

# Synthesis of Silver Nanocrystals by a Modified Polyol Method

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**ABSTRACT:** A modification of the polyol method has been shown to result in improved efficiency and enhanced kinetics for the synthesis of silver nanocrystals when compared with the traditional polyol method. The Ag nanocrystals produced were characterized using X-ray diffraction and transmission electron microscopy. Accordingly, the exhibited Ag crystal structure, corresponding lattice constants, and resultant particle sizes were determined by these means. In addition, using Fourier transform infrared spectroscopy, it was found that a solid-state reaction between the AgNO<sub>3</sub> and the Poly(vinylpyrrolidone) (PVP) takes place prior to their dissolution in ethylene glycol. Moreover, when crystals grow

under total rest conditions, they do not develop a spherical morphology as in the traditional polyol method, but a well-defined geometric shape showing preferential crystallographic growth directions. Under the experimental conditions of this work, the exhibited nanocrystal shapes were quasi-planar hexagonal. Apparently, PVP interacts with the FCC crystal structure promoting growth on the {100} preferential direction by playing the role of an atomic arranger. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 45–53, 2008

**Key words:** nanocrystal synthesis; silver nanoparticles-silver nanostructures; polyvinylpyrrolidone; polyol method

## INTRODUCTION

Several techniques have been developed for the processing of metallic nanopowders in pure metals or in alloy systems, and they can be classified as physical or chemical. Among the physical methods are atomization,<sup>1</sup> splash quenching,<sup>2</sup> laser ablation,<sup>3</sup> ionic bombardment pulverization,<sup>4</sup> high-vacuum deposition,<sup>5</sup> laser synthesis from gaseous precursors,<sup>6</sup> and mechanical alloying.<sup>7</sup> The chemical methods involve the precipitation of the metallic components from their respective solutions,<sup>8</sup> followed by gas reduction using C, CO, or H<sub>2</sub>,<sup>8–10</sup> as well as the polyol method.<sup>11–14</sup>

Among the different processing methods, the polyol method has been proven to be highly reliable for the synthesis of metallic nanoparticles. However, most published works have been focused on the synthesis itself and on the processed nanomaterials. Hence, there is hardly any published literature on the reaction mechanisms involved between the precursor and the metallic compound from which the nanocrystals are obtained.<sup>11–15</sup> In a recent work,<sup>16,17</sup> it was found that Poly(vinylpyrrolidone) (PVP) plays

an important role in determining the final shape of nanocrystals produced by employing the polyol method. In particular, nanosized spheres and cubes were obtained by these means, but no explanations were given to account for the morphological changes. In the present work, the polyol method was modified by incorporating a solid-state mixing reaction prior to its dissolution in ethylene glycol (in the conventional polyol method the precursor is first dissolved in ethylene glycol and then the metallic compound is added). The modified polyol method was then used in processing Ag nanocrystals and an effort was made to disclose the active mechanisms.

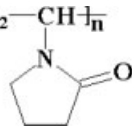
## EXPERIMENTAL METHODS

The raw materials used in this work are given in Table I. For comparison purposes, the modified polyol method as well as the traditional polyol method was investigated in this work.

- *Polyol method.* This method follows the traditional Figlarz polyol method<sup>11</sup> which consists in manually dissolving 1 g of PVP and 100 mg of AgNO<sub>3</sub> in 75 mL of ethylene glycol at 186°C. The solution was mixed for 1 h using a magnetic stirrer (600 rpm) and then it was allowed to rest. Afterwards, at given specific times, the solution

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**TABLE I**  
Chemical Substances Used in This Work

Substance	Chemical formula
Ethylene glycol	HO—CH <sub>2</sub> —CH <sub>2</sub> —OH
Poly(vinylpyrrolidone) (PVP), molecular weight MW = 10,000	$\text{—}[\text{CH}_2\text{—CH}]_n\text{—}$ 
Silver nitrate	AgNO <sub>3</sub>

was centrifuged to get a sample from the sediments. The powders thus obtained are then analyzed and characterized.

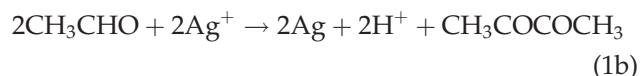
- *Modified polyol method.* The procedure consists in a solid-state mixing of 1 g of PVP with 100 mg of AgNO<sub>3</sub>. The mixture is allowed to react for various times ranging from 10 min to 24 h. Afterwards, the mixture is placed in a sealed dryer container in the absence of light to prevent any photochemical oxidation reactions. The mixture is then manually dissolved in 75 mL of ethylene glycol.

Moreover, there are two implemented variations for the modified polyol method:

1. *Variation A.* The solution was agitated using a magnetic stirrer for 6 h at 186°C in a sealed container and then it was allowed to rest. Samples were taken from this solution at various time intervals.
2. *Variation B.* The solution was allowed to totally rest at 186°C without the intermediate agitation process. Samples were taken from this solution at various time intervals.

The solid-state reactions between the PVP and the AgNO<sub>3</sub> were followed by Fourier transform infrared spectroscopy (FTIR) technique using a Perkin Elmer FTIR System Spectrum GX. The shifting of infrared spectrum bands indicated when a chemical reaction is taking place.

Considering the general chemical reaction<sup>18</sup>:



From the above reactions, each two H<sup>+</sup> requires two Ag cations, in other words, according to this general mechanism for each H<sup>+</sup> one Ag<sup>+</sup> is required to become a single Ag metallic atom.

