

# Effects of Hyperbranched Poly(amido-amine)s Structures on Synthesis of Ag Particles

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**ABSTRACT:** The synthesis of Ag particles stabilized poly(*N,N'*-methylene bisacrylamide *N*-aminoethyl piperazine) (MBA-AEPZ) and poly(*N,N'*-dodecyl diacrylamide *N*-aminoethyl piperazine) (MDA-AEPZ) was reported. The effects of hyperbranched polymer structures and hyperbranched polymer concentrations were studied on the size and size distribution of Ag particles, which were determined from the UV plasmon absorption band and transmission electron microscopic analyses. The data show that slight change

(10.3 and 9.7 nm) and large change on particle size (3.9 and ~200 nm) were observed with increase in concentrations of poly(MBA-AEPZ) and poly(MDA-AEPZ) at the same *M*:*D*, respectively. The difference is explained in terms of a mechanism of structure-dependent stabilization. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 9–13, 2008

**Key words:** silver nanoparticles; hyperbranched poly(amido-amine)s; TEM

## INTRODUCTION

The synthesis of metal nanoparticles is a major research area in nanoscale science and engineering. A better strategy to generate uniform particles is to undergo chemical reduction via microemulsion,<sup>1,2</sup> Langmuir–Blodgett films,<sup>3</sup> polymer protection,<sup>4,5</sup> and so on. The purpose of these methods is to control the size and polydispersity of particles through reducing the surface energy by means of the adsorption of stabilizers such as polymeric ligands or surfactants. Especially interest in colloidal metal nanoparticles protected by polymers is increasing, since these materials offer tremendous options for combining properties stemming from both the inorganic components and the polymers.<sup>6–11</sup> Recently, dendrimer molecules with a well-defined structure have been used as templates to synthesize inorganic nanoparticles as reported by Balogh's group<sup>12</sup> and Crooks' group.<sup>13</sup> Crooks' group and Esumi's group had demonstrated the concept that larger metal particles (>2–3 nm) can be protected by the exterior amine groups of dendrimers.<sup>14</sup> Very recently, the studies of Manna et al.<sup>15</sup>

have refined this model, and very stable silver nanoparticles by the terminal amine groups of dendrimers have been prepared successfully. However, there are few reports to explore effects of polymer architecture on the formation of nanoparticle. In the other way, the ease of hyperbranched polymers preparations makes them more attractive to the practical applications,<sup>16</sup> excepting from a well-defined structure. So here, hyperbranched polymers of poly(MBA-AEPZ) and poly(MDA-AEPZ) were prepared and the effects of their structure on preparation of Ag nanoparticles were studied. It is a value study to design structures of polymers to obtain uniformity and large-scale size of noble metallic particles.

## EXPERIMENTAL SECTION

**Materials:** *N,N'*-methylenebis-acrylamide (MB, 99.9%), *N,N'*-dodecyl diacrylamide (MD, 99%) and *N*-aminoethylpiperazine (AEPZ, 99.9%) were purchased from Aldrich Chemical. Silver nitrate (AgNO<sub>3</sub>, 99.99%) and sodium borohydride (NaBH<sub>4</sub>, 99%) were also purchased from Aldrich Chemical.

