

# Form-Fill-Seal Methodology for Controlled Encapsulation of Small Silver Particles in Hyperbranched Polyglycidol

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**ABSTRACT:** Production of polar hyperbranched polymers and encapsulation of small particles in the hyperbranched polymers is like “forming” pouches and then “filling” these pouches. Modification of the end-groups of the hyperbranched polymers with relative apolar groups is like “sealing” the pouches. In this article, we demonstrated that two methods depending on changed sequences, i.e., Form-Fill-Seal and Form-Seal-Fill methods resulted in different sized small particles with size-dependent properties. By using these approaches, small metal nano-particles can be encapsulated inside polar microzones of dendritic-star polymers taking advantage of the difference in partition coefficients instead of strong interactions between the dendritic polymers and ions. We used the methodology to produce small silver particles encapsulated in hyperbranched polyglycidol (HPG).

The HPG was synthesized via anionic ring-opening multibranching polymerization of glycidol. The “sealing” process was fulfilled by polymerization of  $\epsilon$ -caprolactone initiated from the end groups of HPG. In the Form-Fill-Seal approach,  $\text{Ag}^+$  was filled inside HPG, and then was sealed before reduction to Ag; whereas the “pouch” of HPG was sealed at first, and then  $\text{Ag}^+$  was filled inside HPG by diffusion in the Form-Seal-Fill approach. Mainly nanometer-sized silver particles were formed by the Form-Fill-Seal approach, whereas silver clusters of several atoms were formed in the Form-Seal-Fill approach. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1209–1214, 2009

**Key words:** hyperbranched; nanoparticles; core-shell polymers; water-soluble polymers

## INTRODUCTION

Small silver particles ranging from clusters of several atoms to nanometer-sized metal particles that show strong size-dependent optical properties are recently of huge interest.<sup>1,2</sup> Silver clusters of 2–10 atoms are distinct in strong size-dependent visible fluorescence, which is expected to yield new insights into the practical applications in integrated optical devices for optical storage or in biological labeling or sensor.<sup>3–7</sup> Bigger silver particles than nanometer sizes do not emit visible fluorescence. The most striking phenomenon encountered in the nano-structured silver particles is surface plasmon resonances strongly localized at the interface, which enables the detection of individual molecules by coupling single molecules to nanoparticles.<sup>8</sup> Small silver particles

may also find wide scope of application in the field of catalysts.<sup>9,10</sup>

Synthesis and stabilization of the particles with controlled sizes are critical to the study and application of these small particles. Stabilization of the metal particles is recently achieved of high interest by encapsulation of small metal particles inside highly branched polymers. Dendritic polymers including dendrimers, hyperbranched polymers, and dendritic star polymers are used for encapsulation and templation of nanoparticles.<sup>11,12</sup> In an ideal case of encapsulation, metal ions are pouched inside dendritic polymers, and then were transformed chemically into the desired product. To accomplish this goal, strong interactions between functional groups within the dendritic polymers and ions in solution should exist, for example in dendritic poly(amido-amine) (PAMAM) or poly(propylene imine).<sup>13–16</sup> However, it is reported that this approach does not work for encapsulation of Ag nano-particles inside dendrimers having interiors dominated with tertiary amines. In this case it was possible first to prepare a less noble metal nanoparticle, for example Cu, and then to displace it with Ag.<sup>17</sup> Thus, this approach actually yielded primarily relatively large

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interpolymer particles that were stabilized by multiple dendritic polymers. Recently, we succeeded in formation of silver nanoparticles with tunable spatial distribution at the linear poly(*N*-isopropylacrylamide) corona of a hyperbranched-star polymer.<sup>18</sup>

Dendritic polymers can be transformed into dendritic-star polymers by functionalization of the end groups or end group-initiated polymerization. The dendritic-star polymers can be extracted into a nonpolar phase in which the dendritic-encapsulated particles are preferentially soluble. The dendritic-star polymers dissolved in a nonpolar phase formed many polar microzones. It is possible to encapsulate small metal nano-particles inside polar microzones of dendritic-star polymers taking advantage of the difference in partition coefficients instead of strong interactions between the dendritic polymers and ions. Interpolymer stabilized big particles can be easily separated by this approach. We call this approach as "Form"- "Fill"- "Seal" methodology in this work: (1) "Form" a polar highly branched polymer that can dissolve metal salts, for example hyperbranched polyglycerol (HPG), as a pouch; (2) "Fill" metal ions into the package; (3) "Seal" the package by functionalization of the end groups of the highly branched polymer for nonpolar solubility, by which metal ions can be prevented from being distributed into nonpolar phase. This methodology can be also practiced in different steps, that is, to "seal the pouch" at first, then to "fill" metal ions into the package by diffusion of metal ions into the highly branched polymer.

