal solution on carbon-coated copper grids and dried in vacuum, size measurements were performed manually on TEM images.

### Synthesis of poly[4-(1*H*-tetrazol-5-yl)phenyl acrylate] (3)

Scheme 1 shows the synthetic route used to obtain the polymer with tetrazole pendant groups (polymer 3). The synthesis was carried out in three steps. First, the 4-acryloyloxybenzotrile monomer (1) was obtained by an acylation reaction between 4-cyanophenol and acryloyl chloride. In a second step, compound 1 was polymerized in DMF solution, using AIBN as thermal initiator. Finally, poly(4-acryloyloxybenzotrile) (2) was chemically modified by 1,3-dipolar cycloaddition reaction with ammonium azide to obtain poly[4-(1*H*-tetrazol-5-yl)phenyl acrylate] (3).

**Synthesis of 4-acryloyloxybenzotrile (1).** A 100 mL one-necked flask equipped with a mechanical stirring device was charged with 5 g (41.97 mmol) of 4-cyanophenol and 25 mL of acetone under argon atmosphere, after the dissolution of 4-cyanophenol the mixture was cooled at  $5\text{--}7\text{ }^\circ\text{C}$  in an ice bath, followed by dropwise addition of 3.5 mL (43.27 mmol) of acryloyl chloride and 6.0 mL (42.98 mmol) of triethylamine simultaneously. A white solid precipitate was obtained immediately. The temperature of the exothermic reaction was maintained at  $5\text{--}7\text{ }^\circ\text{C}$  under stirring for 1 h. Finally, the mixture was stirred at room temperature for 24 h. The precipitate was separated by vacuum filtration, washed with acetone, and discarded. The acetone was removed by evaporation to yield a light yellow liquid. The product was purified by chromatographic column on silica with chloroform as mobile phase. After removal of chloroform by rotary evaporation a white solid was obtained. Compound 1 was soluble in organic solvents as ethanol, methanol, acetone, chloroform, DMSO, and DMF. Yield: 5.68 g (78.15%). mp  $69.5\text{ }^\circ\text{C}$ ; <sup>1</sup>H-NMR (400 MHz,  $CDCl_3$ ,  $\delta$ ): 7.71 (d,  $J = 8.87\text{ Hz}$ , 2H; Ar-H), 7.29 (d,  $J = 8.91\text{ Hz}$ , 2H; Ar-H), 6.65 (dd,  $J = 17.28, 3.99\text{ Hz}$ , 1H; HC=CH<sub>2</sub> trans), 6.63 (dd,  $J = 10.45, 17.27\text{ Hz}$ , 1H; HC=CH<sub>2</sub>), 6.09 (dd,  $J = 10.44, 3.99\text{ Hz}$ , 1H; HC=CH<sub>2</sub> cis); <sup>13</sup>C-NMR (100 MHz,  $CDCl_3$ ,  $\delta$ ): 163.57 (C=O), 153.81 (Ar, C-O), 133.89 ( $-HC=CH_2$ ), 133.69 (Ar), 127.16 ( $-CH=CH_2$ ), 122.16 (Ar), 118.65 (C≡N), 109.76 (Ar, C-CN); FT-IR (KBr): 2229 ( $\nu_{C\equiv N}$ ), 1733 ( $\nu_{C=O}$ ), 1633 ( $\nu_{C=C}$  alkene), 1600, 1500, 1400 ( $\nu_{C=C}$  aromatic ring), 1141 ( $\nu_{C-O}$   $\text{cm}^{-1}$ ).



**Scheme 2.** Synthetic route to obtain hexakis[4-(tetrazol-5-yl)phenoxy]cyclotriphosphazene (5).

**Synthesis of Poly(4-acryloyloxybenzonitrile) (2).** In a test tube, 3.25 g of 4-acryloyloxybenzonitrile monomer and 65 mg of AIBN initiator were dissolved in 6 mL of DMF and mixture was bubbled with argon gas for 20 min. The tube was sealed and placed in a water bath at 70 °C for 1 h. After the polymerization reaction the tube was cooled to room temperature and the DMF was eliminated by vacuum distillation obtaining a viscous mixture. The polymer was isolated by precipitation of the viscous mixture in water; finally the polymer purification was made by reprecipitation in methanol. Polymer **2** was obtained as a white powder; and it was soluble in acetone, DMF and DMSO. Yield: 3.21 g (98.84%). mp 138 °C; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ): 7.75 (s, 2H; Ar-H), 7.17 (s, 2H; Ar-H), 2.96 (s, 1H; -CH-); 2.21 (m, 2H; -CH<sub>2</sub>-). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ): 172.78 (C=O), 153.86 (C-O), 134.37 (Ar), 123.16 (Ar), 118.45 (C≡N), 109.45 (C-CN), 39.90 (-CH-CH<sub>2</sub>-), 26.99 (-CH-CH<sub>2</sub>-); FT-IR (KBr, cm<sup>-1</sup>): 2925 -CH<sub>2</sub>-; 2226 νC≡N; 1752 νC=O; 1600, 1500 νC=C aromatic ring; 1126 νC-O.

#### Chemically Modified of Poly(4-acryloyloxybenzonitrile) (3)

In a two-necked flask equipped with mechanical stirring and a condenser, 0.5 g of poly(4-acryloyloxybenzonitrile) were dissolved in 5 mL of DMF. The mixture was heated at 110 °C and then 0.8344 g (15.59 mmol) of ammonium chloride and 1 g (15.38 mmol) of sodium azide were added. The mixture was stirred at 100 °C by 14 h. After that, mixture was distilled under reduced pressure to remove DMF, and 30 mL of CH<sub>2</sub>Cl<sub>2</sub> were added, the formed solid was collected, washed first with acid water (pH 4), then with distilled water, and dried. The polyelectrolyte (**3**) was obtained as an infusible brown powder; and it was insoluble in ethanol, chloroform, acetone, DMF, DMSO, and water, but it was soluble in aqueous solutions of NaOH and NaCl. <sup>1</sup>H-NMR (400 MHz, D<sub>2</sub>O, NaCl anhydrous, δ): 7.68 (s, 2H, Ar-H), 6.90 (s, 2H, Ar-H), 2.75 (m, 3H, CH, CH<sub>2</sub>), <sup>13</sup>C-NMR (100 MHz, D<sub>2</sub>O, NaCl anhydrous, δ): 158.40 (C=N heterocyclic ring), 129.59 (Ar), 116.33 (Ar); FT-IR (KBr): 3421 (νNH), 1721 (νC=O), 1647 (νC=N), 1600, 1514, 1418 (νC=C aromatic ring), 1280 (νN=N), 1181 (νC-O), 1080 cm<sup>-1</sup> (νN-N).