### Synthesize hyperbranched polymer of poly(MBA-AEPZ) and poly(MDA-AEPZ)

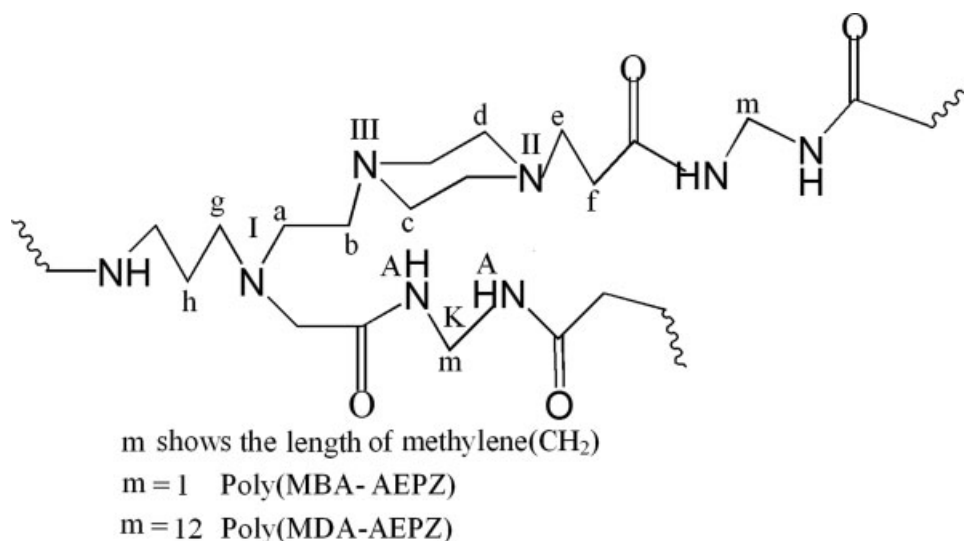
Poly(MBA-AEPZ) and poly(MDA-AEPZ) were synthesized according the previous procedure.<sup>15</sup> When the feed ratio of MDA (or MBA) to AEPZ was 2 : 1, a typical polymerization procedure was as follows: 4 mmol MDA (or MBA) was added to a solution of

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**Scheme 1** Structure characteristic of poly(MBA-AEPZ) and poly(MDA-AEPZ).

2 mmol AEPZ and 4 mL mixture solution containing 70% methanol and 30% water (v/v). The polymerization was performed at 50°C for one day. After then the polymerization was stopped and the solution was concentrated under a reduced pressure, following to precipitate into cold acetone. The product was purified by dissolving in water and precipitating in cold acetone again. The procedure is repeated for three times. At last, the product is dried under vacuum at 40°C for 24 h.

#### Synthesize Ag particles protected by hyperbranched polymer

The synthesis procedure was similar to that reported in the literature<sup>17</sup> as shown in following. Hyperbranched polymer aqueous (or methanol) solution and AgNO<sub>3</sub> aqueous solution were mixed together to produce a reaction mixture. NaBH<sub>4</sub> aqueous solution slowly dropped to the reaction mixture while stirring. The reaction mixture turned to a yellow or brown color within a few seconds after the addition of the first drop of the NaBH<sub>4</sub> solution. The stirring was continued for 2 h to complete the reaction. Finally, we obtained a yellow or brown colloidal solution of hyperbranched polymer-protected particles. The hyperbranched polymer-protected particles were very stable in aqueous and methanol solution at the room temperature for 2 months.

After then, centrifuging (8000 rpm) gave a brown acetone/water soluble precipitates and supernatant solution containing excess hyperbranched polymer and NaH<sub>4</sub>B-derived impurities were extracted. The precipitates were again dissolved into water-methanol mixture. The purification procedure was repeated for three times. The precipitate was redispersible in a water (or methanol).

#### Measurements

Optical measurements were carried out at room temperature on a Shimadzu UV 2200 UV-vis spectrometer using a quartz cell (10 mm path). The spectral background absorption was subtracted by using the UV-vis spectra of the same solvent mixture.

