ORIGINAL PAPER

Water-soluble starlike poly(acrylic acid) graft polymer: preparation and application as templates for silver nanoclusters

Huiqiang Li · Zhanxian Li · Linzhi Wu · Fang Liu · Jie Zhou · Miao Luan · Mingming Yu · Liuhe Wei

Abstract Water-soluble starlike polymers containing concentrated carboxyl groups were conveniently synthesized via the combination of "click" chemistry and atom transfer radical polymerization. The starlike polymer was composed of a shorter polyacrylate main chain and longer poly(acrylic acid) side chains. Alkyne and azide groups were introduced to the structure units of the main chain by esterification and the chain end of the side chain by substitution reaction of NaN_3 to bromine, respectively. By click chemistry between alkyne and azide group, well-defined starlike polymers were obtained. FT-IR, gel permeation chromatography, and ^1H NMR were used to characterize the resulting polymers. Aggregation behavior demonstrated by transmission electron microscopy was observed when the starlike polymers were dispersed in water at pH 7.0–7.5. Using the starlike polymers as templates, water-soluble silver nanoclusters mainly consisting of Ag_2 supported by the generated nanoparticles and carboxyl groups were successfully synthesized. Also, their optical properties and morphology were characterized by UV–vis absorption spectra and TEM.

Keywords Atom transfer radical polymerization · Starlike polymer · Click chemistry · Nanoclusters · Water-soluble polymers

Introduction

Star-shaped polymers, which were first prepared several decades ago have attracted much attention because of their unique properties as compared with those of their
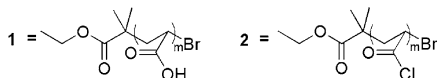
H. Li · Z. Li · L. Wu · F. Liu · J. Zhou · M. Luan · M. Yu (✉) · L. Wei (✉)
Department of Chemistry, Zhengzhou University, Zhengzhou 450001, People's Republic of China
e-mail: yumm@zzu.edu.cn

L. Wei
e-mail: weiliuhe@zzu.edu.cn

corresponding linear counterparts [1]. Nowadays, a wide variety of star polymer architectures with well-defined molecular weights, structural and compositional homogeneity have been prepared due to the development of various controlled polymerization techniques [2, 3], such as ring-opening metathesis polymerization [4], anionic polymerization [5], and controlled living radical polymerization [6–9]. Among these techniques, anionic polymerization is most popularly used to prepare the star polymers with a predetermined arm molar mass. In general, star-shaped polymers can be prepared by different approaches, including "core-first", "arm-first", and "grafting-to" [10]. In the core-first approach (also named from-approach) a multifunctional initiator is employed to simultaneously initiate the polymerization of monomers and then forming the polymer chains [11–15]. The arm-first approach involves use of a multifunctional cross-linker to form the core from which the arm radiates [16–20]. The third strategy combines the controlled polymerization and coupling reaction, providing well-defined arms and cores [21, 22]. These three synthetic methods mentioned above have their own characteristics, thus making them suitable for preparation of the particle-like star polymers. For example, Kanaoka et al. [23] successfully prepared the core cross-linked star polymers in a high yield via the cross-linking of the living poly(isobutyl vinyl ether) and divinyl ether cross-linkers. Moreover, star polymers containing a highly cross-linked core and many arms were synthesized by Gao et al. [24] via a novel method "star from in situ generated core", which belonged to the "core-first" method.

Star-shaped polymers have a molecular structure composed of numerous peripheral arms chemically bonded to a single core [25, 26]. Recently, they have been widely investigated in terms of micellar aggregation in solution because of their well-defined macromolecular architecture [27, 28]. In addition, the aggregates of star polymers which have amino groups, hydroxyl groups or carboxylic acid groups in the side chains have versatile applications in medicine and biology [29–31], catalytical chemistry [32–34], and nanotechnology [35, 36]. For example, Kumacheva's group recently reported fast photoactivated synthesis of stable fluorescent silver nanoclusters [37] and other semiconductor or magnetic nanoparticles [38] by employing polymer microgels with concentrated carboxyl groups as templates. Frey and co-workers [39] synthesized the star-shaped polyglycerol-*block*-poly(acrylic acid) (PG-*b*-PAA) polymers with a core/shell structure, in which the local density of carboxyl groups gradually decreased from core to shell. Using them as templates, they successfully obtained stable silver nanoclusters. Tannenbaum et al. [40] reported that synthetic polymeric matrices are used to guide the formation of stable, monodisperse iron oxide nanoparticles uniformly distributed in the polymeric matrix. Elbjeirami and Omary studied photochemistry of neutral isonitrile gold(I) complexes, modulated photoreactivity by aurophilicity and π-acceptance ability [41]. Kim and Lee [42] reported method of hydrogel-templated growth of large gold nanoparticles, by which, they prepared discrete composite nanoparticles consisting of a large gold core surrounded by a thermally responsive hydrogel polymer.

