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Jiucun Chen[a]; Jiming Xiang[a]; Zhengwang Cai[b]; Huang Yong[b]; Haodong Wang[a]; Lihui Zhang[a]; Wenqian Luo[a]; Hu Min[a]
[a] Department of Chemistry and Chemical Engineering, Ankang University, Ankang, China [b] Department of Agriculture and Life Sciences, Ankang University, Ankang, China

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Synthesis of Hydrophobic Polymer Brushes on Silica Nanoparticles Via the Combination of Surface-Initiated ATRP, ROP and Click Chemistry

JIUCUN CHEN[1,*], JIMING XIANG[1], ZHENGWANG CAI[2], HUANG YONG[2], HAODONG WANG[1], LIHUI ZHANG[1], WENQIAN LUO[1] and HU MIN[1]

[1] *Department of Chemistry and Chemical Engineering, Ankang University, Ankang, China*
[2] *Department of Agriculture and Life Sciences, Ankang University, Ankang, China*

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A fascinating nanoobject, hydrophobic polymer brushes with a hard core of silica nanoparticles and a relatively soft shell of polystyrene-block-poly(ε-caprolactone) (PS-b-PCL), was easily constructed by surface-initiated atom transfer radical polymerization (ATRP) of styrene, ring-opening polymerization (ROP) of ε-caprolactone and click reaction. The structure and morphology of the as-prepared hybrid nanomaterials were characterized and confirmed by FTIR, ^{1}H-NMR, TGA and TEM. We believe that the breakthrough associated with formation of such a complex nanoobject would open a door for the fabrication of novel functional nanomaterials or nanodevices with designable structure and tailor-made properties.

Keywords: Surface-initiated polymerization, ROP, click chemistry, surface modification

1 Introduction

The surface functionalizations of nanomaterials by grafting of polymer are expected to play important roles in the designing of novel organic/inorganic nanocomposite materials (1–3). Polymer grafting techniques provide a very versatile tool to tailor the surface of particles and thus the interfaces between particles and the matrix polymers. These techniques provide control over the type of polymer to be grafted onto the particle surface, surface densities, and chain lengths at the nanometer scale (4). The techniques of covalently grafting polymer chains onto nanomaterials can be categorized into "grafting to" and "grafting from".

The so-called "grafting to" approach has advantages and disadvantages. This approach is experimentally simple and provides better control of the polymerization, but it usually suffers from a lower grafting density (5). In contrast, the "grafting from" technique involves growth of polymer chains from solid surfaces by means of surface-initiated polymerization (SIP) of monomers via various polymerization techniques including atom transfer radical polymerization (ATRP) (6), nitroxide-mediated radical polymerization (NMRP) (7), reversible addition-fragmentation chain-transfer (RAFT) polymerization (8), ring-opening polymerization (ROP) (9), ring-opening metathesis polymerization (ROMP) (10), and anionic polymerization (11). Since the existing grafted polymers will not hinder the diffusion of the small-sized monomers, significantly higher graft densities can be achieved with this technique. On the other hand, the functional groups on the grafted polymers introduced by both approaches are only limited to several types such as hydroxyl, amino, and carboxyl, which is far from complex requirements for functionalization of solid surfaces (12). Hence, to find a novel approach that retains all the integrative advantages while overcoming the disadvantages is urgently needed.

Hence, we present a novel strategy for modifying surfaces with multiple kinds of polymers by a combination of "grafting from" and "grafting to" strategies. Herein, as a typical example, we adopt ATRP and click chemistry as polymerization and coupling tools, respectively, to functionalize the surfaces of silica nanoparticles to demonstrate how the route works.

Recently, copper (I)-catalyzed azide-alkyne 1,3-dipolar Huisgen cycloaddition (CuAAC) has received much attention in the synthesis of a range of functionalized polymers due to high efficiency, high tolerance of functional groups and solvents, as well as moderate reaction temperatures (13, 14). The practicality and versatility of CuAAC

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*Address correspondence to: Jiucun Chen, Department of Chemistry and Chemical Engineering, Ankang University, Ankang 725000, China. Tel: +86-915-3261415; Fax: +86-915-3261415; E-mail: chenjiucun@163.com