Our goal of this work is to practice the "Form"- "Fill"- "Seal" methodology to produce hyperbranched polyglycerol-encapsulated small Ag particles with controllable sizes ranging from clusters of several atoms to nanometer-sized metal particles. We will "seal" the hyperbranched polyglycerol by esterifying the hydroxyl groups via ring-opening reaction of  $\epsilon$ -caprolactone, and the ring-opening reaction is controlled to one caprolactone per hydroxyl group to facilitate the diffusion of Ag ions into hyperbranched cores. No strong interactions between the dendritic polymers and ions are needed in these approaches.

## EXPERIMENTAL

### Measurements

Fourier transform infrared spectra were recorded with an Eouinos 55 spectrometer. 300 MHz <sup>1</sup>H-NMR and 75 MHz <sup>13</sup>C-NMR were performed on an AVANCE 300 spectrometer. UV-vis. absorption and fluorescence spectra were measured by PerkinElmer  $\lambda$ 40 spectrophotometer and RF-5301PC fluorescence spectrophotometer, respectively. Molecular weights

and distributions were determined by gel permeation chromatography (GPC) on a Waters 1515 equipped with three Waters linear styragel columns and 2414 differential refractive index detector. The eluent was DMF at a flow rate of 1.0 mL/min. Transmission electron microscopy (TEM) observations was conducted on a Philips CM 120 electron microscope at an acceleration voltage of 100 kV. X-ray powder diffraction (XRD) analysis was performed on an X'Pert Pro (Philips) D/Max-Ra diffractometer with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm).

### Preparation of small Ag particles encapsulated inside HPG

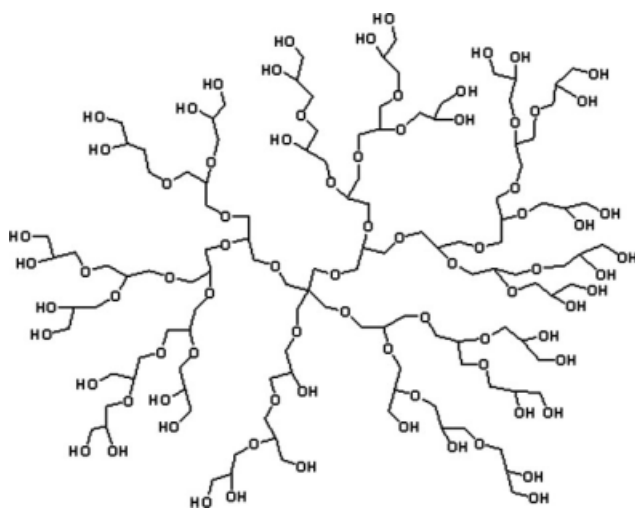
HPG was prepared according to Frey et al.'s work using pentaerythritol as a starting agent.<sup>19</sup> The number average molecular weight of HPG used in this work was 17,000 with a polydispersity of about 1.11 measured by GPC.

1. Form-Fill-Seal (FFS) methodology: HPG was doped with Ag<sup>+</sup>, and then was functionalized by reaction with  $\epsilon$ -caprolactone (CL). Ag<sup>+</sup> was transformed into Ag particles by thermal treatment in the present of multihydroxyl of HPG at 60°C without adding reducing agent.

AgNO<sub>3</sub> (0.1 g) was dissolved in ammonia water solution (10 mL, pH = 10). The AgNO<sub>3</sub> solution was added to a flask with HPG water solution (HPG of 0.330 g in 10 mL distilled water), and then was stirred for 30 min in the dark at room temperature. The mixture was vacuum-dried at 60°C. After  $\epsilon$ -caprolactone of 1 g has been introduced, the flask was sealed under vacuum, and then was kept at 130°C for 24 h. The resulting mixture was dissolved in chloroform/precipitated in excess of cold hexane twice, and then was vacuum-dried. Big intermolecular stabilized particles were removed by filtration.

2. Form-Seal-Fill (FSF) methodology: HPG was functionalized by reaction with  $\epsilon$ -caprolactone (HPG-CL) at first. Ag<sup>+</sup> was diffused into HPG-CL, and then was transformed into Ag particles. HPG-CL was synthesized by the same procedure described in (1) without the addition step of AgNO<sub>3</sub>.