We are particularly interested in core/shell structure of polymers and its application as templates for silver nanoclusters. In this work, we report a novel starlike polyacrylate-*graft*-poly(acrylic acid) (PAA_m-*g*-PAA_n), which was synthesized by
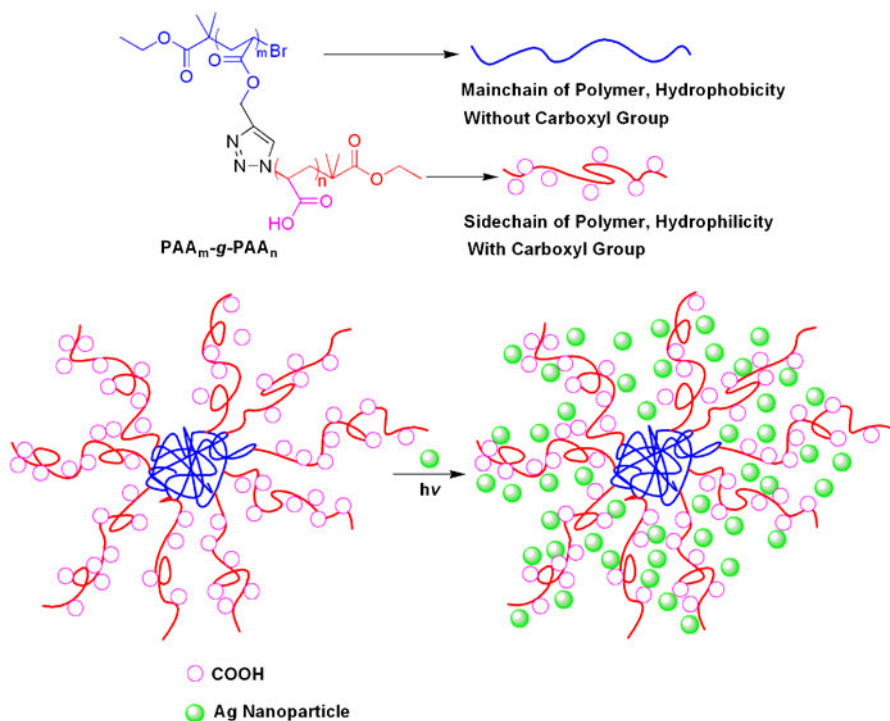
Scheme 1 Synthetic route of starlike polymer

the combination of atom transfer radical polymerization (ATRP) and "click" chemistry (Scheme 1). This synthetic method was proved to be simple and highly efficient. Using the starlike polymers as the templates, we successfully prepared water-soluble Ag nanoclusters (Scheme 2).

Experimental

Materials

Tert-butyl acrylate (*t*-BA) (99%) was purchased from Alfa Aesar and was purified by passing through a basic alumina column to remove the inhibitor. Acetone (Kermel, AR) was dried over 4A molecular sieves overnight and distilled before use. Dichloromethane (Kermel, AR) was disposed following the description in a previous report [43]. Ethyl 2-bromoisobutyrate (EBiB, Alfa Aesar, 98%), *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine (PMDETA, Alfa Aesar, 98%), 2,2'-bipyridine (bpy, Acros, 99%), trifluoroacetic acid (TFA, Alfa Aesar, 99%), propargyl alcohol (Sinopharm Chemical Reagent Co. Ltd., AR), sodium azide (NaN$_3$, Tianjin Kaitong Chemical Reagent Co. Ltd., AR) were used as received.

Scheme 2 Schematic illustration of aggregation of the starlike polymer

Copper(I) bromide was supplied by Aldrich and purified as described previously [43]. All other reagents were purchased from either Sinopharm Chemical Reagent Co. Ltd. or Tianjin Chemical Reagent No. 1 Plant.

Methods

FT-IR spectra were recorded on a NEXUS-470 spectrometer at frequencies ranging from 400 to 4,000 cm^{-1}. Samples were thoroughly mixed with KBr and pressed into pellet form. ^{1}H NMR spectroscopy was performed on a DRX-400 spectrometer. Tetramethylsilane was used as an internal standard. The apparent molecular weights and polydispersities (M_w/M_n) of linear polymers and starlike polymers were determined on an Agilent LC 1200 gel permeation chromatograph (GPC) equipped with Agilent PL columns, a refractive index detector at 38 °C, and THF as the eluent (1.0 mL/min). Transmission electron microscopy (TEM) was performed using a JEM-2100/INCA OXFORD TEM (JEOL/OXFORD) at a 200 kV accelerating voltage. Samples were deposited onto the surface of 300 mesh Formvarcarbon film-coated copper grids. Excess solution was quickly wicked away with a filter paper. In the samples of starlike polymers, the image contrast was enhanced by negative staining with phosphotungstic acid (1.5 wt%). UV–vis absorption spectra were measured on a Persee TU-1901 spectrophotometer at room temperature. The

scanning conditions were as follows: a scanning rate of 50 nm/min, a response time of 1 s, and a bandwidth of 2 nm.

Synthesis of poly(*tert*-butyl acrylate) (P(*t*-BA))

Poly(*tert*-butyl acrylate) was prepared following the method described by Müller et al. [44]. A clean and dry Schlenk tube was charged with CuBr (0.2401 g, 1.67 mmol), PMDETA (0.2900 g, 1.67 mmol), acetone (1.1 mL) and the mixture was sonicated to fully coordinate the catalyst and ligand. Subsequently 2.3596 g (18.4 mmol) *tert*-butyl acrylate and 0.3264 g (1.67 mmol) ethyl 2-bromoisobutyrate (EBiB) were added. The tube was deoxygenated by five freeze–pump–thaw cycles and sealed and placed in a preheated oil bath at 75 °C. The polymerization was quenched after 5 h by cooling and exposure to air. The resulting P(*t*-BA) was isolated by precipitating into a mixture of water and cold methanol (1/1, v/v) and drying under vacuum. ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) = 4.10 (q, –CH$_2$–), 3.74, 2.22, 1.80 (broad, backbone protons of P(*t*-BA)), 1.50 (s, –C(CH$_3$)$_3$), 1.25 (t, –CH$_3$), 1.10 (s, –C(CH$_3$)$_2$–).

Synthesis of poly(propynyl acrylate) (PPA)

The linear poly(*tert*-butyl acrylate) was dissolved in dichloromethane and a fivefold molar excess of TFA was added (with respect to the ester groups). The mixture was stirred at room temperature for 24 h. When hydrolyzed, the polymers precipitated in dichloromethane. They were separated by filtration, washed with dichloromethane, thoroughly dried in vacuum at 40 °C, and characterized using FT-IR. Incomplete hydrolysis was observed, but it did not influence the next experiment. FT-IR (KBr, cm^{-1}): 3,431 (b, –OH), 1,721 (s, –CO–).