led to its inclusion in the class of "click chemistry" as coined by Sharpless et al. (15). The use of click reaction has been extremely fruitful when combined with controlled radical polymerization (CRP) techniques, such as ATRP (16, 17), NMP (18, 19), and RAFT (20, 21). The high yield and specificity of CuAAC allow the quantitative introduction of various functional groups onto polymer backbones with highly defined structures in many cases. So far, there is little literature are reporting on the surface modification of nanoparticles via click chemistry. However, Meldal and coworkers found that click coupling worked well on solid supports (22). Zheng and coworkers synthesized novel β-cyclodextrin covalently modified single-walled carbon nanotubes via a click coupling reaction (23). Brittain and coworker have reported that combined use of click chemistry and RAFT can be used for surface modification by the "grafting to" approach and a click reaction was used to attach polymers onto the surface which produced relatively high grafting density (24). Tasdelen and coworkers prepared polytetrahydrofuran /montmorillonite nanocomposites by two routes: *in situ* cationic ring opening polymerization and a method involving "click" chemistry (25). Moreover, the nanocomposites prepared by the "click" chemistry approach appeared to be thermally more stable than those prepared by *in situ* polymerization and the "click" chemistry method also provided better exfoliation. In our previous work, we reported a facile strategy to prepare chain-end functionality of the grafted polymer chains for surface modification of nanoparticles with functionalized groups through a combination of ATRP and click chemistry (16). Very recently, we reported a facile and useful method to synthesize linear poly(ε-caprolactone) @ attapulgite nanocomposites with well-defined structures by a combination of controlled ring-opening polymerization (CROP) and click chemistry (26).

In this work, ring-opening polymerization (ROP) of ε-caprolactone has been performed to produce alkyne-functionalized poly(ε-caprolactone) and the obtained polymers were subsequently anchored to azido-terminated PSt on the silica nanoparticle surface by a "click" reaction. In principle, this approach can be extended to the combination of azide-modified hydrophilic or hydrophobic polymer brushes on the nanoparticle surface with any other alkyne containing polymers.

2 Experimental

2.1 Materials

ε-Caprolactone (ε-CL, Aldrich) and toluene were dried over calcium hydride for 48 h at room temperature, followed by distillation under reduced pressure just before use. Copper(I) bromide (Shanghai Chemical Reagent Co., A. R. grade) was washed with glacial acetic acid in order to remove any soluble oxidized species, filtered, washed with ethanol, and dried. γ-Aminopropyltriethoxysilane (APTES) (Gaizhou Chemical Industrial Co.) was used as received. Styrene (St) (A.R., Shanghai Chemical Reagent Plant) was washed with 5% NaOH and ion-free water, stirred over CaH_2 overnight, and distilled before use. Tetrahydrofuran (THF) was refluxed over sodium and distilled twice before use. Dimethylformamide (DMF) was dried with magnesium sulfate and distilled under reduced pressure. Triethylamine (A.R., 99%) was dried over barium oxide for 48 h at r.t. and distilled under reduced pressure. Propargyl alcohol, N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA),

2-bromoisobutyryl bromide (BIBB), stannous octoate ($Sn(Oct)_2$), sodium azide were purchased from Aladdin Reagent Co. with the highest purity and used as received without further purification. All other solvents and chemicals were used as supplied without further purification.

2.2 Instruments and Measurements

FTIR spectroscopy patterns were performed on a Dig lab FTS 3000 instrument. The polymers cleaved from the silica particles were dissolved in deuterated chloroform and then characterized with ^{1}H-NMR using a Varian UNITY INOVA-500 FT-NMR spectrometer. The average molecular weights and polydispersity indices of all the samples were measured with a GPC system equipped with a Waters 515 high-performance-liquid-chromatography pump, three Waters Styragel columns (HT2, HT3, and HT4), a Rheodyne 7725i sampler, and a Waters 2414 refractive-index (RI) detector. Narrow PS standards were used to calibrate the GPC system. THF was used as the eluent at a flow rate of 1 mL/min at 35°C. The microstructure of these hybrid nanocomposites was imaged using Hitachi H-600 equipment, TEM samples of particles were prepared by casting one drop of a dilute colloid solution onto a carbon-coated copper grid. Thermogravimetric analysis (TGA) was performed in nitrogen at a heating rate of 10°C/min on a Perkin-Elmer instrument TG/DTA 6300. The polymer grafting (%) (PG, mass ratio of the grafted polymer to the SiO_2 nanoparticles) was determined by TGA and was calculated by Equation 1 (27):

$$\text{Polymer grafting (\%)} = \frac{\text{Organic component/g}}{\text{Bare SiO}_2\text{/g}} \times 100 \quad (1)$$

Where the mass of the organic component was calculated from the TGA weight loss between 150 and 700°C. Weight loss in this regime corresponds to the decomposition of PSt. The mass of bare SiO_2 was assumed to be the retained weight after this decomposition, as measured by TGA.

2.3 Silica Preparation

Spherical submicron-sized SiO_2 particles were prepared according to the method of Stöber et al. (28). The synthesis of SiO_2 was initiated by rapid addition of TEOS to a stirring solution of ethanol (EtOH), aqueous ammonium hydroxide (NH_3) and deionized water. The concentrations of TEOS and NH_3 were fixed at 0.2 M, and the H_2O concentration at 5 M. Stirring at ambient temperature was continued for 48 h to produce the opalescent SiO_2 dispersion herein referred to as the alcosol. The solid content i.e., SiO_2 %, w/v, was established by accurately measuring known volumes of the alcosol and evaporating to dryness *in vacuo* (1×10^{-3} Torr), thus removing all traces of reagents and solvents. The remainder of the alcosol was treated further in the surface modification process.