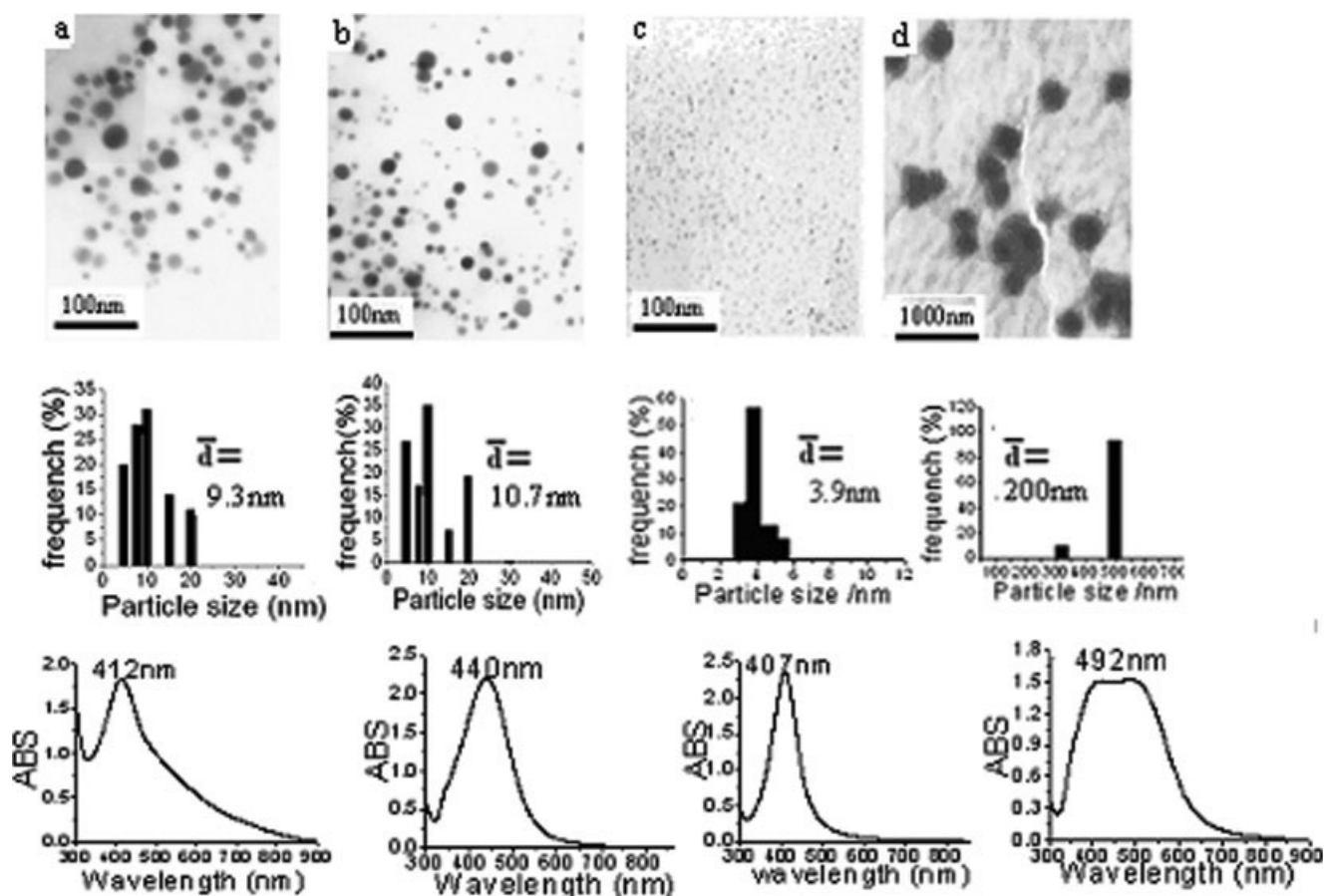
Specimens for transmission electron microscopy (TEM) were prepared by spreading a small drop (1 mL) of a 10 times dilution (in a 1 : 2 in volume of water : methanol mixture) of the colloidal solutions onto standard copper grids coated with a thin amorphous carbon film and letting the drop dry almost completely in air for nearly 1 h. The specimens were placed onto a grid holder. The size and morphology of the particles were observed at room temperature on a Hitachi H-800 electron microscope operating at 100 kV. The size distribution was derived from histograms.

<sup>13</sup>C NMR was performed using an inverse-gated broadband decoupled (INVGATE) program.

Gel permeation chromatography (GPC) was carried out on a Waters 2690 apparatus with two columns in series (waters Ultrahydrogel 250,200) and a Waters 410 refractive index detector using 0.5M acetic acid/0.5M sodium acetate as the eluent at a flow rate of 0.50 mL/min. The molecular weights were calibrated against poly(ethylene oxide) standards.

**TABLE I**  
 Characteristic Data for Hyperbranched Poly(amido-amine)s

Sample	$M_w$	$M_w/M_n$	Polymerization degree ( $n$ )
Poly(MBA-AEPZ)	7918	3.11	18
Poly(MDA-AEPZ)	11270	3.8	20



**Figure 1** TEM images (A–D) of Ag colloidal particles are shown and correspond to samples of PB-1, PB-2, PD-1, and PD-2 as shown in Table II, respectively. Corresponding size distribution and UV spectrum are also shown.

