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Facile synthesis of thiol-terminated poly(styrene-*ran*-vinyl phenol) (PSVPh) copolymers via reversible addition-fragmentation chain transfer (RAFT) polymerization and their use in the synthesis of gold nanoparticles with controllable hydrophilicity

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ABSTRACT

A facile approach to prepare thiol-terminated poly(styrene-*ran*-vinyl phenol) (PSVPh) copolymers and PSVPh-coated gold nanoparticles is reported with the goal of creating stabilizing ligands for nanoparticles with controlled hydrophilicity. Dithioester-terminated poly(styrene-*ran*-acetoxystyrene) copolymers were synthesized via RAFT polymerization using cumyl dithiobenzoate as a chain transfer agent. These copolymers were converted to thiol-terminated PSVPh copolymers by a one step hydrazinolysis reaction using hydrazine hydrate to simultaneously convert dithioester-terminal and acetoxy-pendant groups to thiol-terminal and hydroxyl-pendant groups, respectively. Spectroscopic observations including NMR and IR confirm end- and pendant-group conversion. PSVPh-coated gold nanoparticles were synthesized in the presence of a mixture of thiol-terminated PSVPh and PSVPh copolymers containing disulfides as stabilizing ligands in a water/toluene, two-phase system. The size and size distribution of core gold nanoparticles were determined by TEM and image analysis. The hydrodynamic radius of PSVPh-coated gold nanoparticles was also determined by dynamic light scattering experiment, which confirms the particle analysis by TEM. This procedure provides a facile technique to control the polarity and hydrophilicity of metal nanoparticle surfaces and could prove critical in advancing the control of nanoparticle placement in biological and hierarchically ordered systems, such as diblock copolymers.

1. Introduction

Thiol-terminated polymers or polymers containing disulfides have been of great interest in polymer science for biological, electronic, and optical applications, since they can bind with metals such as gold and silver by specific interactions [1,2]. For example, thiol-terminated polymers stabilize gold nanoparticles due to the strong interactions between sulfur and gold due to their soft character [3]. Thus, successful preparation of thiol-terminated polymers enables the incorporation of the versatile functionalities of polymers onto the surfaces of metal nanoparticles. Furthermore, the thiol-functionalized polymers prevent gold nanoparticles from forming aggregates during nanoparticles synthesis, and can be used to control the size of nanoparticles [4].

Incorporation of functionalized gold nanoparticles in a polymer matrix have attracted much attention, in that controlled dispersion of nanoparticles can lead to tailored structures of nanocomposites, and thus result in a material that is useful in specific applications of nanocomposites, including chemical sensors, catalysts, or substrates in electronic devices [5,6] For example, Krasteva et al. [7]. developed chemical sensors using layer-by-layer self-assembly of multilayers composed of gold nanoparticles and three kinds of dendrimers; hydrophobic polyphenylene (PPh) dendrimer, hydrophilic poly(amidoamine) (PAMAM) dendrimers, and amphiphilic poly(propylene imine) (PPI) dendrimers. Each film of the Au/dendrimer nanocomposites was tested as a chemical sensor by dosing with vapors of toluene, 1-propanol, or water. Au/PPh sensors showed the highest resistance when exposed to toluene vapor, Au/PAMAM with 1-propanol, and Au/PPI with water. The increased

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resistance results from the increase of interparticle distances as dendrimers absorb analyte vapor and swell the polymer chains.

Furthermore, incorporation of nanoparticles in block copolymers as a matrix has been of recent interest, as the microphase-separated morphologies of block copolymers can lead to highly ordered placement of nanoparticles [8–10]. For example, Kramer and co-workers[11] reported sequestering either polystyrene (PS)-coated gold nanoparticles or gold nanoparticles coated with a 1:1 mixture of PS and poly(2-vinyl pyridine) (PVP) chains in poly(-styrene-*b*-2-vinyl pyridine) (PS-*b*-P2VP) diblock copolymers, which microphase-separated into lamellar phases. In this work, PS-coated gold nanoparticles located at the center of the PS domains in the diblock copolymers. On the other hand, PS/PVP-coated gold nanoparticles were dispersed at the interface of PS lamellar domains and PVP lamellar domains in the diblock copolymers.

Recent theoretical and experimental studies reveal that the morphologies of nanocomposites composed of nanoparticles and block copolymers can be designed by controlling entropic contributions to the nanoparticles placement by varying particle size, and by controlling enthalpic contributions between the polymer and nanoparticles by varying particle coatings [12,13]. For example, Wiesner and co-workers[14] prepared nanocomposites composed of silica nanoparticles and poly(isoprene-block-ethylene oxide) (PI-*b*-PEO) block copolymers. They reported that the final morphologies of the nanocomposites were determined by the morphologies of block copolymers when the diameter of the particles was relatively small compared with radius of gyration of PEO chains ($R_{g,PEO}$) in the block copolymers. On the other hand, larger particles than the PEO chains altered nanocomposite morphologies from lamellar to onion-like or cylindrical phases. This change in morphology is ascribed to the loss of entropy of PEO chains as they attempt to circumvent the large particles, which becomes too great to maintain the initial morphologies of the block copolymers without particles [12]. Additionally, Kim et al. [4]. reported controlling the sequestration of polystyrene-coated gold nanoparticles in poly(-styrene-*b*-2-vinylpyridine) diblock copolymers (PS-*b*-P2VP) by varying the chain density of polystyrene attached on gold nanoparticles. They reported that gold nanoparticles with low PS chain density (less than 1.3 chains/nm^2) located at the interface between PS and P2VP domains due to a favorable interaction between a bare gold and P2VP chains, while gold nanoparticles with high chain density located in PS domains.