HPG-CL (0.122 g) and AgNO<sub>3</sub> (0.102 g) were dissolved in a mixture of benzene (200 mL) and tetrahydrofuran (THF, 400 mL). After having been kept in the dark over night, the solution was exposed to <sup>60</sup>Co  $\gamma$ -irradiation to transform Ag<sup>+</sup> into Ag. After THF was carefully removed, a clear yellow solution was obtained after filtration.

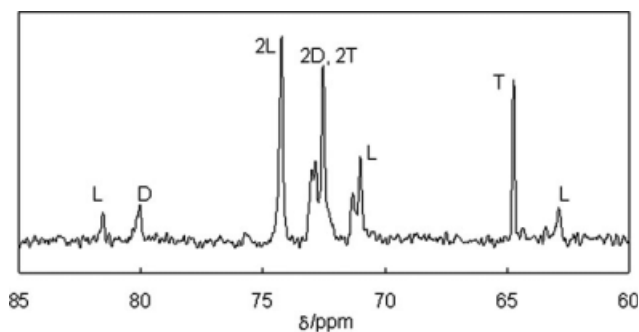


**Scheme 1** Schematic structure of hyperbranched polyglycidol (HPG).

## RESULTS AND DISCUSSION

### Synthesis of HPG and HPG-CL

The number average molecular weight of HPG used in this work was 17,000 with a polydispersity of about 1.11 measured by GPC. According to the literature, hyperbranched polymers with molecular weight less than 3000 were too small for guest encapsulation.<sup>20–23</sup> The schematic structure of hyperbranched polyglycidol (HPG) was illustrated in Scheme 1. Pentaerythritol was incorporated as core unit. The resulting structure was hyperbranched and consists of perfect dendritic (D), linear (L), and terminal (T) units that could be incorporated at each



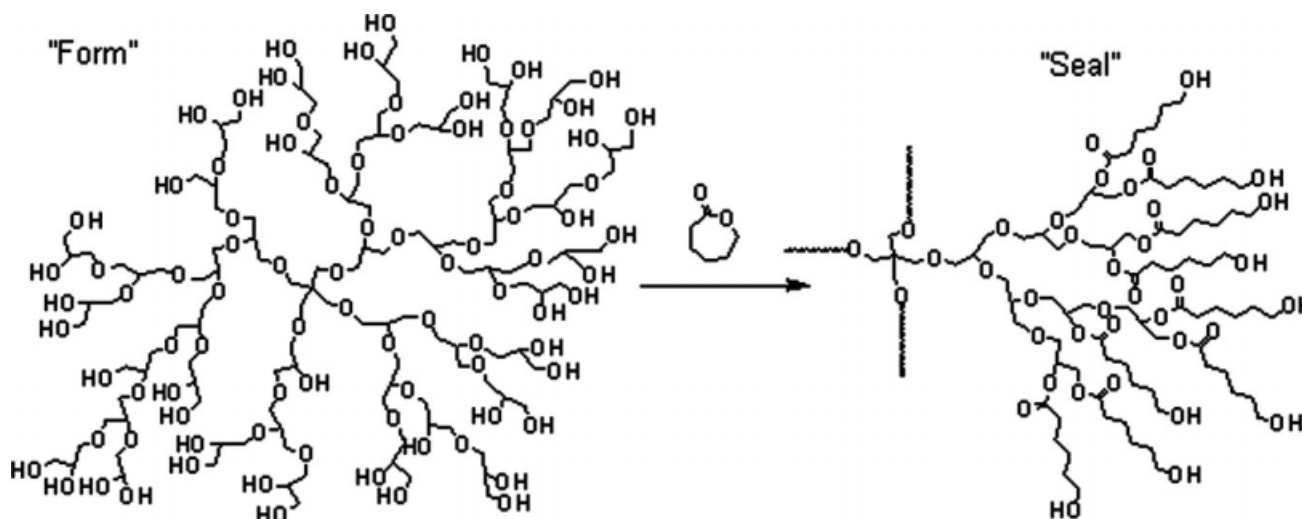
**Figure 1**  $^{13}\text{C}$ -NMR of HPG in  $\text{D}_2\text{O}$ .

position of the structure. The degree of branching (DB) of HPG was measured by using a quantitative  $^{13}\text{C}$ -NMR technique. The  $^{13}\text{C}$ -NMR of HPG was shown in Figure 1. The assignments of  $^{13}\text{C}$ -NMR peaks to structural units have been discussed in details in the literature. The DB of HPG synthesized in this work was calculated as 0.45 according to eq. (1):

$$\text{DB} = \frac{2D}{2D + L} \quad (1)$$

where D, L represent the fractions of dendritic and linear units, respectively.