The hydrolyzed linear P(*t*-BA) (**1**) and tenfold molar excess of thionyl chloride were stirred at 55 °C for 12 h. The excess thionyl chloride was removed by evaporating under vacuum. Due to the instability of the acylating oligomers, they were directly used in the next reaction without characterization. The chlorine side chain end-terminated oligomer (**2**) was added into 40 mL THF (dry) before the flask was immersed into an ice-water bath. Under magnetic stirring, 0.34 mL (0.077 mmol) propargyl alcohol in 1.1 mL TEA was slowly added dropwise into this mixture during a 5-min period. The reaction mixture was allowed to stir for 48 h at room temperature. During this period, the reaction mixture slowly turned into a brown color and the insoluble TEA salt precipitated out. After filtration to remove the solid, the polymer product was precipitated three times in a mixture of water and cold methanol (1/1, v/v) to remove the excess propargyl alcohol. The precipitate was dissolved in dichloromethane and dried in anhydrous MgSO$_4$ overnight. After removal of the dichloromethane, a reddish brown viscous product was obtained and dried at 40 °C under vacuum overnight. GPC: M_n = 2,144 g/mol, M_w = 2,987 g/mol, M_w/M_n = 1.39. FT-IR (KBr, cm^{-1}): 3,290 (m, $\equiv$C–H), 2,129 (w, C$\equiv$C), 1,731(s, –CO–). ^{1}H NMR (CDCl$_3$, 400 Hz): δ (ppm) = 4.69 (s, –CH$_2$–), 4.10 (m, –CH$_2$–), 3.57, 2.00, 1.83 (P(*t*-BA) backbone), 2.53 (s, $\equiv$C–H), 1.25 (s, –C(CH$_3$)$_2$–), 1.16 (t, –CH$_3$).

Synthesis of poly(*tert*-butyl acrylate)-N$_3$ (P(*t*-BA)-N$_3$)

A typical procedure for synthesis of poly(*tert*-butyl acrylate)-N$_3$ is briefly described. P(*t*-BA) was dissolved in 40 mL DMF before twofold molar excess of sodium azide was added. The reaction mixture was stirred magnetically at 65 °C for 48 h and filtered to remove excess sodium azide. DMF was removed by rotary evaporation. The obtained solid was extracted three times with ethyl acetate and water, and the organic phase was dried with anhydrous MgSO$_4$ overnight. After removal of ethyl acetate, poly(*tert*-butyl acrylate)-N$_3$ was isolated, and the structure was verified by FT-IR and ^{1}H NMR. FT-IR (KBr, cm^{-1}): 2,111 (s, –N$_3$), 1,731 (s, –CO–). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) = 4.10 (q, –CH$_2$–), 1.49 (s, –C(CH$_3$)$_3$), 1.25 (t, –CH$_3$), 1.14 (s, –C(CH$_3$)$_2$–), 2.25, 1.74 (broad, backbone protons of P(*t*-BA)).

Synthesis of starlike PAA$_m$-*g*-PAA$_n$ polymers

A typical procedure for synthesis of poly(acrylic acid) was started with the ratio of reagents [PPA$_m$]$_0$/[P(*t*-BA)$_n$-N$_3$]$_0$/[CuBr]$_0$/[bpy]$_0$ = 5/5/1/2. The click coupling reactions between P(*t*-BA)$_n$-N$_3$ (0.8689 g, 0.17 mmol) and PPA$_m$ (0.0250 g, 0.17 mmol for alkyne units) were conducted in a 100 mL single-neck round flask with 40 mL isopropanol as solvent and CuBr/bpy as catalyst. After stirring for 72 h at 60 °C, the polymer solution was exposed to air, evaporated to remove solvent isopropanol, and extracted three times with ethyl acetate and water. The organic phase was dried over anhydrous MgSO$_4$ overnight. The solvent was removed by rotary evaporation, and the final product was dried under vacuum at 40 °C. Finally the obtained products were hydrolyzed following the same procedure as the synthesis of PPA$_m$, to yield the starlike poly(acrylic acid) polymer. FT-IR (KBr, cm^{-1}): 3,431 (b, –OH), 1,721 (s, –CO–). ^{1}H NMR (DMSO, 400 Hz): δ (ppm) = 12.25 (s, –COOH), 8.22 (s, Ar–H), 4.69 (s, –CH$_2$–), 4.00 (s, –CH$_2$–), 3.47, 2.05, 1.89 (broad, PAA backbone), 1.43 (broad, –CH$_3$), 1.25 (s, –C(CH$_3$)$_2$–).

Synthesis of water-soluble Ag nanoclusters using photoreduction strategy

A typical procedure of the preparation of Ag nanoclusters using photoreduction strategy was described as follows. The pH of a 2-mL aqueous solution of starlike PAA$_m$-*g*-PAA$_n$ polymer (the concentration of carboxyl groups ca. 0.1 M) was adjusted to 7.0–7.5. Then 1 mL of AgNO$_3$ aqueous solution was added slowly dropwise. After stirring for 30 min at room temperature, 2 mL of the mixture was transferred into a cleaned quartz cuvette and subjected to UV-irradiation for acquired time intervals.

Results and discussion

Synthesis and characterization of water-soluble starlike polymers

By using click reactions, starlike polymers can be synthesized by two strategies, in the same manner as molecular brushes [45]. The first approach is to use

azido-terminated long polymer chains to react with alkyne-containing oligomers. The opposite approach is that an alkyne-terminated long polymer chains react with an azido-functionalized oligomer. In this article, the former strategy was applied, which proved to be a feasible and highly efficient for the synthesis of starlike polymers. The synthetic strategy for the preparation of starlike polymers is illustrated in Scheme 1.

