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Dynamic polymer brushes on the surface of silica particles†

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Synthesis of cleavable PS brushes on the surface of silica particles was reported in this paper. Atom transfer radical polymerization (ATRP) initiator was anchored onto the surface of silica particles *via* dynamic imine bond, and PS brushes were prepared by surface ATRP of styrene. PS brushes could be cleaved from the surface of silica particles in the presence of trifluoroacetic acid. Based on the dynamic properties of imine bonds, pyrene-labeled silica particles were prepared through dynamic exchange reaction between PS brushes and 1-pyrenecarboxaldehyde. Moreover, silica particles with PS and fluorescein-labeled poly(methyl methacrylate) mixed polymer brushes were synthesized by dynamic exchange reaction. This research demonstrates that dynamic covalent chemistry provides an efficient method for the preparation of ''dynamic'' polymer brushes on silica particles.

Introduction

Over the past few decades, synthesis of polymer brushes on the surface of inorganic nanoparticles has attracted much interest due to the improvement of the properties of the materials. Basically, there are two techniques to prepare polymer brushes on the surface of nanoparticles: (1) the ''grafting to'' method, where the polymer chains are grafted to the surface by reaction with the functional groups on the nanoparticles, and (2) the ''grafting from'' method, where the polymer chains grow from the surface of initiator-modified nanoparticles. Because of the steric hindrance imposed by the grafted polymer chains in the ''grafting to'' method, polymer brushes with high grafting density on the nanoparticles are prepared by the ''grafting from'' method.[1–3] Various polymerization methods, including anionic polymerization,[4] cationic polymerization,[5] ring-opening polymerization,[6] reversible addition-fragmentation chain transfer (RAFT) polymerization[7] and atom transfer radical polymerization (ATRP),[8–11] have been used to prepare polymer brushes on the surface of nanoparticles. Because of the better control over the molecular structures, ATRP was used widely in the preparation of polymer brushes.[10,12–16]

Recently, preparation of silica particles with multi-functional groups or different macromolecular brushes have aroused a lot of interest for their potential applications in many fields. particles with asymmetric morphology, also known as Janus particles,[17] have received much attention due to their applications in colloidal science.[18] Janus particles can be prepared by many different strategies, such as modifying the two hemispheres step-by-step after immobilizing the particles on the substrate, Pickering emulsion method, and electrohydrodynamic jetting in combination with a two-phase side-by-side spinneret tip, *etc*.[19] Another type of silica particle with different polymer brushes was reported by Zhao and co-workers.[11] They anchored a Y-type initiator onto the surface of silica, and synthesized PtBA/PS polymer brushes by ATRP and nitroxide-mediated radical polymerization (NMP). The molar ratio of PtBA chains to PS chains on silica was kept at 1 : 1. Randomly distributed mixed polymer brushes were also prepared on silica particles. Minko and co-workers prepared mixed polymer brushes by free radical polymerization.[20]

Dynamic covalent chemistry relates to chemical reactions carried out reversibly under conditions of equilibrium control.[21] The formation and dissociation of the ''dynamic'' bonds can be controlled by the physical or chemical conditions of the environment. For example, disulfide is responsive to the redox conditions,[22–26] alkoxyamine has an equilibrium at high temperature,[27–29] hydrazone and imine bonds have a broken and reborn balance in acidic conditions,[30–34] and a combination of two of them can allow better control over the structures and properties of the materials.[35–37] Dynamic covalent chemistry has been used in the synthesis of functional polymers and nanostructures with dynamic properties. Lazny and co-workers reported the immobilization of aldehydes and ketones onto the polymeric supports *via* hydrazone.[32] Fulton and co-worker synthesized diblock polymers possessing amino or aldehyde functions within one of their blocks by RAFT polymerization, and core cross-linked