#### Synthesis of Hexakis[4-(tetrazol-5-yl)phenoxy] Cyclotriphosphazene (5)

Scheme 2 shows the synthetic route used to obtain a macroelectrolyte with tetrazole rings. Compound (**5**) was synthesized in two steps. First, hexakis[4-(4-cyanophenoxy)cyclotriphosphazene] (**4**) was synthesized according with the procedure described in the literature.<sup>26</sup> In the second step, compound (**5**) was synthesized via 1,3-dipolar cycloaddition reaction.

In a round-bottom flask equipped with a condenser and a magnetic stir bar 1.1 mmol of compound **4** were dissolved in 10 mL of DMF. After, 7 mmol of ammonium chloride and 7 mmol of sodium azide were added. The heterogeneous solution was stirred at reflux by 7 h and then the mixture was concentrated under reduced pressure. The residue was dissolved in dichloromethane and was extracted with a solution of NaOH 10%. The aqueous phase was transferred to an ice bath while concentrated H<sub>2</sub>SO<sub>4</sub> was added until reach an acid pH. The precipitate formed was filtered and dried to give a yellow and infusible powder which corresponds to the compound **5**. Yield (1.03 g) 78.5%. <sup>1</sup>H-NMR (400 MHz, D<sub>2</sub>O + Na<sub>2</sub>CO<sub>3</sub> anhydrous, δ): 6.81 (d, 2H, Ar), 7.54 (d, 2H, Ar); <sup>13</sup>C-NMR: (100 MHz, D<sub>2</sub>O + Na<sub>2</sub>CO<sub>3</sub> anhydrous, δ) 150.7, 121.6, 128.6, 126.9 (C aromatic), and 161.3 (C tetrazole ring). FT-IR (KBr): 944 (νP-O-Ar), 1205, 1187, and 1165 (νP=N), 1268 (νN=N, tetrazole) γ 1019 cm<sup>-1</sup> (νN-N).

#### Synthesis of Silver and Gold Nanoparticles

Au and Ag nanoparticles were synthesized by colloidal method using the polyelectrolyte (**3**) and macroelectrolyte (**5**) as stabilizer agents. In order to perform these syntheses, five solutions were prepared: 10<sup>-3</sup>M HAuCl<sub>4</sub>·3H<sub>2</sub>O, 10<sup>-3</sup>M AgNO<sub>3</sub>, 1000 mg/L of polymer **3** in NaOH 0.2M, 10<sup>-3</sup>M of compound **5** in 10<sup>-2</sup>M NaOH, and 10<sup>-2</sup>M NaBH<sub>4</sub>, as a reducing agent.

For the synthesis of Au nanoparticles with the polymer **3**, 1 mL of HAuCl<sub>4</sub>·3H<sub>2</sub>O solution, and 2.5 mL of polymer **3** solution were mixed in a glass vial. The mixture was stirred and then 0.2 mL of NaBH<sub>4</sub> solution was added. Ag nanoparticles were prepared mixing 1 mL of AgNO<sub>3</sub> solution with 2 mL of polymer **3** solution. Then 0.2 mL of NaBH<sub>4</sub> solution was added.

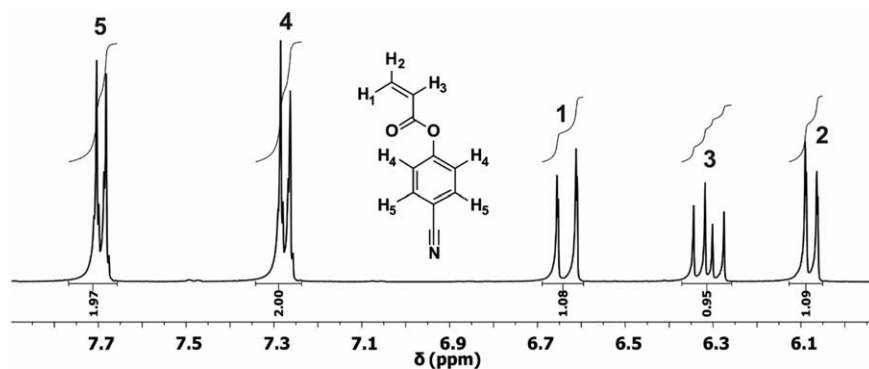


Figure 1.  $^{13}\text{C}$ -NMR spectrum of 4-acryloyloxybenzonitrile (1) recorded at 400 MHz in  $\text{CDCl}_3$ .

The synthesis of Au and Ag nanoparticles with the compound 5 was carried out by mixing of 2 mL of solutions  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  or  $\text{AgNO}_3$  with 2 mL of compound 5 solution. Finally, 0.3 mL of  $\text{NaBH}_4$  freshly solution was added. The synthesis of metallic nanoparticles was carried out at room temperature. The obtained solutions were monitored by UV-vis spectroscopy at different time intervals. The size and shape of metallic nanoparticles were studied by TEM.

## RESULTS AND DISCUSSION

### Characterization of Poly[4-(1H-tetrazol-5-yl)phenyl acrylate] (3) and Precursors

$^1\text{H}$ -NMR spectrum of 4-acryloyloxybenzonitrile monomer (1) is shown in Figure 1. The diagnostic signals for this compound were observed between 6.65 and 6.08 ppm, which indicate the

incorporation of the acrylic moiety. These signals were assigned using first order coupling constants analysis.

The  $^{13}\text{C}$ -NMR spectrum of 1 (Figure 2), shows eight signals in the range of 163.58–109.75 ppm. The assignment of the signals was realized by mean of NMR in two dimensions. The signals observed at 163.57, 133.89, and 127.16 ppm were assigned to  $\text{C}=\text{O}$  and  $-\text{CH}=\text{CH}_2$ , respectively, and confirm the formation of acrylic ester.

