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Comb−Coil Polymer Brushes on the Surface of Silica Nanoparticles

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During the past decade, surface modification of inorganic nanoparticles by attachment of polymer brushes has attracted much interest due to the improvement of the properties of the nanoparticles, especially the dispersion and stability of the particles in various solvents. Recently, many groups reported preparation of polymer brushes on the surface of gold nanoparticles,[1] magnetic nanoparticles,[2] and silica nanoparticles.[3] There are two principal techniques to graft polymer brushes on the surface of the inorganic particles: (1) the "grafting to" method, where the end-functionlized polymers react with the functional groups on the inorganic particle surface, and (2) the "grafting from" method, where the polymer chains grow from the initiator-modified inorganic particle surface. Because of the steric hindrance imposed by the grafted polymer chains, it is difficult to prepare polymer brushes with high graft density on the particle surface using the "grafting to" method. However, in the "grafting from" method polymer chains grow from the initiators that have been initially anchored to the particle surface, and the grafted chains will not hinder the diffusion of the small molecular monomers to the reaction sites, so the polymer brushes with higher graft density can be obtained.

In recent years, there have been increasing research activities in the use of various polymerization methods to grow polymer chains on the silica particle surface. These methods include anionic polymerization,[3b] cationic polymerization,[3d] ring-opening polymerization,[3c] radical polymerization,[3e] and atom transfer radical polymerization (ATRP).[4−8] Because ATRP allows better control over the molecular weight and distribution of the target polymer, much attention has been paid to the use of this polymerization method in the synthesis of polymer brushes from a surface. Recently, Matyjaszewski's group reported an improved ATRP method, activators generated by electron transfer (AGET) ATRP.[9] In a typical AGET ATRP system, an alkyl halide is used as initiator, and a transition metal complex in its oxidatively stable state (e.g., Cu^{2+}/ligand) is used as catalyst. The activator is generated by using an electron transfer to reduce the higher oxidation state transition metal. In their experiments tin(II) 2-ethylhexanoate and ascorbic acid were used as the reducing agents. The AGET ATRP method has all benefits of normal ATRP and remains tolerant to air during sonication, so it will be very useful in the preparation of polymer brushes on the silica nanoparticles surface.

In this paper we report the first synthesis of comb−coil polymer brushes on the surface of silica nanoparticles. In this approach two steps are involved. At the first step, poly(2-hydroxyethyl methacrylate) (PHEMA) brushes on the surface of ATRP-initiator-anchored silica nanoparticles were prepared using ATRP. At the second step using a combination of ring-opening polymerization and AGET ATRP, poly(DL-lactide)−poly(*n*-butyl acrylate) ((PLA−PBA) comb−coil polymer brushes were synthesized from the backbone and the terminal site of PHEMA brushes, respectively. This process is illustrated in Scheme 1. To synthesize PHEMA polymer brushes, ATRP-initiator-anchored silica nanoparticles were prepared by a reaction of original silica particles with 3-(triethoxysilyl)propylamine and followed by another reaction with 2-bromoisobutyryl bromide. PHEMA brushes were synthesized by ATRP. PLA comb and PBA coil were synthesized by a combination of ring-opening polymerization and AGET ATRP (Scheme 1). The hydroxyl groups on PHEMA chains can be used in the ring-opening polymerization of LA, and the bromide

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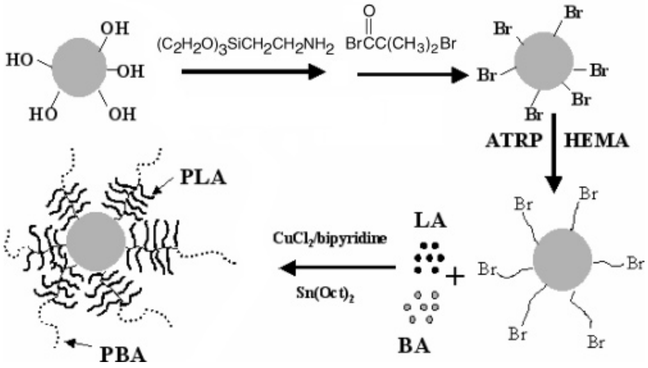
Scheme 1. Schematic Representation for the Preparation of Comb−Coil Polymer Brushes on the Surface of Silica Nanoparticles



groups at the end of PHEMA chains can be used as initiators in AGET ATRP of BA. In this polymerization system, the Cu^{2+}/bipyridine complex was used as catalyst for AGET ATRP, and tin(II) 2-ethylhexanoate was used as a reducing agent. Meanwhile, tin(II) 2-ethylhexanoate was also used as catalyst for the ring-opening polymerization of DL-lactide (LA). So the ring-opening polymerization of LA at the backbone of PHEMA chains and AGET ATRP of BA at the end of PHEMA chains were taken place in the same polymerization system (Scheme 1). In this case each monomer should independently propagate via two different mechanisms (ring-opening and radical) and form different structures (comb structure at the backbone of PHEMA and coil structure at the end of PHEMA chain).