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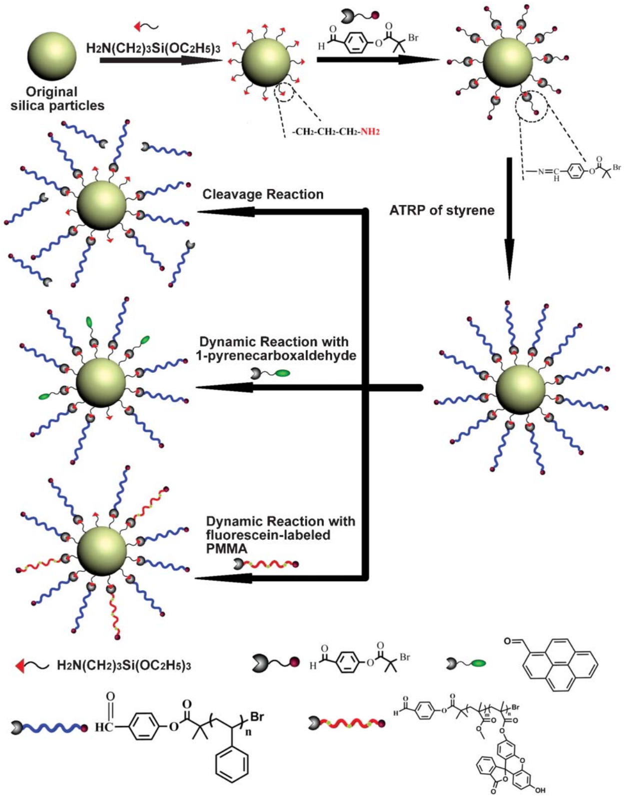
star polymers can be formed by using the dynamic imine bonds as the linker.[33] Lehn and co-workers reported the change of color and fluorescence at the interface of two different polyhydrazone polymer films, induced by hydrazone bond exchange and component recombination through the interface.[35]

The synthesis of cleavable polymer brushes provides direct characterization of the polymer brushes on solid substrates and facile modifications of the surface of the solid substrates,[38] so the dynamic polymer brushes will find potential applications in surface and medical sciences. Herein, we report the preparation of the cleavable polymer brushes on silica particles based on the dynamic properties of the imine bond. An imine bond formed by the condensation of an amine and an aldehyde group can be used as a dynamic covalent bond. ATRP initiator was anchored onto the surface of the silica particles by reaction of 4-formylphenyl 2-bromoisobutyrylate (FPBIB) and amine-modified silica particles. After ATRP of styrene, PS brushes grafted to the surface of silica particles *via* imine bonds were prepared by the "grafting from" method, and the structure of the polymer brushes was analyzed after cleavage of the polymer brushes from solid substrates. In this research, silica particles with PS brushes and pyrenyl groups on the surface can be prepared through dynamic exchange reaction between PS coated silica particles and 1-pyrenecarboxaldehyde. Scheme 1 shows an outline for the preparation of cleavable PS brushes on silica nanoparticles and dynamic exchange reactions.



Scheme 1 Schematic representation for the preparation of cleavable PS brushes on silica particles, and dynamic exchange reactions between PS brushes and 1-pyrenecarboxaldehyde, and PS and aldehyde-terminated fluorescein-labeled poly(methyl methacrylate) (f-PMMA).

Experimental

Materials

Tetraethyl orthosilicate (TEOS) was purchased from Tian Jin Institute of Chemical Agents and was distilled before use. Styrene (99%) was purchased from Tian Jin Institute of Chemical Agents. It was purified by washing with aqueous solution of NaOH, drying over $MgSO_4$, and distilling under reduced pressure. Triethylamine (TEA, Tianjin Chemical Reagent Co., AR) was dried with CaH_2 and distilled before use. CuBr (99.5%) purchased from Guo Yao Chemical Company, was purified by washing with glacial acetic acid and dried in a vacuum oven at 100 °C. *p*-Toluenesulfonic acid (*p*-TsOH, 99.5%) was purchased from Tianjin Jinke Chemical Co.; 4-hydroxybenzaldehyde (99%) was purchased from J&K Scientific Ltd.; fluorescein methacrylate (FMA, 97%), *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA, 99%) and 3-(triethoxysilyl)propylamine were purchased from Aldrich; 2-bromoisobutyryl bromide (98%), 1-pyrenecarboxaldehyde (99%) and trifluoroacetic acid (TFA, 99%) were purchased from Alfa Aesar. All the above chemicals were used as received.

