Copolymers of styrene and gold nanoparticles†

Xiwen Zhang, Li Liu, Jia Tian, Jian Zhang and Hanying Zhao*

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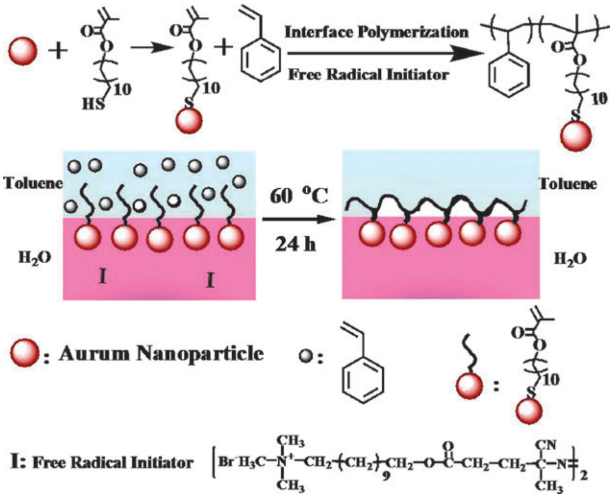
The use of stoichiometrically functionalized gold nanoparticles (AuNPs) as building units in polymerization reaction is described; the obtained copolymers, comprised of AuNPs and polystyrene, behave differently in various solvents, micellar structures with PS cores and AuNPs corona are obtained in water.

Nanoparticles are recognized to have potential applications in electronics, optics, genomics, proteomics, biomedical and bioanalytical areas.[1] Gold nanoparticles (AuNPs) are the most stable metal nanoparticles, and present many fascinating properties such as size-related electronic, magnetic and optical properties (quantum size effect), and find many applications in catalysis and biology.[2] AuNPs can be used as elementary building blocks in the bottom-up approach of nanotechnology, and they are materials with important potential applications as well as being promising building block candidates in the 21st century.[2] In the past two decades preparation of AuNPs/polymer hybrid materials has been investigated widely.[2,3] In these years controlled functionalization on the surface of nanoparticles is becoming a powerful tool in the synthesis of new materials. For example stoichiometrically functionalized AuNPs were prepared by surface polymerization method.[4] The stoichiometrically functionalized AuNPs were also used as building blocks or reacting units in the polymerization. AuNPs with a single functional group on the surface were employed in the fabrication of a "nanonecklace" structure.[5] Stoichiometric functionalized AuNPs were used as chemical handles to form nanoparticle chains through coupling with a bifunctional amine.[6]

Herein, a new versatile route for the synthesis of AuNPs-polystyrene (PS) copolymers is presented. Polymers with known number of AuNPs on the polymer chains were synthesized by free radical polymerization. The outline for the synthesis of the copolymers is shown in Scheme 1. The citrate-capped AuNPs were prepared by reduction of $HAuCl_4$ with borohydride in aqueous phase.[7] The AuNPs prepared in aqueous phase are dispersed well in water and are hydrophilic particles. AuNPs with mono-vinyl groups (AuNPs monomer) were obtained *via* the ligand exchange between 11-mercaptoundecyl methacrylate (MUMA) moieties and the equivalent amount of AuNPs. Subsequently, free radical copolymerization of AuNP monomers and styrene initiated by an ammonium free radical initiator yielded copolymers of styrene and AuNPs.

Because of the steric hindrance and low concentration of vinyl groups on the surface of AuNPs, it is difficult to conduct copolymerization of styrene and AuNPs monomers in a homogeneous phase. In a mixture of water and toluene, the AuNP monomers tend to locate at the liquid–liquid interface due to the long carbon chain (C_{11}) of MUMA and the hydrophilic AuNPs (Fig. S2 and S3 in ESI†). The local concentration of AuNP monomers at the liquid–liquid interface is much higher than that in the homogeneous phase. A water-soluble quaternary ammonium free radical initiator was employed in the polymerization. The decomposition of the initiator was in the aqueous phase, and only free radicals diffusing to the liquid–liquid interface were able to initiate the copolymerization of styrene and AuNPs monomer. Thus, the possibility of homopolymerization of styrene was avoided by using this method. In the polymerization, styrene was dissolved in toluene and the copolymerization of styrene and AuNPs was conducted at the interface of toluene and water.

