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# Grafting polystyrene onto silica nanoparticles via RAFT polymerization

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## Abstract

Reversible addition–fragmentation chain transfer (RAFT) polymerization was used to graft polystyrene (PS) onto silica nanoparticles. A novel route was used to prepare the RAFT agent, 2-butyric acid dithiobenzoate (BDB) by substitution of dithiobenzoate magnesium bromide with sodium 2-bromobutyrate under alkali condition in aqueous solution. Epoxy groups were covalently attached to silica nanoparticles by condensation reaction of 3-glycidyloxypropyltrimethoxysilane (GPS) with the hydroxyl on the silica particle surface. RAFT agent functionalized nanoparticles were produced by ring-open reaction of the epoxy group with the carboxyl group of BDB. Then, PS chains with controlled molecular weights and narrow polydispersities (less than 1.1) were grown from the RAFT agent anchored nanoparticle surface. FT-IR, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) results showed that PS chains grew from silica particles by surface RAFT polymerization.

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*Keywords:* RAFT polymerization; Silica; Surface initiation polymerization

## 1. Introduction

Exploitation of the fascinating properties of inorganic nanoparticles, such as optical, magnetic and electronic properties requires the particles to be dispersed homogeneously. The best way to avoid aggregation is to graft polymer chains onto the particles covalently, forming organic–inorganic hybrid materials. Those hybrid materials composed of inorganic core and organic polymer shell have intrigued interest for the combination of the properties of both the inorganic particles and the polymer such as solubility and easy processing [1–5].

Generally, chemically grafting techniques include the ‘‘grafting to’’ and ‘‘grafting from’’ methods. ‘‘Grafting to’’ involves the reaction of appropriate end-capped functional groups or side pendant groups in the polymers with the particles. This method is simple, but the graft density is fairly low because the diffusion of polymer chains to the surface of the particles is hindered sterically [6,7]. This limitation can be circumvented by the ‘‘grafting from’’ method, in which initiating groups are anchored onto the surface of the particles followed by in situ polymerization. Because the chain radicals are consistently on the surface of the grafted polymers, and the diffusion of the smaller monomers is easier relatively, the graft density is determined by density of the initiating groups, and generally, higher graft density can be achieved [8,9]. A variety of polymerization techniques, including conventional free radical [10], cationic [11], anionic [12], ring-opening [13–15] and controlled radical polymerizations (CRPs) have been used to graft the polymers onto the surface of different inorganic particles. Among those different methods, CRPs reveal advantages because they can control the architecture, molecular weight and molecular weight distribution in comparison with the conventional radical polymerization and they are simple on operation procedure and versatile on monomers in comparison with the ionic polymerizations.

Among the CRPs, nitroxide-mediated polymerization (NMP) and atom transfer radical polymerization (ATRP) have been used to graft polymers from solid surface. There are a large

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number of reports on grafting the polymers onto the solid surface by NMP and ATRP [16−23]. Comparing to the NMP and ATRP, the reversible addition−fragmentation chain transfer (RAFT) polymerization displays the advantage on compatibility with a wide range of monomers including functional monomers and free of transition metal ion contamination. Up to date, RAFT polymerization has been successfully used to graft various polymer chains on different solid surface. Dithiobenzoate was anchored to the multiwalled carbon nanotubes (MWNTs), and following grafted polymers on the MWNTs by RAFT polymerization [23,24]. Skaff et al. applied RAFT polymerization in the preparation of polymer-grafted CdSe nanoparticles using trithiocarbonate functionalized CdSe particles as RAFT agent [25]. RAFT polymerization was also used to modified surface of gold nanoparticle [26,27], cotton [28], cellulose [29], and silica wafer [30,31]. As to silica particles, Li et al. reported the preparation of polymer-grafted silica nanoparticles by "graft from" method via RAFT polymerization by attaching R group of RAFT agent to silica particles. But the RAFT agent was synthesized in low yield via a multi-step process [32]. They reported another method to prepare the dithiobenzoate-anchored silica via the reaction of 2-mercaptothiazoline-activated 4-cyanopentanoic acid dithiobenzoate (CPDB) with amino-functionalized silica nanoparticles [33]. While Perrier et al. synthesized well-defined homopolymer and diblock copolymer grafted onto silica particles by Z-supported RAFT polymerization [34].

In this article, we report an easy and facile method for preparation of RAFT agent anchored silica nanoparticles, and then it was used in the RAFT polymerization of St for synthesis of PS grafted silica nanoparticles. The kinetics and graft efficiency were investigated.

## 2. Experimental section

### 2.1. Materials

All reagents were of analytical grade and purchased from Shanghai Chemical Reagent Co. Carbon disulfide was dried with calcium chloride, and then distilled. Hexane was dried with calcium chloride and distilled before use. Styrene (St) was refluxed with calcium hydride overnight and distilled under reduced pressure. Tetrahydrofuran (THF) was distilled from a purple sodium ketyl solution. Methyl isobutyl ketone (MIBK) was distilled after drying with calcium chloride. Tetraethoxysilane (TEOS) was distilled under reduced pressure before use. 3-Glycidyloxypropyltrimethoxysilane (GPS) and other reagents were used as received without further purification.

