

# Synthesis and Characterization of Novel Silver/L-Phenylalanine-Based Optically Active Polyacrylate Nanocomposite

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**ABSTRACT:** Novel bioactive and optically active poly(*N*-acryloyl-L-phenylalanine) (PAPA) was synthesized by atom transfer radical polymerization. PAPA-silver (Ag) nanocomposites have been successfully prepared via *in situ* reducing Ag<sup>+</sup> ions anchored in the polymer chain using hydrazine hydrate as reducing agent in an aqueous medium. By controlling of the amount of Ag<sup>+</sup> ions introduced, we have produced an organic/inorganic nanocomposite containing Ag nanoparticles with well controlled size. Nanocomposites were characterized by X-ray diffraction (XRD), UV-Vis spectrophotometry, transmission electron microscopy, and

Fourier transform infrared. XRD pattern showed presence of Ag nanoparticles. The PAPA/Ag nanocomposites with 1 : 10 silver nitrate (AgNO<sub>3</sub>) : PAPA ratio revealed the presence of well-dispersed Ag nanoparticles in the polymer matrix. All of these Ag nanoparticles formed are spherical and more than 80% of them are in the range of 15–25 nm. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4491–4495, 2012

**Key words:** silver nanoparticles; optically active polymers; poly(*N*-acryloyl-L-phenylalanine); reducing agent; atom transfer radical polymerization

## INTRODUCTION

Metal nanoparticles have been noted in the last years, for their attractive electrical, optical, and mechanical properties and they have a wide range of applications in various sectors including catalysts, electronics, chemical sensors, and so forth.<sup>1–6</sup> Generally, the metal cations are first complexed with a certain polymer, and then reduced *in situ* using various reducing agents to form the stable colloidal polymer/metal nanocomposites. Here the polymers acted as stabilizers, templates, or protecting agents. Many approaches have been employed for preparing metal nanoparticles.<sup>7–13</sup> One of the most extensively used techniques is chemical method.<sup>14,15</sup>

In comparison with other metals, Ag has the highest thermal and electrical conductivity, and has been widely used in catalysis, sensors, photonics, elec-

tronics, photography, and biological labeling. Since, Ag nanoparticles possess an outstanding biocompatibility and low toxicity, so it has been employed for the purpose of biology such as antibacterial agents, DNA sequencing, surgical instruments (e.g., catheters), and surface modification of endoprosthesis, heart valves, and so on.<sup>16–18</sup> Exploration of the optical properties of Ag nanoparticles is very striking; since, the Ag nanoparticles powerfully absorb in the visible region owing to its surface plasmon resonance. Ag nanoparticles are often synthesized by reducing Ag salt via reducing agents in aqueous solution.<sup>19</sup>

Optically active polymers received much attention because of its distinctive chiral structures (e.g., helix), which resemble those of naturally occurring materials such as proteins, nucleic acids, and amino acids. An important application of these macromolecules is chiral recognition.<sup>20–23</sup> This ability of chiral polymers has been utilized in various forms of catalytic and separation chemistry. Amino acid-based synthetic polymers are expected to show a diversity of chemical and biochemical functions such as biocompatibility and biodegradability similarly to those of polypeptides and form secondary structures such as helices.<sup>24,25</sup> We synthesized a series of optically active polymers bearing amino acid moieties via

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introducing amino acid units in polymer backbone.<sup>26–28</sup>

Herein, we present a simple and efficient method for the preparation of Ag nanoparticles having an amino acid moiety in the side chain. Ag has been reduced via *in situ* technique in aqueous PAPA solution using reductive agent such as hydrazine hydrate and the resulting Ag nanoparticles were stabilized and well dispersed in the solution. The synthesized samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and UV-Vis absorption spectroscopy.

## EXPERIMENTAL

### Materials

All chemicals were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical.

### Techniques

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR, 500 MHz) spectrum was recorded in DMSO-*d*<sub>6</sub> solution using a Bruker (Germany) Avance 500 instrument. FTIR spectra were recorded on (Jasco-680, Japan) spectrophotometer. UV-Vis spectra were recorded on a UV/Vis/NIR spectrophotometer, JASCO, V-570, XRD was done by using CuK $\alpha$  radiation on a PW3040 Model. TEM was done on a Jeol model 1200 EX instrument operating at a voltage of 120 kV. The size distribution of the Ag nanoparticles in composite was determined by Image Tool software. Molecular weight distributions were measured by size exclusion chromatography, the elution rate was 1 mL/min and standard polystyrene (PS) was used for calibration.