2.4 Preparation of ATRP Initiator-Immobilized Silica Particles (SiO_2-Br)

In situ surface modification of the SiO_2 particles was performed by an addition of excess silane coupling agent, APTES (10 mmol/g SiO_2 directly into the alcosol, with continued stirring for 24 h at ambient temperature. The APTES -modified SiO_2 was purified by repeated centrifugation and washing with EtOH (6000 rpm for 20 min) to remove any excess NH_3 and APTES. The obtained powder, APTES–SiO_2 was air dried *in vacuo* (1×10^{-3} Torr) prior to being used in the polymer encapsulation process.

Initiator-immobilized silica particles were synthesized as follows: into a 100 mL dried round-bottom flask, 1 g APTES–SiO_2 was ultrasound dispersed in 50 mL chloroform for 10 min, then the mixture was cooled down to 0°C in an ice-water bath and 2 mL of triethylamine was added. A solution of 3 mL 2-bromoisobutyryl bromide and 5 mL chloroform was added dropwise over 20 min and the mixture was stirred at room temperature for 24 h. The product was washed by centrifugations/redispersions for three times in ethanol and dried in vacuum at room temperature for 24 h. The elemental analysis results of C and N indicated that about 0.503 mmol initiator groups per gram of SiO_2–Br were immobilized.

2.5 Graft Polymerization of PS from Initiator-Immobilized Silica Particles (SiO_2-PS-Br)

0.8 g of SiO_2-Br, 0.072 g (0.50 mmol) of CuBr, 0.087 g (0.50 mmol) of PMDETA and 50 mL of dry toluene were placed in a dry 100 mL flask. The flask was evacuated and thrice filled with Ar gas. After this procedure, 5.73 ml (50 mmol) of styrene was injected into the flask using a syringe. The flask was immersed in an oil bath at 110°C and the contents were stirred for 2 h. After the polymerization, the PS-coated SiO_2 sample (SiO_2-PS-Br) was separated by centrifugation, then the pruduct was extracted for 24 h to remove the physical adsorption polymer from the surface of silica. SiO_2-PS-Br sample was obtained and drying overnight under vacuum.

2.6 Preparation of Aido-PS Modified Silica Particles (SiO_2-PS-N_3)

In a typical reaction, 0.60 g of the PS-coated silica particles was dispersed in 25 mL of DMF. 0.20 g of sodium azide was added, and the reaction mixture was stirred at 80°C for 16 h. After cooling to room temperature and the particles were recovered by centrifugation at 3000 rpm for 30 min. Purification of SiO_2-PS-N_3 was carried out using three rounds of centrifugation interspersed with redispersion and washing with deionized water, and finally dried in vacuum.

2.7 Synthesis of Propargyl-Terminated PCL by ROP

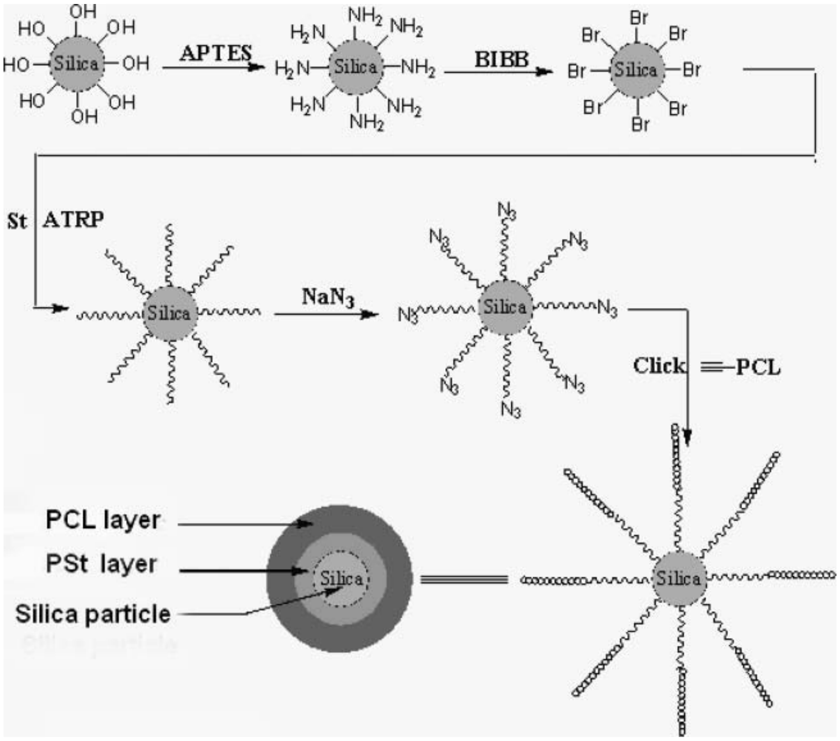
The propargyl-terminated PCL was prepared by ring-opening polymerization of ε-CL in toluene with $Sn(Oct)_2$ as a catalyst and propargyl alcohol as an initiator as the reported procedure (29). The polymerization was performed in a glovebox with a water content of less than 0.1 ppm. In a typical procedure, propargyl alcohol (0.070 g, 1.25 mmol) and ε-CL (14 g, 125 mmol) were added to freshly dried toluene (50 mL) in a flask, and then $Sn(Oct)_2$ (0.254 g, 0.63 mmol) was added and the flask was then placed in a thermostated oil bath at 100°C for 6 h. After the polymerization, the mixture was cooled to room temperature, precipitated into an excess amount of methanol, filtered off, and dried at room temperature in a vacuum oven for 48 h ($Mn = 9300$, $Mw/Mn = 1.1$).