MUMA was synthesized by a reaction of 11-mercapto-1-undecanol and methacrylic acid, and used in the synthesis of AuNP monomers. In order to graft only one vinyl group on each nanoparticle, an equivalent amount of MUMA was added into the AuNP solution at a very low concentration. After stirring for 2 h, an aqueous solution of free radical initiator, toluene and styrene were added, successively. Copolymerization of AuNP monomers and styrene was performed at the interface of toluene and water. No agglomeration occurred during the polymerization. The molecular weight and molecular weight distribution of a typical copolymer were 72 kg mol^{-1} and 1.35, determined by gel permeation chromatography (GPC) using polystyrene as standard support and tetrahydrofuran as solvent



Scheme 1 Outline for the synthesis of copolymer of styrene and gold nanoparticles.

Department of Chemistry, Nankai University, 300071 Tianjin, China. E-mail: hyzhao@nankai.edu.cn; Fax: 862223498703; Tel: 8622 2349 8703

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(Fig. 1(a)). The ^{1}H NMR spectrum of a copolymer is shown in Fig. 1(b). Assuming there is one ammonium group at the end of each polymer chain, integration of the ^{1}H NMR signals allowed the calculation of the repeating unit number of styrene and the average number of AuNPs on each copolymer chain. The calculation result indicated that the repeating unit number of styrene in the copolymer was 548 (ESI†). According to the ratio of the peak area at 3.99 ppm corresponding to methylene protons on MUMA units (peak c in Fig. 1(b)) to that at 4.24 ppm corresponding to methylene protons adjacent to the quaternary ammonium group at the end of the polymer chains (peak b in Fig. 1(b)), there were about five AuNPs on each copolymer chain (Fig. 1(b)). In this research three copolymers were prepared by using the ammonium free radical initiator (Table S1 in ESI†). Only the copolymer with five pendant AuNPs on each chain was used as a model copolymer for further research in this paper.

Transmission electron microscopy (TEM) was used to characterize the AuNP monomers, the copolymer and the self-assembly of the copolymer in a selective solvent. A TEM image revealed that the AuNP monomers had a narrow size distribution and well-defined shape (Fig. 2(a)). The average diameter of the nanoparticles is around 5.0 nm. The purified copolymer is highly soluble in THF and CH_2Cl_2, indicating that the AuNPs are dispersed well in organic solvents after copolymerization with styrene. TEM observation also showed that the size of AuNPs did not change after the polymerization (Fig. 2(b)), which proved that there were no fusions of AuNPs

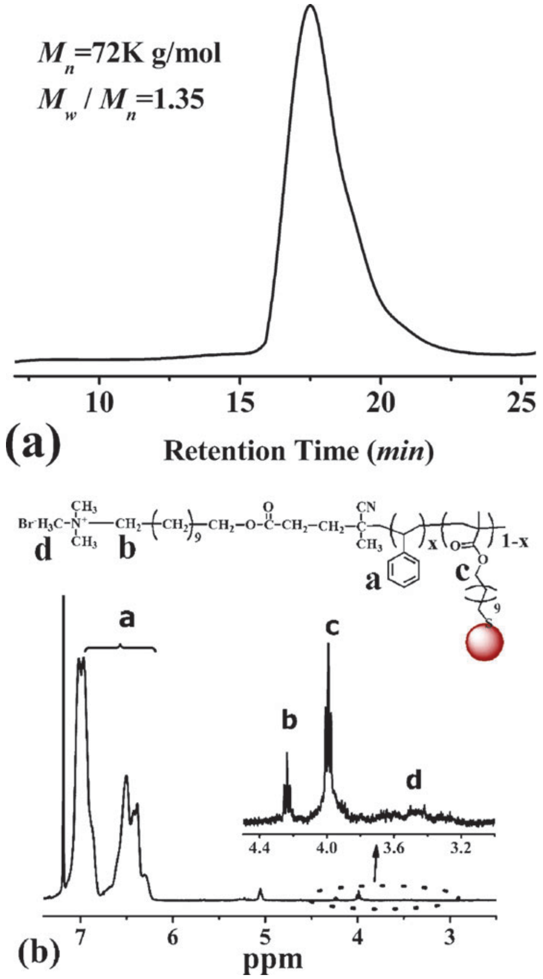

Fig. 1 (a) A GPC curve and (b) ^{1}H NMR spectrum of a copolymer of styrene and gold nanoparticles.