Thus, nanoparticles coated with polymers of versatile functionalities can be a key material to achieve desired morphologies, and thus properties, of nanocomposites by tailoring enthalpic parameters within nanocomposite systems. Nanoparticles with polar functionality are of particular interest to form supramolecular, non-covalent intermolecular interactions between the nanoparticles and polymer matrices. For instance, the incorporation of metal nanoparticles into bio-responsive and biomaterials will require exquisite control of the polarity the nanoparticles surface in order to control their dispersion and placement in these promising matrices. Unfortunately, the synthesis of nanoparticles that afford this control is nontrivial, and requires the ability to tune the distribution and content of polar functionalities within the stabilizer ligand.

In our recent work, we have shown that the extent of intermolecular hydrogen bonding between the PSVPh matrix and nanoscale additives can be optimized by controlling the composition of poly(styrene-*ran*-vinyl phenol) random copolymers (PSVPh). These results have been shown to be broadly applicable, having been applied to the dispersion of liquid crystalline polymers [15], multi-walled nanotubes [16], single-walled nanotubes [17,18], and montmorillinite clays in a polymer matrix [19]. The improved extent of non-covalent interactions results in optimized dispersion as well as optimal mechanical, thermal, and electrical properties of the resultant nanocomposites. Therefore, we plan to utilize this fundamental understanding to design optimal ligands for gold nanoparticles based on PSVPh, to enable their efficient dispersion in diblock copolymer matrices and bio-based materials by maximizing the extent of non-covalent interactions between the nanoparticle ligands and polymer matrix.

For example, such ligands will provide a mechanism to investigate the ability to tune enthalpic attractions between the gold nanoparticles and one phase of the diblock copolymer on the accessible nanocomposite morphologies. The correlation of morphology with the extent of non-covalent enthalpic attractions between a nanoparticle and a component of a diblock copolymer has not been previously examined and yet can potentially provide a heretofore inaccessible avenue to novel diblock nanocomposite loadings and morphologies.

However, the synthesis of thiol-terminated PSVPh copolymers (PSVPh-SH) as well as gold nanoparticles coated with PSVPh copolymers has not been previously reported. This may result from the difficulty in synthesizing polymers with both thiol-terminal and hydroxyl-pendant groups. In this study, we suggest a simple and useful strategy to prepare PSVPh-SH copolymers via reversible addition-fragmentation chain transfer (RAFT) polymerization [20–22]. A common chain transfer agent in the RAFT process is a thiocarbonylthio compound, which can lead to degenerative transfer with propagating polymeric radicals [23]. Subsequently, intermediate radicals are fragmented to polymers with thiocarbonylthio end groups and a new radical [23,24]. The overall RAFT process results in polymers with thiocarbonylthio end groups, which can be converted to thiols by hydrolysis [23,25]. This conversion of dithioesters to thiols has opened a facile pathway to synthesize thiol-terminated polymers and to stabilize gold nanoparticles by utilizing the thiol-terminated polymers as a stabilizing ligand [26–29].

We report here our attempts to synthesize thiol-terminated PSVPh ligands using controlled free radical techniques. Atom transfer radical polymerization was attempted first, where the hydrazinolysis to the thiol and pendant –OH groups were sequentially implemented. These methods proved disappointing, and we then turned to RAFT polymerization, where a facile method to synthesize thiol-terminated PSVPh copolymers via RAFT polymerization, and subsequent hydrazinolysis using hydrazine hydrate was identified. Subsequently, gold nanoparticles coated with these PSVPh copolymers were synthesized by using thiol-terminated PSVPh copolymers and PSVPh copolymers containing disulfides as a stabilizing ligand.

2. Experimental

2.1. Gel permeation chromatography (GPC)

The molecular weight of the synthesized polymers were determined using gel permeation chromatography on a PL-GPC 120 (Polymer Laboratories, Varian Inc., Amherst, MA, USA) with two PLgel 5 micron mixed-B columns with a calibration of polystyrene standards with narrow molecular weight distribution in tetrahydrofuran (THF) as the elution solvent.

2.2. Nuclear Magnetic Resonance (NMR)

The analysis of the structure of the terminal and pendant groups of the synthesized copolymers was conducted by collecting the ^{1}H NMR spectra of copolymers dissolved in deuterated chloroform using a Bruker spectrometer operating at 300 MHz. Samples for NMR were prepared by dissolving 7 mg of polymers in 1 mL of deuterated chloroform. Each copolymer sample was scanned 1024 times to clearly obtain peaks generated from end groups of the copolymers with low molecular weight.

2.3. Infrared (IR) spectroscopy

The structure of the synthesized copolymers was also characterized by Fourier transform infrared spectroscopy (Varian 4100 FT-IR). Copolymer samples were scanned 16 times with the range of 400–4000 cm^{-1} wavenumber at 4 cm^{-1} resolution. Spectroscopic information was corrected for KBr background information. Samples for IR were prepared by mixing 5 mg of copolymers with 95 mg of potassium bromide (KBr) and compressing this mixture into an IR pellet.

2.4. Transmission electron microscopy (TEM) of gold nanoparticles

The synthesized gold nanoparticles were characterized by transmission electron microscopy (TEM, Hitachi H800) with an acceleration voltage of 100 KeV. To examine the gold nanoparticles coated with either PSVPh or poly(styrene-*ran*-acetoxystyrene) copolymers by TEM, a dilute solution of the gold nanoparticles in toluene (5 mg/mL) was prepared. One drop of this solution was placed on porous carbon films supported by copper grids [32]. These films were dried in air to evaporate the solvent. Size and size distribution were determined by analyzing TEM images of the gold nanoparticles using Image J software by assuming that particles are spheres. The range of particle area was set to be from 3 to 100 nm^2. The degree of circularity, a measure of the degree that the particles approach a circle was set to be from 0.8 to 1.0 for PSVPh-coated gold nanoparticles.