Considering that the pH is related to the concentration of atomic hydrogen in the solution [H<sup>+</sup>], the

amount of precipitated metallic nanosized Ag particles was estimated by measuring the pH of the solution at various times, using a pH-meter ICM Corning, according the equation:

$$1[\text{H}^+] \frac{\text{mol}}{\text{l}} \left( \frac{107.8682 \text{ g Ag}}{1 \text{ mol Ag}} \right) \left( \frac{1000 \text{ mg}}{\text{g}} \right) = C_{\text{Ag}} \text{mgL} \quad (2)$$

However, this is a semiquantitative method, since a nonaqueous solution is being used and some inaccuracy can always be introduced by using pH values in the 0–14 scale. At the same time, it is a helpful way to measure the relative efficiencies when comparing the different variations of the polyol methods.

X-ray diffraction (XRD) of the powders produced by these methods was carried out using a X-Ray Philips X'Pert diffractometer, with a vertical goniometer using the Cu Kα (λ = 1.54051 Å) radiation. In addition, the morphology of the nanosized powders was investigated by transmission electron microscopy (TEM) using a Philips CM 200 microscope, operating at 200 kV. This enabled determinations of the powder crystal structure and the corresponding lattice parameters. The samples examined under the TEM were Ag nanosized powders collected and dried for 24 h in a filtering paper in the absence of light and placed on a Veco Cu 100 mesh grid. Image analyses were carried out from TEM micrographs using an Omnimet III image analyzer in order to measure the size distributions of the silver particles. In this case, 10 optical fields were analyzed to ensure reliable statistical results.

## RESULTS

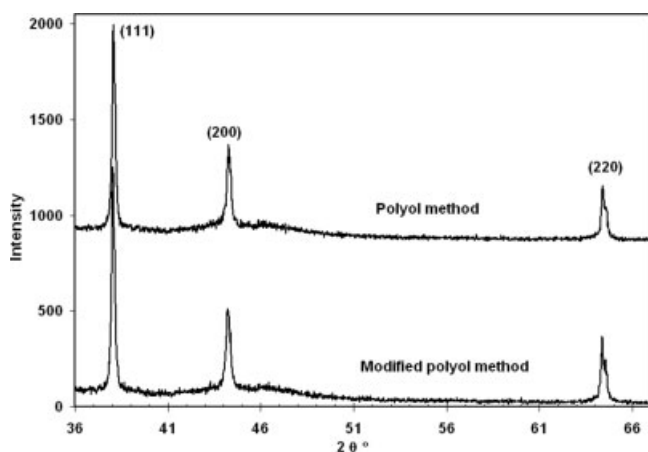
### X-ray diffraction

Preliminary results show that both polyol methods (traditional and modified) can be used to synthesize pure Ag nanoparticles, as seen in Figure 1. In this figure, the XRD patterns correspond to Ag powders after a synthesis period of 3 months. In both methods, silver nanocrystals were obtained with a lattice parameter,  $a_{\text{FCC}} = 0.40729$  nm, and an estimated atomic radius of 0.144 nm in agreement with reported values for metallic Ag.<sup>19,20</sup> However, the processing reaction kinetics is not the same, nor the exhibited nanocrystal morphology. There are intrinsic differences in each of the polyol methods and they are described in the next section.

### Morphology and size of Ag nanoparticles

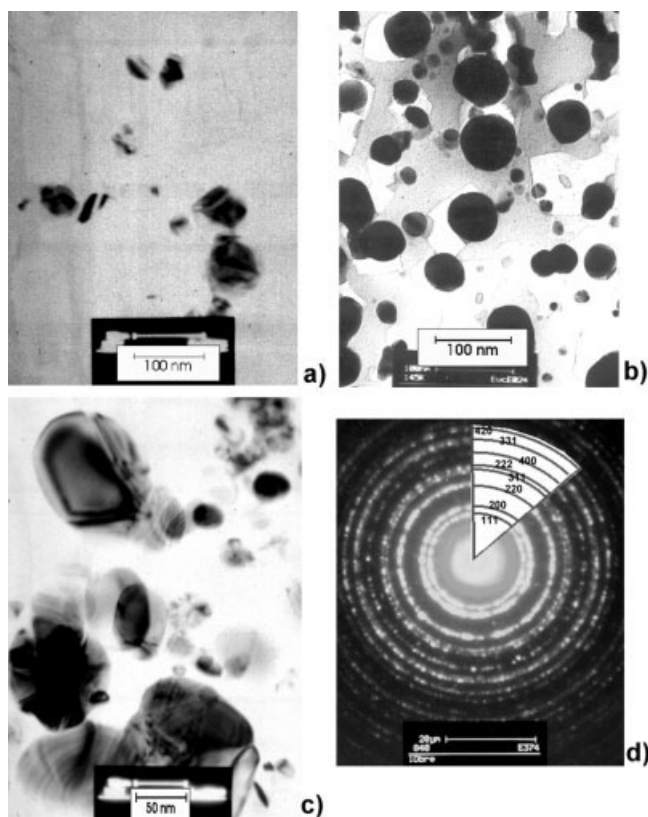
#### Polyol method

Figure 2(a–d) is TEM micrographs of the Ag nanoparticles obtained by the traditional polyol method



**Figure 1** X-ray diffraction patterns of silver powders produced by polyol and modified polyol method after 3 months of synthesis.

at several reaction times. Figure 2(a) shows particles in the early stages of formation, where a quasi-spherical morphology is dominant. At increasing times the morphology becomes clearly spherical, with the particles maintaining a nanometric size, even at times as long as 3 months [Fig. 2(b,c)]. As expected for metallic silver, XRD [Fig. 2(d)] shows