Synthesis of 4-formylphenyl 2-bromoisobutyrylate (FPBIB)

4-Formylphenyl 2-bromoisobutyrylate was synthesized by using a procedure similar to previous literature.[39] 4-Hydroxybenzaldehyde (1.06 g, 8.68 mmol) was dissolved in anhydrous DMF (20 mL) in a round-bottom flask, and excess triethylamine (7.0 mL, 50.33 mmol) was added. The solution was cooled in an ice bath, and 2-bromoisobutyryl bromide (6 mL, 48.5 mmol) was added slowly to the solution. After stirring for 48 h, the white precipitate was filtered off, and the solution was concentrated under reduced pressure. The concentrated solution was further purified by silica gel column chromatography with a mixture of petroleum ether/ethyl acetate/dichloromathane (10 : 1 : 1, v/v/v) as the eluent. The yield of the product is about 33%. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 10.02(s, 1H); 7.97, 7.95(s, 2H); 7.34, 7.32(s, 2H); 2.11(s, 6H).

Preparation of silica particles

The spherical silica particles used in this research were prepared by using the Stöber method.[40] To a 1000 mL flask were added 500 mL of ethanol, 10 mL of water, and 36 mL of ammonia solution (25%). After stirring at 40 °C for 2 h, 30 mL of TEOS was added to the solution. The mixture was stirred at 40 °C overnight, and silica particles were prepared. The silica particles were collected by centrifugation (10 000 rpm, 15 min) and washed by ethanol and water for at least five times. The particles were then dried at 110 °C under vacuum.

Preparation of ATRP initiator-modified silica particles

In a round bottom flask, bare silica particles (2.15 g) were dispersed in dry toluene after 30 min of sonication, and 3-

(triethoxysilyl)propylamine (7.5 g) was added to the solution dropwise. The solution was stirred at 95 °C for 22 h. After the reaction, the particles were filtered and washed by ethanol until no blue precipitants were observed upon addition of Cu^{2+} to the upper solution, which indicates that all the excess 3-(triethoxysilyl)propylamine was removed.

In order to prepare ATRP initiator-modified silica particles, the amine-modified silica particles (0.82 g) were dispersed in 10 mL of THF; after 1 h of sonication, *p*-TsOH (9.8 mg, 0.057 mmol) and FPBIB (0.10 g 0.38 mmol) were added into the dispersion at room temperature. The reaction was conducted at 70 °C for 20 h. After the reaction, the particles were collected by centrifugation.

ATRP of styrene on the surface of silica particles

ATRP initiator-modified silica particles (30 mg), styrene (4.0 mL, 35 mmol) and toluene (2 mL) were mixed in a Schlenk flask, the dispersion was degassed by one freeze-pump-thaw cycle. CuBr (2.8 mg, 0.019 mmol) and PMDETA (4.0 μL, 0.019 mmol) were dissolved in 2 mL of dry DMF, and 0.2 mL of the solution was added into the dispersion under nitrogen atmosphere. The solution was degassed by three freeze-pump-thaw cycles. The surface ATRP of styrene was conducted at 110 °C for 24 h. The polymerization was stopped by exposure of the solution to air.

Preparation of aldehyde-terminated f-PMMA

Fluorescein-labeled PMMA was synthesized by ATRP of MMA and FMA using FPBIB as initiator. PMDETA (35 μL, 0.167 mmol) was dissolved in 2 mL of MMA monomer (18.83 mmol), and then CuBr (0.023 g, 0.16 mmol) was added under nitrogen atmosphere. After stirring for 15 min, the solution was added to a mixture of toluene (2 mL), FPBIB (0.052 g, 0.19 mmol) and FMA (0.0141 g, 0.0353 mmol) under nitrogen atmosphere. The solution was degassed by three freeze-pump-thaw cycles, and ATRP of MMA and FMA was conducted at 70 °C for 6.5 h. The polymerization was stopped by exposure of the solution to air. After removal of solvent under reduced pressure, copper ions were removed with neutral alumina column chromatography by using CH_2Cl_2 as eluent. The product was isolated by pouring the polymer solution into cold diethyl ether. After filtration, the polymer was dried under vacuum. The average molecular weight and PDI of the polymer are 15 k and 1.11, respectively. GPC trace of the polymer is shown in Fig. S1 (ESI†).

Cleavage reaction of PS polymer brushes

The cleavage reaction of PS-coated silica particles was conducted using a method similar to previous literature.[3] PS-coated silica particles (0.015 g) were dispersed in 1 mL of THF under sonication, and TFA (0.4 mL) was added to the dispersion. The dispersion was stirred at 50 °C for 24 h. The silica particles were collected by centrifugation (10 000 rpm, 15 min), washed by THF and dried under vacuum. After separation, an equimolar amount of triethylamine was added to the cleaved polymer solution to neutralize TFA. The cleaved PS was concentrated by evaporating the solvent, and solid PS was obtained by adding the polymer solution into 6-fold of methanol.