2.8 "Click" Coupling Reaction Between Propargyl-Terminated PCL and Azido-PS Modified Silica Particles (SiO_2-PS-b-PCL)

Azido-PS modified silica particles(0.5 g), propargyl-terminated PCL (2.88 g, 0.31 mmol), and THF (20 mL) were added in a round-bottomed flask and stirred. Following a brief sonication, solutions of 0.005 g (0.031 mmol) of $CuSO_4$ in 0.5 mL of water and 0.022 g (0.11 mmol) of sodium ascorbate in 1 mL of water were added, and the mixture was heated at 70°C overnight. The particles were recovered by centrifugation at 3000 rpm for 30 min. Then they are redispersed in water and the mixture was centrifuged; this cycle was repeated four times. Finally, the particles were placed in a Soxhlet extractor and extracted with THF for 18 h and dried in vacuum.

2.9 Cleavage of the Polymer Brushes from the Silica Particle Surfaces

Generally phase transfer agent Aliquat 336 was required to transfer the HF in the aqueous phase to the organic phase to efficiently etch the silica of polymer grafted silica particles (30). In this work, a slightly modified procedure was used to cleave the polymer from the silica nanoparticles. In the modified procedure, a relatively large amount of THF was used as the cosolvent for both the polymer grafted silica



Sch. 1. Illustration of the synthesis route of hydrophobic polymer brushes on silica nanoparticles.

and HF(aq) solution. Phase transfer agent Aliquat 336 was not used since it has a GPC molecular weight of ∼1000 which will overlap with the low molecular weight polymer fraction, thereby complicating the molecular weight and polydispersity calculations.

In a typical experiment, polystyrene grafted silica particles (50 mg) were dissolved in THF (3 mL). HF (0.2 mL, 49% in aq) was added, and the solution was allowed to stir at room temperature overnight (Caution: HF is highly toxic and great care must be taken when handling). The solution was poured into a PTFE Petri dish and allowed to stand in a fume hood overnight to evaporate the volatiles. The recovered PSt was then subjected to GPC analyses. Similar procedures were used to recover PS-N_3 and PS-b-PCL.

3 Results and Discussion

The general synthesis route for growing hydrophobic polymer brushes on SiO_2 via ATRP, ROP and click chemistry was described in Scheme 1. For this, first, the initiating sites (SiO_2-Br) of ATRP were first introduced onto the surface of SiO_2, followed by *in situ* ATRP of styrene and then the terminal bromides of PSt grafted SiO_2 were substituted with azido groups. As the second step, the azido-terminated PSt on the silica particles were reacted with propargyl-terminated PCL via click reaction.

The ROP of ε-CL was performed in the presence of the catalyst $Sn(Oct)_2$ and an initiator propargyl alcohol in toluene at 100°C. The structural characteristics of the obtained PCL has been determined by ^{1}H-NMR and GPC analysis. The characteristic signals of $HC{\equiv}C{-}$, $HC{\equiv}C{-}CH_2{-}$, and $-CH_2{-}OH$ appear at 2.45, 4.70, and 3.65 ppm in the ^{1}H-NMR spectrum of PCL (Fig. 1a), respectively. This verified that the ROP of ε-CL was successful. Furthermore, by GPC analysis, the PCL precursor had a low polydispersity index (Fig. 1b). So, the propargyl-terminated PCL can be prepared by the ROP of ε-CL initiated with propargyl alcohol and in the presence of the catalyst $Sn(Oct)_2$.