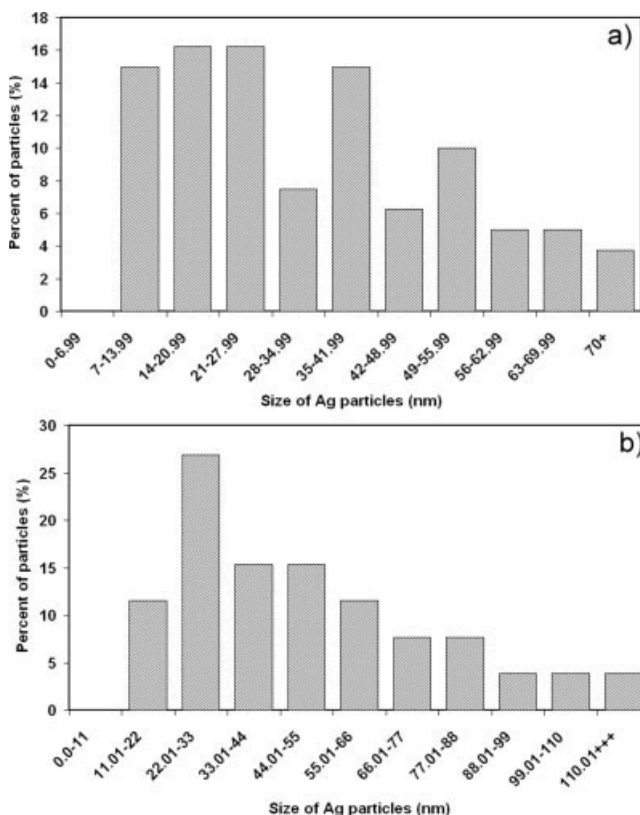
**Figure 2** TEM micrographs showing Ag nanoparticles obtained by polyol method (bright field): (a) 2 h, (b) 8 h, (c) 3 months, (d) electron diffraction pattern obtained from a group of silver nanocrystals.

that the crystal structure of the nanocrystals is FCC with an average lattice parameter of 0.410 nm.

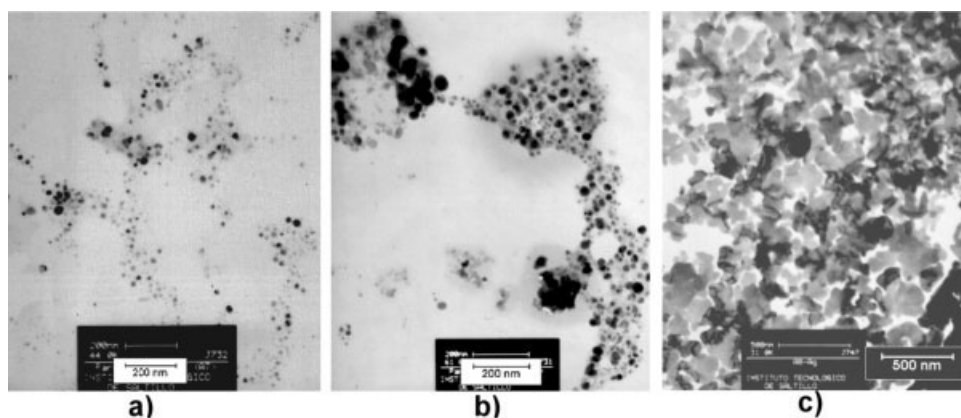
After 8 h of synthesis, the size distribution indicates two predominant average sizes [Fig. 3(a)], indicating two probable formation stages; (a) large-sized particles probably formed during the agitation process and continue to increase in size during the resting period, while increasing Ag atoms came out of solution, and (b) new particles form during this stage, giving rise to the smaller sizes. After 3 months of synthesis [Fig. 3(b)], the particles have increased in size.

#### Modified polyol method

*Variation A.* Figure 4 shows TEM micrographs of Ag nanocrystals obtained by the modified polyol method (variation A). In the early stages, and similar to the conventional polyol method, the Ag nanocrystals develop a spherical shape [Fig. 4(a)] for up to 24 h of synthesis [Fig. 4(b)]. The Ag nanocrystals continue to grow by the addition of  $\text{Ag}^+$  cations, reduced to metallic silver, and after 336 h, their morphology shifts from spherical to irregular, probably as a result of particle coalescence as shown in Figure 4(c).



**Figure 3** Size distribution of particles obtained by polyol method: (a) 8 h, average size 33 nm; (b) 3 months, average size 50 nm.



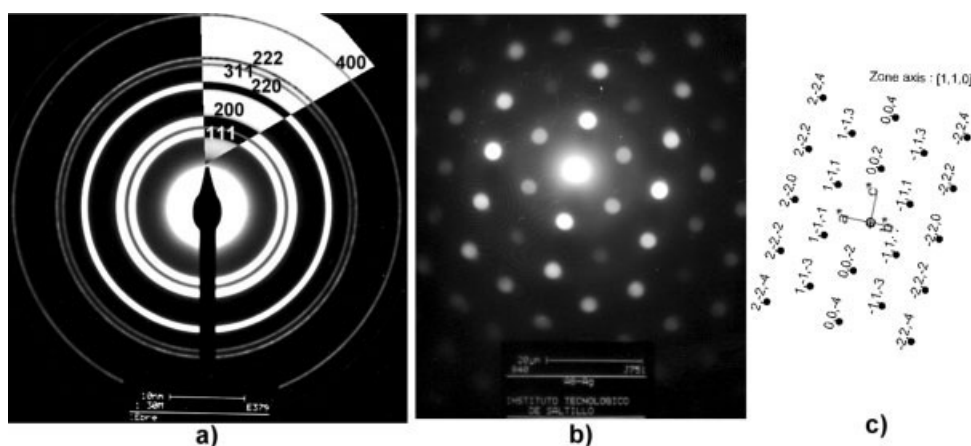
**Figure 4** TEM micrographs showing Ag nanoparticles obtained by modified polyol method (variation A) (bright field): (a) 4 h, (b) 24 h, (c) 336 h.

