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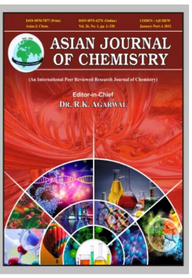

Micelles of Polymeric Ionic Liquid Block Copolymer as Templates for Preparation of Gold Nanoparticles

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The ionic liquids block copolymers polystyrene-block-poly(N-ethyl-4-vinyl pyridinium bromide) {PS-*b*-P[E-VP]Br} was synthesized by one step quaternization of prefabricated polystyrene-block-poly(4-vinylpyridine) and bromoethane. The PS-*b*-P[E-VP]Br formed the micelles with polystyrene as a core and polymeric ionic liquid P[E-VP]Br as a shell in neutral aqueous solution. The composite of gold nanopartices and polymeric micelles were obtained *via in situ* reduction of polymeric ionic liquid shell adsorbed $AuCl_4^-$ with $NaBH_4$ in neutral water. The size and morphology of micelles and outer gold nanopartices were investigated by using dynamic laser scattering, transmission electron microscope and UV-visible spectrum. The obtained gold nanopariticles have been determined to be coated on the surface of micelles and had a small quantum size (6-8 nm) and narrow distribution.

Keywords: Ionic liquids, Block copolymers, Self-assemble, Micelles, Gold nanoparticles.

INTRODUCTION

Gold nanoparticles (GNPs) have been extensively investigated due to their special optical, electronic, catalytic and biocompatible properties, as well as their perspective application in green-catalysis[1-2], cancer therapy[3-4], drug delivery[5-6], molecular recognition and sensors[7], *etc*. The particle size and dispersion of gold nanopartices are important for the properties and applications mentioned above. Commonly, the stable gold nanopartices are prepared by reduction of tetrachloroaurate ions under the action of the satbler or template to avoid aggregation or agglomeration[8-10]. So, proper choice of satbler or template is curial in the control of the size and dispersion of gold nanopartices by chemical methods.

Recently, as a novel stabler, polymeric ionic liquids (PILs)[11] have been reported that because they could provide both steric and electrostatic effects for preparing controlled size and shape of gold nanopartices[12]. Those special effects come from the combining of unique chemical and physical properties of ionic liquids and polymers. Besides the effective protection from the long-chain structure of polymers, the cation group ionic liquids on the main chain of macromolecules, such as pyridinium, imidazolium and ammonium, can provide a stable electrostatic repulsion among the resulting polymeric ionic liquid-gold nanopartices to prevent the aggregation of gold nanopartices. For example, Shan *et al.*[13] obtained 2-4 nm gold nanopartices by polyethylenimine-functionalized ionic liquid as stabler. The produced gold nanopartices showed a potential application in bioelectroanalysis. Buaki *et al.*[14] used liposomes by polymerization of an imidazolium ionic liquid as microreactors for preparation of 10-15 nm gold nanopartices and application in catalysis alcohol oxidation. The reported gold nanopartices stabilized by polymeric ionic liquids have been confirmed to be a high stability in neutral water, which is quite important for the applications in bioscience and biotechnology.