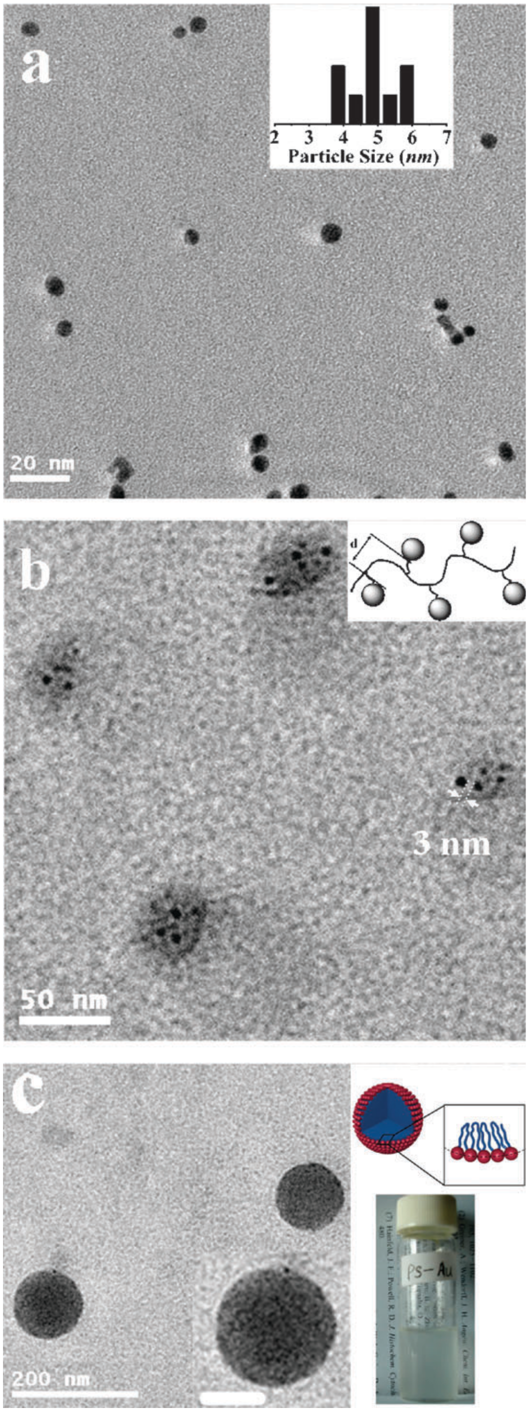

Fig. 2 Transmission electron microscopy (TEM) images showing (a) the size of gold nanoparticle monomers (the particle size was determined by counting at least 150 particles), (b) the morphology of gold nanoparticle copolymers in THF, and (c) the aggregation morphology and a scheme for gold nanoparticle copolymers in H_2O. The image at lower right shows a colloidal solution of self-assembled PS-Au nanoparticle copolymers in water. The scale bar on the TEM image in the inset of Fig. 2(c) represents 50 nm.

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during the copolymerization.[8] Stoichiometric functionalization of AuNPs plays a key role in the preparation of nanoparticle copolymers with well defined structure.[9] The TEM image of the nanoparticle copolymer revealed confined AuNPs in the coil structures of PS chains (Fig. 2(b)). The interparticle distance (defined as the distance between the two nearest particles) in a polymer chain was measured on TEM as shown in Fig. 2(b). The distance varies from 3 to 5 nm, proving that AuNPs are covalently grafted to the backbone of polymer chains. The interparticle distance is determined by the length of the polystyrene chain between two AuNPs.

The copolymer chains are composed of hydrophobic PS segments and pendant hydrophilic AuNPs, so they may be able to self-assemble into micelle-like structure in selected solvents. A colloidal solution was obtained by adding 6-fold of water into a THF solution of AuNPs-PS copolymer (image is shown at the lower right of Fig. 2(c)). TEM observation (Fig. 2(c)) indicated the aggregated structure of AuNPs-PS copolymers with an average diameter of around 100 nm. The core part of the structure is composed of collapsed PS chains and the corona is composed of hydrophilic AuNPs. The hydrophilic AuNPs stabilize the structure. Due to the high density of the AuNPs in the corona, it is difficult to observe isolated single AuNPs. However, at a high magnification the AuNPs in the structure could be identified (inset in Fig. 2(c)). The aggregation structure of the copolymer chains is also schematically shown in Fig. 2(c). Therefore, the copolymerization of nanoparticle monomers and traditional organic monomers is a novel way to prepare new materials, and could bring new insight to views into the structures and properties of the polymer hybrids.

AuNPs-PS copolymers were prepared by copolymerization of AuNPs and styrene monomer at the liquid–liquid interface. Extension of this fundamental new concept to other nanoparticles (Ag, Cu, CdSe, ZnSe) with monofunctional vinyl groups is under way. A variety of monomers will be used in the copolymerization of nanoparticles. The utilization of these materials in biological applications based on the specific binding between nanoparticles and biological molecules is being investigated in this laboratory. The broad availability of nanoparticle monomers will enable the preparation of a novel class of hybrid materials and will certainly provide novel materials with interesting structure–property relationships.

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