The electron diffraction patterns, shown in Figure 5, clearly show the crystalline nature of the particles. Accordingly, a lattice parameter of 0.40729 nm for the FCC Ag and an average atomic size of 0.1439 nm were estimated from these patterns [Fig. 5(a)]. In addition, there is a remarkable size increment from 20.3 to 158.7 nm as evidenced from the size distributions shown in Figure 6.

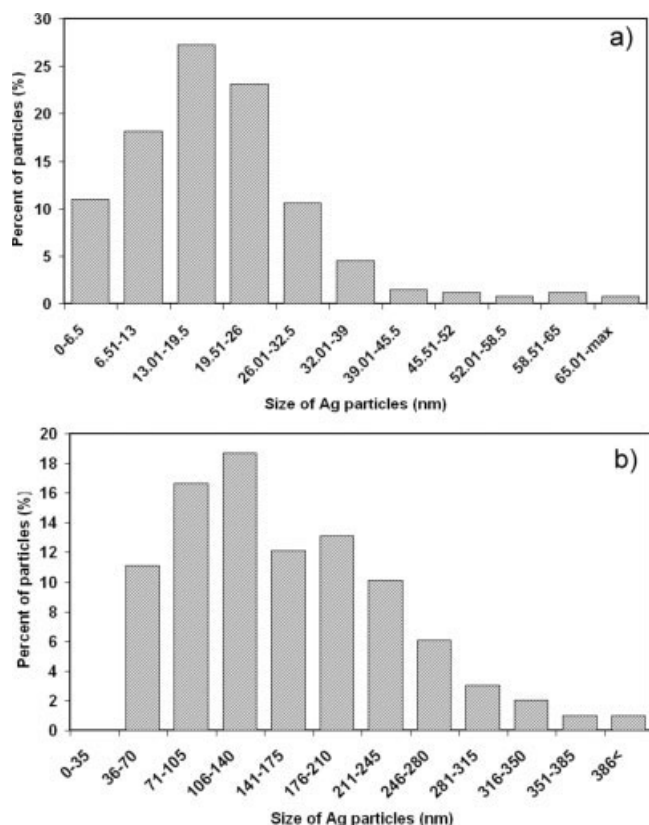
*Variation B.* Figure 7 are TEM micrographs of Ag nanocrystals obtained by the modified polyol method (variation B). Similar to the early stages found in the polyol method, the Ag nanocrystals develop a spherical shape [Fig. 7(a)], yet at longer times the particles are no longer spherical. After 24 h of synthesis, the particles start becoming elongated. Since the liquid solution is not moving and remains at rest, the particles clearly grow following preferential crystallographic directions, as seen in Figure 7(c,d). At growing times of or above 144 h, the particles develop well-defined geometrical shapes.

The crystalline nature of these particles is clearly evident by the electron diffraction patterns of Figure 8. The average lattice parameter calculated from a group of crystals shown in Figure 7(a) was 0.4127 nm, typical of FCC Ag. Moreover, by considering only a single crystal, such as the one shown in Figure 7(f), the measured Ag FCC lattice parameter was 0.1417 nm, for a [110] zone axis.

Tsuji et al.<sup>21</sup> have shown that the shape of Ag nanocrystals, when obtained by polyol methods, greatly depends on the molecular weight of the PVP (and its different chain lengths). Accordingly, in 10K PVP (such as the one used in this work) the formation of Ag nanocrystals with leaves or plate-like shapes is highly favored, while the use of heavier PVP molecular weights (40–360K), promotes rod-like or wire-like shapes. Also, in FCC crystals, equilibrium shapes obey well-defined crystallographic relations that favor a reduction in interfacial energy, as found in high-temperature annealing of single crystals, where {100} and {111} facets are exposed.<sup>22</sup> In



**Figure 5** Electron diffraction patterns of Ag nanocrystals obtained by the modified polyol method (variation A). (a) Ring patterns for a large group of nanocrystals after 168 h of synthesis. (b, c) Electron diffraction pattern corresponding to one single crystal, as the ones shown in Figure 4(c).



**Figure 6** Size distribution of particles obtained by modified polyol method (variation A): (a) 24 h, average size 20.3 nm; (b) 336 h, average size 158.7.

the case of nanocrystals, a heat treatment is not required since the experimental conditions enable the atoms to incorporate into preferential crystal plane orientations according to the equilibrium shape.

In this case, PVP plays a critical role as its highly movable chains enable the Ag atoms to readily reach positions where the conditions for crystal growth are preferential. In the case of relatively low molecular weights (as in 10K PVP chains), spherical shapes can be readily substituted by planar hexagonal shapes. In this case, PVP preferentially adsorbs on {111} facets and growth occurs along {100} directions, in a similar way to the triangular crystals obtained by Tsuji et al.<sup>21</sup> In addition, the Ag nanocrystals grown under the modified polyol method conditions are expected to have the lowest Gibbs free energies according to theoretical estimations for FCC single crystals,<sup>23</sup> leading to the hexagonal shapes shown in Figure 7(f).

The Ag particle nanosize distribution obtained by the modified polyol method, variation B, is shown in Figure 9. The distribution shows a predominant average particle size of 10.12 nm after 4 h of synthesis [Fig. 9(a)]. At longer synthesis times, the particle size becomes increasingly homogeneous and the statisti-

cal frequency is reduced, indicating possible coalescence, where the smaller particles dissolve in the liquid and the Ag atoms later incorporate onto the large-sized particles as seen in Figure 9(b).