### Preparation of PAPA

The polymers were prepared by atom transfer radical polymerization (ATRP) in deionized (DI) water/methanol solution.<sup>29</sup>

Mixture of 2-hydroxyethyl-2'-methyl-2'-bromopropionate (HMB) (0.012 g, 0.057 mmol) and APA monomer (1.00 g; 4.56 mmol) were dissolved in 2 mL of a 50:50 (v/v) methanol/double distilled water mixture, then 5% NaOH was added to achieve pH = 8. This solution was degassed by passing dry nitrogen gas, then 2,2'-bipyridine (bpy) ligand (0.023 g; 0.15 mmol) and Cu<sup>I</sup>Br catalyst (0.008 g; 0.056 mmol) was added rapidly. Upon addition to these reagents a dark brown solution was created. An exothermic polymerization reaction started immediately leading to an increase in viscosity of the mixture,

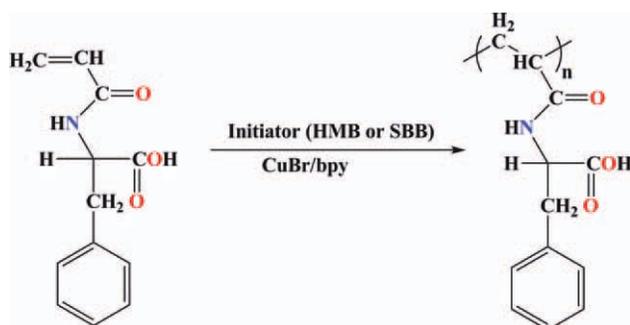
and it was observed by sensing the vessel of reaction. After 2 h the mixture was exposed to air. The dark brown reaction solution turned blue, indicating aerial oxidation of Cu(I) to Cu(II). The polymer solution was diluted with 5 mL of water and was mixed with about 1 g of silica gel and was stirred for 1 h. Then it was filtered off and was acidified with a solution of concentrated HCl (12N) to provide white solid polymers. The resulting polymers were washed with cold THF to remove traces of residual APA monomer and/or unreacted initiator, affording PAPA in high yield. FTIR (KBr): 3376 (s), 3206–2760 (s, br), 2945 (s), 1730 (s), 1654 (s), 1602 (s), 1384 (s), 1326 (m), 1084 (s), 1046 (s), 880 (m) cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  1.30 (CH<sub>2</sub>, br), 2.05 (CH, br), 2.96 (CH, diastereotopic proton of methylene, br), 3.43 (CH, diastereotopic proton of methylene, br), 4.41 (C–H chiral center, br), 7.25 (aromatic protons, s), 8.43 (amidic proton, s), 12.71 (acidic proton, s, br) ppm.

### Preparation of the Ag/PAPA nanocomposite

In a typical experiment, salt PAPA (0.1 g) was dissolved in DI water (5 mL). An aqueous solution of AgNO<sub>3</sub> (0.1M, 5 mL) was prepared and added to the PAPA solution, thus maintaining the weight ratio between AgNO<sub>3</sub> and PAPA approximately equal to 1 : 1. These two solutions were then allowed to stir together for about 10 min. The solution was evacuated and then purged with nitrogen. Dilute aqueous solution of hydrazine hydrate was separately prepared and were introduced to the PAPA/AgNO<sub>3</sub> solution in appropriate quantities (1 : 1 with respect to AgNO<sub>3</sub>) by a syringe. The color of the solutions changed to golden-yellow due to reduction of Ag<sup>+</sup> to Ag<sup>0</sup>. Stirring was continued under inert atmosphere at room temperature for another 30 min. The films of the solutions were prepared by evaporation of the solvent at 100°C. The nanocomposites also prepared at ratio of PAPA to AgNO<sub>3</sub>, 2, 4, 6, 8, and 10, respectively.