2.5. Dynamic light scattering (DLS) of copolymers and gold nanoparticles

The hydrodynamic radius (R_h) of the synthesized copolymers and the PSVPh-coated gold nanoparticles in toluene at 25 °C were measured using dynamic light scattering in toluene (PD 5000, Precision Detectors Inc., Bellingham, MA, USA). A laser of 683 nm wavelength was used as a light source, and light scattered by the sample was detected at 65°. Copolymer or gold nanoparticle solutions in toluene were prepared with the concentration of 5 mg/mL for copolymers and 2.7 mg/mL for nanoparticles. These solutions were filtered using Millipore PTFE membrane filters with pore size of 0.2 micron [29], and centrifuged at 14,000 rpm for 30 min, before they were injected into the DLS sample holder. Each sample was scanned 120 times, and the mean R_h was determined by averaging the R_h values from at least 10 different experiments.

2.6. Synthesis of cumyl dithiobenzoate (CDB)

Cumyl dithiobenzoate was prepared by a method derived from that of Oae et al. [30]. Dithiobenzoic acid[31] (11.1 g, 72.0 mmol) and α-methylstyrene (10.4 g, 88.0 mmol) excess) were dissolved in carbon tetrachloride (40 mL), and the resulting solution was purged with nitrogen and stirred at 70 °C for 5 h. The crude product was obtained as a dark-purple oil in 69% yield and was subsequently purified by column chromatography (neutral alumina packing, hexanes as eluent).

2.7. Synthesis of dithioester- terminated poly(styrene-ran-acetoxystyrene) copolymers via RAFT polymerization

Styrene, 4-acetoxystyrene, anhydrous 1,4-dioxane, 2,2′-azobisisobutyronitrile (AIBN), petroleum ether, and hydrazine hydrate were purchased from Aldrich, and utilized as received without further purification. Styrene (monomer, 9.7 g, 93.3 mmol, 51 equiv.), 4-acetoxystyrene (2.7 g, 16.6 mmol, 9 equiv.), CDB (chain transfer agent, 500 mg, 1.84 mmol), AIBN (30 mg, 0.1 equiv.), and anhydrous dioxane (solvent, 3 g) were added to a two-neck, round bottom flask. All reactants were degassed by freeze and thaw repeated 3 times. Polymerization was then conducted under nitrogen in an oil bath at 65 °C for 15 h. After 15 h, the resultant solution was quenched in liquid nitrogen to stop polymerization, and polymers were purified by precipitating in petroleum ether. A reddish polymer powder was obtained after filtration, and dried under vacuum at 70 °C for 24 h. The molecular weight of the resultant copolymers was determined by gel permeation chromatography (GPC), exhibiting a number average molecular weight (Mn) of 5100 (g/mol), weight average molecular weight (Mw) of 6400 (g/mol), and PDI of 1.25.

2.8. Hydrazinolysis of dithioester-terminated poly(styrene-ran-acetoxystyrene) to PSVPh copolymers

The one step hydrazinolysis reaction was conducted to convert both dithioester-terminal and acetoxy-pendant groups to thiol and hydroxyl groups respectively. In a typical hydrazinolysis reaction, 1.2 g of dithioester-terminated poly(styrene-*ran*-acetoxystyrene) copolymers was completely dissolved in 23 mL of dioxane, and then 10 mL of hydrazine hydrate ($NH_2NH_2xH_2O$) was added dropwise into the polymer solution. This mixture was vigorously stirred under nitrogen gas flow for 5 days at room temperature. The polymer was then precipitated in cold methanol, and filtered. The resultant, white polymer powder was obtained after drying in air overnight, followed by drying under vacuum at 80 °C for 24 h. After hydrazinolysis, it was found by spectroscopy and GPC that the final product is the mixture of thiol-terminated PSVPh copolymers and PSVPh copolymers containing disulfides.

2.9. Synthesis of PSVPh-coated gold nanoparticles using thiol-terminated polymers and disulfide containing polymer mixtures

Gold nanoparticles with surfaces that are coated with PSVPh copolymers were synthesized using a mixture of thiol-terminated PSVPh copolymers and PSVPh copolymers containing disulfides as the stabilizing ligand. This synthesis procedure was developed to mimic the process reported by Brust et al. [32]. and Bockstaller et al. [33,34], which is a water-toluene, two phase synthesis procedure. In this reaction, hydrogen tetrachloroaurate(III) hydrate, sodium borohydride, and tetraoctylammonium bromide (Sigma–Aldrich) were used as received. An aqueous solution of hydrogen tetrachloroaurate ($HAuCl_43H_2O$, 9 mg in 3 mL water, 8.83 mmol/L) was mixed with a solution of tetraoctylammonium bromide in toluene ($N(C_8H_{17})_4Br$, 110 mg in 8 mL toluene, 25 mmol/L), which is a phase transfer agent in this reaction [34]. This mixture was vigorously stirred for 3 h until the tetrachloroaurate was completely transferred from the aqueous phase to the toluene layer, which can be verified by the appearance of the reddish color of the toluene layer. The organic phase was separated from the two-phase (water/toluene) system. Thiol-terminated PSVPh copolymers and PSVPh copolymers containing disulfides (125 mg, 0.025 mmol) were then added to the separated toluene layer, and 2 mL of THF was added to this polymer solution. Addition of THF was needed to increase the solubility of PSVPh copolymers containing polar-pendant groups in toluene. An aqueous solution of sodium borohydride ($NaBH_4$, 75.6 mg in 2 mL water, 1 mol/L) and 5 drops of hydrazine was quickly added while this mixture was vigorously stirred. With the addition of reductant, a color change of the solution was observed from yellow-red to dark-purple. This mixture was stirred for 17 h, and the organic phase was then separated. This separated solution was evaporated to 1 mL using a rotary evaporator. The final product was precipitated in cold methanol, and the dark brown product was filtered. Any unbound PSVPh copolymer ligands were removed by washing with a mixture of ethanol and THF (5:1) once briefly, and ethanol several times. The final PSVPh-coated gold nanoparticles were dried under vacuum at 70 °C for 6 h.