### Chemical reactions

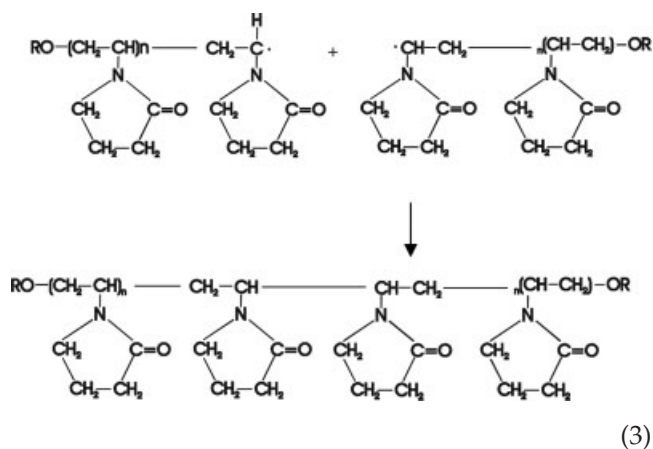
The FTIR infrared absorption spectrum of the PVP before any reaction shows a shift in the signal corresponding to C=O of the amide group from a frequency of  $1680.0\text{ cm}^{-1}$  to  $1659.67\text{ cm}^{-1}$ . This is due to water absorption, which was not eliminated during drying as seen in Figure 10. When PVP is mixed with  $\text{AgNO}_3$ , prior to dissolution in ethylene glycol, a shift in this frequency to  $1642.09\text{ cm}^{-1}$  takes place, indicating a solid-state interaction between the  $\text{AgNO}_3$  molecules with the PVP chains (see Fig. 11). This interaction can be attributed to the formation of a coordination complex compound.

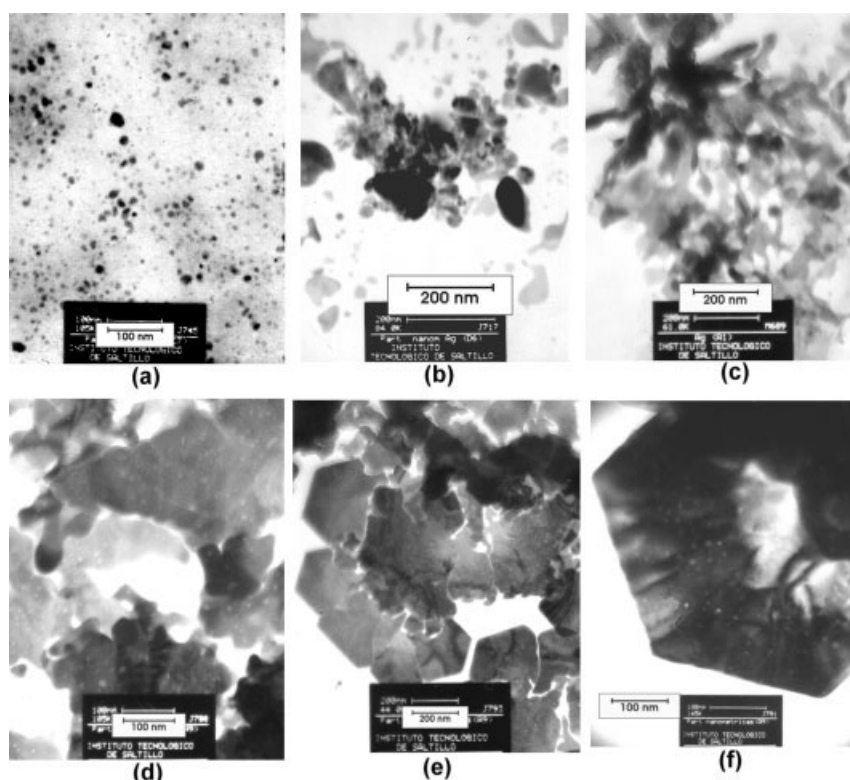
A similar result was found by Li et al.<sup>17</sup> using a poly(1,8-diaminonaphthalene) polymer to synthesize silver nanocrystals. In this case, as a first step, adsorption and complexation between  $\text{Ag}^+$  and amine/imine groups take place, while the final stage is a redox reaction between  $\text{Ag}^+$  and the  $-\text{NH}_2$  groups of the polymeric chains. Moreover, Sun and Xia<sup>16</sup> consider the role of PVP as a facilitator for the  $\text{AgNO}_3$  reaction and its possible role in organizing the Ag atoms to form crystals, while Patel et al.<sup>18</sup> also suggest the role of PVP in controlling the particle size and in its ability to reduce Ag by itself.

### Hypothesis on possible chemical reactions in the modified polyol method

To account for the experimental outcome, a proposed chemical mechanism is provided to account for the reduction of  $\text{AgNO}_3$  and for the formation of silver nanocrystals in the modified polyol method.

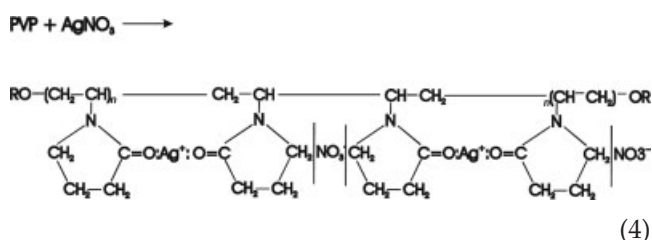
Once the PVP polymer is available in the present form, a polymerization reaction takes place according to:





**Figure 7** TEM photomicrographs of Ag nanoparticles obtained by a modified polyol method (variation B) (bright field): (a) 4 h, (b) 24 h, (c) 48 h, (d) 144 h, (e, f) 3 months.