## RESULTS AND DISCUSSION

PAPA was synthesized via ATRP in the presence of CuBr/bpy catalyst system and HMB or sodium-4-(bromomethyl)benzoate (SBB) as initiators in pH = 8 at room temperature (Scheme 1). The molecular weight and molecular weight distribution of some homopolymer samples are shown in Table I. The <sup>1</sup>H-NMR spectrum of PAPA shows the characteristic resonance of acidic and amidic protons at 12.71 and 8.43 ppm, C–H chiral center at 4.41 ppm, two diastereotopic hydrogens of methylene group at 2.96, and 3.43 ppm, backbone methine proton at 2.05 ppm, and backbone methylene protons at 1.30 ppm.

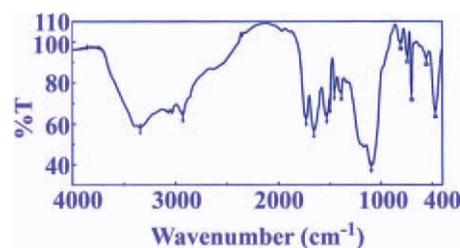


**Scheme 1** Synthesis of PAPA via ATRP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Novel optically active PAPA-Ag nanocomposites were successfully prepared by *in situ* reducing  $\text{Ag}^+$  ions anchored in the polymer by the deprotonized carboxylic acid groups ( $\text{COO}^-$ ). The resulting golden-yellow solutions are stable over a long period of time, thus showing the nanoparticle have no propensity to agglomerate.

It can be seen that the asymmetric stretching band of COOH occurs at the  $1730\text{ cm}^{-1}$  in the FTIR spectrum of PAPA, while it shifts to low wavenumber  $1600\text{ cm}^{-1}$  in the FTIR spectrum of Ag ions-PAPA. It indicated that complexation took place between the  $\text{COO}^-$  groups and  $\text{Ag}^+$  ions. It is also found that the characteristic absorptions of PAPA and Ag nanoparticle/PAPA composite are quite similar (Fig. 1).

A typical XRD pattern of Ag nanoparticle/PAPA composite with ratio of PAPA to  $\text{AgNO}_3$  10 to 1 shows the presence of the diffraction peaks corre-



**Figure 1** FTIR spectrum of Ag/PAPA nanocomposite with ratio of PAPA to  $\text{AgNO}_3$ , 10 to 1. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

sponding to the, 111, 200, 220, 311 planes. The two peaks with  $2\theta$  values of  $38^\circ$  and  $44.5^\circ$  correspond to two crystal planes, 111 and 200, of metallic crystalline silver, respectively.<sup>1,2,30</sup> All diffraction peaks in this XRD pattern (Fig. 2) can be well indexed as face-centered cubic (fcc) Ag with peak positions, indicating that the fcc structure of the Ag is preserved in this nanocomposite. The intensity of the peaks of silver nanoparticles decreases with a decrease in silver nanoparticles concentration at different compositions.

The morphology of Ag nanoparticles dispersed in the matrix of polymer is studied using TEM. Figure 3 illustrates TEM images and size distribution of Ag nanoparticles dispersed in the matrix of polymer with ratio of PAPA to  $\text{AgNO}_3$ , 10 to 1. The TEM image clearly reveals the presence of Ag nanoparticles and their uniform distribution in the polymer matrix. The mean diameter of the particles was found to be in the range of 15–25 nm. No regions

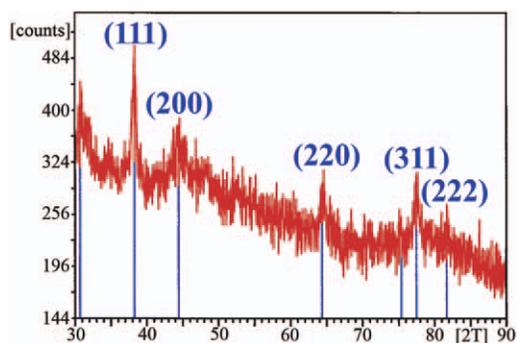
**TABLE I**  
Summary of Conversion, Molecular Weight, and Polydispersity Data for Homopolymerization of APA Using Two Initiators in Various Ratio Water and Methanol at Room Temperature<sup>a</sup>