The primary amino groups were introduced onto particle surface by a reaction with 3-(triethoxysilyl)-propylamine (Scheme 1). The elemental analysis result shows that the nitrogen content is about 0.93%, which means the concentration of amino groups on the surface is about 0.66 mmol/g. This result keeps consistent with the literature report.[3a] ATRP-initiator-anchored silica particles were prepared after a reaction of aminated silica particles with 2-bromoisobutyryl bromide. The elemental analysis result shows that the bromide content on the silica particle surface is about 6%. This result indicates that on the particle surface the amount of ATRP initiator is roughly the same as that of amino group.

Thermogravimetric analysis (TGA) result indicated that the weight retention of ATRP-initiator-anchored silica nanoparticles at 800 °C was about 90%. But it has to be pointed out that part of the weight loss of the modified silica particles is due to the continued condensation reaction and associated water loss.[8,10] If the weight retention of the residue at 800 °C is used as the reference, the weight retention of PHEMA brushes on the surface is about 76%, and that of the comb−coil polymer brushes is about 50%.

Comb−coil polymer/silica composite was etched by HF acid, and the polymer was measured by ^{1}H NMR. Figure 2 shows the ^{1}H NMR spectrum of the comb−coil polymer. In Figure 2 the peak at 3.8 ppm assigned to methylene protons adjacent to the −OH group in PHEMA basically disappears, which indicates the successful ring-opening reaction of LA by −OH group on PHEMA backbone. In the spectrum the peaks at 5.16 ppm (d) and at 2.28 ppm (e) represent the methine protons in PLA and PBA backbone, respectively.[11] Using these two peaks, it can be calculated that the molar ratio of LA to BA is about 1:0.36. The peak at 4.36 ppm (b) is attributed to the methylene group of PHEMA. Using this peak and the peak at 5.16 ppm (d), the molar ratio of PHEMA repeating units to PLA repeating units can be obtained. Assuming all the −OH groups take part in the ring-opening polymerization, there are 20 LA repeating units on each PHEMA repeating unit, or the average molecular weight of PLA comb chain is about 1400.

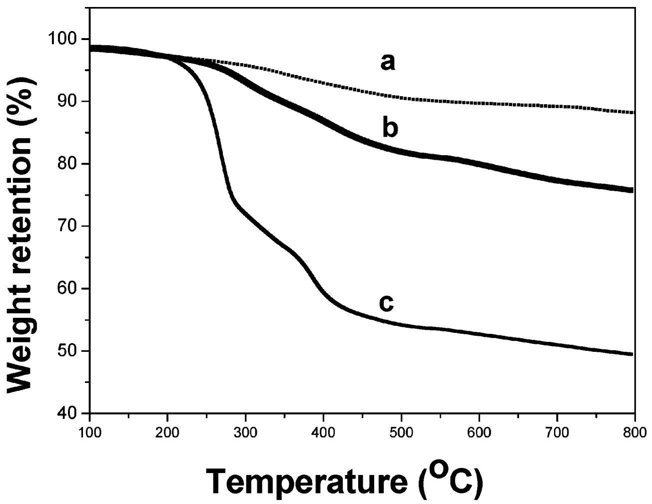


Figure 1. Thermogravimetric analysis of (a) ATRP-initiator-anchored silica nanoparticles, (b) PHEMA brushes on the surface of silica nanoparticles, and (c) PLA−PBA comb−coil polymer brushes on the surface of silica nanoparticles.

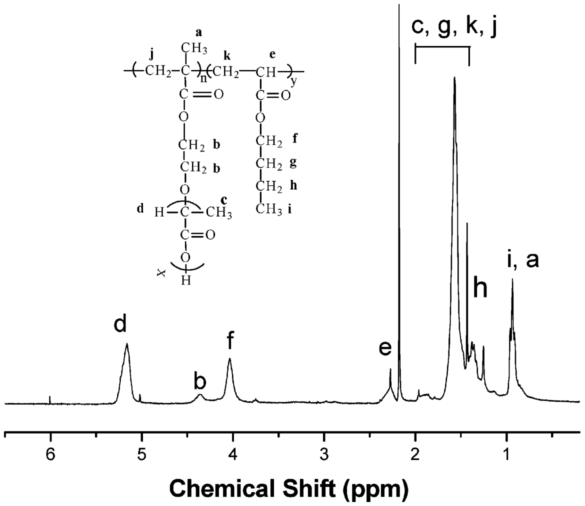


Figure 2. ^{1}H NMR spectrum of PLA−PBA comb−coil polymer.

The molecular weight of the etched polymer was also measured by GPC. The GPC result shows that the molecular weight (M_n) of the comb−coil polymer is about 44 000 and the polydispersity is about 1.55.