The polymeric chain can react with  $\text{AgNO}_3$  (modified polyol method) or can follow the traditional polyol method. In the modified polyol method PVP chains can react in the solid state with  $\text{AgNO}_3$  as shown in the following chemical reaction:

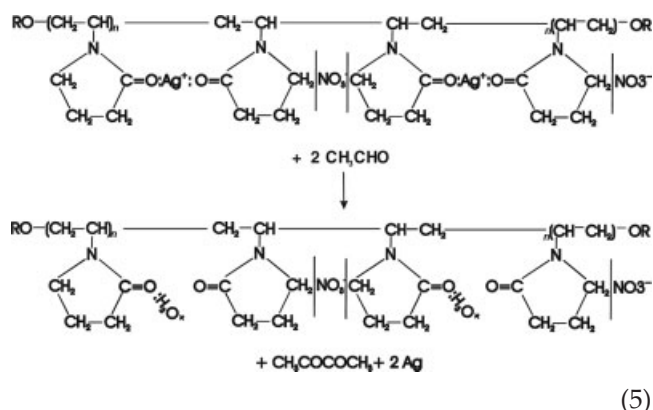


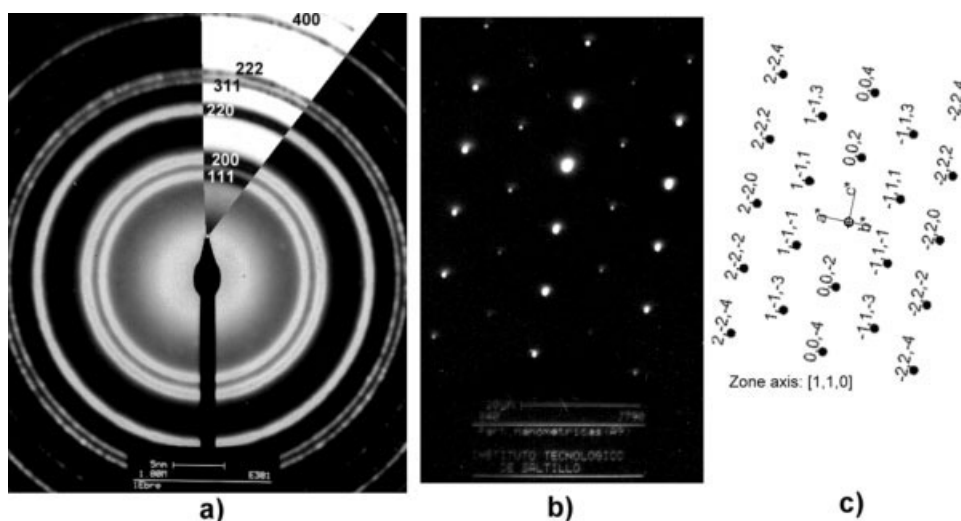
where two carbonyl groups of the amide group, belonging to two repetitive units of PVP chain, interact with silver ions to form a coordination complex compound.

From the stoichiometry of the proposed model, it can be seen that a single  $\text{AgNO}_3$  molecule reacts with two rings, corresponding to two PVP units. Taking into account the corresponding atomic weights, this PVP segment yields 222.28714 g. Hence, for 1 g of added PVP based on the stoichiometry of the system, 0.7642 g of  $\text{AgNO}_3$  is required for full reaction. In this work, 100 mg of  $\text{AgNO}_3$  (0.100 g) were added ensuring that there is an excess amount of PVP to promote a complete reaction.

The reaction between PVP and  $\text{AgNO}_3$  manifests as shifts of the amide group frequency (Fig. 11). PVP is a polymer whose molecular chains are highly mobile, enabling  $\text{Ag}^+$  ion interactions and the formation of metallic silver. In particular, the IR shows that a solid-state reaction takes place between the PVP and the  $\text{AgNO}_3$ . Accordingly, it is expected that a change in the number of Ag ions reacting with PVP (different stoichiometry) will lead to increasing shifts on the amide peak.

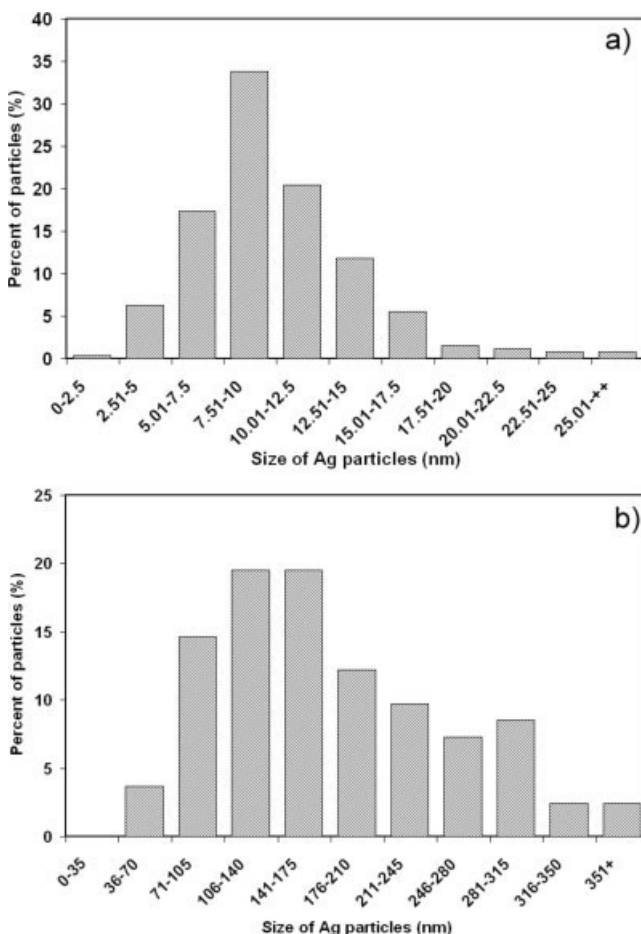
Once the mixture is dissolved in ethylene glycol, it is relatively easy to reduce the adsorbed Ag ions and to precipitate them as metallic silver, according to reaction (1b):