The most important evidences of polymerization of monomer (1) were obtained from its  $^1\text{H}$ -NMR spectrum. In this spectrum, there were no signals between 6.08 and 6.65 ppm, which indicate the disappearance of the vinyl group. Broad signals between 1 and 3 ppm were observed and assigned to the

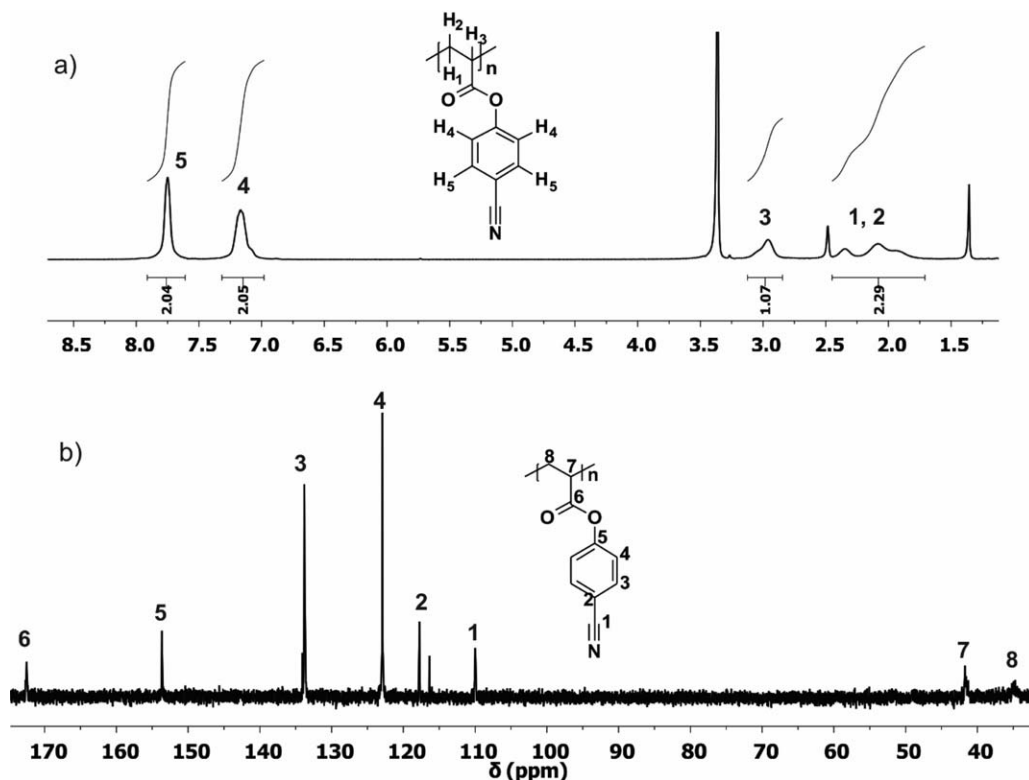
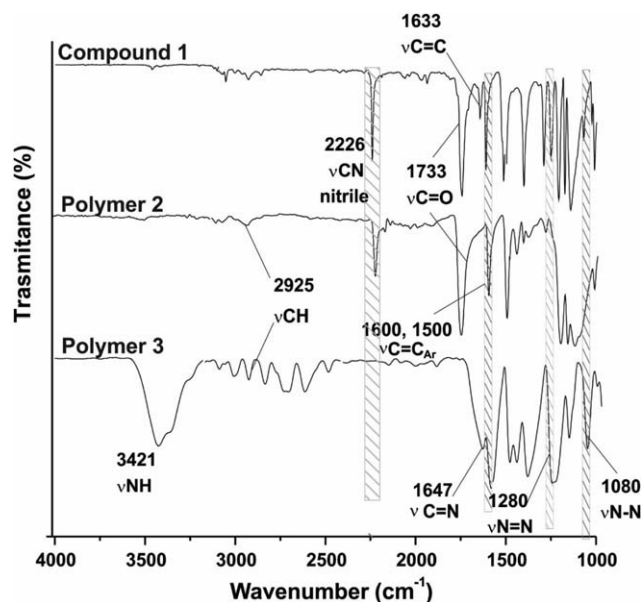


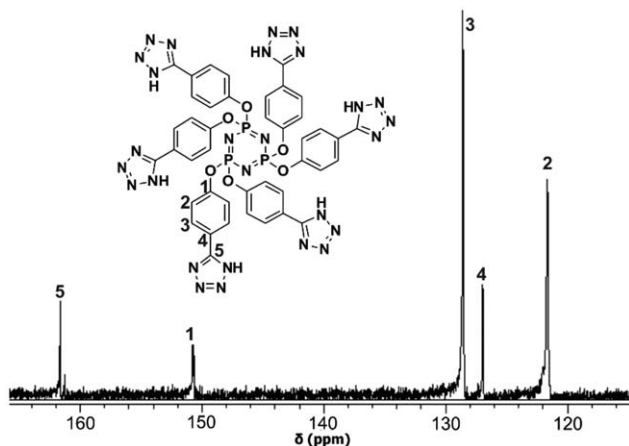
Figure 2. (a)  $^1\text{H}$ -NMR spectrum of poly(4-acryloyloxybenzonitrile) (1) recorded at 400 MHz in  $\text{DMSO-d}_6$  and (b)  $^{13}\text{C}$ -NMR spectrum of 1 recorded at 100 MHz in  $\text{acetone-d}_6$ .



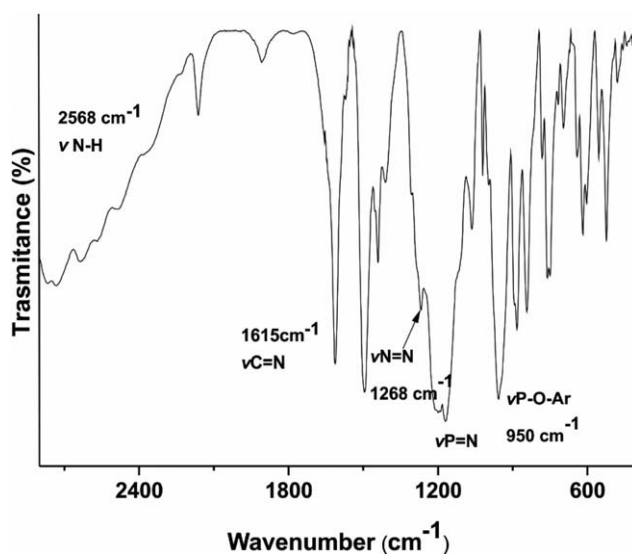
**Figure 3.** FT-IR spectra of poly[4-(1H-tetrazol-5-yl) phenyl acrylate] (3) and starting materials.

protons of methyne and methylene groups of backbone chain. The  $^{13}\text{C}$ -NMR spectrum of polymer 2 also confirms the formation of the polymer by the disappearance of signals attributed to vinyl group (133.89 and 127.16 ppm). In addition, a signal at 26.99 ppm was observed and assigned to carbon of methylene group of polymer backbone. Signals at 172.78 and 118.45 ppm indicate that carbonyl and cyano groups remain in the polymer (2) structure.