To prepare the alkyne-containing core precursor PPA_m, the azido-terminated arm precursor $P(t\text{-BA})_n\text{-}N_3$, and $P(t\text{-BA})$ were synthesized. As shown in Table 1 and Fig. 2a, all of these polymers had very narrow polydispersity index (PDI). $P(t\text{-BA})$ with the lowest molecular weight (entry 1) was employed to prepare core precursor PPA_m. The GPC traces indicated that there was no obvious change of apparent molecular weights between $P(t\text{-BA})$ and PPA_m in THF, which was in accordance with the actual situation after esterification, although the apparent molecular weights was a little higher than the theoretical molecular weights.

For the synthesis of azido-terminated arm precursor $P(t\text{-BA})_n\text{-}N_3$, $P(t\text{-BA})$ (entry 2) with narrow PDI (Table 1; Fig. 2a) were synthesized, followed by transformation of bromine chain-end groups into azido groups via reaction with NaN_3 in DMF. Target polymers were synthesized by coupling azido-terminated $P(t\text{-BA})_n\text{-}N_3$ and alkyne-containing PPA_m. To synthesize starlike polymers, the molar ratio of $P(t\text{-BA})_n\text{-}N_3$ to alkynyl groups was set to 1:1. As compared with brush polymers [44], the grafting density, however, was confirmed not to be largely affected in this condition, because the functional groups of the core precursor with low molecular weight were easy to react. Initially, the click reaction was carried out incompletely even in a long reactive time using the mixture of THF/H_2O (v/v, 1/1) the solvent and $CuSO_4 \cdot H_2O$/sodium ascorbic acid (NaAsc) as the catalyst system, which might be attributed to the relatively poor solubility of PPA_m and $P(t\text{-BA})_n\text{-}N_3$ in this solvent. When isopropanol was employed as a replacement of the mixture of THF/H_2O, however, click coupling of the alkynyl and azide groups was complete 72 h. It can be seen from the infrared spectra of $P(t\text{-BA})_n\text{-}N_3$, PPA_m, and $PAA_m\text{-}g\text{-}PAA_n$ (Fig. 1) that the strong absorption peak at 2,112 cm^{-1} assigned to stretched vibration of –N_3 [46] and the strong absorption peaks at 3,300 and 2,129 cm^{-1} assigned to stretched vibration of $-C\equiv CH$, respectively, are disappeared in the infrared spectra of

Table 1 Characterization and properties of the series of $P(t\text{-BA})$

Entry	$[M]_0/[I]_0/[CuBr]_0/[PMDETA]_0$[c]	Conv.[d] (%)	$M_{n,\ GPC}$[e]	$M_{n,\ NMR}$[f]	M_w/M_n	DP[g]
1[a]	11/1/1/2	64	1800	1100	1.10	7
2[b]	23/1/1/2	65	2800	2100	1.18	15

[a] Polymer **1** is employed to the preparation of core precursor (PPA_m)

[b] Polymers **2** is employed to the preparation of arm precursors ($P(t\text{-BA})_n\text{-}N_3$)

[c] M and I denote the monomer (t-BA) and EbiB, respectively

[d] Calculated from ^1H NMR spectroscopy (400 MHz) recorded in $CDCl_3$ at 20 °C

[e] Measured by GPC in THF with polystyrene standards

[f] From ^1H NMR spectroscopy (400 MHz) in $CDCl_3$ at 20 °C
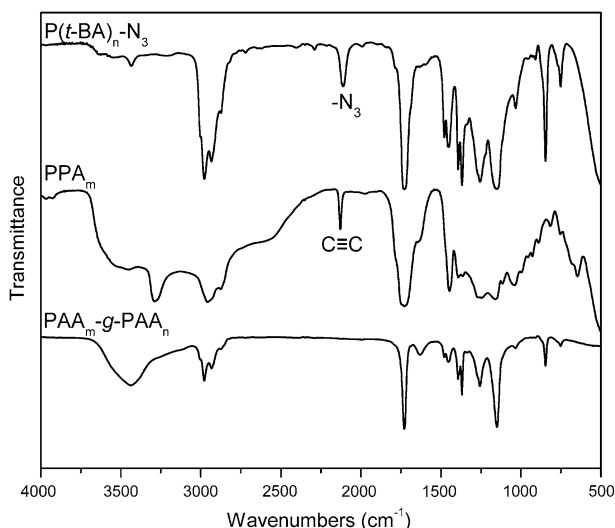
[g] Calculated from $M_{n,\ NMR}$

Fig. 1 FT-IR spectra of P(t-BA)$_n$-N$_3$, PPA$_m$, and PAA$_m$-g-PAA$_n$

PAA$_m$-g-PAA$_n$. A new absorption at about 1,600–1,640 cm^{-1} typical of the triazole ring appeared [46], which seemed not to be obvious because of its incorporation with strong absorption peak of the carbonyl group. In addition, the star polymers showed the distinct stretching bands at 3,432 cm^{-1} (–OH) and 1,712 cm^{-1} (C=O) for the arms, and the strong absorption at 2,977 and 2,863 cm^{-1} for the initiators. The GPC analysis proved that the unreacted trace P(t-BA)$_n$-N$_3$ and/or PPA$_m$ component can be completely removed from the resulting starlike polymer by simple extraction with ethyl acetate and deionized water and then dialysis. Also, the unimodal and symmetrical elution peak of the purified starlike polymer apparently shifted toward a lower elution time region in comparison with that of the original PPA$_m$ and P(t-BA)$_n$-N$_3$ precursors, as shown in Fig. 2b, which also convincingly revealed the click reaction was successful. In summary, all these results indicate that the click conjugation between alkyne-containing core precursors and azide-terminated arm precursors provides a versatile strategy for synthesizing water-soluble starlike polymers.