Figure 2 shows spectra obtained by FTIR spectroscopy for silica particles, SiO_2-PS-Br, SiO_2-PS-N_3, and SiO_2-PS-b-PCL. Chidsey and coworkers used quantitative FTIR spectroscopy in their detailed investigation of the catalyzed click reaction on gold electrodes (31). Williams and coworkers recently chose to quantitatively assess the azide/triazole surface coverage on the particles over the course of the cycloaddition reaction using FTIR spectroscopy, which is highly sensitive and able to examine molecules that remain attached to the particle surface (32). As shown in Figure 2, FTIR spectroscopy provided clear evidence for the step-by-step surface modification.Figure 2b shows a IR spectrum of PSt-grafted hybrid nanocomposite, in which the absorption bands assigned to C-H stretch (ca. 3025 cm^{-1}) from the aromatic rings, C-H stretch (ca. 2900 cm^1 from the alkyl portions, and C=C stretch (ca. 1634 cm^{-1}) are clearly

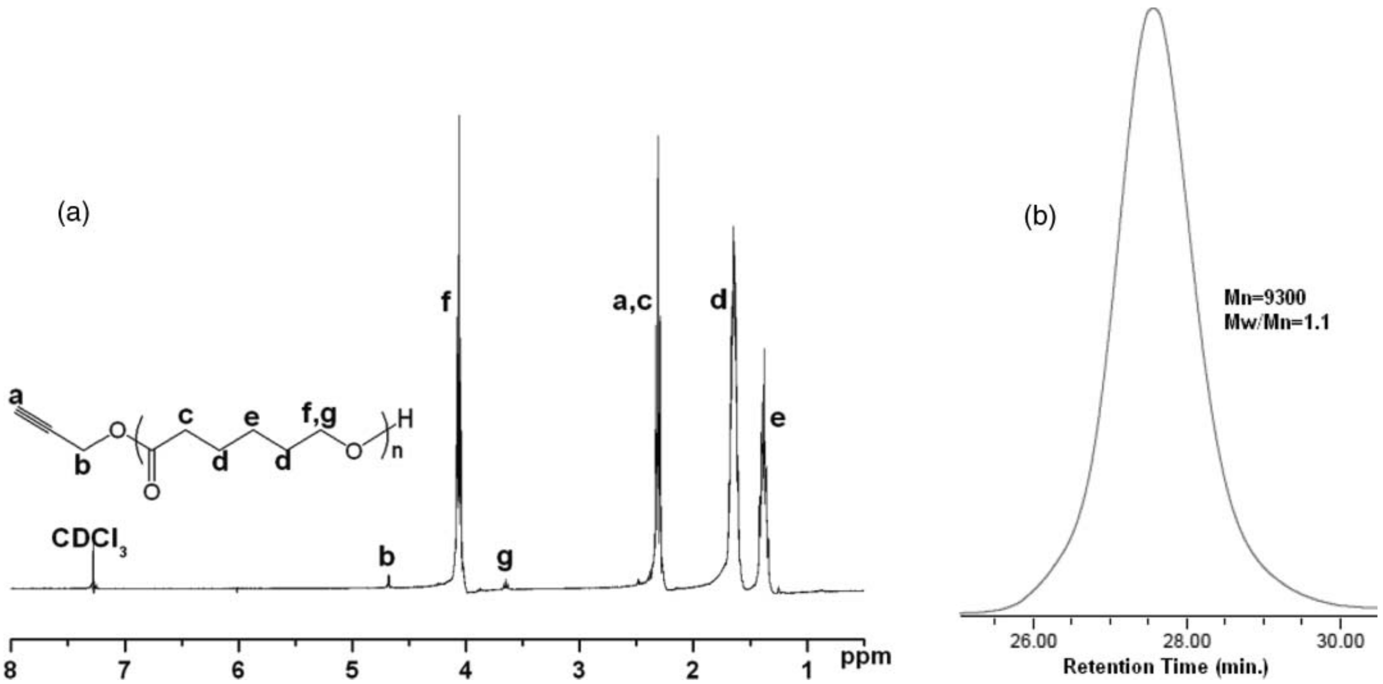


Fig. 1. (a) ^{1}H-NMR spectra and (b) GPC trace of the propargyl-terminated PCL.

observed. The adsorption peak at 1108 cm^{-1} results from S–O stretching of silica When the bromide was substituted with azide by reaction with sodium azide, an azide group was verified by an IR adsorption at 2100 cm^{-1} (Fig. 2c). As shown in Figure 2d, comparing to SiO_2-PS-N_3, the peak at 2100 cm^{-1} from–N_3 almost disappears while the peaks at 3300 c^{-1} and 1731 cm^{-1} from –OH and C=O groups appear in the IR curve of SiO_2-g-(PSt-b-PCL), indicating that the cycloaddition reaction was successful.

^{1}H-NMR spectroscopy also proved the success of cycloaddition reaction and the structure of polymers. After the cycloaddition reaction, new peaks from the 1,2,3-triazole and other functional groups from PCL appear. All the peaks in the spectrum can be ascribed to the protons labeled on the structure as shown in Figure 3.