2.10. Synthesis of thiol-terminated PSVPh copolymers by ATRP followed by thiolation or hydrazinolysis

We first attempted to synthesize thiol-terminated PSVPh copolymers via atom transfer radical polymerization (ATRP) followed by thiolation or hydrolysis. Our attempts were conducted with two different approaches starting with different monomers. First, the synthesis of thiol-terminated PSVPh was attempted by first synthesizing bromine-terminated poly(styrene-*ran*-acetoxystyrene) copolymers via ATRP, and followed by subsequent individual hydrazinolysis and thiolation reactions. The details of these reactions are provided as supplemental information.

Additionally, the synthesis of PSVPh-SH copolymers was attempted by first synthesizing bromine-terminated poly(styrene-*ran*-4-tert-butoxystyrene) copolymers via ATRP, followed by the thiolation of the copolymers to thiol-terminated poly(styrene-*ran*-4-tert-butoxystyrene) copolymers, and the subsequent hydrazinolysis of the thiol-terminated poly(styrene-*ran*-4-tert-butoxystyrene) to PSVPh-SH. The details of this reaction are also provided as supplemental information.

3. Results and discussion

3.1. Attempts to synthesize thiol-terminated PSVPh copolymers via atom transfer radical polymerization (ATRP)

The synthesis of thiol-terminated poly(styrene-*ran*-vinyl phenol) copolymers was first attempted starting with bromine-terminated poly(styrene-*ran*-acetoxystyrene) copolymers. Our experimental results indicate that the conversion of the acetoxy groups of the copolymer to hydroxyl groups and the conversion of the bromine-end groups of this copolymer to thiol-end groups were not successful. NMR data suggests that the hydrazinolysis of the copolymers using hydrazine hydrate results in a loss of end groups of the copolymers, and the acetoxy groups of the copolymers are not stable under thiolation using thiourea and NaOH. The details of these experimental results are described in the supporting information. Thus, the synthesis of PSVPh-SH was next attempted starting with poly(styrene-*ran*-4-tert-butoxystyrene) copolymers with bromine-end groups, which was selected as it is expected that the ether bonds of the tert-butoxystyrene groups will be more stable under thiolation than the ester bonds of the acetoxystyrene groups [35].

The results of this study indicate that the conversion of the bromine-end groups of poly(styrene-*ran*-4-tert-butoxystyrene) to thiol-end groups by thiolation was complete. However, the conversion of the tert-butoxy groups of the thiol-terminated poly(styrene-*ran*-4-tert-butoxystyrene) copolymers to hydroxyl groups was not successful. Furthermore, NMR data suggests that the hydrazinolysis impacts the thiol-end group of the thiol-terminated copolymers. The details of these experimental results are also presented and discussed in the supporting information section. While incomplete conversion of the hydrazinolysis reaction may result from insufficient reaction time and/or insufficient amount of HCl for hydrazinolysis, it was determined that the synthesis for PSVPh-SH copolymers via RAFT polymerization followed by hydrazinolysis would be a more facile approach and thus became the focus of our studies.

3.2. Synthesis for PSVPh-SH copolymers via RAFT polymerization, followed by hydrazinolysis

To improve the efficiency and facility of the synthesis the thiol-terminated PSVPh copolymers, we implemented a one step hydrazinolysis to convert both dithioester-terminal and acetoxy-pendant groups of dithioester-terminated poly(styrene-*ran*-acetoxystyrene) copolymers to thiol-terminal and hydroxyl-pendant groups, respectively. This strategy can be rationalized in that the labile dithioester groups can be converted to thiol groups by hydrolysis using a nucleophile such as an amine [22]. Furthermore, acetoxy-pendant groups of the copolymers can be converted to hydroxyl groups using NH_2NH_2 [36]. Thus, we prepared dithioester-terminated poly(styrene-*ran*-acetoxystyrene) copolymers via RAFT polymerization, and selected hydrazine hydrate as a reducing agent for the one step hydrazinolysis reaction. Fig. 1 shows the overall synthesis reaction to prepare PSVPh-SH copolymers. As can be seen, dithioester-terminated poly(styrene-*ran*-acetoxystyrene) copolymers were synthesized using cumyl dithiobenzoate as a chain transfer agent via RAFT polymerization. One step hydrazinolysis using hydrazine hydrate then followed the polymerization.

The formation of dithioester-terminal and acetoxy-pendant groups of the poly(styrene-*ran*-acetoxystyrene) copolymers after RAFT polymerization was confirmed by NMR. Fig. 2 (A) shows the ^{1}H NMR spectrum of the dithioester-terminated copolymers. In this figure, the aromatic protons in the dithioester end groups are present at a chemical shift of 7.8 ppm [20,21]. The methine proton next to the dithioester chain ends is evidenced by peaks at 4.8 ppm [20]. Additionally, a chemical shift of around 2.3 ppm indicates the presence of 3 methyl protons in the acetoxy-pendant groups of the copolymers. Furthermore, the mole fraction of acetoxy groups in the dithioester-terminated poly(styrene-*ran*-acetoxystyrene) copolymers was calculated to be 19.7% [37].

Fig. 2 (B) shows the ^{1}H NMR spectrum of PSVPh-SH copolymers after hydrazinolysis. In this figure, the peak around 7.8 ppm associated with the aromatic protons in the dithioester chain end disappears. The peak indicating methine protons next to the end groups also disappears. This NMR data therefore indicates that the dithioester-terminal groups of the copolymers were converted to thiol-end groups by hydrazinolysis. Additionally, this conversion of dithioester chain ends to thiols was confirmed by color change of the copolymers after hydrazinolysis (reddish-pink → clear). Furthermore, the acetoxy proton peaks around 2.3 ppm disappear, which indicates that the acetoxy-pendant groups were converted to hydroxyl groups. Therefore, this NMR data indicates that both dithioester and acetoxy groups were converted to thiol and hydroxyl groups by this one step hydrazinolysis reaction.