The hydroxyl end groups of HPG were transformed into 6-hydroxy-hexanoic ester groups by ring-opening reaction of  $\epsilon$ -caprolactone initiated from the end hydroxyl groups. The process was illustrated in Scheme 2. The ring-opening reaction was controlled to one caprolactone unit per hydroxyl end group to facilitate the diffusion of Ag ions into hyperbranched cores. The number average molecular weight of the actually obtained HPG-CL was 36,000 with polydispersity of about 1.2 measured by



**Scheme 2** "Sealing" HPG with  $\epsilon$ -caprolactone.

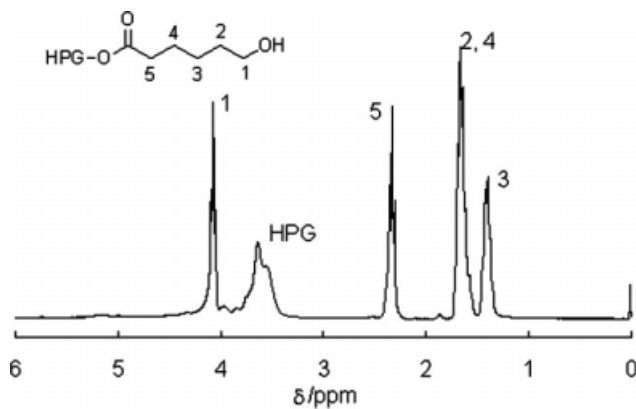


Figure 2  $^1\text{H-NMR}$  of HPG-CL in  $\text{CDCl}_3$ .

GPC. The actual grafting degree was about 0.8 CL unit per hydroxyl end group according to NMR and GPC results based on the difference in molecular weights between HPG-CL and acetylated HPG in which the hydroxyl end groups of HPG are totally acetylated.<sup>24</sup> Figure 2 was the 300 MHz  $^1\text{H-NMR}$  of HPG-CL measured in  $\text{CDCl}_3$ . The obtained HPG-CL became soluble in chloroform, THF, and benzene etc. When HPG-CL was dissolved in a nonpolar solvent, HPG will form a polar microzone for dissolving Ag salts in a nonpolar solution.

### Ag particles by FFS methodology

The morphology of silver particles formed by FFS methodology was observed by TEM. Figure 3 showed the TEM image and a size-distribution histogram of silver particles. Two groups of particles with different sizes were found in the TEM image, one with an average diameter of about 7 nm, whereas another one with an average diameter of about 40 nm. The bigger sized particles were large