**Figure 8** Electron diffraction patterns of Ag nanocrystals obtained by the modified polyol method (variation B). (a) Electron diffraction pattern of Ag nanocrystals shown in Figure 7(a). (b) Electron diffraction pattern of single crystal shown in Figure 7(f) and its corresponding indexes (c).

The previous adsorption of  $\text{Ag}^+$  on the PVP chains would then facilitate the formation of Ag nanocrystals.



**Figure 9** Particle size distribution of Ag nanocrystals obtained by a modified polyol method (variation B): (a) 4 h, (b) 3 months.

### Kinetics

The relative amounts of precipitated metallic silver as a function of time are shown in Figure 12. Notice from this figure that the highest achieved efficiency can be attributed to the modified polyol method. As shown in Figure 11, there is evidence of a chemical interaction between  $\text{AgNO}_3$  and PVP when these substances are mixed prior to dissolution in ethylene glycol (variations A and B of the modified polyol method). According to the proposed solid-state chemical interaction, the carbonyl groups of the amide group, belonging to the repetitive PVP chains, interact with  $\text{Ag}^+$  to form a coordination complex compound. These reactions would create a state in which  $\text{Ag}^+$  ions can also be reduced to  $\text{Ag}^0$  to form extremely fine Ag embryos.

When the mixture containing the PVP-Ag coordination complex compound is dissolved in ethylene glycol, the mobility of the organic chains increases favoring the interaction between silver embryos and the  $\text{Ag}^+$  ions, while the reduction reaction continues to take place. Accordingly, silver embryos will continue to grow becoming metallic crystals, while an increasing number of Ag atoms become part of the crystals. It is also expected that the Ag embryos would act as substrates in promoting the growth of Ag particles.

In the Figlarz's polyol method, the solid-state reaction is not present and the rate of formation of Ag crystals is rather sluggish, as observed when comparing the three different curves shown in Figure 12. It is important to mention that five samples were taken for each experimental condition. The average values correspond to the points shown in Figure 12, and there is relatively small experimental statistical data dispersion.

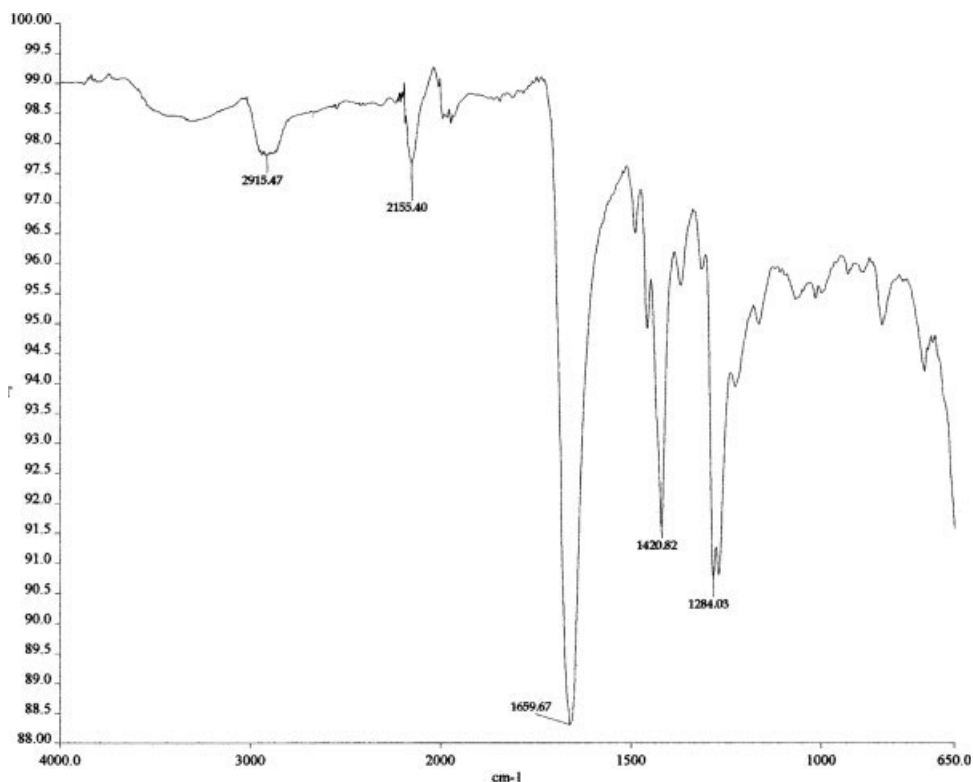


Figure 10 FTIR infrared absorption spectrum of PVP.