IR further confirmed the formation of hydroxyl-pendant groups by the reduction of acetoxy groups. Fig. 3 shows the IR spectrum of the dithioester-terminated poly(styrene-*ran*-acetoxystyrene) before hydrazinolysis and the thiol-terminated PSVPh copolymers after hydrazinolysis. It is clearly shown in Fig. 3 that the peaks around 3100–3700 cm^{-1} denoting hydroxyl (O–H) group stretching vibration in PSVPh copolymers are present after hydrazinolysis, but were absent in the dithioester-terminated poly(styrene-*ran*-acetoxystyrene) copolymers. Additionally, the peaks around 1200 and 1760 cm^{-1}, which indicate C–O and C=O group stretching vibration in the acetoxystyrene pendant groups before hydrazinolysis respectively, became very weak or disappeared after hydrazinolysis, further verifying that the acetoxy-pendant group is reduced to hydroxyl groups by the hydrazinolysis reaction.

Fig. 4 shows the GPC curves of the copolymers before and after hydrazinolysis. As can be seen in this Figure, a peak indicating a component with higher molecular weight than the original copolymer is observed at around 13,000 (g/mol) after the 5day

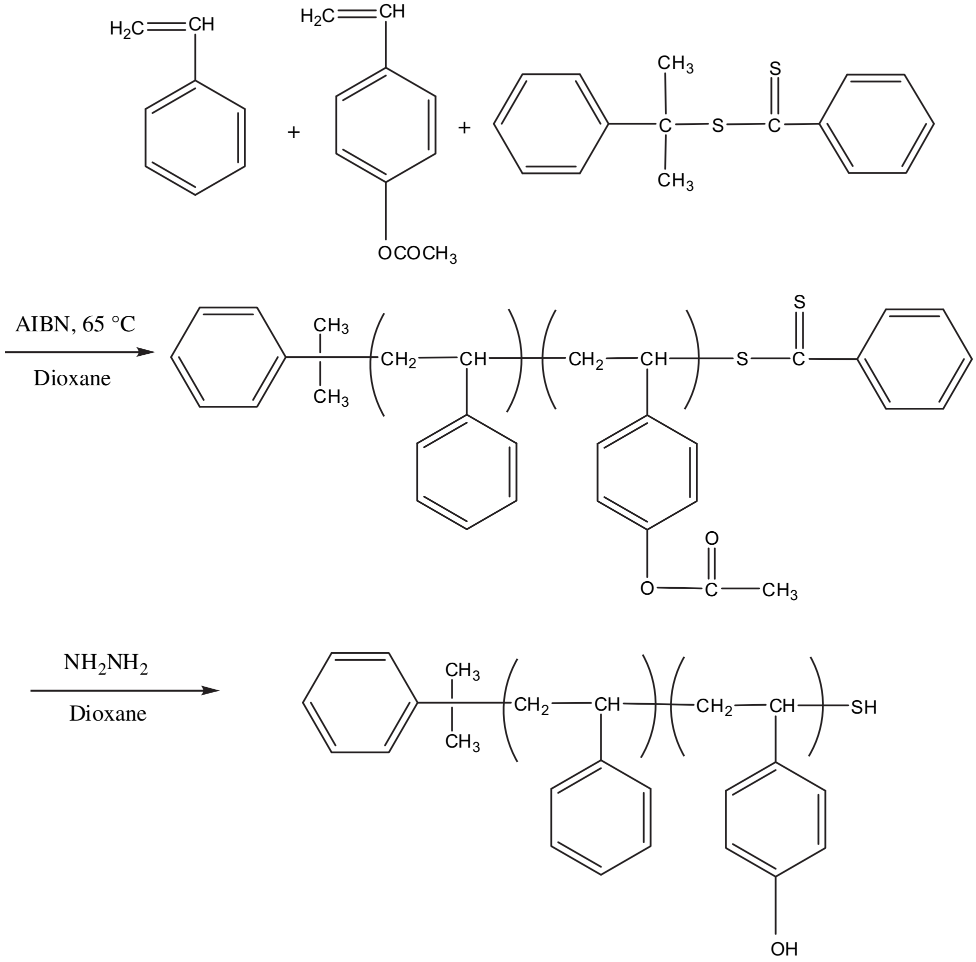

Fig. 1. Overall scheme for the synthesis of thiol-terminated PSVPh copolymers via RAFT polymerization, followed by one step hydrazinolysis using hydrazine hydrate.

hydrazinolysis reaction, in addition to the original peak indicating the starting material around 5800 (g/mol). The appearance of the higher molecular weight peak at double the molecular weight of the starting polymers suggests the formation of disulfides during the hydrazinolysis reaction [38]. Thiols can be easily oxidized, and two oxidized thiols can readily link together to form corresponding disulfides [2,38]. This characteristic of thiols has been previously observed in thiol-terminated polymers. For example, Kim et al. [38]. suggested the formation of a disulfide linkage during the hydrazinolysis reaction to convert dithioester-terminated poly(-styrene-*ran*-2-vinyl pyridine) (PS-r-P2VP) copolymers to thiol-terminated PS-r-P2VP copolymers using hexylamine in dry THF under nitrogen flow. To further analyze the formation of these larger molecular weight materials, the GPC curve of PSVPh copolymers after hydrazinolysis was deconvoluted and analyzed to determine the fraction of thiols and disulfides, as shown in Fig. 4. The areas under the two Gaussian curves are used to estimate that the final product of the hydrazinolysis is composed of 52% disulfides and 48% thiols. It should be emphasized that this estimation is not precise as the use of the area under the curves does not take into account the mass-sensitive response of the RI detector.

This ratio could certainly be optimized by limiting the reaction time of the hydrazinolysis to shorter time than 5 days. This was attempted, where the hydrazinolysis reaction was performed for 1 and 18 h. However, it was found that neither 1 h nor 18 h was sufficient to completely hydrolyze the acetoxy-pendant groups to hydroxyl groups, as evidenced by NMR studies. Thus, the product of the hydrazinolysis reaction after 5 days was used to determine its suitability to act as a ligand in the formation of gold nanoparticles, and the optimization of this hydrazinolysis procedure is currently ongoing in our lab.