$[\alpha]_{\text{Hg}}^{25\text{b}}$	$[\alpha]_{\text{Na},589}^{25\text{b}}$	Molecular weight			Conversion (%)	Time (h)	Solvent $\text{H}_2\text{O} : \text{MeOH}$	Initiator
		$M_w/M_n$	$M_n^c$ (theory)	$M_n$ (SEC)				
+45.08	+17.46	–	–	–	81.2	1	50 : 50	SBB
+45.21	+20.22	1.1	18,700	17,500	98.6	2	50 : 50	SBB
+45.22	+20.28	–	–	–	98.6	4	50 : 50	SBB
+45.68	+20.44	–	–	–	98.7	6	50 : 50	SBB
+46.62	+20.72	–	–	–	99.3	8	50 : 50	SBB
+46.34	+21.16	–	–	–	99.4	10	50 : 50	SBB
+48.34	+21.96	1.3	23,100	17,800	100.0	12	50 : 50	SBB
+37.11	+18.43	1.1	23,100	17,600	99.1	2	100 : 0	SBB
+36.27	+18.69	1.2	12,400	14,400	81.5	2	0 : 100	SBB
+37.44	+21.43	–	–	–	81.5	1	50 : 50	HMB
+37.63	+21.94	1.2	16,200	14,500	83.4	2	50 : 50	HMB
+37.48	+21.69	–	–	–	83.6	4	50 : 50	HMB
+37.26	+22.53	–	–	–	84.8	6	50 : 50	HMB
+37.68	+25.68	–	–	–	86.9	8	50 : 50	HMB
+38.42	+25.94	–	–	–	87.3	10	50 : 50	HMB
+37.87	+24.47	–	–	–	89.0	12	50 : 50	HMB

<sup>a</sup>  $[\text{APA}]_0 = 2.28\text{M}$  and the molar ratio of initiator:  $\text{CuBr} : \text{bpy}$  was 2 : 2 : 5.

<sup>b</sup> Measured at a concentration of 0.5 g/dL in DMF at  $25^\circ\text{C}$ .

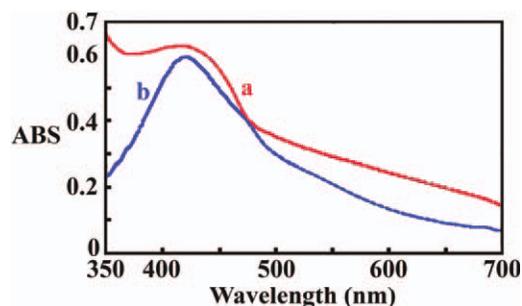
<sup>c</sup>  $M_n$  (theory) =  $219.2([\text{APA}]_0/[\text{initiator}]) \times \% \text{Conversion}/100 + M_w$  (initiator).



**Figure 2** XRD of Ag/PAPA nanocomposite with ratio of PAPA to  $\text{AgNO}_3$ , 10 to 1. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

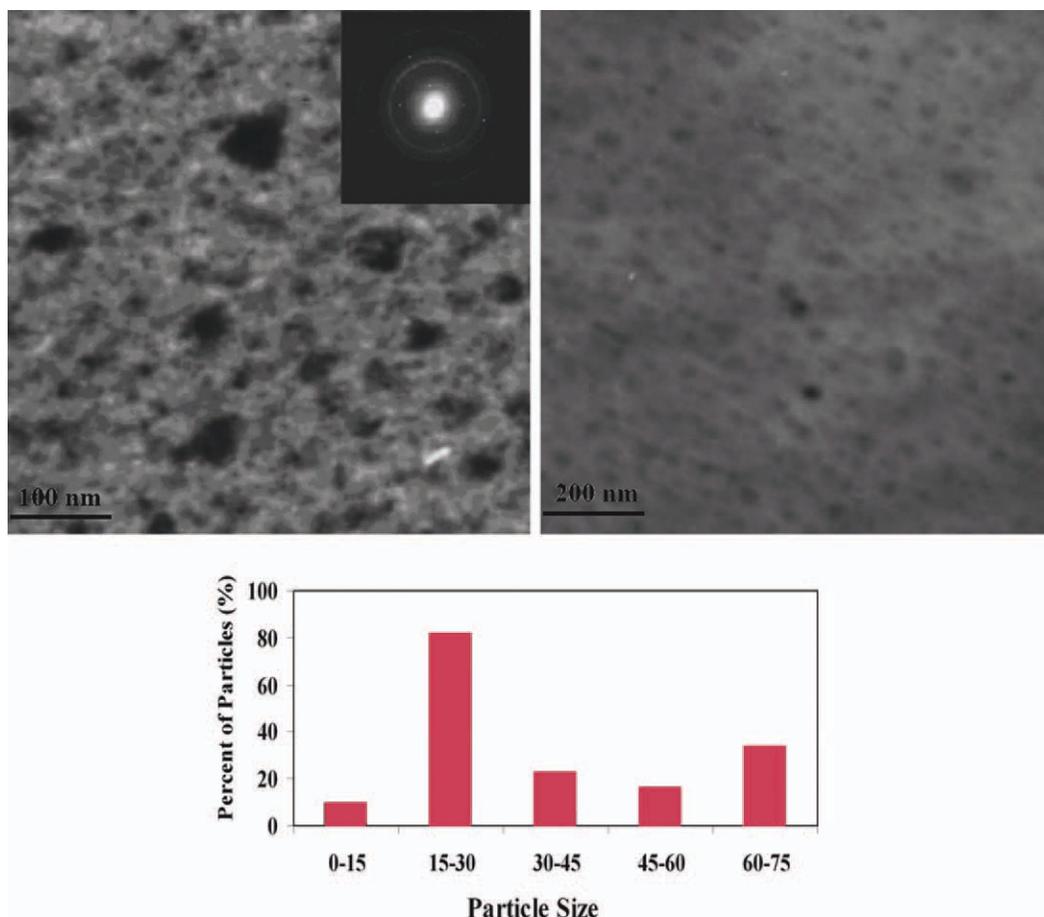
containing only polymer or Ag nanoparticles were detected from analysis of TEM image of the sample, indicating that the composites have good uniformity. XRD and TEM results confirm the formation of polymer-Ag nanoparticle composites with a good dispersion of the nanoparticles within the polymer matrix.