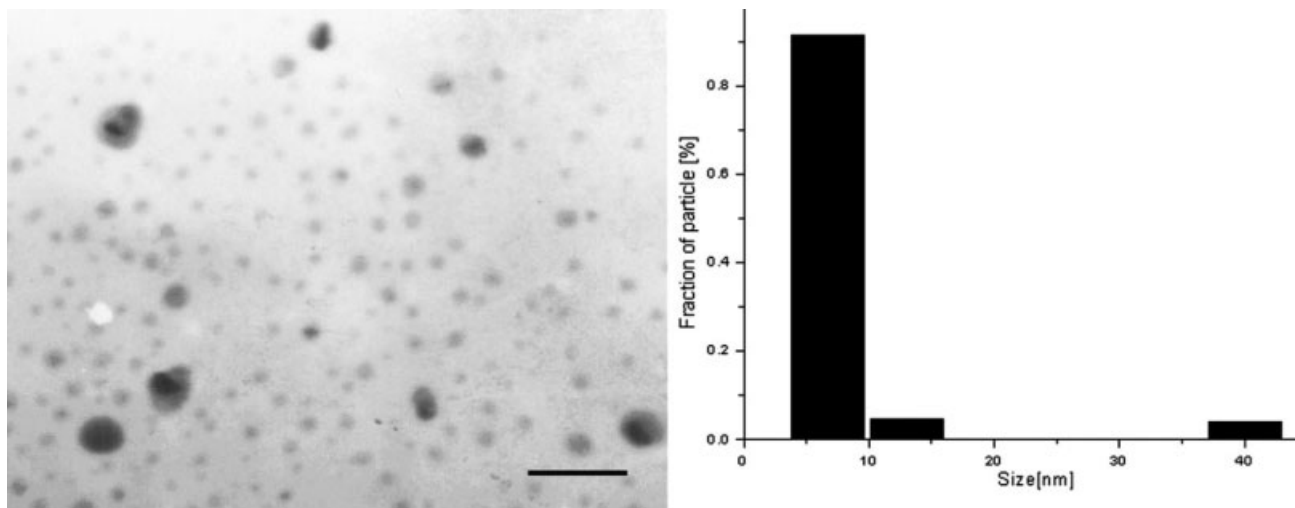


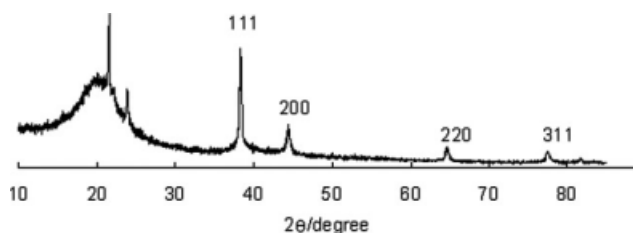
Figure 3 TEM picture of Ag particles by Form-Fill-Seal methodology. The bar is 50 nm.

interpolymer particles without question. The smaller sized particles were regarded as being encapsulated in the hyperbranched molecules. Note that all the silver nanoparticles were stable without flocculation or aggregation for several months, suggesting HPG-CL served as a very effective protective agent for silver nanoparticles.

XRD was used to examine the crystal structure of the sample. The XRD pattern of the as-synthesized product was shown in Figure 4. The diffraction peaks of former one could be indexed to the (111), (200), (311), and (222) planes of the face centered cubic structure of silver with lattice constant  $a = 4.076 \text{ \AA}$ , which was smaller than the reported values of bulk silver crystals (the standard values from JCPDS (04-0783):  $a = 4.086 \text{ \AA}$ ). The sharp peaks existed in the range of  $10\text{--}30$  degrees were due to the crystals of PCL while the broad one arose from the uncrystallized polymer, HPG. The average size of the particles could be calculated by Scherer formula,  $L = 0.9 \gamma / B \cos \theta$ , where  $\theta$  is the diffraction angle,  $\gamma$  is the wavelength of the X-ray, and  $B$  is the full width at the half maximum.<sup>25</sup> The average size calculated according to peak (111) is about 4.6 nm, which was smaller than the result obtained from TEM observation.

Figure 5 showed the UV-vis spectra of the FFS silver sample in  $\text{CHCl}_3$ . The colloidal silver particles exhibited a strong absorption at 434 nm and a weak peak at 255 nm, 434 nm corresponding to the dipole plasma resonance of silver nano-particles, while absorption at 255 nm due to  $\text{Ag}_{\text{nm}}^{x+}$  clusters of several atoms. A fluorescence spectrum of the sample in a  $\text{CHCl}_3$  solution was presented in Figure 5, which showed a strong peak at 340 nm when being excited at 240 nm. The peak at 340 nm was assigned to the radiative recombination of Fermi level electrons and sp or d band holes.<sup>26</sup>



