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Preparation of platinum nanoparticles using star-block copolymer with a carboxylic core

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Abstract

Well-defined star polymers containing a functionalized core supply a molecular nanocavity and may be used to control formation of inorganic nanoparticles. Herein, platinum (Pt) nanoparticles of 2–4 nm were prepared by using (poly(acrylic acid)-*b*-polystyrene)$_6$ (PAA-*b*-PS)$_6$ amphiphilic star block copolymer as a novel single molecular stabilizer. This PAA core functionalized star polymer was obtained by hydrolysis of (poly(*tert*-butyl acrylate)-*b*-polystyrene)$_6$ (P*t*BA-*b*-PS)$_6$, which was synthesized by sequential atom transfer radical polymerization (ATRP) of *tert*-butyl acrylate and styrene with an initiator bearing six 2-bromoisobutyloxyl groups. Pt(IV) ions were loaded by ion exchange to the core of the star polymer and Pt nanoparticle stabilized by single star polymer was produced by a reduction with $NaBH_4$.

Keywords: Star-block copolymer; Platinum nanoparticles; Preparation; Unimolecular micelle

1. Introduction

Nanoparticles of transition metals and related compounds have attracted a great attention of academic area and application field owing to their special properties which are greatly different from the properties of their bulk materials [1,2]. Rare metal nanoparticles are very important catalysts of chemical reactions [3]. The properties of the nanoparticle catalysts depend not only on the size, the polydispersity, and the shape, but also on the surface environment [3–6]. Platinum (Pt) nanoparticle shows fascinating catalytic properties which have been widely studied [4–6]. In order to prepare Pt nanoparticles with small size, narrow size distribution, and long-term stability, researchers have applied various polymers including homopolymers, copolymers, dendrimers, and hyperbranched polymers as the stabilizers [1,3–5,7]. In recent years, block copolymers have been widely investigated for their potential application in nanotechnology and nanomaterials [8–10]. When the block copolymer dissolves in a selective solvent above the critical micelle concentration (cmc), it can aggregate into well-defined micelles of core–shell structure [1,8–14]. The core of the micelle becomes a “nanoreactor” for the formation of metal nanoparticles. The micelle structure and nanoparticle thereafter may be controlled by varying the composition of block copolymers. As one micelle is formed by the aggregation of many polymer chains, the stability of micelle and the nanoparticles prepared by block copolymer micelles depend on the concentration, temperature, pH value, solvent, and even some small molecules or ions [8–14]. Mark and co-workers have prepared palladium and platinum nanoparticles using polystyrene-*b*-poly(methacrylic acid) amphiphilic block copolymers. The particle size and morphology were found to be affected by the metal precursor counter ions and pH values of the solution [13,14].

Star polymer is a simplest branched polymer with several polymer chains linked to a core as its arms [15,16]. If the arms are amphiphilic, the star polymer is called amphiphilic star-block copolymer. Depending upon synthetic approach, the star polymers prepared by controlled polymerization have low distribution; their arm number and functionalities can be controlled during the polymerization. As showed in Fig. 1, $(AB)_n$ and A_nB_n are two common star-block copolymers. These star

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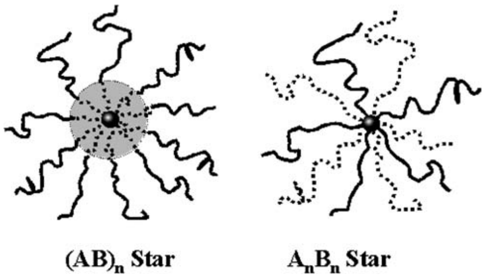

Fig. 1. Star block copolymers of different forms.

polymers are expected to be a new stabilizer for preparing metal nanoparticles. However, very few star polymers have been used for such purpose so far. Youk et al. have applied a (polystyrene-*b*-poly(2-vinylpyridine))$_n$ star-block copolymer, (PS-PVP)$_n$, to prepare gold nanoparticles [17]. Gorodyska et al. have prepared palladium nanoparticles with star polystyrene-*b*-poly(2-vinylpyridine) copolymer (PS$_7$-PVP$_7$) [18]. Both PS-PVP star copolymers in different form were prepared by arm-first approach, of which the core was formed by microgelation of divinyl chemicals. However, the arm numbers of the star polymers thus prepared were not well-controlled. It has been confirmed recently that the core of the star polymers of low polydispersities by arm-first approach has a rather broad distribution after the arms have been removed [19,20]. In addition, only poly(vinylpyridine) was applied as the functional segment to chelate with metals.