UV-Vis spectroscopy is a valuable technique, for the characterization of metal nanoparticles. The formation of Ag nanoparticles was confirmed by the



**Figure 4** UV-Vis absorption spectra of Ag/PAPA nanocomposite, (a) 1 : 1  $\text{AgNO}_3$  : PAPA and (b) 1 : 10  $\text{AgNO}_3$  : PAPA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

UV-Vis spectra of the samples. Figure 4 represents the UV-Vis spectra of Ag/PAPA nanocomposite solutions with two ratios of PAPA to  $\text{AgNO}_3$ , 1 to 1 and 10 to 1; this figure shows a broad absorption band at  $\lambda_{\text{max}}$  428 nm. In this region, no peak was observed in the UV-Vis spectrum of PAPA alone. In addition, the height of this peak gives direct information about the metallic Ag concentration in the solution. This characteristic peak is due to the



**Figure 3** TEM images and size distribution of Ag/PAPA nanocomposite with ratio of PAPA to  $\text{AgNO}_3$ , 10 to 1. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

oscillation of conduction band electrons of Ag known as the surface plasmon effect.<sup>31</sup> It is important to mention that, only at a ratio of 1 : 10 AgNO<sub>3</sub> : PAPA, the shape of the plasmon band was almost symmetrical, suggesting that the nanoparticles merely at this ratio were well-dispersed and spherical-shaped. However, for the other ratios the aggregation and elongated nanoparticles led to broad absorption peaks. With extending time, the absorbance of Ag/PAPA nanocomposite solutions increased regularly and no shift was observed in wavelength towards longer or shorter, this shows that particles are highly stable. This method has many advantages in comparing with the works reported in literature such as green conditions for example organic solvent as well as stabilizer were not used, which decreases cost and energy of the production. Furthermore, Ag nanoparticles were readily dispersible in aqueous media with the same stability reported elsewhere.<sup>32-34</sup>

### CONCLUSIONS

To conclude, the synthesis of biocompatible and biodegradable optically active Ag/PAPA nanocomposite by a simple and easy route via *in situ* reducing the Ag<sup>+</sup> ions anchored to deprotonized carboxylic acid groups with hydrazine hydrate is described. TEM image revealed that the particles dimension is nanometer regime and they are uniformly distributed. UV-Vis spectrum of the Ag/PAPA nanocomposite solution with ratio of 1 : 10 AgNO<sub>3</sub> : PAPA showed the surface plasmon resonance absorption band. Therefore, this method opens up a simple and rapid procedure for the fabrication of optically active Ag nanoparticles/polymer containing amino acid groups for the biomedical applications.

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