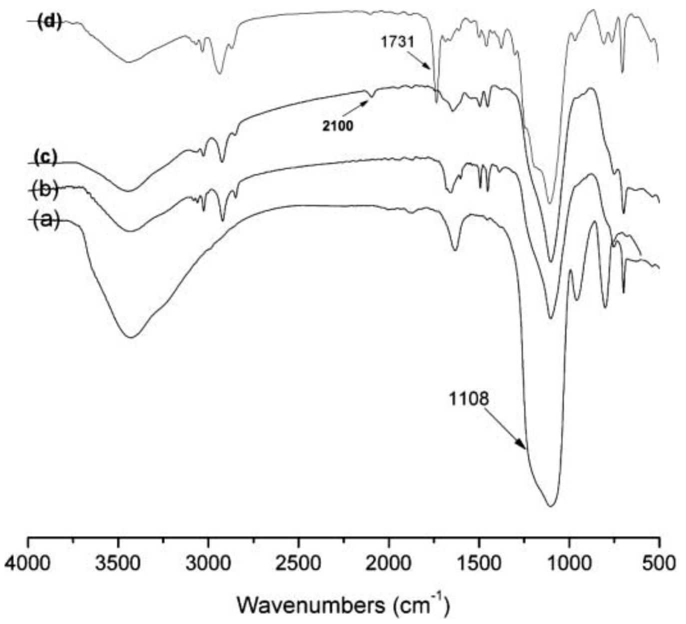


Fig. 2. FTIR spectra of (a) SiO_2, (b) SiO_2-PS-Br, (c) SiO_2-PS-N_3, and (d) SiO_2-PS-b-PCL.

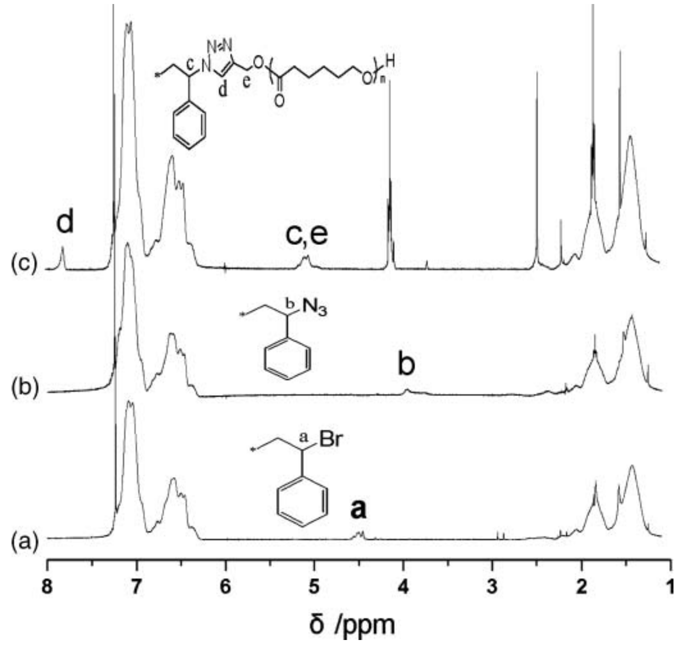


Fig. 3. ^{1}H-NMR spectra of (a) SiO_2-PS-Br, (b) SiO_2-PS-N_3, and (c) SiO_2-PS-b-PCL.

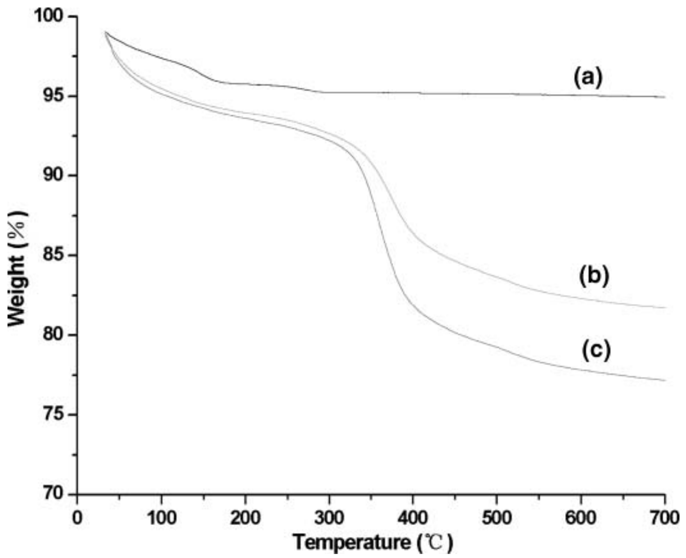


Fig. 4. TGA curves of (a) SiO_2, (b) SiO_2-PS-Br, and (c) SiO_2-PS-b-PCL.