Aggregation of starlike PAA$_m$-g-PAA$_n$ polymers

Both the morphology and the average size of the aggregates from the poly(acrylic acid) starlike polymers were investigated by the techniques of TEM and the corresponding size-distribution histograms were shown in Fig. 3. This figure shows that the poly(acrylic acid) starlike polymers are spherical particles, 11–16 nm in size. In water at pH 7.0–7.5, the hydrophobic segments will aggregate together and the hydrophilic parts arrange outside, so core/shell structure was obtained (Scheme 2). Notably, these starlike polymers can be functionalized for the preparation of silver nanoparticles or nanoclusters because the charged carboxyl
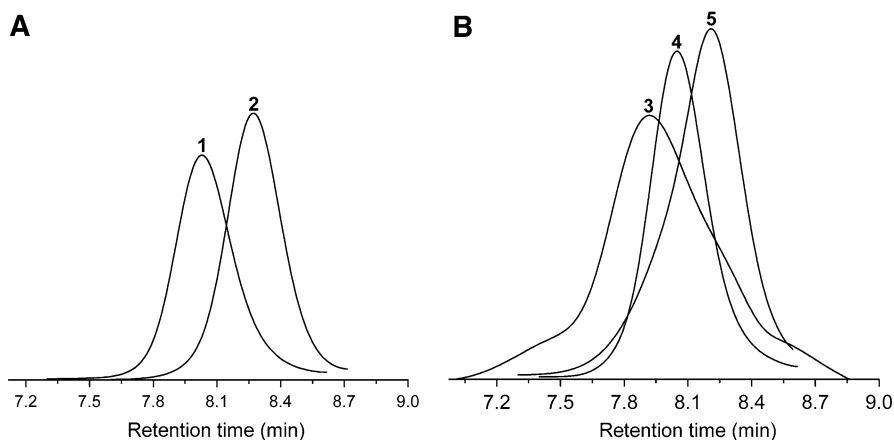
Fig. 2 GPC traces of **a** P(t-BA) with DP 15 (*1*) and 7 (*2*); **b** PAA$_m$-g-PAA$_n$ (*3*), P(t-BA)$_n$-N$_3$ (*4*), and PPA$_m$ (*5*)
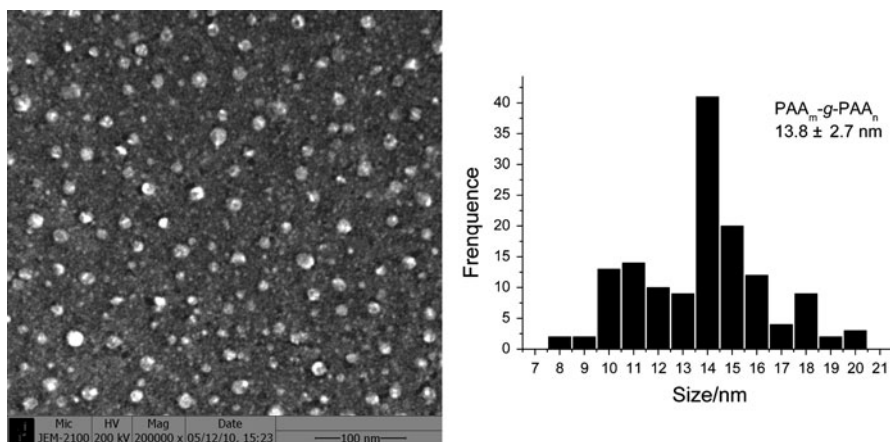

Fig. 3 TEM photographs and corresponding size-distribution histograms of starlike polymer PAA$_m$-g-PAA$_n$ in water at pH 7.0–7.5

groups of arms segments exhibit a strong affinity to Ag$^+$ ions [39]. This concept has been widely used for the immobilization of Ag$^+$ ions to provide Ag source for further reduction reactions by employing chemical reductant, optical irradiation or other ways [37, 47, 48]. In addition, since a core/shell structure can be obtained from the starlike polymers PAA$_m$-g-PAA$_n$, when they are used as the templates to prepare silver nanoparticles, the "cage effect" can be anticipated.

Preparation of water-soluble silver nanoclusters used by poly(acrylic acid) graft polymer templates

Water-soluble silver nanoclusters were synthesized by using water-soluble starlike polymers as templates in the presence of UV-irradiation. In general, photochemistry