Transmission electron microscopy (TEM) results confirmed the formation of comb−coil polymer brushes on the surface of silica particles. The specimens for TEM measurement were prepared by dipping the copper grids into the diluted solution of grafted (or bare) silica nanoparticles in THF and evaporating in air. To increase the contrast, the comb−coil polymer chains were stained by exposing in hydrazine vapor for 6 h and OsO_4 vapor for 3 h.[12] Figure 3a shows a TEM image of bare

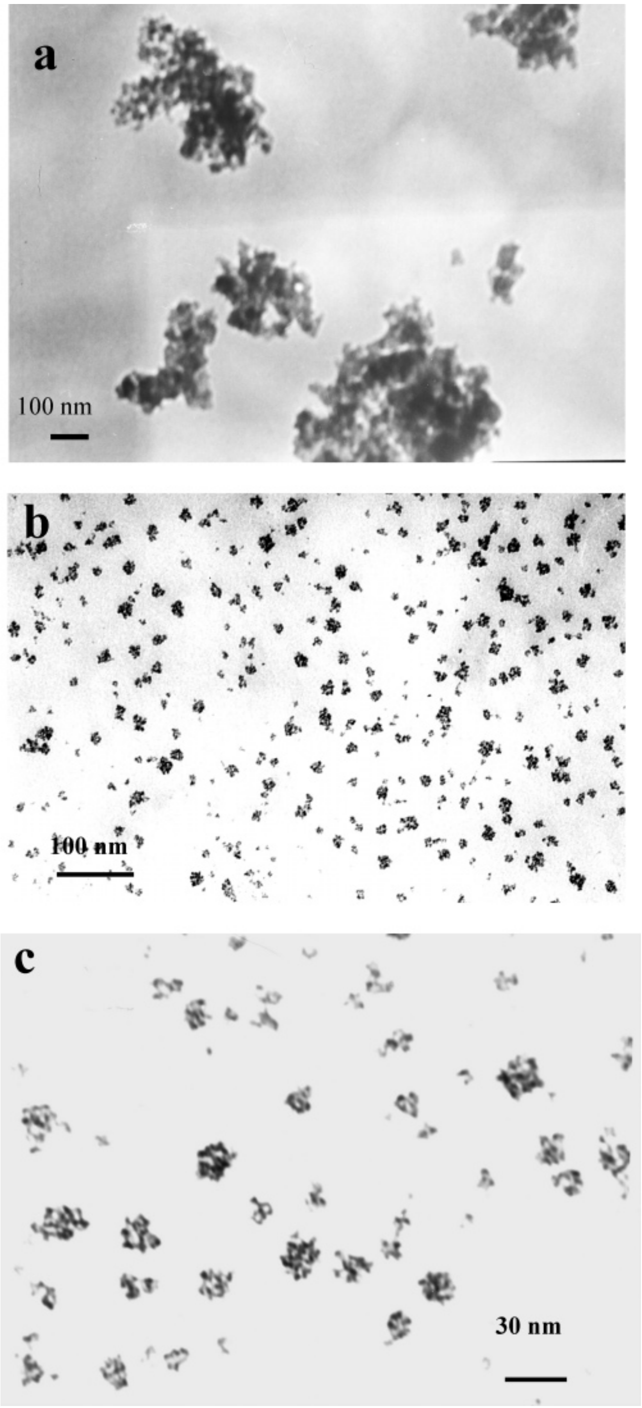


Figure 3. TEM images of bare silica particles (a) and comb−coil polymer grafted silica particles (b, c). Part c is a magnified TEM image of comb−coil polymer grafted silica particles.

silica particles. The bare silica particles were observed as aggregates with an average size of several hundred nanometers. In Figure 3a no isolated bare silica particles can be found. In contrast, silica particles with comb−coil polymer brushes were observed to have fine dispersion, and the particle size ranges from 20 to 30 nm. To observe the particles clearly, a magnified TEM image was shown as Figure 3c. On the particles surface the comb−coil polymer brushes form wormlike structure. Molecular brushes tend to form rodlike conformation due to the steric repulsion of side chains. This type of structure was also observed by many people in their study of molecular brushes.[13] Here, it is difficult to measure the length of the comb−coil polymer, but the width of the structure is measured to be around 1.2 nm.

In summary, we have described an effective and novel method to synthesize comb−coil polymer brushes on the surface of silica nanoparticles. For the synthesis of comb−coil polymer on the particle surface, PHEMA polymer brushes were prepared by ATRP method. On the basis of a combination of AGET ATRP and ring-opening polymerization, PLA−PBA comb−coil polymer brushes were prepared from the backbone and the end of PHEMA chains, respectively. The comb−coil polymer brushes form wormlike structure on the silica particle surface. It is obvious that our approach can be extended to other systems, such as Au nanoparticles. This type of polymer modified nanoparticles may find their applications in the area of biomaterials, chemical mechanical polishing (CMP), etc.

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Supporting Information Available: Experiments details and two control experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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