Dynamic reaction between PS-coated silica particles and 1-pyrenecarboxaldehyde

PS-coated silica particles (20 mg) were dispersed in 1 mL of THF under sonication, and 1-pyrenecarboxaldehyde (0.0034 g, 1.5×10^{-5} mol) was added to the dispersion. After stirring at room temperature for 30 min, 0.1 mL of TFA was added to the dispersion. The dynamic exchange reaction was conducted at 50 °C for 24 h. The silica particles were collected by centrifugation (10 000 rpm, 15 min), washed by THF and dried under vacuum.

Dynamic reaction between PS-coated silica particles and aldehyde-terminated f-PMMA

PS-coated silica particles (8.60 mg) were dispersed in 1 mL of THF under sonication, and then 0.3 mL of TFA was added to the dispersion. After stirring at room temperature for 30 min, aldehyde-terminated fluorescein labeled PMMA (25.4 mg) was added to the dispersion. After stirring at room temperature for 4 h, TEA was added to stop the reaction. The silica particles were collected by centrifugation (10 000 rpm, 15 min), washed by THF and dried under vacuum.

Preparation of pickering emulsion

Silica particles with PS and f-PMMA mixed polymer brushes (1.0 mg) were dispersed in 1 mL of decalin by sonication, and then 0.1 mL of distilled water was added into the dispersion forming a stable Pickering emulsion.

Results and discussion

A scheme for the synthesis of cleavable PS brushes on silica particles is shown in Scheme 1. FPBIB was synthesized by a reaction between 4-hydroxybenzaldehyde and 2-bromoisobutyryl bromide.[39] Chemical structure and ^1H NMR spectrum of FPBIB were shown in Fig. S2, ESI.† Spherical silica particles with an average diameter of 150 nm were prepared by using the Stöber method.[40] Amino groups modified silica particles were prepared by reaction of the silica particles and 3-(triethoxysilyl)propylamine. The elemental analysis result shows that the nitrogen content is 0.45 wt%. ATRP initiator was anchored onto the silica particles through dynamic imine bond after a reaction between aldehyde groups of FPBIB and the primary amino groups on silica particles. The bromine content measured by ionic chromatogram was 0.504 wt%.

Thermogravimetric analysis (TGA) curves of original, amine-modified, and ATRP initiator-modified silica particles are presented in Fig. 1. They are found to have 7.2 and 8.7 wt% volatile materials on amine-modified and ATRP initiator-modified silica particles, so after reaction, 1.5 wt% FPBIB is attached to the silica particles. A TEM image of the original silica particles is shown in Fig. 2(a). The TEM result shows that the average size of the original silica particles is about 150 nm.

PS polymer brushes on the silica particles were prepared by *in situ* ATRP. The possible free PS was removed by washing with THF and followed by repeated sonication and centrifugation cycles. After polymerization, PS was successfully grafted to

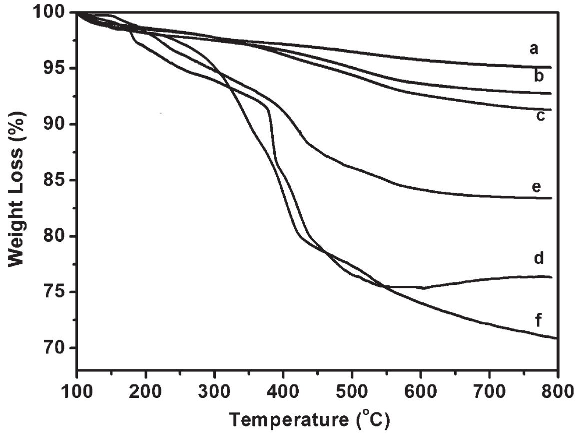


Fig. 1 TG thermograms of unmodified silica particles (curve a), amine-modified silica particles (curve b), ATRP initiator-anchored silica particles (curve c), PS-coated silica particles (curve d), silica particles after cleavage reaction (curve e) and silica particles with mixed polymer brushes (curve f).