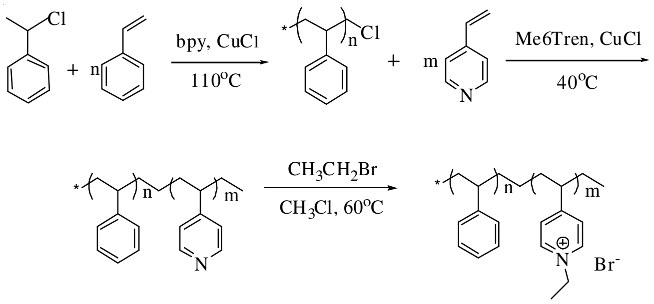
Polymeric micelles have been widely reported as a good template for controlling the size, shape and distribution of gold nanopartices because of their special core-shell structure[15-17]. The micelles composite with gold nanopartices can not only combine with their own unique properties, but these properties can be tailored for specialized applications simply by modulating the structure of polymer or assembly method. Gold nanopartices could be distributed in different parts of the micelles, incorporated into the core or coated on the shell. For example, the micelles of polystyrene-*block*-poly(4-vinyl pyridine) (PS-*b*-P4VP) have been repeatedly used to preparation of gold nanopartices. We obtained gold nanopartices[18,19] in the core of micelle by self-assembled PS-*b*-P4VP in toluene, where the P4VP as the micellar core and polystyrene as the shell. On the other hand, Chen *et al.*[19] reported formation of gold nanopartices on the surface of micelle by P4VP as shell in acidic aqueous solution. It has been found that gold nanopartices stabilized on the surface of micelle have more wide application value because the substrate was easy to access the active surface of gold nanopartices and the properties may be modulated by changing the solubility of coordination segment[20,21].

Herein, *in situ* anchoring gold nanopartices onto the polymeric ionic liquids shell of micelle is investigated, where micelles formed by self-assembly of ionic liquid block copolymer polystyrene-block-poly(4-vinyl-N-*n*-ethyllpyridinium bromide). The cotaed gold nanopartices have been determined and had a small quantum size (6-8 nm) and narrow distribution. The micellar shells combine special properties of gold nanopartices and polymeric ionic liquids and have potential applications in the fields of biotechnology, catalysis and sensor.

EXPERIMENTAL

Styrene, 4-vinyl pyridine and CuCl are purchased from Aldrich and purified according to ref.[22]. *Tris*[2-(dimethylamino)ethyl]amine (Me_6TREN) was synthesized according to ref.[23]. Sodium borohydride ($NaBH_4$), hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$) and bromoethane were purchased from Aldrich Co. Other solvents were of analytical grade and are used as received without further purification.

Preparation of the PS-*b*-P[E-Py]Br: The block copolymer polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) was synthesized by sequent ATRP of styrene and 4-vinylpyridine according to previous report[24]. Then, polystyrene-block poly(4-vinyl-N-*n*-ethyllpyridinium bromide) (PS-*b*-P[E-Py]Br) was prepared by a step quaternization of prefabricated polystyrene-block-Poly(4-vinylpyridine). Under nitrogen atmosphere and magnetic stirring, PS-*b*-P4VP(2g) was added into a solution of bromoethane (2 mL) in chloroform (20 mL). After the mixture was reacted at 60 °C for 120 h, the resulting solution was poured into colder diethyl ether (200 mL) to precipitate the product. The precipitate was filtered and dried *in vacuo* to obtain PS-*b*-P[E-Py]Br. The synthesis procedures are illustrated in **Scheme-I**.



Scheme-I: Schematic representation for synthesis of PS-*b*-P[E-Py]Br

Preparation of the PS-*b*-P[E-Py]Br micelles: The PS-*b*-P[E-Py]Br/DMF solution with a concentration of 0.1 wt % was first prepared by dissolving 0.02 g polymer in 20 mL DMF. After stirred overnight, the deionized water was added into the solution with a rate of 7s/d under vigorous stirring. When the solution turn to turbid, the addition was stop and indicating the occurrence of micellzation of block copolymers. The micelle solution was allowed to keep overnight and then, adding 5 times deionized water. The resultant micelles solutions were loaded in dialysis bags and dialyzed against deionized water for 7 days to remove DMF. Finally, the micelles solutions ware fixed at a concentration of 0.2 mg/mL.

Fabrication of hybrid composites: The aqueous solution (4.5 mg/mL) of $HAuCl_4$ was added into 10 mL micelle aqueous solution (0.02 mg/mL). The ratio of $AuCl_4^-$ to pyridinium was controlled at 1:7 and 1:5. After gently stirring for 24 h at room temperature, 10-fold excess of aqueous solution of $NaBH_4$ was then quickly added and the stirring was continued for 24 h. The color of solution turn from yellow to wine, which indicated the *in situ* formation of gold nanopartices in the micelles solution. The excess $NaBH_4$ was removed by dialysis.