3.3. Synthesis of gold nanoparticles stabilized by a mixture of thiol-terminated PSVPh and PSVPh copolymers containing disulfides

It has been demonstrated that polymers containing disulfides, as well as thiol-terminated polymers, are effective stabilizing ligands in the synthesis of gold nanoparticles, and thus the product of the hydrazinolysis reaction was used to synthesize gold nanoparticles. For instance, disulfides have been utilized in recent experimental studies to stabilize metal nanoparticles such as gold and silver, or to functionalize the surfaces of gold nanoparticles [29,39,40]. Lee and co-workers [39] reported the preparation of gold or silver nanoparticles in the presence of *n*-octadecyl disulfides, $(C_{18}S)_2$, as a stabilizing agent. They observed that the size and size distribution of gold nanoparticles that were synthesized using *n*-octadecanethiols, $C_{18}SH$ were similar to those of nanoparticles synthesized using *n*-octadecyl disulfides as the ligand, suggesting that disulfides can effectively stabilize gold surfaces, comparable to that of thiols. Additionally, Mangeney et al. [40]. functionalized gold nanoparticles with poly(acrylamide)s containing disulfide-terminal groups. They found that the surfaces of the gold colloids could effectively be coated with those polymers due to strong

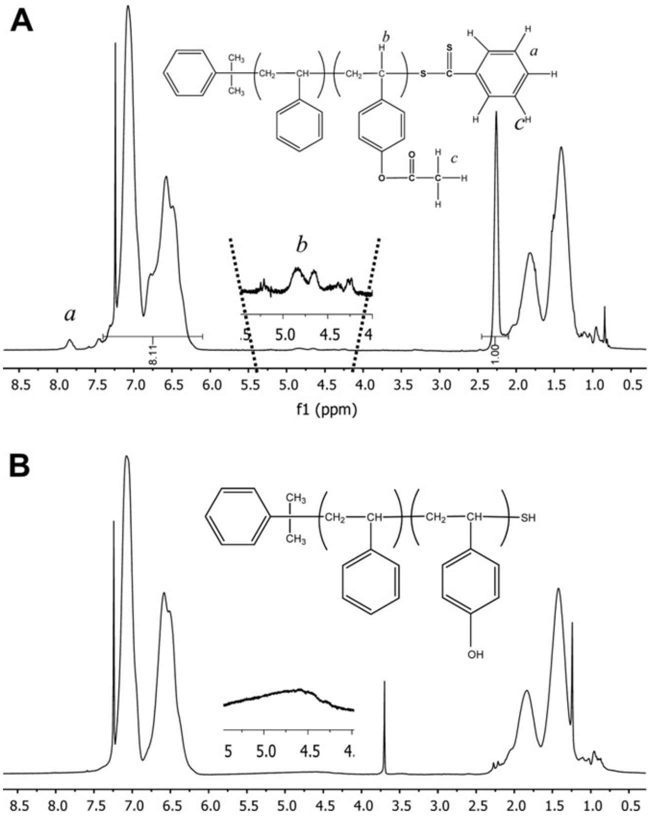

Fig. 2. ^{1}H spectrum of (A) dithioester-terminated poly(styrene-*ran*-acetoxystyrene) from RAFT polymerization and (B) of thiol-terminated PSVPh copolymers after hydrazinolysis.

interactions between the gold and the sulfur from disulfide-terminal groups.

Therefore gold nanoparticles coated with PSVPh-SH and PSVPh copolymers containing disulfides were synthesized in a water-toluene two-phase system using the mixture of thiol-terminated PSVPh and disulfides that resulted from the hydrazinolysis. These gold nanoparticles were characterized by TEM to analyze their size and size distribution. Fig. 5 shows a representative TEM image of the PSVPh-coated gold nanoparticles. Additionally, Fig. 6 shows the size and size distribution of the gold nanoparticles, which were determined using Image J software (1.34 s) by counting 459 particles, where an average diameter of 5.7 nm with standard deviation of 2.2.was found As can be seen in Figs. 5 and 6, the size of the gold nanoparticles was well-controlled in the presence of the mixture of thiol-terminated PSVPh and PSVPh copolymers containing disulfide bridges. This data indicates that polymers containing disulfides mixed with thiol-terminated polymers can be utilized to stabilize gold nanoparticles and to control their size. While this is in agreement with previous work, where disulfides or thiols are effective at passivating gold nanoparticles during particle synthesis, our results indicate that *mixtures* of thiol and disulfides effectively stabilize gold nanoparticles, suggesting that any competition between the thiol and disulfide does not inhibit the nanoparticle stabilization process.

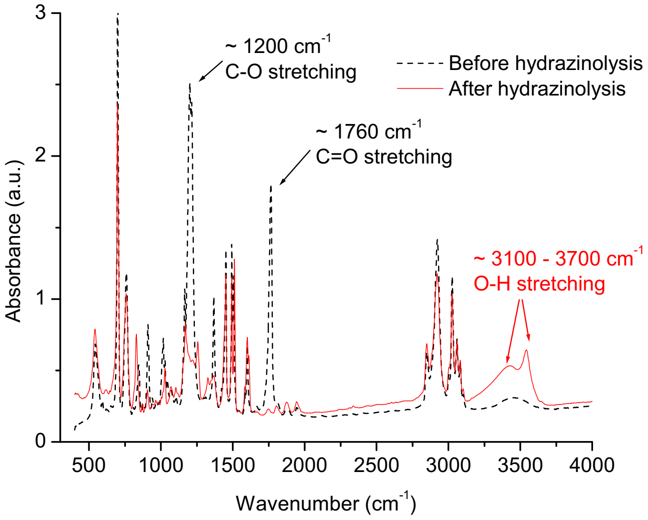

Fig. 3. IR spectrum of dithioester-terminated poly(styrene-*ran*-acetoxystyrene) before hydrazinolysis and PSVPh-SH copolymers after hydrazinolysis.