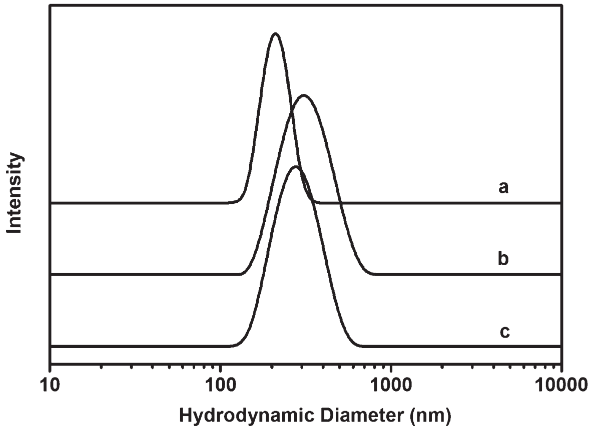


Fig. 3 Size distributions of ATRP initiator-anchored silica particles (curve a), PS-coated silica particles (curve b) and silica particles after cleavage reaction (curve c).

the surface of silica particles as proved by TGA, DLS and TEM. The TGA curve of silica particles with PS brushes is shown in Fig. 1 (curve d). After ATRP of styrene, it is found to have ~23.6 wt% weight loss, which means the weight percentage of PS grafted to the surface of silica particles is about 14.9 wt%. The grafting density of PS is calculated to be about 1.08 chains nm^{-2}. A TEM image of the silica particles after surface ATRP was presented in Fig. 2 (b). On the image, PS brush layers on the silica particles are observed clearly, and the thickness of the PS layer ranges from 8 to 10 nm. DLS results also prove the success of the polymerization. DLS curve of ATRP initiator-modified silica particles is shown in Fig. 3 (curve a). The modified silica particles possess a unimodal size distribution with a hydrodynamic diameter range from 129 to 345 nm. However, after surface ATRP, the hydrodynamic diameter of the particles ranges from 140 to 748 nm with an average value at about 290 nm (Fig. 3). In comparison with ATRP initiator-modified silica particles, the average size increased about 77 nm. Therefore, the surface ATRP of styrene was successfully conducted on the silica particles.

In order to investigate the dynamic properties of the polymer brushes, PS brushes were cleaved from the surface of silica particles in an acidic environment. The cleavage reaction was conducted by dispersing the PS-coated particles into a mixture of THF/trifluoroacetic acid (TFA) (v/v, 1 : 0.4) *via* vigorous mixing. After stirring at 50 °C for 24 h, the particles were removed from the cleaved polymer chains by centrifugation and repeated washing with THF. The cleaved PS was characterized by GPC (Fig. 4) and ^{1}H NMR (Fig. S3 in ESI†). The GPC result shows that the number average molecule weight of PS is about 11 k and the molecular weight distribution is about 1.29. TGA curve of silica particles after cleavage of PS is

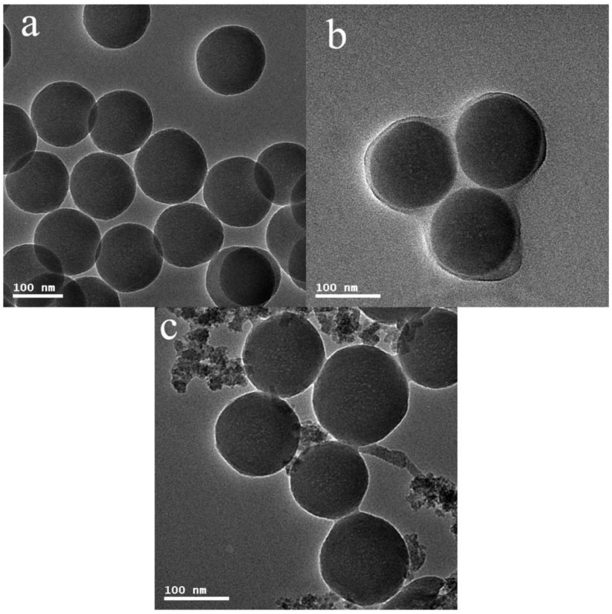


Fig. 2 (a) A TEM image of the original silica particles prepared by the Stöber method; the average diameter is about 150 nm. (b) A TEM image of PS coated silica particles. (c) A TEM image of silica particles after cleavage reaction.