The structure of (AB)$_n$ star molecule is very interesting since its core supplies a functionalized nanospace which is surrounded by the corona if the inner block bears functionalities and number of arms is large enough [21,22]. It is an unimolecular micelle just like a small core–shell micelle of block copolymer with its core being covalent linked and with no cmc. Moreover, its core can be much smaller than that of block copolymer micelle. Such star polymers with an unimolecular cavity are also similar to the well-known dendrimers which have been used as nanoreactors in preparing nanoparticles [23,24]. However, dendrimers are synthesized through stepwise organic reactions which are tedious and time consuming; in contrast, the star polymers are prepared much easier.

Herein (PAA-*b*-PS)$_6$ star-block copolymer with six arms and a carboxyl core was synthesized by a core-first approach via atom transfer radical polymerization (ATRP). Since an initiator bearing six initiating groups was used, the arm number and the block compositions were tailor-made. Such novel functionalized star polymer was used as a stabilizer to prepare Pt nanoparticles by applying PAA cavity in the star. The synthesis of polymers and Pt nanoparticles was shown in Fig. 2. Another motivation of using carboxyl groups to stabilize Pt nanoparticles is for potential catalytic reaction with the Pt nanoparticles as a catalyst. It has been reported that the microenvironment of metal colloids greatly affects the catalytic activity and substrate selectivity [25]. Liu et al. have found that asymmetric hydrogenation of methyl pyruvate catalyzed by Pt colloid in presence of acetic acid resulted in 100% conversion and 93.6% enantiomeric excess value [26]. Besides stabilizing the Pt nanoparticles, the PAA core in the star polymer applied here may supply a carboxylic acid microenvironment which may enhance the potential catalytic properties of the Pt particles.

2. Materials and methods

2.1. Materials

ATRP initiator, Br$_6$ (Fig. 2), was synthesized according to Ref. [27]. Styrene (St) and *tert*-butyl acrylate (*t*BA) were stirred over CaH$_2$ overnight and distilled under reduced pressure. CuBr was purified by washing with acetic acid and acetone. N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA, 99%) was purchased from Aldrich. Trifluoroacetic acid (TFA, 99%) was provided by Fluka and sodium borohydride (NaBH$_4$) was purchased from Sigma. Other commercially available reagents were used as received.

2.2. Measurements

Gel permeation chromatography (GPC) was performed by a set of a Waters 515 HPLC pump, a Waters 2414 refractive index detector, and combination of Styragel HT-2, HT-3, and HT-4, effective molecular weight range is 100–10,000, 500–30,000, and 5000–600,000, respectively. THF was used as eluent at a flow rate of 1.0 ml/min at 35 °C. Polystyrene standards were used for the calibration. ^{1}H NMR spectra were recorded on a Bruker DMX300 spectrometer in CDCl$_3$ at room temperature. Transmission electron microscopy (TEM) was performed on a JEM-100CXII instrument. Specimens were pre-

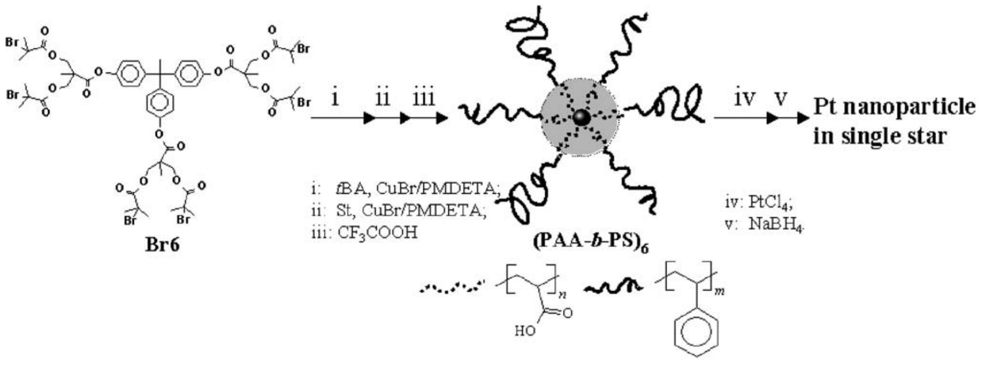

Fig. 2. Synthesis of (PAA-*b*-PS)$_6$ star block copolymer by ATRP.