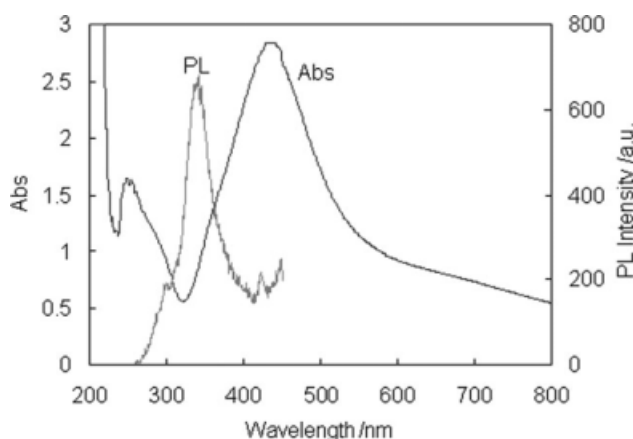


**Figure 4** XRD pattern of silver particles stabilized by hyperbranched polymers obtained by Form-Fill-Seal approach.

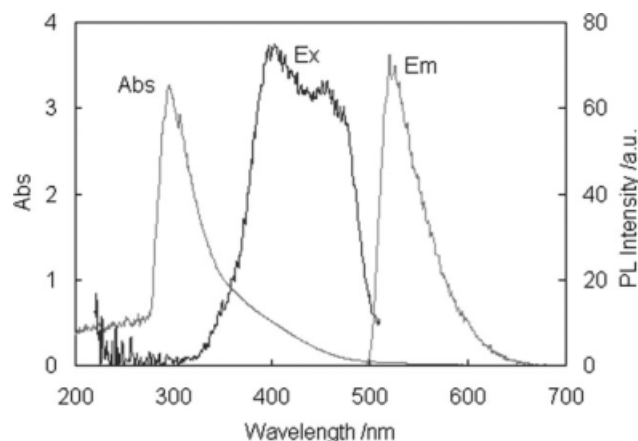
### Ag particles by FSF methodology

In the FSF approach, a “pouch” was sealed in a non-polar phase at first, and then silver ions were filled into the “pouch” by diffusion, finally silver ions were reduced to silver atoms after exposure to the irradiation of  $^{60}\text{Co}$ .<sup>27</sup>

Figure 6 showed the UV-vis spectra and photoluminance spectra of the FSF silver sample in benzene. The maximum absorption peak at 300 nm and the emission band at 520 nm conformed to the fluorescence spectra of silver atoms in inert gases matrices.<sup>28</sup> According to literature,<sup>29</sup> the 300 nm absorption band was caused by trimeric silver. It was supposed that in the solution of HPG-CL and silver ions in a nonpolar solvent, silver ions were diffused inside the HPG-CL molecule. The Ag ions located at the spherical of hyperbranched polymers with higher mobility could be reduced and aggregate into nano-particles, whereas Ag ions inside the protection molecules could be reduced as Ag clusters of several atoms. Figure 7 showed the TEM image of silver particles prepared by FSF methodology. TEM image showed a big spherical frame of which was composed by several HPG-CL molecules, and the surface was surrounded by a few silver nano-particles formed by intermolecular stabilization. The diameters of frame and silver nano-particle



**Figure 5** UV-vis absorption and photo-luminescence spectra of silver particles in  $\text{CHCl}_3$  via Form-Fill-Seal approach.

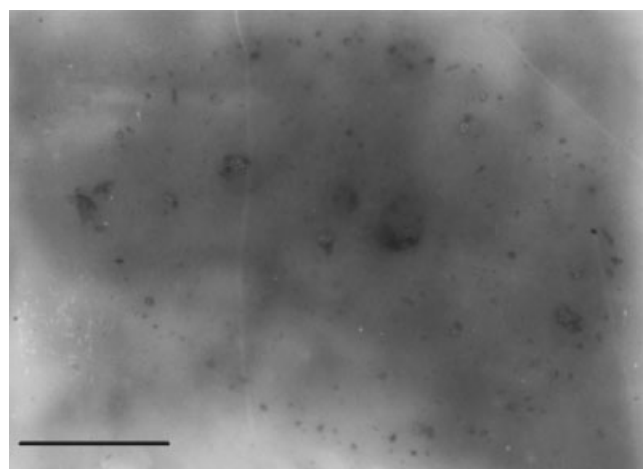


**Figure 6** UV-vis absorption (Abs), photo-excitation (Ex) and emission (Em) spectra of Form-Seal-Fill silver sample in benzene.

aggregates were about 5  $\mu\text{m}$  and 60 nm, respectively. The Ag clusters inside the hyperbranched polymers could not be discerned by TEM, however, background shadow of the TEM pictures indicated the existence of Ag clusters. The Ag clusters were alike photographic developers to show the big spherical frame composed by several HPG-CL molecules. Mainly Ag clusters of several atoms were formed in FSF approach.

### CONCLUSIONS

In this article, we successfully prepared two kinds of nanometer-sized silver particles by FFS and FSF methodology. The former method inclined to prepared silver nano-particles with an average diameter of no more than 10 nm. In the FSF method, mainly silver clusters of several atoms were obtained as encapsulated inside the hyperbranched polymers. The two kinds of nanometer-sized silver particles



**Figure 7** TEM of Ag particles prepared by Form-Seal-Fill method. The bar is 1  $\mu\text{m}$ .

showed different absorption and emission characteristics. The protective polymer introduced in the synthesis of silver particles is biocompatible or biodegradable, so those emissive soluble silver nanoparticles have potential for biological labeling and light emitting sources in nanoscale optoelectronics applications.

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