reduction has recently been of interest as an approach for the preparation of fluorescent metal nanoclusters, because it works at mild conditions and does not produce other by-products [49]. In this article, novel starlike polymers were utilized to concentrate, stabilize, and solubilize Ag nanoclusters in deaerated aqueous solutions, and this method was quite simple and highly reproducible. By mixing 2 mL aqueous solution of starlike polymer (the concentration of carboxyl groups ca. 0.1 M) and 1 mL of 0.1 M aqueous silver nitrate into a 25 mL of cleaned one-neck round bottom flask and then adjusting pH to 7.0–7.5 with 0.1 M aqueous NaOH solution, silver ions readily interacted with the starlike polymer. The samples were deaerated by bubbling with argon for at least 30 min at room temperature. 2 mL of the mixture solution was transferred to a quartz cuvette and diluted with another 2 mL of distilled water. The molar ratio of acrylic acid groups to Ag^+ ions was about 2.5:1. Subsequently, photoreduction was carried out under UV-irradiation at 365 nm for various time intervals. During the total irradiation, the color of the solution gradually changed from colorless to light yellow, then to purple, and finally to dark reddish brown in accordance with the results of UV–vis spectra of the solution of the starlike poly(acrylic acid) graft polymer doped with Ag^+ ions after UV-irradiation for different intervals of time (Fig. 4). Results of UV–vis spectra can be ascribed to characteristic of the surface plasmon band of silver nanoparticles with dimensions larger than ca. 2–3 nm [50–52]. The emergence of this absorption band revealed larger silver nanoparticles appearing after 73 min irradiation in our experimental conditions. The distinct absorption band at about 450 nm observed in our work has not been reported for silver nanoparticles [47, 53–55], but it was observed by Maretti and Scaiano et al. [56] for Ag nanoclusters synthesized in TFA and cyclohexylamine and assigned to absorption by photoreduced silver nanoclusters Ag_2 [57, 58]. They believe that this absorbance is not due to the silver plasmon band but rather to the presence of small silver clusters, although previous
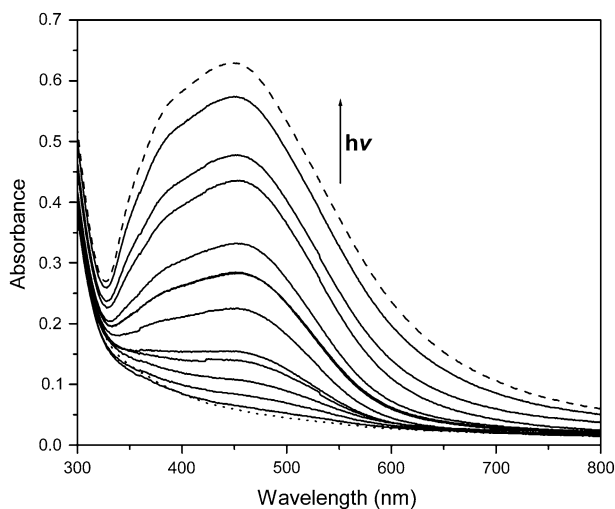

Fig. 4 UV–vis spectra of starlike poly(acrylic acid) graft polymer aggregates after mixing with Ag^+ ions and UV-irradiating them for various time intervals
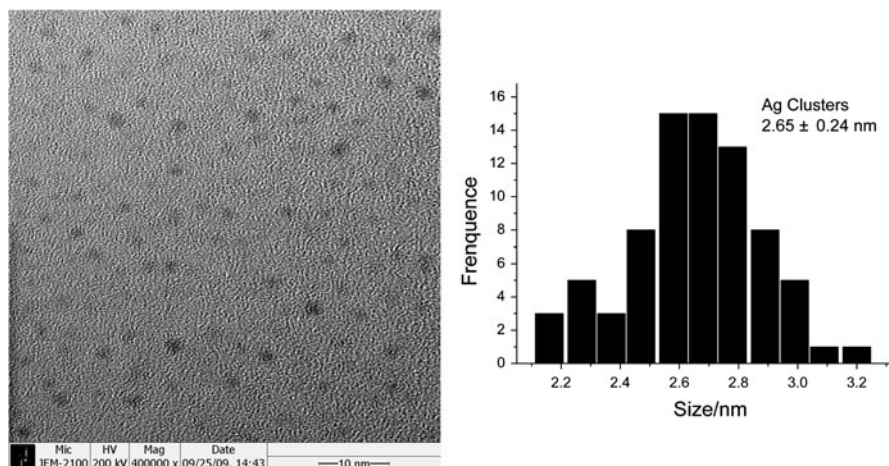
Fig. 5 TEM image of Ag nanoparticles formed after 115 min irradiation and corresponding size-distribution histograms

studies have identified absorbance band at 442 nm [59], which corresponds well to the absorption they observed in their case at around 450 nm. Similarly, we also ascribe the absorption band (about 450 nm in Fig. 4) to Ag_2 clusters supported by the generated nanoparticles and carboxyl ions of the starlike polymer arms. From TEM image and corresponding size-distribution histograms (Fig. 5), about 2.65 nm Ag nanoparticles are obtained after 115 min UV-irradiation in poly(acrylic acid) graft polymer aggregate. Ag nanoparticles are uniform, spherical particles. "Cage effect" protects the nanoclusters in solution, which is important that such nanoclusters are stable for future application [38].

Conclusions

In summary, we have demonstrated a synthesis of Ag nanoclusters from well-defined starlike poly(acrylic acid) graft polymer, prepared via the combination of ATRP and "click" chemistry, using UV-light as the reductant reagent, which has mild reducibility. When the solutions of poly(acrylic acid)/Ag was subjected to UV-irradiation of 365 nm, Ag_2 nanoclusters supported by the generated nanoparticles and carboxyl ions of starlike polymer arms were obtained. "Cage effect" of starlike poly(acrylic acid) graft polymer makes Ag nanoclusters stable and prevents further growth of nanoclusters.

References

1. Schaefgen JR, Flory PJ (1948) Synthesis of multichain polymers and investigation of their viscosities. J Am Chem Soc 70(8):2709–2718