Comparing both modified methods, where the only difference is the magnetic stirring step, it is found that the kinetics of silver crystals formation is

modified. From the expected role of PVP in ordering metallic atoms, a possible hypothesis would be that during the early stages of solution mixing, the syn-

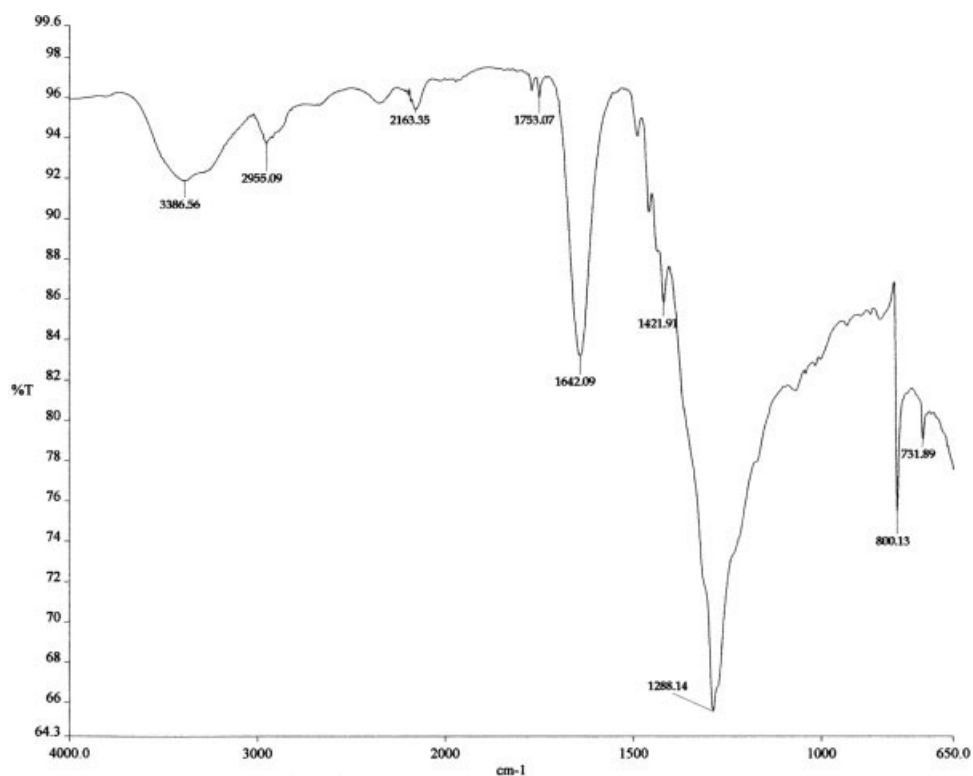
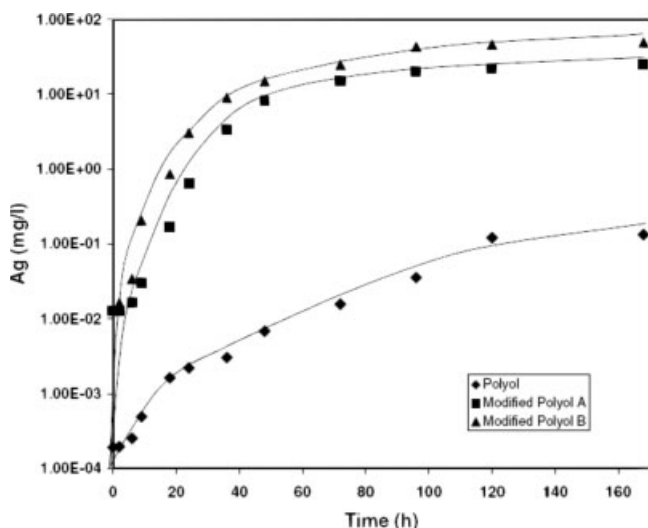


Figure 11 FTIR infrared absorption spectrum for the PVP + AgNO<sub>3</sub> after 1 h of solid-state reaction.





**Figure 12** Amount of metallic Ag precipitated as a function of synthesis time.

this process would not only prevent the union of  $\text{Ag}^+$  ions. It would also modify the length and order of PVP chains making the formation of Ag crystals increasingly difficult.

In contrast, when the solution is at rest, avoiding magnetic agitation, the electromagnetic field of the crystals will have a strong effect promoting the attraction between silver atoms. Once the reactants are dissolved and the solution is kept at rest, the crystals will continue to grow by coalescence. Accordingly, the combined effect of previous solid-state mixing and rest, after total dissolution, leads to an increase in the rate of crystal formation, resulting in enhanced kinetics (see Fig. 12). Finally, it is important to mention that all the mechanisms proposed in the literature do not consider PVP as taking part in the reduction process, nor the quantification of obtained metallic silver or other metals by similar polyol methods.

## CONCLUSIONS

In the present work, the traditional polyol method was modified by introducing a solid-state intermediate solution mixing step. The modified polyol method was then used in the synthesis of Ag nanocrystals using PVP (10K) and silver nitrate. It was found that the modified polyol method exhibits improved efficiency and enhanced kinetics when compared with the traditional polyol method. Experimental evidence of solid-state interaction between the PVP and silver nitrate was found by FTIR. This interaction was explained as due to the adsorption of silver ions to the PVP polymeric chains and to the possible formation of a PVP-Ag coordination complex compound. Once the mixture is dissolved in ethylene glycol, the coordination

complex compound promotes a relatively fast formation of silver nanocrystals. Apparently, PVP plays an important role in arranging metallic atoms during the formation of silver nanocrystals. In particular, it enables the crystals to achieve their thermodynamically stable geometrical shapes. Under the experimental conditions of this work, the exhibited nanocrystal shapes were quasi-planar hexagonal. Apparently, PVP interacts with the FCC crystal structure promoting growth on the {100} preferential direction. Finally, the crystal structure and lattice parameters of the Ag nanocrystals as determined by X-ray and electron diffraction patterns indicated that they are similar to those corresponding to standard pure silver bulk samples.

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