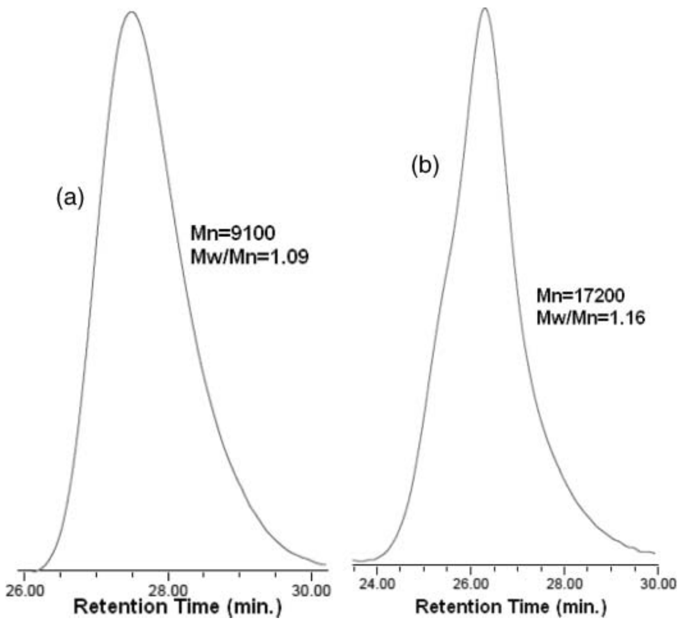


Fig. 5. GPC traces of (a) PSt and (b) PS-b-PCL.

The thermogravimetric analysis (TGA) for bare silica, SiO_2-PS and SiO_2-g- (PSt -b- PCL) is shown in Figure 4. The weight loss below 200°C , due to the physisorbed water and residual organic solvent, was 7.4% for bare SiO_2 (Fig. 4a). After the polymerization, the reaction mixture was diluted with toluene, and the particles were extracted thoroughly with toluene and then filtered to remove soluble ungrafted polymers. Washing was done until no polymer was found in the filtrate. The weight fractions of organic moieties of the modified SiO_2 particles were measured with TGA, and the obtained values are 11.6 wt% (Fig. 4b) and 15.7 wt% (Fig. 4c) for modified SiO_2-PS-N_3 and the click-modified SiO_2 nanoparticles, respectively. And, the percentage of grafting (PG) was found to be 24.1% calculated from Equation 1, according to the TGA analysis.

In order to understand the growth characteristics of the surface-initiated polymerizations via ATRP and click reaction techniques and the molecular parameters of the grafted polymers, the polymers were cleaved from the surfaces at their points of attachment by treatment with HF solution. ATRP of PSt was carried out using SiO_2–Br as an initiator in the presence of CuBr/PMDETA as a catalyst in bulk at 110°C for 2 h. As described in the literature, the polymerization was stopped at rather low monomer conversion in order to obtain a polymer with a high degree of terminal halogen functionality (33, 34). Previous reports indicated that at low monomer conversions (conversion $< 40\%$), the bromine end-functionality of PSt prepared with ATRP was over 90% (34, 35). The polystyrene was degrafted from the silica and GPC was used to calculate molecular weight and polydispersity (Fig. 5a). Monomer conversion was 24%. Then the bromide end-functionality of PSt was quantitatively converted to azide end group. By GPC analysis, the synthesis of the SiO_2-PSt-N_3 precursors involved no molecular weight reduction because narrow symmetrical signals were observed at the same position as the starting SiO_2-PSt-Br precursors. Finally, using click chemistry strategy, an azide end-functionalized SiO_2-PSt-N_3 and propargyl-terminated PCL was reacted to give constructing hydrophobic polymer brushes on the surfaces of silica nanoparticles. The well-defined hydrophobic polymer brushes was also cleaved from the silica particles by the same procedure as the PSt. The cleaved polymer had a number-average molecular weight of 17200 and a PDI of 1.16 (Fig. 5b).

The morphologies of bare silica particles and functional silica particles modified by ATRP and click chemistry were investigated using TEM. Dispersions of colloidal silica were prepared via the Stöber method with a size of approximately 100 nm as evidenced by TEM (Fig. 6a). The PSt–SiO_2 material was used further in the preparation of silica–core hybrids. We selected a short polymerization time since our objective was to prepare thinly coated SiO_2 particles. TEM micrographs showed that the PSt–SiO_2 particles were encapsulated during the polymerization of St with the evident formation of a thin PSt coating, thus yielding SiO_2 core–shell PSt particles (Fig. 6b). After reaction of SiO_2-PSt-N_3 with propargyl-terminated PCL, TEM images were also taken to examine dispersion at a particle scale. As shown in Fig. 6c, in SiO_2-g-(PSt-b-PCL) particles, silica particles are completely encapsulated with the polymers, and most of the hybrid particles appear to be roughly spherically symmetric, although several of the larger particles are seen to form aggregation due to hydrogen bonding.