2. Ouchi M, Terashima T, Sawamoto M (2009) Transition metal-catalyzed living radical polymerization: toward perfection in catalysis and precision polymer synthesis. Chem Rev 109(11):4963–5050
3. Blencowe A, Tang JF, Goh TK, Qiao GG (2009) Core cross-linked star polymers via controlled radical polymerisation. Polymer 50(1–2):5–32
4. Ternat C, Kreutzer G, Plummer CJG, Nguyen TQ, Herrmann A, Ouali L, Sommer H, Fieber W, Velazco MI, Klok HA (2007) Amphiphilic multi-arm star-block copolymers for encapsulation of fragrance molecules. Macromol Chem Phys 208(2):131–145
5. Hadjichristidis N, Iatrou H, Pitsikalis M, Mays J (2006) Macromolecular architectures by living and controlled/living polymerizations. Prog Polym Sci 31(12):1068–1132
6. Moad G, Rizzardo E, Thang SH (2005) Living radical polymerization by the RAFT process. Aust J Chem 58(6):379–410
7. Tsarevsky NV, Matyjaszewski K (2007) "Green" atom transfer radical polymerization: from process design to preparation of well-defined environmentally friendly polymeric materials. Chem Rev 107(6):2270–2299
8. Debuigne A, Poli R, Jérôme C, Jérôme R, Detrembleur C (2009) Overview of cobalt-mediated radical polymerization: roots, state of the art and future prospects. Prog Polym Sci 34(3):211–239
9. Hawker CJ, Bosman AW, Harth E (2001) New polymer synthesis by nitroxide mediated living radical polymerizations. Chem Rev 101(12):3661–3688
10. Blencowe A, Tan JF, Goh TK, Qiao GG (2009) Core cross-linked star polymers via controlled radical polymerisation. Polymer 50(1):5–32
11. Moinard D, Taton D, Gnanou Y, Rochas C, Borsali R (2003) SAXS from four-arm polyelectrolyte stars in semi-dilute solutions. Macromol Chem Phys 204(1):89–97
12. Danko M, Libiszowski J, Wolszczak M, Racko D, Duda A (2009) Fluorescence study of the dynamics of a star-shaped poly (-caprolactone)s in THF: a comparison with a star-shaped poly (l-lactide)s. Polymer 50(10):2209–2219
13. Hawker CJ (1995) Architectural control in "living" free radical polymerizations: preparation of star and graft polymers. Angew Chem Int Ed Engl 34(13–14):1456–1459
14. Weberskirch R, Hettich R, Nuyken O, Schmaljohann D, Voit B (1999) Synthesis of new amphiphilic star polymers derived from a hyperbranched macroinitiator by the cationic 'grafting from' method. Macromol Chem Phys 200(4):863–873
15. Lapienis G (2009) Star-shaped polymers having PEO arms. Prog Polym Sci 34(9):852–892
16. Zhang X, Xia J, Matyjaszewski K (2000) End-functional poly (tert-butyl acrylate) star polymers by controlled radical polymerization. Macromolecules 33(7):2340–2345
17. Radke W, Gerber J, Wittmann G (2003) Simulation of GPC-distribution coefficients of linear and star-shaped molecules in spherical pores. 2. Comparison of simulation and experiment. Polymer 44(3):519–525
18. Themistou E, Patrickios CS (2008) A cleavable network based on crosslinked star polymers containing acid-labile diacetal crosslinks: synthesis, characterization and hydrolysis. Macromol Chem Phys 209(10):1021–1028
19. Gao H, Matyjaszewski K (2006) Synthesis of star polymers by a combination of ATRP and the "click" coupling method. Macromolecules 39(15):4960–4965
20. Xia J, Zhang X, Matyjaszewski K (1999) Synthesis of star-shaped polystyrene by atom transfer radical polymerization using an "arm first" approach. Macromolecules 32(13):4482–4484
21. Rother M, Barqawi H, Pfefferkorn D, Kressler J, Binder WH (2010) Synthesis and organization of three-arm-star PIB-PEO block copolymers at the air/water interface: Langmuir- and Langmuir-Blodgett film investigations. Macromol Chem Phys 211(2):204–214
22. Gao H, Min K, Matyjaszewski K (2007) Synthesis of 3-arm star block copolymers by combination of "core-first" and "coupling-onto" methods using ATRP and click reactions. Macromol Chem Phys 208(13):1370–1378
23. Kanaoka S, Sawamoto M, Higashimura T (1991) Star-shaped polymers by living cationic polymerization. 1. Synthesis of star-shaped polymers of alkyl and vinyl ethers. Macromolecules 24(9):2309–2313
24. Gao H, Matyjaszewski K (2008) Synthesis of star polymers by a new "core-first" method: sequential polymerization of cross-linker and monomer. Macromolecules 41(4):1118–1125
25. Hadjichristidis N (1999) Synthesis of miktoarm star (μ-star) polymers. J Polym Sci A: Polym Chem 37(7):857–871
26. Hirao A, Hayashi M, Loykulnant S, Sugiyama K, Ryu SW, Haraguchi N, Matsuo A, Higashihara T (2005) Precise syntheses of chain-multi-functionalized polymers, star-branched polymers, star-linear

block polymers, densely branched polymers, and dendritic branched polymers based on iterative approach using functionalized 1,1-diphenylethylene derivatives. Prog Polym Sci 30(2):111–182

27. Choi I, Gunawidjaja R, Suntivich R, Tsitsilianis C, Tsukruk V (2010) Surface behavior of PSn(P2VP-b-PtBA)n heteroarm stars. Macromolecules 43(16):6818–6828

28. Beyer FL, Gido SP, Uhrig D, Mays JW, Tan NB, Trevino SF (1999) Morphological behavior of A2B2 star block copolymers. J Polym Sci B: Polym Phys 37(24):3392–3400

29. Groll J, Ademovic Z, Ameringer T, Klee D, Moeller M (2005) Comparison of coatings from reactive star shaped PEG-stat-PPG prepolymers and grafted linear PEG for biological and medical applications. Biomacromolecules 6(2):956–962

30. Groll J, Amirgoulova EV, Ameringer T, Heyes CD, Röcker C, Nienhaus GU, Möller M (2004) Biofunctionalized, ultrathin coatings of cross-linked star-shaped poly (ethylene oxide) allow reversible folding of immobilized proteins. J Am Chem Soc 126(13):4234–4239

31. Qiu S, Huang H, Dai XH, Zhou W, Dong CM (2009) Star-shaped polypeptide/glycopolymer biohybrids: synthesis, self-assembly, biomolecular recognition, and controlled drug release behavior. J Polym Sci A: Polym Chem 47(8):2009–2023