pared by dropping the colloid solution on a copper grid covered with a carbon film and then evaporating the solvent. The particle size distribution was obtained on the basis of the measurements of about 150 particles. X-ray diffraction patterns (XRD) were recorded by a Rigaku D/Max-2400 diffractometer at 40 kV and 100 mA employing Cu$K\alpha$ radiation. The specimen was prepared by rotary evaporating the solvent of colloid solution and crushing into powder with agate mill. A slightly modified commercial laser light scattering (LLS) spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He–Ne laser ($\lambda_0 = 632$ nm) was used. The sample solutions were filtered through a 0.45 µm PTFE membrane prior to use. The solutions were put in 10 mm diameter glass cells.

2.3. Synthesis of star poly(t-butyl acrylate) (PtBA)$_6$

In a 25 ml Schlenk flask, Br_6 (47.3 mg, 0.03 mmol) and CuBr (13.7 mg, 0.09 mmol) were purged three times with N_2. Acetone (0.66 ml) and a solution of PMDETA (19.5 µl, 0.09 mmol) and *t*BA (2.65 ml, 18.0 mmol) were deoxygenated by bubbling with N_2 for 30 min and transferred into the Schlenk flask with a syringe. The flask was placed in an oil bath at 60 °C for 3.5 h with stirring. The reaction was terminated by cooling to room temperature and exposing to air. The catalyst was removed by passing through alkaline alumina column. The sample was precipitated from 7:3 methanol/water and dried in vacuum at 40 °C. Dried product: 1.05 g. Monomer conversion: 43.4%.

2.4. Synthesis of star PtBA-b-PS (PtBA-b-PS)$_6$

In a 50 ml Schlenk flask, (P*t*BA)$_6$ (1.00 g, 0.03 mmol) and CuCl (18.0 mg, 0.18 mmol) were purged three times with N_2. A solution of PMDETA (38 µl, 0.09 mmol) and St (20.8 ml, 0.18 mol) was deoxygenated by bubbling with N_2 for 30 min and transferred into the Schlenk flask with a syringe. The flask was placed in an oil bath at 100 °C for 9 h with stirring. The catalyst was removed by passing through alkaline alumina. The sample was precipitated from methanol and dried under vacuum at 40 °C. Dried product: 2.88 g. Monomer conversion: 11.3%.

2.5. Preparation of star PAA-b-PS (PAA-b-PS)$_6$

(P*t*BA-*b*-PS)$_6$ (2.0 g, 4.2 mmol of *t*BA unit) was dissolved in methylene chloride (25 ml) and TFA (1.62 ml, 21.2 mmol) was transferred into the solution. After stirring at room temperature for 24 h, the solution was concentrated, the polymer was precipitated from ethanol and dried under vacuum at 50 °C.

2.6. Preparation of Pt nanoparticles

(PAA-*b*-PS)$_6$ (158.3 mg) was dissolved in tetrahydrofuran (THF, 32.8 ml). NaOH (15.6 mg, NaOH:AA = 7:10, molar ratio) was added into the solution with stirring overnight at room temperature. Then three parts of the above solution of 10 ml were transferred into three flasks of 25 ml. Different amounts of $PtCl_4$ (0.02 mol/L) solution of THF were transferred into each flask with Pt:AA molar ratio of 1:10, 1:20, and 1:40, respectively. The solutions were stirred overnight at room temperature. Then $NaBH_4$ in 1-(2-methoxyethoxy)-2-methoxyethane (0.3 mol/L), which was about 10 times of $PtCl_4$ (molar ratio), was introduced into each flask. The solution turned to brown immediately. Half an hour later, 10 µl of solution was taken for preparing TEM samples. The colloid solutions were stored in sealed containers at room temperature.