Characterization: The ^1H NMR spectra of the polymers in $CDCl_3$ and DMSO were recorded on a Bruker AV300 spectrometer operating at 300 MHz for protons. PDI ware characterized by a Waters 600 E gel permeation chromatography (GPC) analysis system equipped with waters 2414 refractive index detector at 30 °C, where N,N-dimethylformamide (DMF) was used as the eluent at flow rate of 1 mL/min and linear polystyrene as the calibration standard. Transmission electron microscopy (TEM) was conducted by using a Philips T20ST electron microscopy at an acceleration voltage of 200 kV. Thin films were prepared by dipping a drop of the solution onto a carbon-coated copper grid and then volatilizing the solution at room temperature. UV-visible absorption spectrum was obtained using a Perkin-Elmer UV-visible spectrometer (Lambda 20). Dynamic laser scattering (DLS) measurements were performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000 AT) at 532 nm at room temperature.The sample was filtered through a 0.45 µm Millipore filter into a clean scintillation vial.

RESULTS AND DISCUSSION

Recently, the ionic liquid block copolymers have received much attention due to their novel properties, such as the anionic sensitivity of ionic liquids and the self-assembly properties of block copolymers[25]. The preparation of ionic liquid block copolymers has been reported through reversible addition-fragmentation chain transfer polymerization of ionic liquid monomer[26] or the quaternization of block copolymers with the pyridine[27] or imidazole[28]. Here, the PS-*b*-P4VP is firstly synthesized by sequent ATRP and then PS-*b*-P[E-Py]Br is obtained by a step quaternization of prefabricated PS-*b*-P4VP. The GPC traces of the macroinitiator PS-Cl and PS-*b*-P4VP is shown in Fig. 1. From Fig. 1, the number mean molecular weight (Mn) of PS-Cl is 7900 and PS-*b*-P4VP is 18500. The PDI is 1.15 and 1.27 respectively. The composition of the PS-*b*-P4VP can be denoted as PS78-*b*-P4VP101(the subscript indicating the number of the repeating units). Fig. 2 is the ^1H NMR spectrum of PS-*b*-P4VP and (PS-*b*-P[E-Py]Br. From Fig. 2b, after quaternization, the characteristic proton integrals of pyridinium (c, d) shifts about 1 ppm to down-field compared with that of pyridine on Fig. 2a due to deshielding effect[29]. The emergence of e at 4.69 is ascribed to the $-N-CH_2^-$ and the increase proton integrals f at 1.2-2.1 is caused by-CH_3. The mole ratio of d to e is about 0.98, which indicate that the 98 % group pyridine be quaternized.