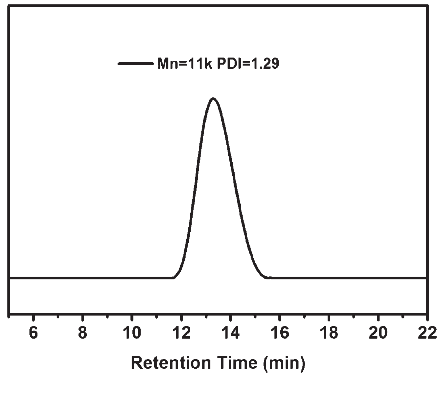


Fig. 4 GPC trace of PS cleaved from the surface of PS-coated silica particles.

presented in Fig. 1 (curve e). TGA results show that the weight loss of the silica particles after cleavage reaction is about 16.5 wt%, which is smaller than the silica particles before cleavage reaction (curve d in Fig. 1). After the reaction, the grafting density of PS decreased from 1.08 to 0.58 chains nm^{-2}. This result means not all PS chains are cleaved from the silica surface due to the dynamic property of the imine bond in the acidic environment.[41] A TEM image of the silica particles after cleavage of PS is shown in Fig. 2 (c). In comparison to the PS-coated silica particles, the disappearance of the polymer layers on silica particles indicates the cleavage of PS chains from the silica surface and the decrease of the grafting density of PS brushes. In the meanwhile, PS phases cleaved from the silica particles are observed on the TEM image. The DLS result also supports the successful cleavage of PS from the silica particles. As shown in Fig. 3 (curve c), after the cleavage reaction, the size distribution of silica particles is shifted to a smaller size range. The change in size is attributed to the cleavage of PS from the silica surface.

Dynamic covalent chemistry is based on reversible covalent bonds, and the formation and dissociation of the bonds can be controlled through environmental change, so dynamic covalent chemistry not only provides a method to prepare cleavable polymer brushes on silica particles but also provides a method to prepare surface-labeled functional particles. The amino groups produced after dissociation of imine groups can be used in the formation of new imine bonds, and new functional groups or polymer chains can be grafted to the surface of the silica particles. In this research 1-pyrenecarboxaldehyde was added into the dispersion of PS-coated silica particles in the presence of TFA, and pyrene-labeled silica particles were prepared. On the surface of particles both PS chains and pyrenyl groups were grafted to the silica particles *via* imine bonds (Scheme 1).

The UV-vis absorption (spectrum a) and fluorescence emission spectrum (spectrum b) of the pyrene-labeled silica particles are shown in Fig. 5. In the UV-vis spectrum, the absorptions of PS and pyrenyl groups are observed. The amount of pyrenyl groups on silica particles was determined quantitatively by comparing the absorption at 343 nm for the pyrene-labeled silica particles to a standard absorption curve made from known amounts of 1-pyrenecarboxaldehyde in THF (Fig. S4, ESI†). Based on the UV-vis results, the content of pyrenyl groups on silica particles was calculated to be about 0.05 mmol g^{-1}. The emission spectrum of the silica particles shows the typical monomer emission peaks at 377, 383, 388, 397 and 418 nm. The UV-vis and fluorescence results demonstrated that the fluorescence-labeled silica particles were successfully prepared by the dynamic exchange reaction between polymer-modified silica particles and 1-pyrenecarboxaldehyde.

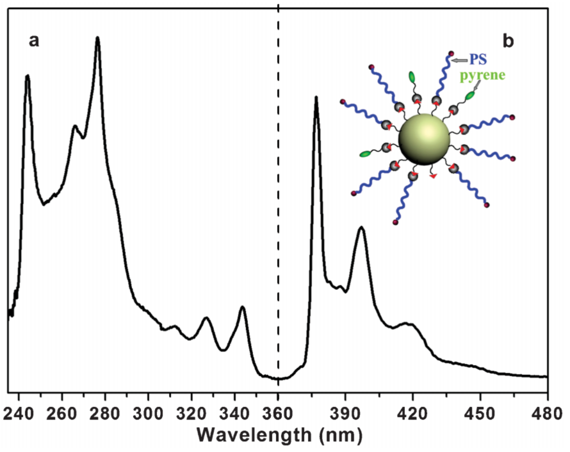


Fig. 5 The UV-vis absorption (a) and fluorescence emission spectrum (b) of the silica particles after dynamic reaction with 1-pyrenecarboxaldehyde in THF. Excitation wavelength was set at 343 nm.