3. Results and discussion

3.1. Preparing (PAA-b-PS)$_6$

Fig. 3 shows the GPC traces of (P*t*BA-*b*-PS)$_6$ star polymer and its precursor (P*t*BA)$_6$. It indicated that the synthesis of the star polymers by core-first ATRP approach is efficient. By comparing ^{1}H NMR spectra of (P*t*BA)$_6$ and (P*t*BA-*b*-PS)$_6$ in Figs. 4a and 4b, the second PS segments were introduced as expected. The composition of two segments may be estimated by comparing the peak area of PS protons at 6.3–7.2 ppm and that of P*t*BA protons at 2.0–2.3 ppm. The properties of (P*t*BA-*b*-PS)$_6$ star polymer were summarized in Table 1. It may be found that the polydispersities of (P*t*BA)$_6$ and (P*t*BA-*b*-PS)$_6$ were narrow, indicating that the well-defined star polymers have been obtained. Molecular masses given by monomer conversion agreed well with that by ^{1}H NMR analysis. After hydrolysis, *tert*-butyl groups of *t*BA segments disappeared completely as demonstrated by ^{1}H NMR spectrum (Fig. 4c) and FT-IR spectra. Each arm of the star polymer contained ca. 47 AA units and ca. 110 St units.

Depending upon the composition and solvent, the star polymer (PAA-*b*-PS)$_6$ in solution may have two forms: unimolecule and its aggregate. If a good solvent for both segments is used, unimolecule would be the main form [21,22]. Since THF is a good solvent for PS segments and may dissolve PAA, it is possible that present star polymer forms molecular dispersion in THF. A similar star polymer, (poly(acrylic acid)-*b*-poly(methyl methacrylate)$_6$, which formed unimolecular micelle, has been

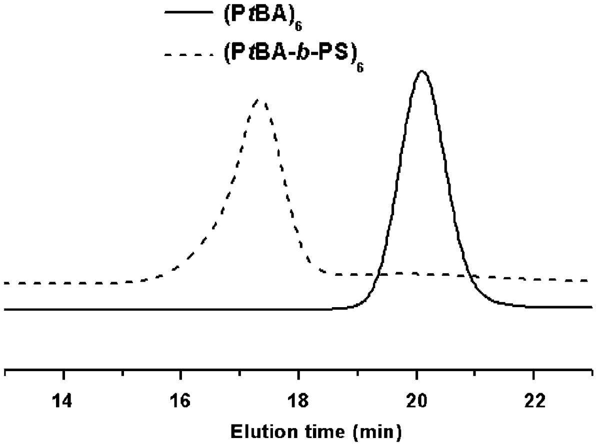

Fig. 3. The GPC curves of (P*t*BA)$_6$ and (P*t*BA-*b*-PS)$_6$.

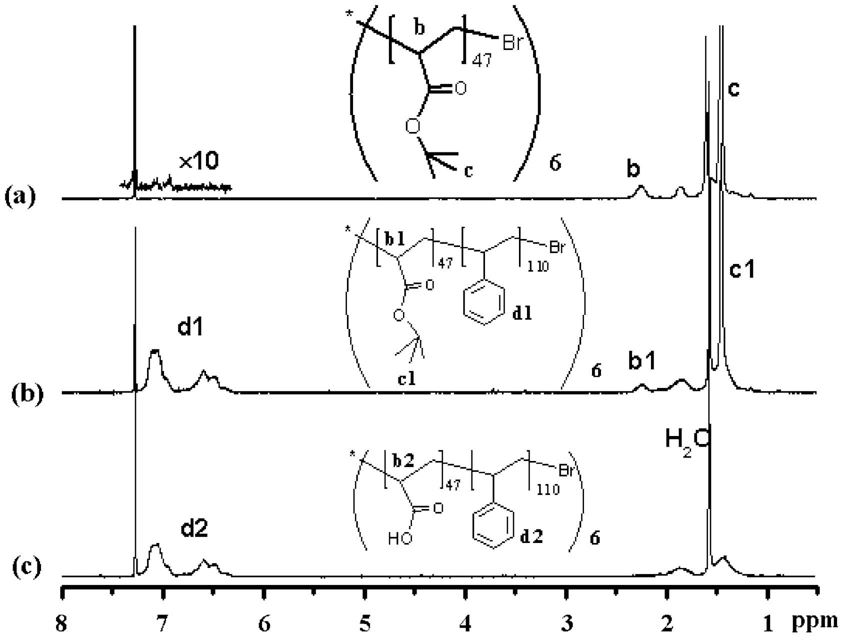

Fig. 4. The ^{1}H NMR spectra of (a) $(\mathrm{P}t\mathrm{BA})_6$, (b) $(\mathrm{P}t\mathrm{BA}\text{-}b\text{-}\mathrm{PS})_6$, and (c) $(\mathrm{PAA}\text{-}b\text{-}\mathrm{PS})_6$.