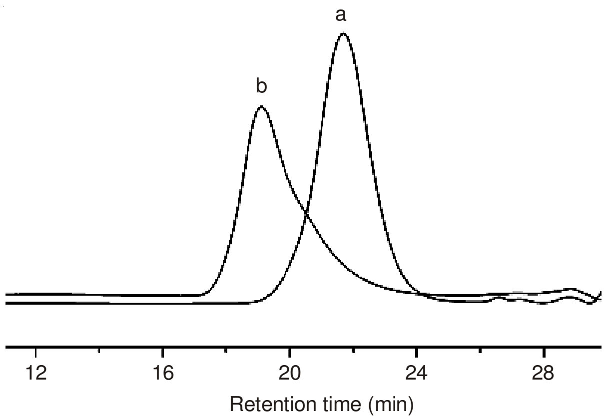


Fig. 1. GPC traces for PS-Cl (b) and PS-*b*-P4VP (a) in DMF at room temperature

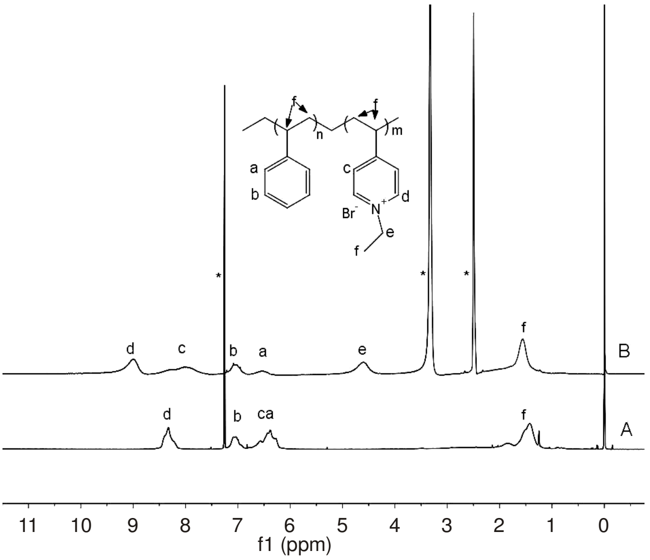


Fig. 2. ^{1}H NMR spectrum of PS-*b*-P4VP (a) in $CDCl_3$ and PS-*b*-P[E-Py]Br (b) in DMSO

Characterization of micelles and gold nanopartices: The amphi-philic block copolymers can self-associate to form micelle-like structure with a hydrophobic block as a core and a hydrophilic as a shell, which is easy to be materialized through a selective solvent method. Although Meristoudi and Pispas[20] reported that gold nanopartices could coate on the surface of micelles formed by PS-*b*-P4VP with polystyrene as the core and P4VP as the shell, the gold nanopartices must been stabilized in acid aqueous solution due to the weak electrolyte of P4VP. Here, the polymeric ionic liquids block of P[E-Py]Br has a structure ion liquid with pyridinium as cation on polymer main chain and bromide (Br$^-$) as the counteranion, which solubility is found to be not influenced by pH values in water. In addition, those electrostatic effects have a special role on the preparation and stability of gold nanoparticles. The forming process of gold nanopartices/micelle composites is shown in **Scheme-II**. Firstly, (PS-*b*-P[E-Py]Br is self-assembled into micelles with polystyrene as a core and P[E-Py]Br as shell in natural aqueous solution; and then the $AuCl_4^-$ is adsorbed on the P[E-Py]Br shell block by the an anion displace. Finally, adding reluctant $NaBH_4$ makes the formation of composites with shell coating gold nanopartices.

The block P[E-Py]Br is soluble in water but block polystyrene is insoluble, thus block copolymers PS-*b*-P4VP would self-assemble in water and form micelles with polystyrene as a core and P[E-Py]Br as a shell. The hydrodynamic diameter distribution of the micellar solution is measured by dynamic laser scattering and the result is shown in Fig. 3. The average diameter is about 60 nm with the size distribution range of is 39-79 nm.