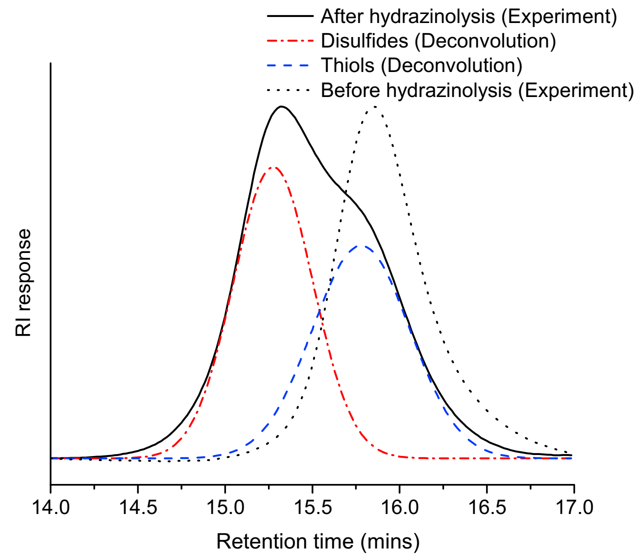

Fig. 4. GPC curves of copolymers before and after hydrazinolysis. Deconvoluted curves from the SH-PSVPh copolymer data are also shown.

This is not surprising, as the adsorption of a polymer with the adsorbing group in the middle of the polymer chain has been shown to adsorb much more slowly than the comparable end-

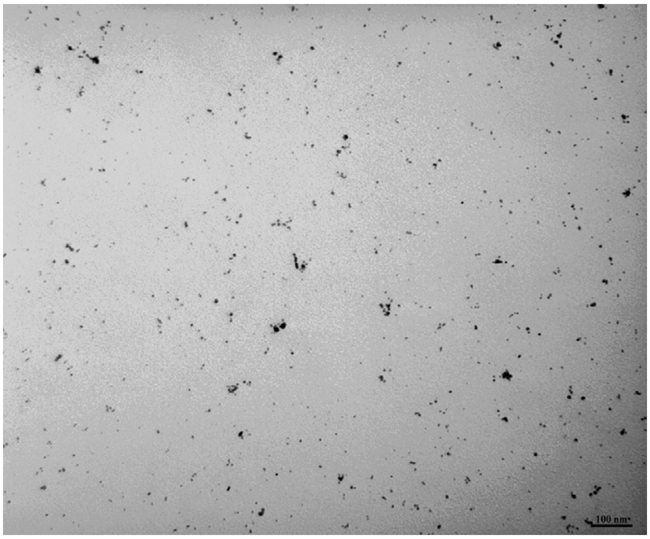

Fig. 5. Representative TEM image of gold nanoparticles coated with PSVPh copolymers. (Scale bar: 100 nm).

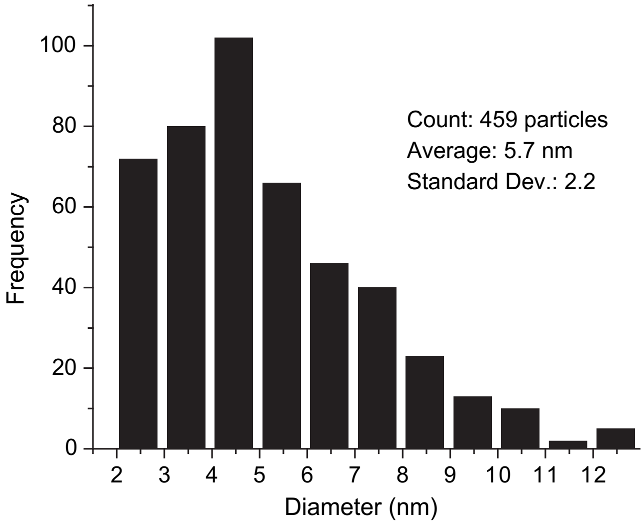

Fig. 6. Size and size distribution of gold nanoparticles coated with PSVPh copolymers.

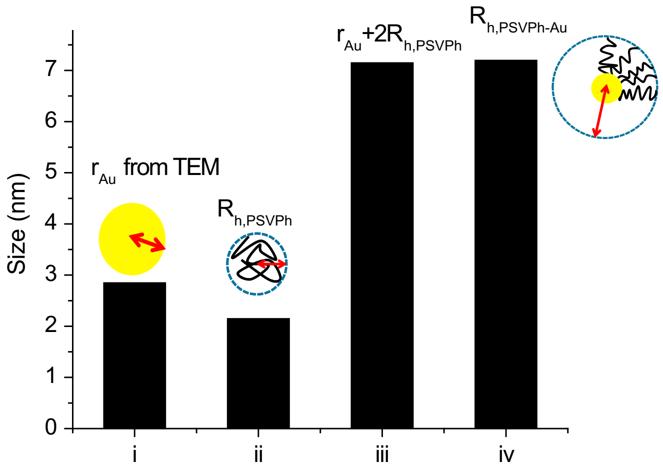

Fig. 8. Comparison of experimental results from TEM and DLS. (i) average radius of core Au nanoparticles, r_{Au}, from TEM, (ii) R_h of PSVPh, $R_{h,PSVPh}$, from DLS, (iii) $r_{Au} + R_{h,PSVPh}$, and (iv) R_h of PSVPh-coated Au nanoparticles, $R_{h,PSVPh-Au}$.

functionalized polymer[41] as well as to adsorb fewer chains [41,42]. Thus, in our system, it is expected that the PSVPh-SH molecules will adsorb onto the gold nanoparticle much more quickly and be more plentiful than the disulfide containing PSVPh molecules, providing a system that can effectively stabilize nanoparticle formation.