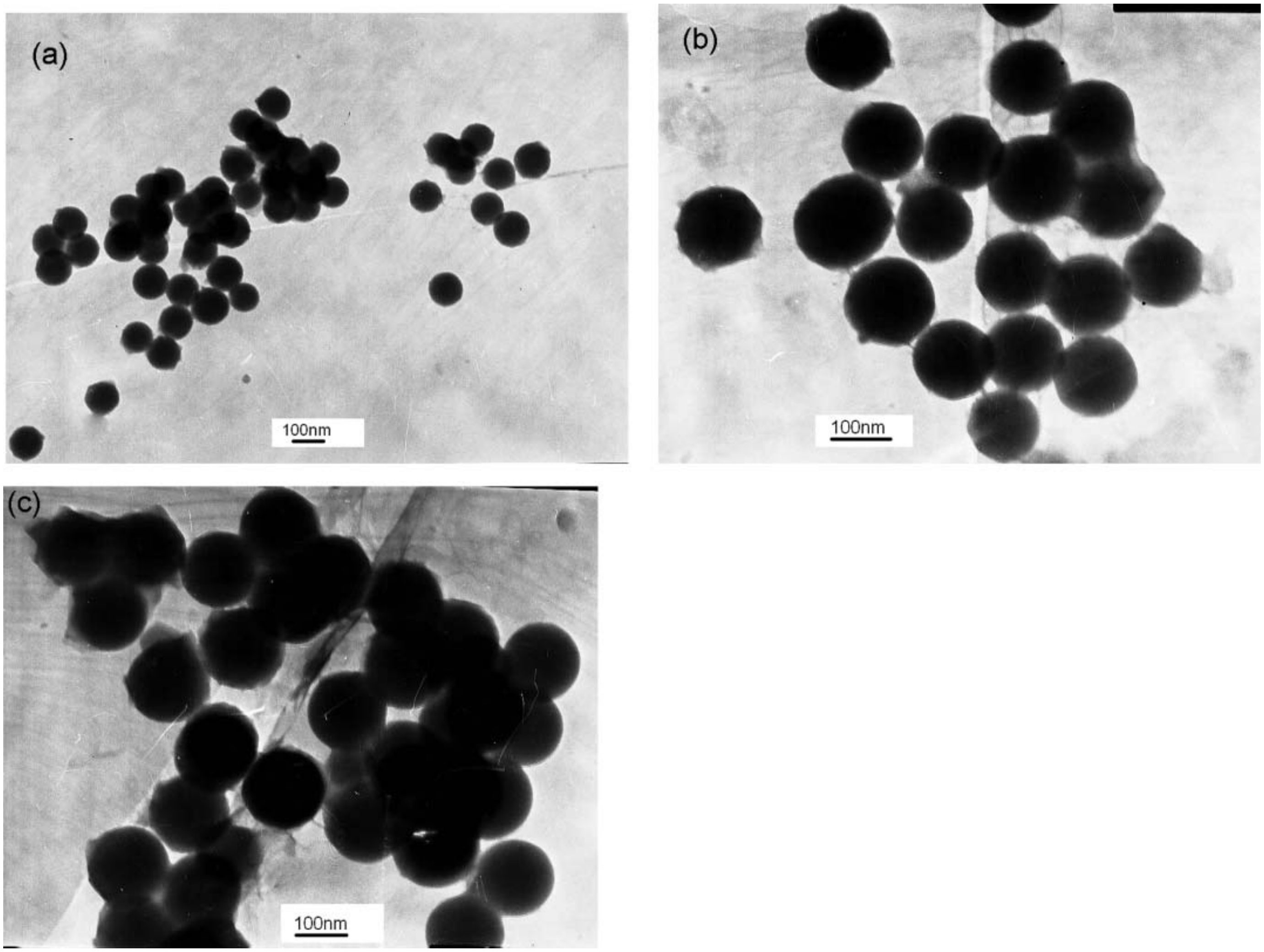


Fig. 6. TEM micrographs of (a) Stöber silica spheres, (b) SiO_2-PS, and (c) SiO_2-PS-b-PCL.

4 Conclusions

Hydrophobic block polymer brushes on silica nanoparticles were successfully prepared via surface-initiated atom transfer radical polymerization of styrene, ring-opening polymerization of ε-caprolactone and click reaction. The surface of the silica nanoparticles was modified with polystyrene brushes via the "grafting from" approach. The terminal bromides of PSt-grafted silica nanoparticles were then substituted with azido groups. The propargyl-terminated PCLs were subsequently anchored to azido-terminated PSt on the silica nanoparticle surface by copper (I)-catalyzed azide-alkyne 1,3-dipolar Huisgen cycloaddition. There is no doubt that the same protocol as that in the case of silica nanoparticles can be easily extended to modify other topological (e.g., linear, spherical, and flat) surfaces.

Acknowledgments

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