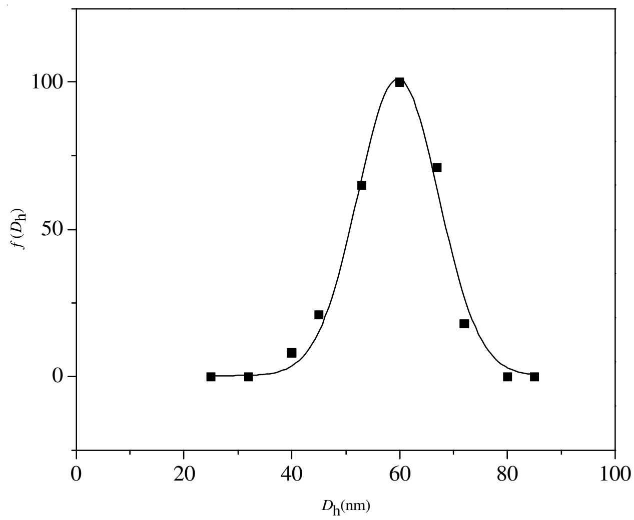
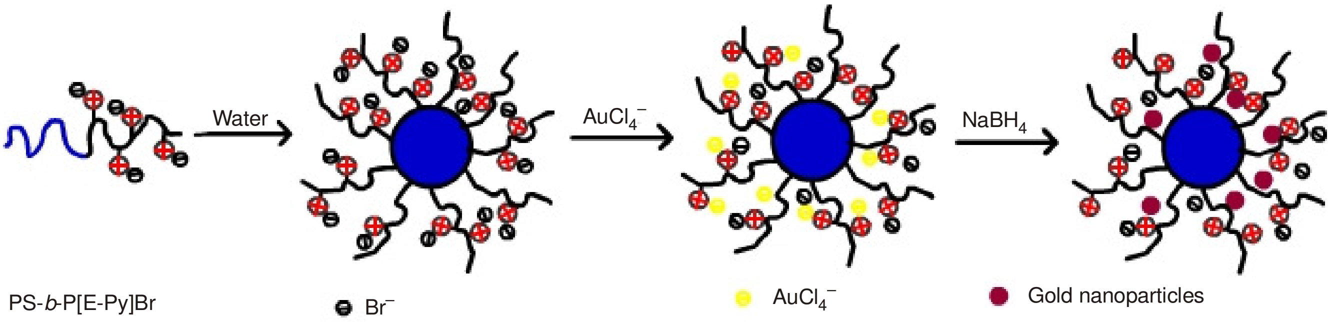


Fig. 3. Hydrodynamic diameter distributions of the micelles. Polydispersity index is about 0.12

The TEM image of the micelle is shown in Fig. 4. The micellar aggregates are uniform sphere and the mean diameter measured from the TEM is about 45 nm. The size determined from the TEM is smaller than that measured from the dynamic



Scheme-II: Schematic representation of the formation of PS-*b*-P[E-Py]Br micelles and gold nanoparticles

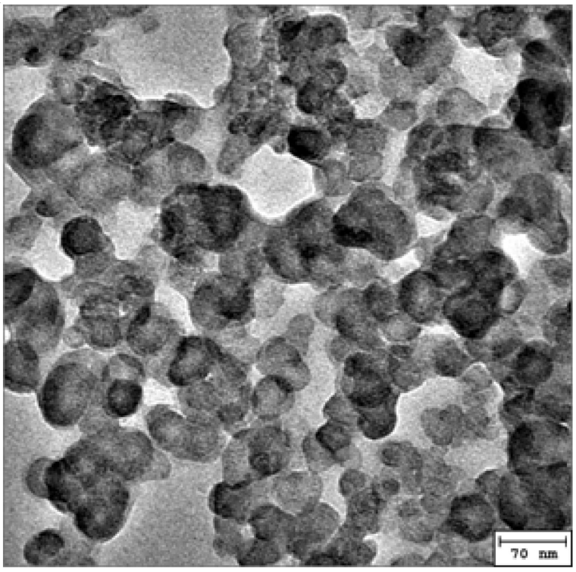


Fig. 4. TEM image of PS-*b*-P[E-Py]Br micelle in nature aqueous solution

laser scattering (Fig. 3), the possible reason may be ascribed to the TEM result obtaining from a dry state. The dynamic laser scattering result shows the hydrated state of the micelle, in which the ionized P[E-Py]Br keeps stretched due to electrostatic repulsion. In addition, the spherical micelle are accumulated together in TEM, which may be ascribed to the shell polymer of one micelles intertwine with the others when the evaporation of water reduced the electrostatic repulsion.