The  $^1\text{H}$ -NMR spectrum of polyelectrolyte (3) shows characteristic signals of aromatic protons and from the polymer backbone. The  $^{13}\text{C}$ -NMR spectrum of (3) showed a signal at 158.40 ppm, which was assigned to carbon atom of heterocyclic ring. Figure 3 shows the FT-IR spectra of 1, 2, and 3. Spectrum of compound 1 showed absorption bands in 1733 and 1633  $\text{cm}^{-1}$  due to  $\text{vC=O}$  vibration of ester and  $\text{vC=C}$  of alkene group, respectively, which are absent in the structure of 4-cyanophenol and

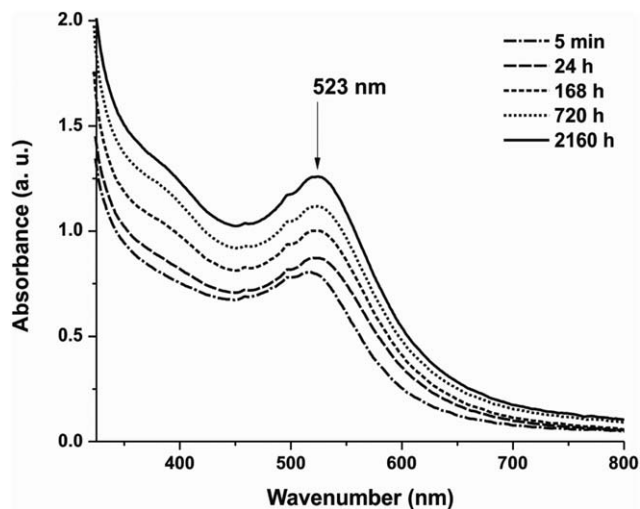


**Figure 4.**  $^{13}\text{C}$ -NMR spectrum of compound 5 recorded at 400 MHz in  $\text{D}_2\text{O}$ - $\text{Na}_2\text{CO}_3$  (anhydrous).