3.4. *Dynamic light scattering of copolymers and gold nanoparticles*

The hydrodynamic radii (R_h) of dithioester-terminated poly(styrene-*ran*-acetoxystyrene) copolymers, thiol-terminated PSVPh copolymers, and PSVPh-coated gold nanoparticles in toluene at 25 °C were determined by dynamic light scattering (DLS). Fig. 7 shows a scheme to illustrate the relationship between the R_h of the copolymers and of the PSVPh-coated gold nanoparticles. The average R_h of the copolymers in toluene decreased after hydrazinolysis, where the R_h of the dithioester-terminated poly(styrene-*ran*-acetoxystyrene) copolymers was 2.37 nm, and the R_h of the PSVPh-SH copolymers was 2.15 nm. This DLS data indicates, not surprisingly, that the PSVPh copolymer chains with *ca.* 20 mol% polar, hydroxyl-pendant groups tend to shrink in non-polar toluene, relative to the poly(styrene-*ran*-acetoxystyrene) copolymer chains before hydrazinolysis.

This result, however, appears to contradict the GPC data, which indicate the coupling of thiols to form disulfides, which should result in, on average, larger polymer chains, and thus an increase in R_h. However, these two data points can be rationalized by considering that the disulfide containing PSVPh will adsorb at their center point and form brushes that are nearly as extended as the end-functionalized PSVPh-SH. In fact, theoretical calculations[42] estimate that the center-adsorbing chain will extend ~90% as far from the surface as a comparable end-functionalized that is ½ the length, the precise conditions of our study. Thus, the increased chain length of the potential adsorbate does not result in an increase in the resultant brush length. The decrease in the R_h of PSVPh copolymers in toluene can be explained due to the repulsive interaction between the pendant, polar –OH moieties in PSVPh copolymers and the non-polar solvent. It is important to emphasize that this is not the only mechanism by which the PSVPh can decrease in size, for instance intramolecular hydrogen bonding among vinyl phenol groups of a chain may also cause a contraction of the PSVPh chain.

To further verify this analysis, the average R_h of the gold nanoparticles coated with PSVPh copolymers was measured and found to be 7.2 nm. This DLS data agrees with the DLS and TEM

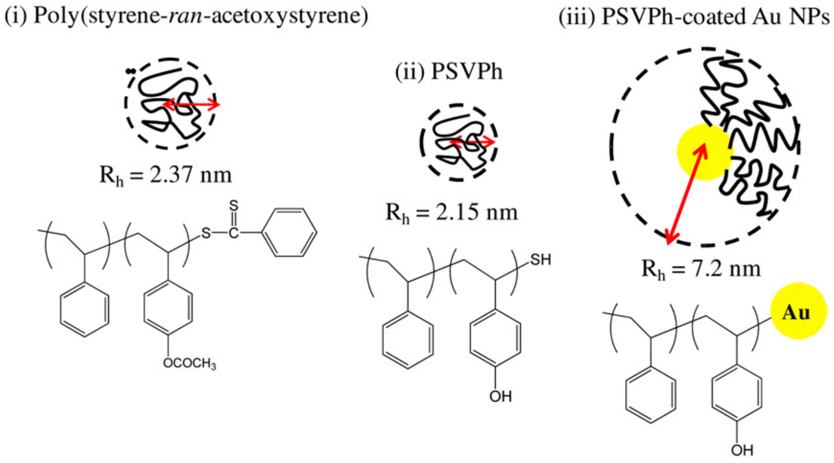

Fig. 7. Scheme to illustrate hydrodynamic radius of the copolymers before and after hydrazinolysis, and of the PSVPh-coated gold nanoparticles.

data of the PSVPh copolymers, as shown in Fig. 8. The average radius of the core gold nanoparticles was determined to be 2.85 nm by TEM analysis. The R_h of the PSVPh copolymers, which form the corona around the core gold nanoparticles, was determined to be 2.15 nm. The sum of radius of the core gold and hydrodynamic diameter of PSVPh copolymers is 7.15 nm, which is sufficiently close to the R_h of gold nanoparticles coated with PSVPh copolymer as determined by DLS. (7.2 nm) Therefore, the DLS data further verifies that the synthesized PSVPh-coated gold nanoparticles are composed of core gold nanoparticles surrounded by PSVPh copolymer coronas.

4. Conclusions

We report here the successful synthesis of thiol-terminated PSVPh copolymers with polar-pendant groups, which are mixed with PSVPh copolymers containing disulfides, by RAFT polymerization followed by one step hydrazinolysis using hydrazine hydrate. Our NMR and IR data confirm the conversion of both dithioester-terminal and acetoxy-pendant groups to thiol and hydroxyl groups, respectively. Additionally, gold nanoparticles coated with PSVPh copolymers were synthesized utilizing a mixture of thiol-terminated copolymers and copolymers containing disulfides as the stabilizing ligand. The TEM and DLS results indicate that the nanoparticles were composed of core gold nanoparticles and PSVPh ligands. Thiol-functionalized PSVPh copolymers containing a targeted amount of hydrophilic-, polar-pendant groups may have versatile applications, including in biological systems. The polarity of the resultant stabilizing ligands can be readily controlled by the composition of the initial poly(-styrene-*co*-acetoxystyrene) copolymer, and thus this method provides a facile approach to create stabilizing ligands with controlled hydrophilicity, enabling the fabrication of metal nanoparticles that can be tailored to sequester in local environments in proteins and other biomacromolecules. Similarly, gold nanoparticles coated with PSVPh copolymers can be an important material to study the physics of the impact of supramolecular, non-covalent intermolecular interactions on the final morphologies in nanocomposites that are composed of gold nanoparticles and diblock copolymers.

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Supplementary data

Supplementary data associated with this article can be found in the online version doi:10.1016/j.polymer.2010.01.033.

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