The size, shape and surrounded environment of the gold nanoparticles can be inferred by measuring the surface plasmon resonance (SPR) using UV-visible spectrophotometer. UV-visible absorption spectra of the gold nanoparticles prepared by two ration of $AuCl_4^-$ to pyridium (1:7 and 1:5) are presented in Fig. 5. In this study, the two samples are prepared at the same condition, thus the surface plasmon resonance is directly related to the sizes of the gold nanopartices in composites. From Fig. 5a the absorbance peak of the 1:7 are located at position of about 516 nm and the 1:5 at position about 520 nm. This result indicates the obtained gold nanopartices are a spherical particles with diameters at 10 nm or smaller[30].

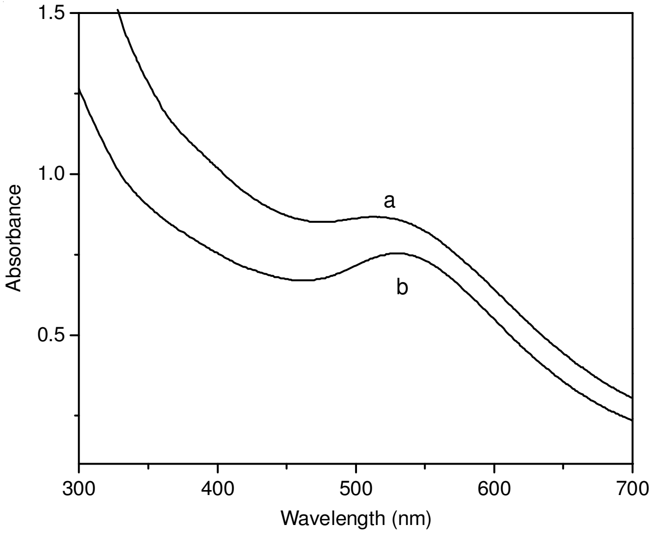


Fig. 5. UV-visible spectra of two gold nanopartices-micelle composite solutions with initial molar ratio of 1/5 (a); 1/7 (b) of $AuCl_4^-$ to E-Py in nature aqueous solution

The micelles are stable in the neutral water due to their polyelectrolyte shells, which composite of a pyridinium cation and counteranion of bromide. Through a anion exchange, the added $AuCl_4^-$ can be adsorbed onto the P[E-Py]Br shell block