32. Terashima T, Ouchi M, Ando T, Sawamoto M (2010) Thermoregulated phase-transfer catalysis via PEG-armed Ru (II)-bearing microgel core star polymers: efficient and reusable Ru (II) catalysts for aqueous transfer hydrogenation of ketones. J Polym Sci A: Polym Chem 48(2):373–379

33. Chi Y, Scroggins ST, Fre chet JMJ (2008) One-pot multi-component asymmetric cascade reactions catalyzed by soluble star polymers with highly branched non-interpenetrating catalytic cores. J Am Chem Soc 130(20):6322–6323

34. Rodionov V, Gao H, Scroggins S, Unruh DA, Avestro AJ, Fréchet JMJ (2010) Easy access to a family of polymer catalysts from modular star polymers. J Am Chem Soc 132(8):2570–2572

35. Ding J, Wang L, Yu H, Huo J, Liu Q, Xiao A (2009) Controllable formation of nanorods through electrostatic-assisted assembly of star poly (methacrylic acid) induced by surfactants. J Phys Chem C 113(9):3471–3477

36. Guillemet B, Faatz M, Gröhn F, Wegner G, Gnanou Y (2006) Nanosized amorphous calcium carbonate stabilized by poly (ethylene oxide)-b-poly (acrylic acid) block copolymers. Langmuir 22(4):1875–1879

37. Zhang J, Xu S, Kumacheva E (2005) Photogeneration of fluorescent silver nanoclusters in polymer microgels. Adv Mater 17(19):2336–2340

38. Zhang J, Xu S, Kumacheva E (2004) Polymer microgels: reactors for semiconductor, metal, and magnetic nanoparticles. J Am Chem Soc 126(25):7908–7914

39. Shen Z, Duan H, Frey H (2007) Water-soluble fluorescent Ag nanoclusters obtained from multiarm star poly (acrylic acid) as "molecular hydrogel" templates. Adv Mater 19(3):349–352

40. Tannenbaum R, Zubris M, Goldberg EP, Reich S, Dan N (2005) Polymer-directed nanocluster synthesis: control of particle size and morphology. Macromolecules 38(10):4254–4259

41. Elbjeirami O, Omary MA (2007) Photochemistry of neutral isonitrile Gold(I) complexes: modulation of photoreactivity by aurophilicity and π-acceptance ability. J Am Chem Soc 129(37):11384–11393

42. Kim JH, Lee TR (2007) Hydrogel-templated growth of large gold nanoparticles: synthesis of thermally responsive hydrogel-nanoparticle composites. Langmuir 23(12):6504–6509

43. Bernaerts KV, Willet N, Van Camp W, Jérôme R, Du Prez FE (2006) pH-Responsive diblock copolymers prepared by the dual initiator strategy. Macromolecules 39(11):3760–3769

44. Schön F, Hartenstein M, Müller AHE (2001) New strategy for the synthesis of halogen-free acrylate macromonomers by atom transfer radical polymerization. Macromolecules 34(16):5394–5397

45. Gao H, Matyjaszewski K (2007) Synthesis of molecular brushes by "grafting onto" method: combination of ATRP and click reactions. J Am Chem Soc 129(20):6633–6639

46. Meng Z, Hendrickson GR, Lyon LA (2009) Simultaneous orthogonal chemoligations on multiresponsive microgels. Macromolecules 42(20):7664–7669

47. Henglein A, Giersig M (1999) Formation of colloidal silver nanoparticles: capping action of citrate. J Phys Chem B 103(44):9533–9539

48. Hao E, Kelly KL, Hupp JT, Schatz GC (2002) Synthesis of silver nanodisks using polystyrene mesospheres as templates. J Am Chem Soc 124(51):15182–15183

49. Karadas F, Ertas G, Ozkaraoglu E, Suzer S (2005) X-ray-induced production of gold nanoparticles on a SiO₂/Si system and in a poly (methyl methacrylate) matrix. Langmuir 21(1):437–442

50. Kamat PV (2002) Photophysical, photochemical and photocatalytic aspects of metal nanoparticles. J Phys Chem B 106(32):7729–7744

51. Mallin MP, Murphy CJ (2002) Solution-phase synthesis of sub-10 nm Au-Ag alloy nanoparticles. Nano Lett 2(11):1235–1237
52. Scaiano J, Aliaga C, Maguire S, Wang D (2006) Magnetic field control of photoinduced silver nanoparticle formation. J Phys Chem B 110(26):12856–12859
53. Padalkar S, Capadona J, Rowan S, Weder C, Won YH, Stanciu LA, Moon RJ (2010) Natural biopolymers: novel templates for the synthesis of nanostructures. Langmuir 26(11):8497–8502
54. Richards CI, Choi S, Hsiang JC, Antoku Y, Vosch T, Bongiorno A, Tzeng YL, Dickson RM (2008) Oligonucleotide-stabilized Ag nanocluster fluorophores. J Am Chem Soc 130(15):5038–5039
55. Guo W, Yuan J, Dong Q, Wang E (2009) Highly sequence-dependent formation of fluorescent silver nanoclusters in hybridized DNA duplexes for single nucleotide mutation identification. J Am Chem Soc 132(3):932–934
56. Maretti L, Billone PS, Liu Y, Scaiano JC (2009) Facile photochemical synthesis and characterization of highly fluorescent silver nanoparticles. J Am Chem Soc 131(39):13972–13980
57. Fedrigo S, Harbich W, Buttet J (1993) Optical response of Ag_2, Ag_3, Au_2, and Au_3 in argon matrices. J Chem Phys 99(8):5712–5717
58. Rabin I, Schulze W, Ertl G (1998) Light emission during the agglomeration of silver clusters in noble gas matrices. J Chem Phys 108:5137
59. Rabin I, Schulze W, Ertl G (1999) Absorption spectra of small silver clusters Ag_n ($n \geq 3$). Chem Phys Lett 312(5–6):394–398