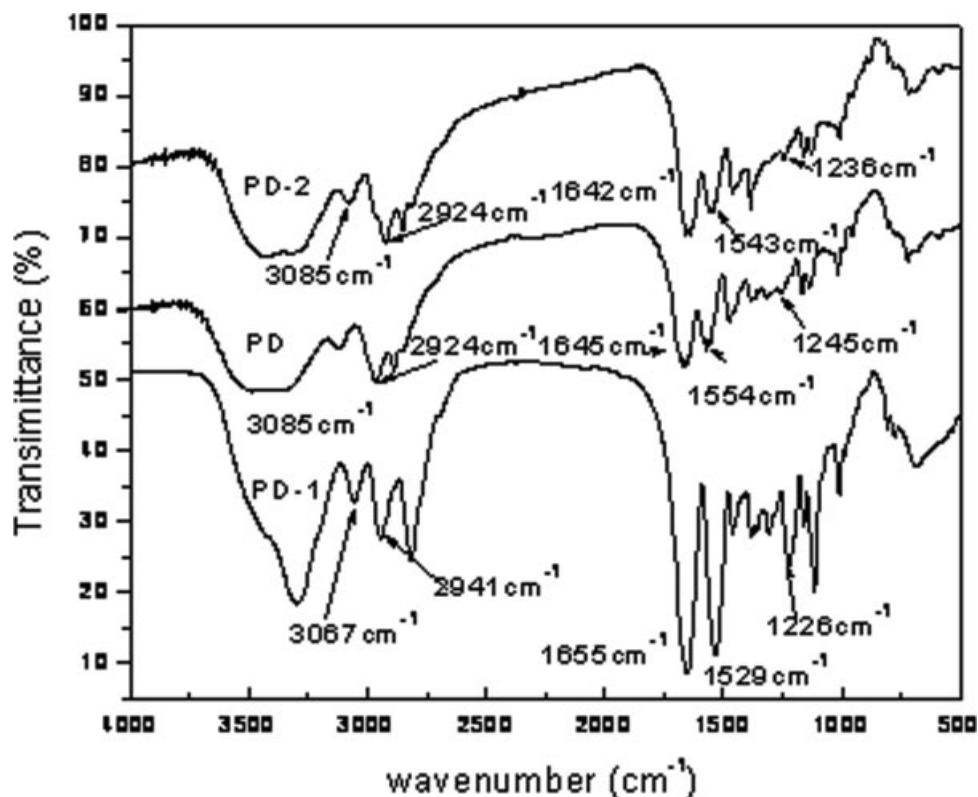
## RESULTS AND DISCUSSION

Novel hyperbranched poly(amido-amine)s containing tertiary amines in the backbones and double bonds as terminal groups were synthesized via the Michael addition polymerizations of trifunctional amines with diacrylamide. Furthermore, the different structure of these poly(amido-amine)s was designed to investigate the effect on preparation of silver particles and shown in Scheme 1. Their structures were verified by  $^{13}\text{C}$  NMR a (50.0–51.0 ppm, 1C), b (54.0–55.0 ppm, 1C), c (52.0–52.5 ppm, 1C), d (51.5–52.0 ppm, 1C), e (52.5–53.0 ppm, 1C), f and h (32.0–33.0 ppm, 2C), g (53.5–54.0 ppm, 2C), and k (44.0–45.0 ppm, 12C or 1C). Their molecular weight ( $M_w$ ) and its distribution ( $M_w/M_n$ ) are shown in Table I. The poly(MBA-AEPZ) can dissolve in water well. In opposition, the poly(MDA-AEPZ) can not dissolve in water and easily dissolve in methanol for long methylene chain with 12. So, to obtain stable Ag particles, water and water/methanol (1 V : 15 V) mixture act as reaction solution in the presence of poly(MBA-AEPZ) and poly(MDA-AEPZ), respectively. Their average size, size distribution, and corresponding UV spectrum are compared in Figure 1. The formation of Ag particles was proved by UV

spectra and TEM analyses. The characteristic bands from 410 to 490 nm corresponding to well-known surface plasmon resonance of Ag particles are observed. On all TEM images, one can see that particles mainly have a spherical shape and are characterized by a size distribution close to Gaussian. The A and B TEM images show that the average particles sizes are 9.3 and 10.7 nm, respectively. The results are also concluded in Table II. It shows the slight decrease ( $\sim 1.4$  nm) in size with in increase concentration of poly (MBA-AEPZ), suggesting that effect of polymer concentration on the size of particles is slight. The Ag nanoparticles were formed outer poly(MBA-AEPZ) for their average size be larger than 5 nm, which has