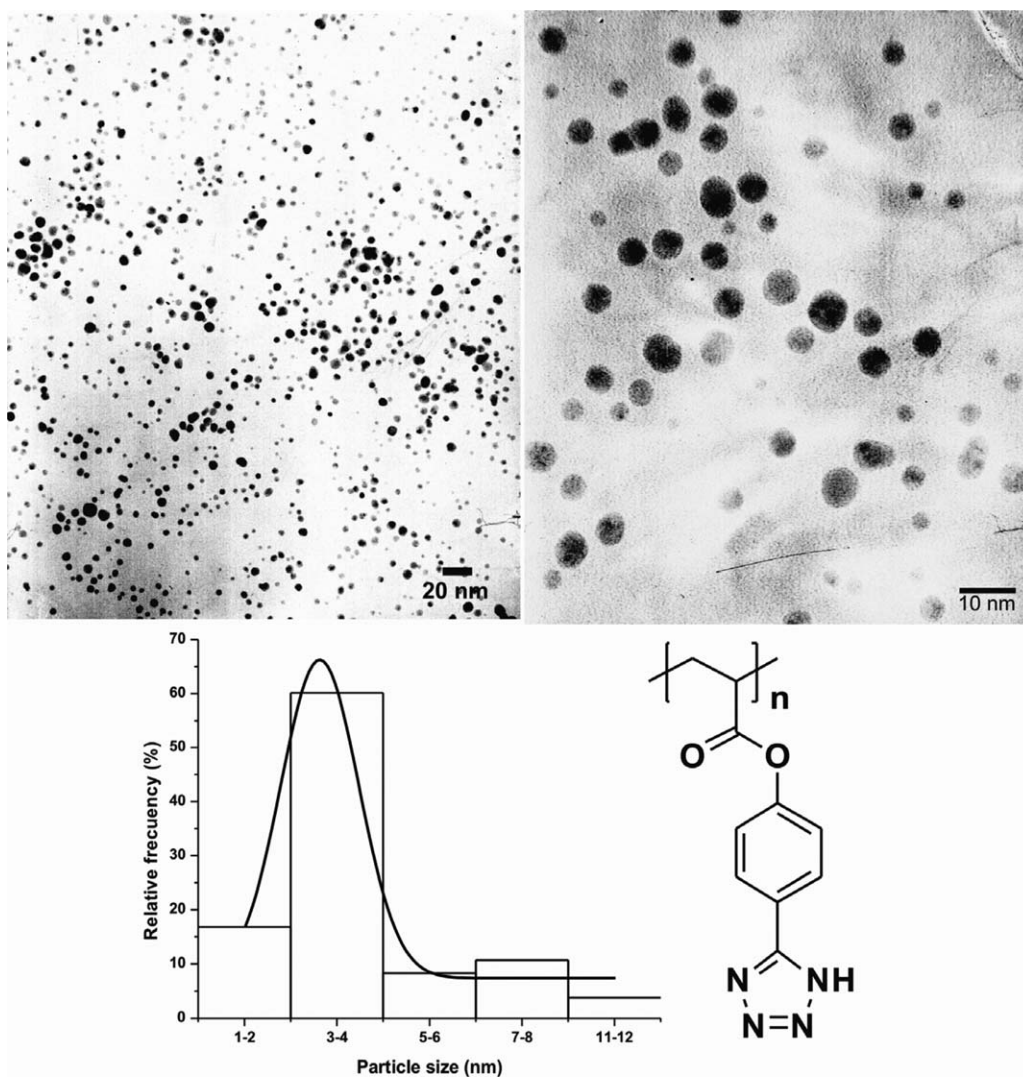


**Figure 5.** FT-IR spectrum of compound 5.

confirmed the obtaining of the desired molecule. The absorption band in 2226  $\text{cm}^{-1}$  was attributed to  $\text{vC}\equiv\text{N}$  vibration of nitrile group and the absorption band in 1600  $\text{cm}^{-1}$  was assigned to  $\text{vC=C}$  of aromatic ring. After polymerization, the absorption band of  $\text{vC=C}$  vibration disappear, and a band at 2925  $\text{cm}^{-1}$  (attributed to  $\text{vC-H}$  vibration of methylene group from the polymer backbone) was observed. The FT-IR spectrum of polymer 2 also showed the absorption bands of  $\text{vC}\equiv\text{N}$  of nitrile group at 2226  $\text{cm}^{-1}$  and  $\text{vC=C}$  vibrations at 1600  $\text{cm}^{-1}$  from the aromatic ring. The conversion of nitrile to tetrazole rings by chemical modification was confirmed from FT-IR spectrum of polyelectrolyte (3). This spectrum shows an absorption band at 1647  $\text{cm}^{-1}$  attributed to  $\text{vC=N}$  vibration as well as other characteristic bands of tetrazole ring (1280, 1080, and 3421  $\text{cm}^{-1}$ ). In addition, the spectrum of polyelectrolyte (3) shows the absence of the absorption band due to  $\text{vC}\equiv\text{N}$  vibration (2226  $\text{cm}^{-1}$ ) of nitrile group. These evidences confirm the



**Figure 6.** Temporal evolution of UV-vis spectrum of Au nanoparticles stabilized by polymer 3.



**Figure 7.** TEM images of Au nanoparticles synthesized with polymer 3 and the size distribution of the Au nanoparticles in them.

successful modification of nitrile groups by 1,3-dipolar cycloaddition reaction.

#### Characterization of Hexakis[4-(tetrazol-5-yl)phenoxy]Cyclotriphosphazene (5)

The  $^{13}\text{C}$ -NMR spectrum of 5 shows five signals (Figure 4), one of them at 161.3 ppm attributable to carbon atom of the heterocyclic ring,<sup>6</sup> which confirm the nitrile to tetrazole conversion. This amount of signals indicates that all branches have the same structure and the nitrile-tetrazole conversion was complete. The FT-IR of compound 5 (Figure 5) shows typical bands of tetrazole ring ( $1268\text{ cm}^{-1}$   $\nu\text{N}=\text{N}$ ;  $1019\text{ cm}^{-1}$   $\nu\text{N}-\text{N}$ ) and no bands were observed for nitrile group, which confirms the complete conversion.

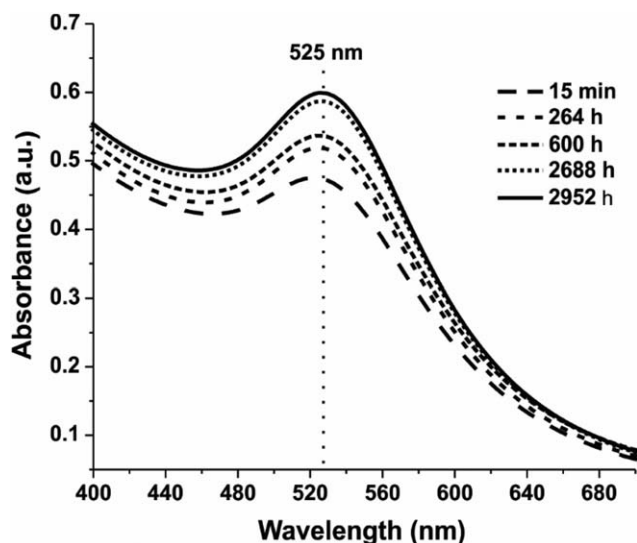
#### Synthesis and Characterization of Metallic Nanoparticles

Formation of Au and Ag nanoparticles using the polyelectrolyte (3) and compound (5) which contain tetrazole rings bonded covalently to the structure, was monitored in situ by UV-vis absorption spectroscopy since is well known that noble metal

nanoparticles exhibit a strong absorption band in the UV-vis region due to Surface Plasmon Resonance (SPR).

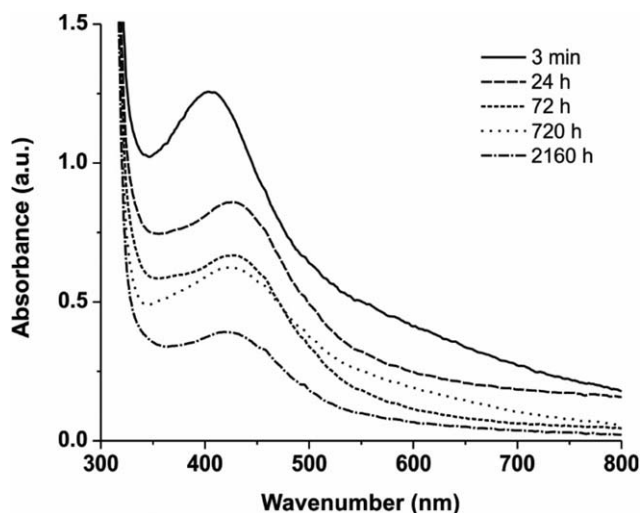
#### Synthesis and Stabilization of Au Nanoparticles with Polyelectrolyte 3 and Compound 5.

Figure 6 shows the temporal evolution of UV-vis spectrum of Au nanoparticles synthesized with polyelectrolyte (3). The figure shows the UV-vis spectra of colloidal solution taken at different time intervals after mixing the solution of  $\text{NaBH}_4$  with the solution formed by  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  and the polyelectrolyte (3) at room temperature. Five minutes after adding  $\text{NaBH}_4$ , the spectrum of colloidal solution shows an absorption band in 517 nm which corresponds to SPR band of Au nanoparticles. The width of the absorption band correspond to SPR indicated that the distribution of nanoparticles size is narrow, this affirmation was confirmed from TEM images. This absorption band is the principal evidence of reduction of  $\text{Au}^{3+}$  ions and formation of gold nanoparticles. With the increase in the reaction time, the SPR band shifts gradually from its starting point to 523 nm during the first hours of reaction, whereas its intensity increases.