Table 1
Characterization of $(\mathrm{P}t\mathrm{BA}\text{-}b\text{-}\mathrm{PS})_6$ star-block copolymer[a]

Polymer[b]	$M_{n\mathrm{NMR}}$[b]	$M_{n\mathrm{conv}}$[c]	M_w/M_n[d]
$(\mathrm{P}t\mathrm{BA}_{47})_6$	36,100	33,300	1.05
$(\mathrm{P}t\mathrm{BA}_{47}\text{-}b\text{-}\mathrm{PS}_{110})_6$	106,300	105,400	1.08

[a] *t*BA and St conversions were 43.4 and 11.3%, respectively.

[b] $M_{n\mathrm{NMR}}$ and degree of polymerization were obtained by ^{1}H NMR spectra, P*t*BA block was determined from the ratio of integrated peak areas of initiator peak around 7 ppm and the P*t*BA peak at 2.2 ppm, PS block was determined from the ratio of integrated peak areas of PS protons at 6.3–7.2 ppm and P*t*BA protons at 2.2 ppm.

[c] Estimated by monomer conversion, $M_{n\mathrm{conv}} = M_{n\mathrm{initiator}} + ([\mathrm{monomer}]/[\mathrm{initiator}]) \times M_{n\mathrm{monomer}} \times \mathrm{conversion}$.

[d] Given by GPC.

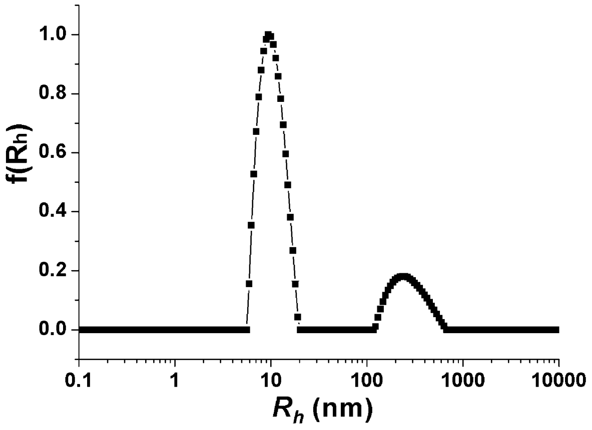

Fig. 5. CONTIN analysis from the DLS correlation functions of $(\mathrm{PAA}\text{-}b\text{-}\mathrm{PS})_6$ at concentration of 0.5 mg/ml in THF.

reported [21]. DLS was applied here to confirm that this star polymer was a molecular dispersion in solution. For 0.5 mg/ml of $(\mathrm{PAA}\text{-}b\text{-}\mathrm{PS})_6$ solution in THF, CONTIN analysis of light scattering (Fig. 5) gave a bimodal size distribution. R_h of the main part was of 10 nm, corresponding to the unimer star polymer. A large particle, $R_\mathrm{h} = 260$ nm, coexisted as well, indicating the formation of the aggregates. Since the light scattering is more sensitive to large particles, the number of the aggregates should be much less than the unimer star polymer. This result is similar to the results in a recent research, which revealed that the solvent property influences the micellization behavior of a $(\mathrm{AB})_n$ star polymer. In a poor selective solvent, unimolecular micelle formed for the star polymer of low molecular weight but it coexisted with multimolecular micelle for the sample of high molecular weight [22].

3.2. Preparing Pt nanoparticles

Different amounts of Pt(IV) ions were introduced into the core of the star polymer and Pt nanoparticles were produced by the reduction as described in Section 2. The Pt particles were nearly monodispersed and their particle sizes given by TEM analysis were 4.2 ± 1.3, 2.9 ± 0.9, and 1.9 ± 0.8 nm for the amount of Pt ions loading of 1:10, 1:20, and 1:40 (Pt:AA unit), respectively. Lower Pt loading produced smaller Pt particles. Fig. 6 shows the TEM micrographs of Pt nanoparticles from 1:40 loading (Pt:AA = 1:40). The inset is an enlarged area, from which it is interesting to observe the core–shell structure. The dark spots, surrounded by a gray corona of the star polymer, were Pt particles and most of the Pt particles were located at the center of a star polymer. The shell diameter was ca. 9 nm and this value agreed to that of the individual star polymers given by DLS. No large Pt particles were observed, supporting the results of DLS that the aggregation of star polymer was neglectable. It was of note that not every star polymer has a Pt particle in it. This may be ascribed to the uneven distribution of Pt ions before or after reduction.