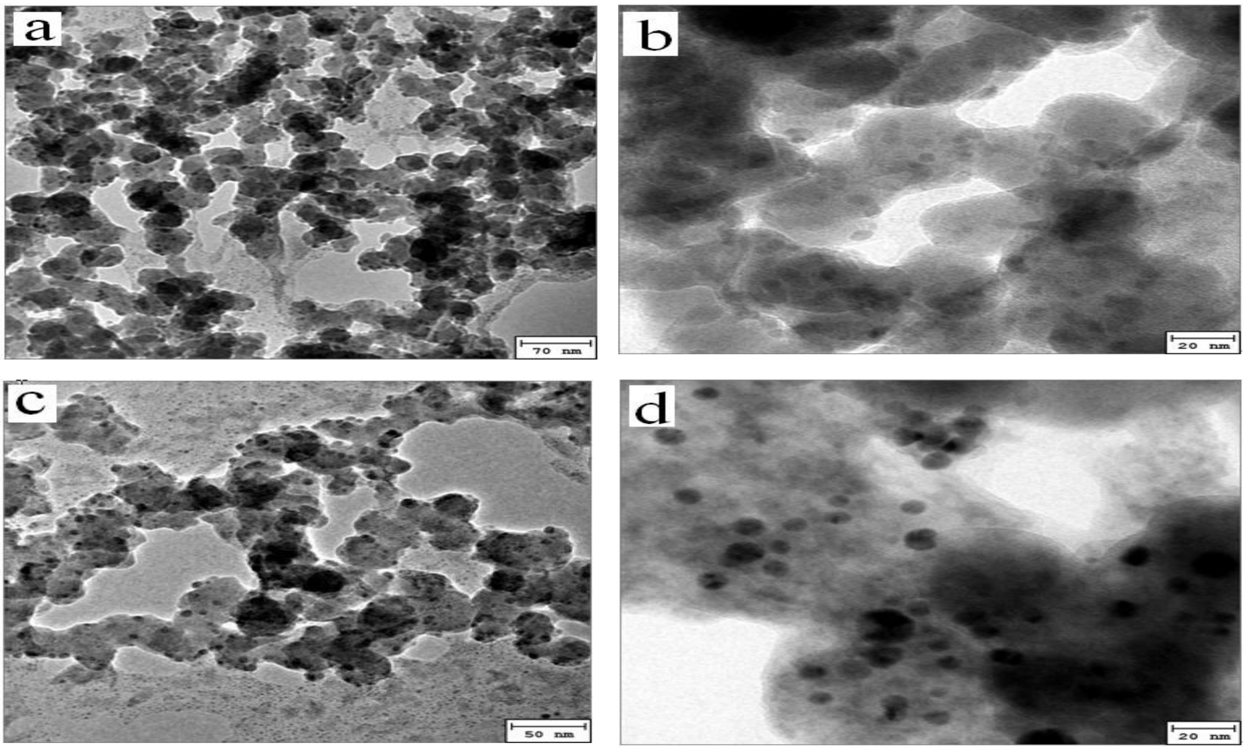


Fig. 6. TEM graphs of immobilization gold nanoparticles on shell of micelles formed by 1/7 (a, b) and 1/5 (c, d) of $AuCl_4^-$ to [E-Py]Br

and the same result has been found in the Lu *et al.*[31] reports. Adding reluctant $NaBH_4$, the nucleation and growth of gold nanopartices relate directly to the environment protected by the polymeric ionic liquids shells. Two different amounts of gold have been introduced into the shell and reduced them to produce gold nanopartices.

The TEM image gives a direct proof that gold nanopartices forming on the surface of micelles. Fig. 6a displays TEM pictures of micelles composite gold nanopartices prepared by the ration of $AuCl_4^-$ to pyridium at 1:7 and Fig. 4b shows a partly enlarged view of Fig. 6a. It is evident that the gold nanopartices located in the micelle surface from Fig. 6a. After coating gold nanopartices on the surface, the micellar size are 35-40 nm and a little smaller than the original. This can be explained that the negative charge of the gold nanopartices prepared by reduction of $NaBH_4$ partially crosslinks the P[E-Py]Br shell by ionic interaction and makes the shell shrunken[31]. From Fig. 6b, the gold nanopartices have a dimension of ca. 4-5 nm, uniform sphere and evident narrow size distribution. Fig. 6c and Fig. 6d is the TEM image of gold nanopartices prepared at the ration 1:5. The gold nanopartices still have a uniform sphere and evident narrow size distribution while the size slightly increases to 6-8 nm.

Here, the $AuCl_4^-$ is absorbed on the P[E-Py]Br shell block by the anion displace and then the nucleation of the gold nanopartices takes immediately place when the excess $NaBH_4$ was added in the solution. Although the process would cause a slight P[E-Py]Br segment crosslinking and the micelles contraction, the electrostatic interaction from the rest of ionic liquid group can prevent the aggregation of gold nanopartices.

Conclusion

The ionic liquids block copolymers PS-*b*-P[E-Py]Br has been prepared by a step quaternization reaction of PS-*b*-P4VP. The stable micelles structure could be formed in the nature aqueous with the polystyrene as a core and P[E-Py]Br as a shell. These polymeric ionic liquids micelles can be as a "nano-reactor" for preparation and stabilization gold nanopartices on the micellar surface. The composite shell of micelle combining the special properties of ionic liquid polymer and gold nanopartices will have the potential in biomedical and catalytic applications.

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