**Figure 8.** Temporal evolution of UV-vis spectra of Au nanoparticles stabilized by compound 5.

After that, the position of SPR band did not shift from its position, because the size and form of Au nanoparticles do not change, and only was observed an increment in its intensity until a reaction time of 2160 h, when the stabilization was reached. The increase in the intensity of SPR band was attributed only to the increase of the concentration of particles formed, whereas the shift in its position was attributed to the increase in the average size of nanoparticles. The Au nanoparticles were stabilized by steric and electrostatic effects. The steric effect is due to the high molecular weight of polymer, and the electrostatic effect is due to negative charges of the polyelectrolyte in all tetrazole rings. The Au nanoparticles stabilized with polymer 3 stayed stable in the colloidal solution for several months and no precipitate was observed. Finally, the solution of polymer 3 and  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  initially was lightly yellow and after adding  $\text{NaBH}_4$  the solution acquired red color. This change of color it is another evidence of formation of gold

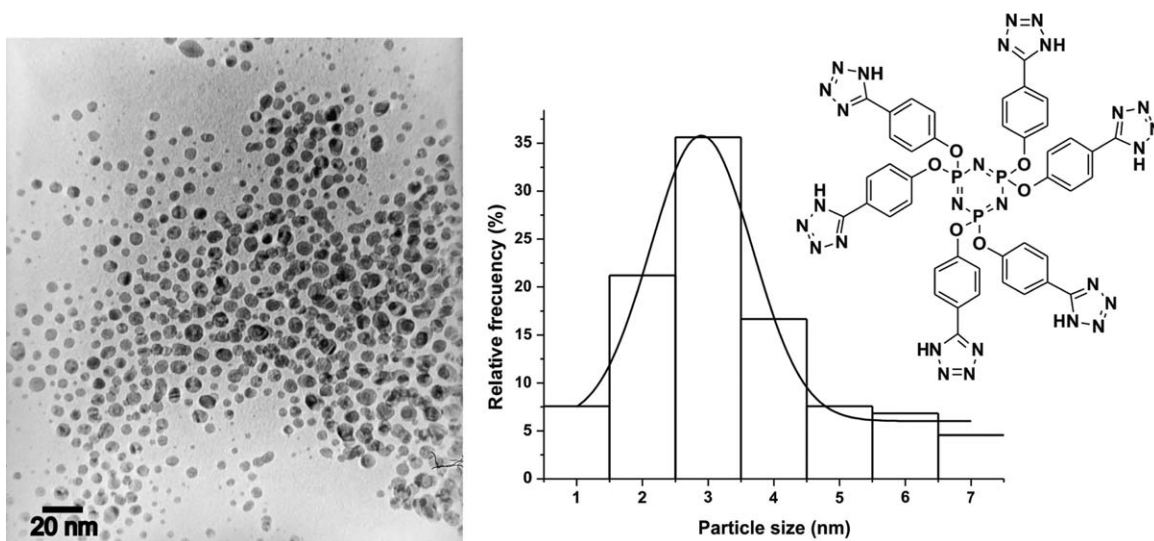


**Figure 10.** Temporal evolution of UV-vis spectra of Ag nanoparticles stabilized by polymer 3.

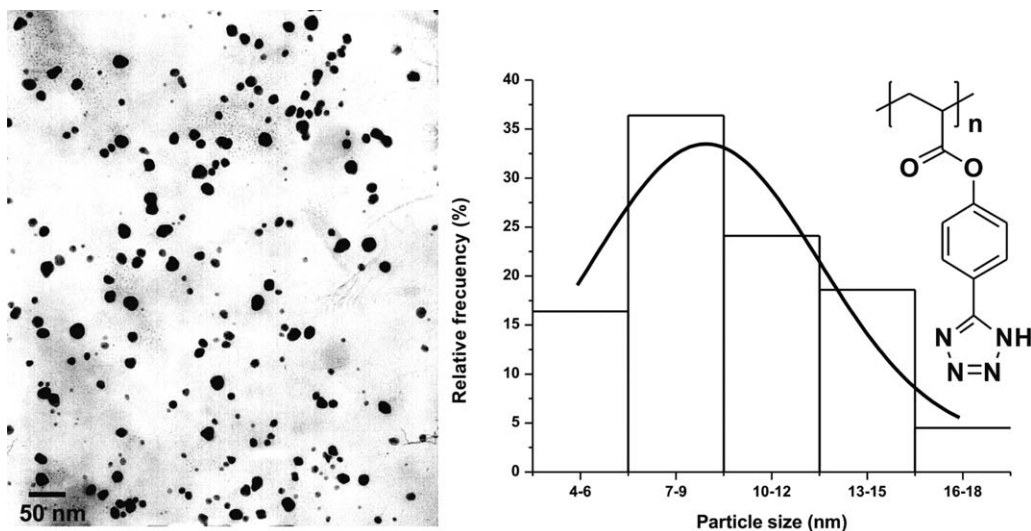
nanoparticles. Any other color change was observed with increasing reaction time.

Figure 7 shows typical TEM images of Au nanoparticles stabilized by polymer 3 in aqueous solution, after 72 h of reaction. TEM images revealed the formation of Au nanoparticles with size in the range of 1.9–10.7 nm, which have quasi-spherical shape and average diameter of 3.8 nm. However, more than 70% of Au nanoparticles are in the range of 1.9–3.65 nm. This results show that polyelectrolyte (3) it is a very good stabilizing agent during the synthesis of Au nanoparticles by colloidal method, forming Au nanoparticles with a shape and size controlled, obtaining a narrow size distribution.

The UV-vis spectra of colloidal solution obtained after mixing  $\text{NaBH}_4$  with the solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  and compound 5 are shown in the Figure 8. In this case, when  $\text{NaBH}_4$  was added to the solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  with compound 5 it acquired a violet color indicating the reduction of  $\text{Au}^{3+}$  ions and the



**Figure 9.** TEM image of Au nanoparticles stabilized by compound 5 and its size particle distribution.



**Figure 11.** TEM image of Ag nanoparticles synthesized with polymer 3 and its size particle distribution.

formation of Au nanoparticles. At 15 min of reaction, the spectrum of the colloidal solution showed the SPR band of Au nanoparticles at 525 nm.

As the reaction time increase, it was observed an increase in the intensity of SPR band as consequence of the increase of the concentration of nanoparticles formed. After 4 months, the system reached the stabilization, because the intensity and shift of SPR band does not change, and precipitates were not formed indicating high stability of the colloidal solution. The UV-vis spectra revealed a slowly reduction of Au ions with macroelectrolyte 5, because the intensity in de SPR band increased slowly, however the control in size and form of Au nanoparticles was better than polyelectrolyte 3, this was confirmed from TEM image (Figure 9).

The characterization by TEM showed that compound (5) was able to control the size and shape of the Au nanoparticles too. Figure 9 shows a typical TEM image of Au nanoparticles stabilized by compound 5 at 264 h of reaction. The image revealed the formation of Au nanoparticles with quasi-spherical shape. Finally, the image showed that Au nanoparticles have a small size between 1 and 7 nm and an average size of 3.3 nm.