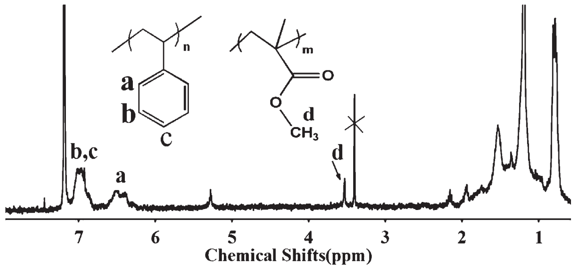


Fig. 6 ^{1}H NMR spectrum of PS and f-PMMA mixed polymer brushes cleaved from silica particles. The spectrum was recorded in $CDCl_3$.

Silica particles with mixed polymer brushes were also prepared by dynamic exchange reaction between PS-coated silica particle and aldehyde-terminated f-PMMA. f-PMMA was synthesized by ATRP of MMA and FMA by using FPBIB as initiator.[42] The mixed polymer brushes were cleaved by TFA in THF solution, and purified by precipitating in methanol. Fig. 6 shows the ^{1}H NMR spectrum of the mixed polymer brushes dissolved in deuterated chloroform. On the spectrum, the signals representing the phenyl protons on PS chains and methyl protons on f-PMMA were observed, which demonstrated the successful synthesis of mixed polymer brushes on silica particles. TGA results indicated that in comparison to PS-coated silica particles, the weight loss of the silica particles with mixed polymer brushes increased by about 5.6 wt% (curve f in Fig. 1).

Fluorescein is a fluorophore commonly used as a fluorescent tracer for many applications. After grafting of fluorescein-labeled PMMA onto the surface of silica particles, the silica particles will be able to be tracked by using a fluorescence microscope. Because the average size of the silica paerticles is about 150 nm, it is impossible to observe the isolated particles on a fluorescence microscope, however, it is possible to observe aggregation or self-assembly strutures of the particles. In a mixture of water and oil, solid particles are able to self-assemble at the liquid–liquid interface and a Pickering emulsion is prepared. In this research, silica particles with PS and f-PMMA mixed polymer brushes were dispersed in 1 mL of decalin by sonication, and then 0.1 mL of distilled water was added into the dispersion forming a stable Pickering emulsion. In the Pickering emulsion, decalin forms the continuous phase, and water forms the discontinuous phase. The water droplets are

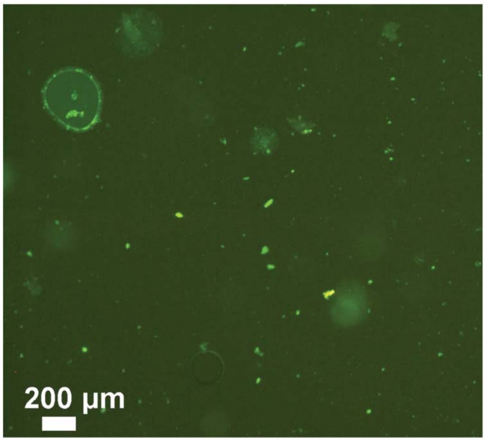


Fig. 7 A fluorescence microscope image of a Pickering emulsion prepared by dispersing silica particles with PS and f-PMMA mixed polymer brushes into a mixture of water and decalin. The volume ratio of water to decalin is about 1 : 10.

stabilized by silica particles. Fig. 7 shows a fluorescence image of water droplets in Pickering emulsion recorded on a fluorescence microscope. In the image, water droplets stabilized by silica particles can be observed on a fluorescence microscope. Besides water droplets, aggregation of silica particles can also be observed in the image. The fluorescence microscopy results offered direct evidence for the successful grafting of fluorescein-labeled PMMA onto the surfaces of silica particles by the dynamic exchange reaction.

Conclusions

In summary, we have demonstrated a practical route for the synthesis of dynamic polymer brushes, which permits post polymerization analysis. Based on the the dynamic properties of imine bonds, pyrene-labeled silica particles and silica particles with mixed polymer brushes were prepared by dynamic exchange reaction. This research offers a straightforward method to characterize polymer brushes on the surface of solid substrates and prepare multi-functional silica particles with diverse properties.

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