**TABLE II**  
Characteristic Data for Hyperbranched Poly(amido-amine)s-Protected Silver Particles

Sample	Polymer concentration ( $\times 10^{-2}$ mM)	Average particles size (nm)
PB-1	3.6	9.3
PB-2	1.8	10.7
PD-1	1.6	3.9
PD-2	3.2	200



**Figure 2** FTIR spectra of free poly(MDA-AEPZ) (PD), corresponding to Ag particles coated with poly(MDA-AEPZ) at concentration of  $1.6 \times 10^{-2}$  mM (PD-1) and  $3.2 \times 10^{-2}$  mM concentration (PD-2).

been reported in previous work.<sup>13,15</sup> However, for Ag particles protected poly(MDA-AEPZ), the change of particle size is large from 3.9 to 200 nm with increase in polymer concentration from  $1.6 \times 10^{-2}$  to  $3.2 \times 10^{-2}$  mM as shown in Table II at same number ratios ( $M : D$ ) of Ag metal ion to terminal primary amino group of the hyperbranched poly(amido-amine)s, respectively. Average size of 200 nm is observed, showing that Ag particles were formed outer poly(MDA-AEPZ) at concentration of  $3.2 \times 10^{-2}$  mM. At the same time, the size of particles protected poly(MDA-AEPZ) was observed to be smaller than 5 nm ( $\sim 3.9$  nm), suggesting that Ag nanoparticles can be formed in the template of hole. It shows that the poly(MDA-AEPZ) can be as template in which the particles was formed and be like low mass molecule stabilizers, which depend on the polymer concentration.

**TABLE III**  
TIR Bands for a Hyperbranched Polymer and Hyperbranched Polymer-Coated on Particles

Assignment	Band positions ( $\text{cm}^{-1}$ )		
	Free PD	PD-1	PD-2
Amine A	3085	3067	3085
	2924	2941	2924
Amine I	1645	1655	1642
Amine II	1554	1529	1543
Amine III	1245	1226	1236

These results are confirmed by the Figure 2, which shows a comparison of the FTIR spectra between 4000 and  $500 \text{ cm}^{-1}$  of free poly(MDA-AEPZ) and poly(MDA-AEPZ) coated on particles. FTIR of silver nanoparticles coated with poly(MBA-AEPZ) has been reported,<sup>15</sup> and here we do not further discuss. The similarity of the features of three spectra confirm (i) the poly(MDA-AEPZ) as an essential component of the composite particles and (ii) the poly(MDA-AEPZ) molecule was not removed after washing the precipitate. From the FTIR spectra analyses as concluded in Table III, all of amines stretching vibration frequencies show a large shift, indicating that Ag nanoparticles were protected by the interaction between Ag and the surface and inside amines of poly(MDA-AEPZ) at polymer concentration of  $1.6 \times 10^{-2}$  mM. However, the bands at 2924 and  $3805 \text{ cm}^{-1}$  correspond to the amine A is unchanged before and after adsorption on the metal particles, suggesting Ag to be protected by surface amides of poly(MDA-AEPZ) at polymer concentration of  $3.2 \times 10^{-2}$  mM. These results indicated the formation of Ag nanoparticles at the inside and outer of poly(MDA-AEPZ), respectively.

## CONCLUSIONS

The Ag colloidal nanoparticles were prepared in the presence of hyperbranched poly(amido-amine)s.

Poly(MBA-AEPZ) with short CH<sub>2</sub> chain (~1) behaves only like low mass molecule stabilizers and protect Ag nanoparticles and poly(MDA-AEPZ) with long CH<sub>2</sub> chain (~ 12) can be as template in which the particles was formed at high polymer concentration, excepting from being like low mass molecule stabilizers. Moreover, when poly(MDA-AEPZ) behaves like low mass molecule stabilizers, it can obtain larger (>100 nm), stabilization and monodispersion particles, resulting from long CH<sub>2</sub> chain, too. The result provides a theory to control polymer structure to obtain a large-scale nanoparticle.

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