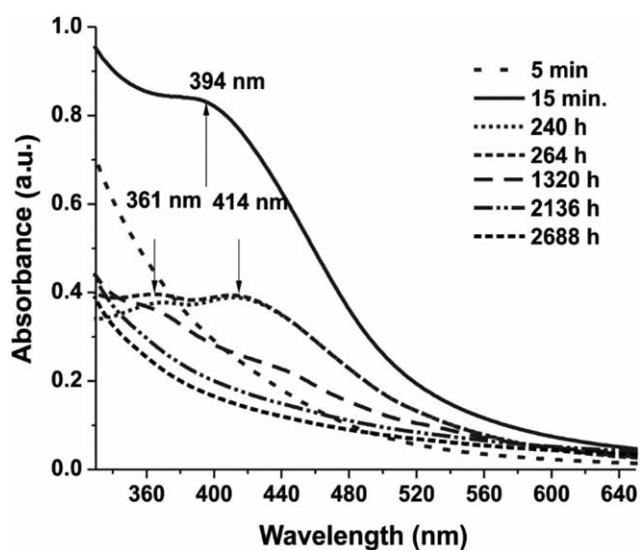
From the above, it is observed that both polyelectrolyte 3 and compound 5 are good stabilizing agent during the synthesis of Au nanoparticles. However, polyelectrolyte 3 led to obtaining Au nanoparticles with lower average diameter than compound 5. This is a consequence of the molecular weight of polyelectrolyte 3, which may control better the growing of Au nanoparticles by steric effect. Further, both colloidal solutions stabilized with polymer 3 and compound 5 showed high stability for several months. The high affinity between tetrazole ring and Au atoms contributes significantly to this high stability.

**Synthesis and Stabilization of Ag Nanoparticles with Polyelectrolyte 3 and Compound 5.** Formation of Ag nanoparticles using the polymer 3 was monitored by UV-vis spectroscopy. Figure 10 shows the temporal evolution of UV-vis

spectrum of the colloidal solution obtaining after adding  $\text{NaBH}_4$  to the solution of  $\text{AgNO}_3$  and polymer 3. The spectrum of colloidal solution at 3 min of reaction shows an absorption band in 402 nm attributed to the SPR band of Ag nanoparticles.

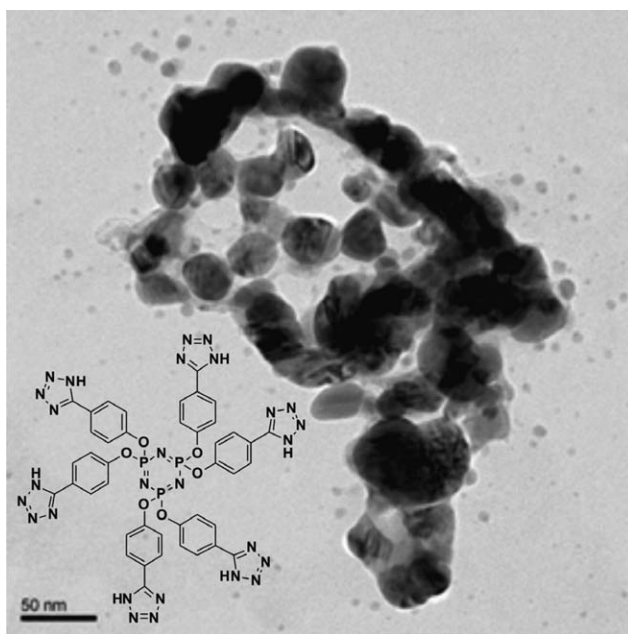
With the increase in reaction time the SPR band showed a shift in its position until 422 nm, due to the increased the size of Ag nanoparticles, and the intensity of SPR band decreased. Simultaneously, the formation of a brown precipitate was observed. This indicates that Ag nanoparticles have low stability in the colloidal solution and they tend to coalesce. However, 2160 h after adding reducing agent, the SPR band did not present more changes, which indicates that the system reaches some condition of stability where Ag nanoparticles do not coalesce.

Figure 11 shows a TEM image of Ag nanoparticles stabilized by polymer 3 after 72 h of reaction. Even when Ag nanoparticles synthesized with the polymer 3 had lower stability than



**Figure 12.** Temporal evolution of UV-vis spectra of Ag nanoparticles stabilized by compound 5.





**Figure 13.** TEM image of Ag nanoparticles synthesized with compound 5.

Au nanoparticles, they were obtained with shape and size controlled. The image reveals the obtaining of Ag nanoparticles with quasi-spherical shape and size between 3.5 and 18.4 nm, the average size was of 9.7 nm. Nonetheless, the control of size of Ag nanoparticles was lower than the control observed in Au nanoparticles, as show the bigger average size and the wider size distribution obtained.

Meanwhile, compound 5 neither was able to stabilize the Ag nanoparticles in the colloidal solution. Figure 12 shows the UV-vis spectra of colloidal solution obtained by mixing  $\text{NaBH}_4$  aqueous with the solutions of  $\text{AgNO}_3$  and compound 5. Five minutes after adding the reducing agent, the colorless solution with compound 5 acquired a yellow color. At the same time, the UV-vis spectrum showed the SPR band at 394 nm due to the presence of Ag nanoparticles. At 240 h, the spectrum of solution showed two SPR bands at 414 nm and 361 nm. They were attributed to Ag nanoparticles with bimodal size distribution. The colloidal solution of Ag nanoparticles stayed stable until complete 600 h. Then, the SPR band in the UV-vis spectrum diminished its intensity until disappear. Simultaneously, the colloidal solution acquired a colorless aspect and the formation of precipitate was observed. Ag nanoparticles stabilized by compound 5 were stable in the colloidal solution only for 25 days.

The characterization of Ag nanoparticles by TEM showed that compound 5 was not able to control the size and shape of Ag nanoparticles. The Figure 13 shows a TEM image of Ag nanoparticles synthesized with compound 5 at 240 h of reaction. As the evolution of UV-vis spectrum suggests, the Ag nanoparticles were obtained with nonuniform size. It can be observed Ag nanoparticles of 5 nm and Ag nanoparticles bigger than 50 nm. The smaller Ag nanoparticles are spherical while the bigger nanoparticles have irregular shape. The TEM images showed too that there is not a well dispersion of nanoparticles

in the system; the bigger Ag nanoparticles are formed by agglomeration of smaller nanoparticles. According with the observations realized by UV-vis, at 240 h of reaction there are big agglomerates of nanoparticles that lead to coalescence and precipitation of Ag nanoparticles.