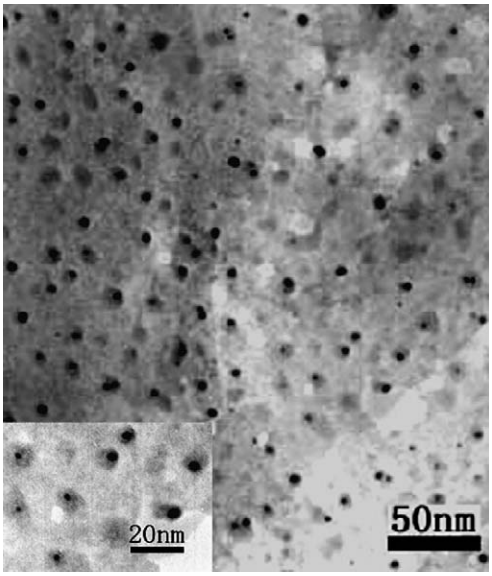

Fig. 6. TEM micrograph of platinum nanoparticles for incorporation of $PtCl_4$ of 1:40 (Pt:AA units) reduced with $NaBH_4$.

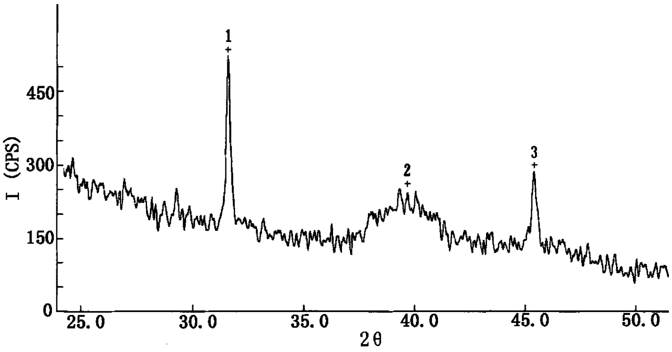

Fig. 7. The XRD spectra of the sample with incorporating 1:10 of $PtCl_4$ to carboxyl and reduced with $NaBH_4$.

TEM analysis was performed again after the Pt nanoparticle in solution was stored at room temperature for a month. The size of Pt nanoparticles from different incorporation ratios of Pt ions, 1:10, 1:20, and 1:40, was 2.9 ± 0.9, 1.9 ± 0.9, and 1.9 ± 0.7 nm, respectively. Sizes from the sample of 1:10 and 1:20 Pt(IV) loading even became smaller and the distributions became narrower. This phenomenon has been observed previously [28,29]. After digestive ripening, a process in which a colloidal suspension in a solvent was refluxed at the solvent boiling temperature in the presence of a surface-active ligand, a highly polydisperse colloid was converted into a nearly monodisperse one.

To make sure the Pt nanocrystals were obtained, the Pt nanoparticles from 1:10 of Pt ion loading were analyzed with XRD after it was reduced. XRD result was shown in Fig. 7, in which peak 2 corresponded to the face center cubic Pt crystals and the diffraction data ($d = 2.2701$ Å) agreed well with corresponding standard data (2.2921) achieved from PDF2 ICDD database. The broad peak was owing to the small sizes of particles. The sharp peaks 1 and 3 were ascribed to the side product NaCl during ions exchange.

4. Summary

A well-defined star-block copolymer with six arms, $(PAA\text{-}b\text{-}PS)_6$, was synthesized by an arm-first approach of ATRP. The star polymer formed unimolecular micelle with PAA block as its core and PS block as its shell in THF solution. Pt nanoparticles of ca. 2.0 nm were prepared with the star molecule as a single molecular reactor. TEM analysis indicated the core–shell structure of the star polymer stabilized Pt particles. It is exciting that PAA functionalized single star polymer can be used as a new stabilizer for formation nanoparticles. The star polymer supplies a molecular cavity instead of the micelle core of many molecules from linear diblock copolymers. Therefore, the cavity is much smaller and can be tailored. Exploring different core functionalized star polymers and their application for formation of inorganic nanoparticles is under way.

Acknowledgments

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