The results indicate that polyelectrolytes with tetrazole ring are not the most appropriate stabilizing agents for the synthesis of Ag nanoparticles. However, polymer 3 is better stabilizing agent for this purpose. Polymer 3 is able to control the size and shape of Ag nanoparticles for short time periods. Meanwhile, compound 5 do not control the growing of Ag nanoparticles and they rapidly coalesce, leading to the precipitation of Ag with the polyelectrolyte forming an organometallic complex.

The lower stability of Ag nanoparticles synthesized with polyelectrolytes containing tetrazole groups may be attributed to the low affinity between tetrazole rings and Ag atoms. The weak interaction between them does not allow stabilize the Ag nanoparticles through steric effects allowing the consequent agglomeration and coalescence.

## CONCLUSIONS

From our results, we can conclude that polymer 3 and compound 5 containing tetrazole group are able to stabilize Au nanoparticles in colloidal solutions and prevent their aggregation and coalescence. Au nanoparticles remained stable in the colloidal solutions for several months, which show their high stability. Further, Au nanoparticles were obtained with shape and size controlled. Colloidal solutions of Ag nanoparticles stabilized by polymer 3 were less stable, but the nanoparticles formed have shape and size controlled and they remain in suspension by several weeks. As it was mentioned before, polymer 3 is the better stabilizing agent than compound 5, but both can be used for successful nanoparticle stabilization.

## ACKNOWLEDGMENTS

The authors acknowledge the financial support through the project CONACyT-CB2011 No. 168071.

## REFERENCES

- Dumur, F.; Guerlin, A.; Dumas, E.; Bertin, D.; Gigmès, D.; Mayer, C. R. *Gold Bull.* **2011**, *44*, 119.
- Tsuji, T.; Thang, D. H.; Nakanishi, M.; Tsuboi, Y.; Tsuji, M. *Appl. Surf. Sci.* **2008**, *254*, 5224.
- Ayyappan, S.; Srinivasa Gopalan, R.; Subbanna, G. N.; Rao, C. N. R. *J. Mater. Res.* **1997**, *12*, 398.
- Kan, C.; Cai, W.; Li, C.; Zhang, L. *J. Mater. Res.* **2005**, *20*, 320.
- Behera, M.; Ram, S. *Appl. Nanosci.* **2014**, *4*, 247.
- Wang, H.; Qiao, X.; Chen, J.; Wang, X.; Ding, S. *Mater. Chem. Phys.* **2005**, *94*, 449.
- Desai, A.; Varade, D.; Mata, J.; Aswal, V.; Bahadur, P. *Colloids Surf. A* **2005**, *259*, 111.

8. Morales, B. E.; Gamboa, S. A.; Pal, U.; Guardián, R.; Acosta, D.; Magaña, C.; Mathew, X. *Int. J. Hydrogen Energy* **2010**, *35*, 4215.
9. Li, Y.; Boone, E.; El-Sayed, M. A. *Langmuir* **2002**, *18*, 4921.
10. Teranishi, T.; Miyake, M. *Chem. Mater.* **1998**, *10*, 594.
11. Gurav, P.; Srinu Naik, S.; Ansari, S.; Srinath, K.; Kishore, A.; Pydi Setty, Y.; Sonawane, S. *Colloids Surf. A* **2014**, *441*, 589.
12. Gual, A.; Delgado, J. A.; Godard, C.; Castellón, S.; Curulla-Ferré, Claver, C. *Catal. Top. Catal.* **2013**, *56*, 1208.
13. Osuna, J.; de Caro, D.; Amiens, C.; Chaudret, B.; Snoeck, E.; Respaud, M.; Broto, J. M.; Fert, A. *J. Phys. Chem.* **1996**, *100*, 14571.
14. Aromí, G.; Barrios, L. A.; Roubeau, O.; Gamez, P. *Coord. Chem. Rev.* **2011**, *255*, 485.
15. Tao, G. H.; Parrish, D. A.; Shreeve, J. N. M. *Inorg. Chem.* **2012**, *51*, 5305.
16. Voitekhovich, S. V.; Serebryanskaya, T. V.; Lyakhov, A. S.; Gaponik, P. N.; Ivashkevich, O. A. *Polyhedron* **2009**, *28*, 3614.
17. Wehlan, M.; Thiel, R.; Fuchs, J.; Beck, W.; Fehlhammer, W. P. *J. Organomet. Chem.* **2000**, *613*, 159.
18. Nichick, M. N.; Voitekhovich, S. V.; Shavel, A.; Lesnikovich, A. I.; Ivashkevich, O. A. *Polyhedron* **2009**, *28*, 3138.
19. Nichick, M. N.; Voitekhovich, S. V.; Shavel, A.; Lesnikovich, A. I.; Ivashkevich, O. A. *J. Phys. Chem. C* **2011**, *115*, 16928.
20. Singh, P.; Kumari, K.; Katyal, A.; Klra, R.; Chandra, R. *Spectrochim. Acta Part A* **2009**, *73*, 218.
21. Thomas, S.; Biswas, N.; Venkateswaran, S.; Kapoor, S.; Naumov, S.; Mukherjee, T. *J. Phys. Chem. A* **2005**, *109*, 9928.
22. Note, C.; Koetz, J.; Kosmella, S.; Tiersch, B. *Colloid Polym. Sci.* **2005**, *283*, 1334.
23. Boraei, A. A. *J. Chem. Eng. Data* **2001**, *46*, 939.
24. García-Serrano, J.; Pal, U.; Herrera, A. M.; Salas, P.; Angeles-Chavez, C. *Chem. Mater.* **2008**, *20*, 5146.
25. Herrera-González, A. M.; Caldera-Villalobos, M.; García-Serrano, J.; Peláez-Cid, A. A. *Des. Monomers Polym.* **2016**, *19*, 330.
26. Carriedo, G. A.; Fernández Catuxo, L.; García Alonso, F.; Gómez Elipe, P.; González, P. A.; Sánchez, G. *J. Appl. Polym. Sci.* **1996**, *59*, 1879.

SGML and CITI Use Only  
DO NOT PRINT