### 2.2. Characterizations

The molecular weight $M_n$ (GPC) and the molecular weight distribution ($M_w/M_n$) were measured on a Waters 2690 gel permeation chromatography (GPC) equipped with microstyragel columns ($10^3$, $10^4$, $10^5$ Å) and Waters RI detector at 30 °C. THF was used as eluent at a flow rate of 1.0 ml/min. Molecular weights were calculated based on monodispersed polystyrene standards. $^1$H NMR spectra were determined on a Bruker DMX-300 nuclear magnetic resonance (NMR) instrument with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. Thermal gravimetric analyses (TGA) were carried out on a PE TGA-7 instrument with a heating rate of 10 °C/min under nitrogen atmosphere. Transmission electron microscopy (TEM) images were made on a JEM-100SX microscopy operated at 100 kV. Particles hydrodynamics radius was determined on spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-$\hat{o}$ digital time correlation (ALV5000) and a cylindrical 22 mW Uniphase He−Ne laser ($\lambda_0 = 632$ nm) as the light source. Elemental analysis was performed on an Elementar Vario EL-III analyzer.

### 2.3. Synthesis of 2-butyric acid dithiobenzoate (BDB)

Into a 250 ml three-necked flask, magnesium turnings (2.4 g, 0.1 mol) were activated by purging purified nitrogen while stirring until the magnesium became gray-black. After diethyl ether (100 ml) was added, the bromobenzene (15.7 g, 0.1 mol) was dropped in 30 min. The mixture was warmed to 40 °C, and after magnesium turnings disappeared completely, carbon disulfide (9 ml) was added in 30 min. After maintaining at 40 °C for 2 h, ice water (100 ml) was added slowly in 15 min. The mixture was stirred for additional 2 h. After filtration, the aqueous phase was separated and washed with diethyl ether for three times (100 ml × 3), and then the aqueous solution was placed in a 500 ml flask in the ice-water bath. Into this solution, a solution of sodium 2-bromobutyrate (20.0 g, 0.1 mol) was added. The reaction was carried out at room temperature (5−12 °C) for 30 h. Concentrated hydrochloric acid (20 ml, 37 wt%) was added. The aqueous phase was extracted with carbon disulfide for three times (100 ml × 3). The extracts were combined; the organic liquid was washed with deionized water for five times (100 ml × 5), and then dried over anhydrous magnesium sulfate overnight. After removal of the solvent (about 250 ml), BDB was crystallized from the solvent as an orange powder (10.1 g, yield: 41%) (sometimes, the product was obtained as a red oil. In this case, 100 ml *n*-hexane was added in the crude product and BDB could be crystallized from the solution when it was frozen in refrigerator). $^1$H NMR (300 MHz, $\delta$, ppm, $CDCl_3$): 7.98−8.03 (d, 2H, *o*-Ar*H*), 7.52−7.59 (t, 1H, *p*-Ar*H*), 7.36−7.43 (*t*, 2H, *m*-Ar*H*), 4.73−4.79 (t, 1H, −C*H*COOH), 2.02−2.23 (m, 2H, $CH_3C\mathit{H}_2$−), 1.10−1.17 (t, 3H, $C\mathit{H}_3CH_2$−). $^{13}$C NMR (300 MHz, $\delta$, ppm, $CDCl_3$): 11.9 (−$\mathit{C}H_3$), 24.2 (−$\mathit{C}H_2$−), 55.1 (−*C*HCOOH), 127.1 (*o*-Ar*C*), 128.5 (*m*-Ar*C*), 132.9 (*p*-Ar*C*), 144.4 (ArC=S*C*), 177.1 (−*C*OOH), 225.9 (−C=S). FT-IR (KBr, $cm^{-1}$): $\nu = 3441$ (OH), 1703 (C=O), 1043 (C=S). Elemental analysis: calculation: C: 54.97%, H: 5.03%. Found: C: 54.55%, H: 4.90%.

### 2.4. Synthesis of silica nanoparticles

Into a 500 ml flask, ethanol (250 ml), deionized water (5 ml) and aqueous ammonia solution (15 ml, 28%) were added. After the mixture was stirred at 40 °C for 2 h, TEOS (14 ml) was added rapidly. The reaction mixture was stirred at 40 °C vigorously overnight. The resulting nanoparticles were isolated by centrifugation, and purified by redispersing in ethanol or water − separated by centrifugation for six cycles, one in ethanol, three in water and two in ethanol. The final products were dried at 110 °C in vacuum oven overnight.

### 2.5. *Preparation of RAFT agent anchored silica nanoparticles*

The GPS-grafted silica nanoparticles are prepared as follows. Silica particles (3.0 g) and freshly distilled MIBK (50 ml) were added into a three-necked flask. The mixture was ultrasonicated for 30 min, and then GPS (1.0 g) was added. The suspension was heated at 85 °C under $N_2$ atmosphere for 12 h, and then cooled to room temperature. The reaction mixture was added into 500 ml hexane, and the precipitate was collected by centrifugation at 4000 rpm for 10 min. The particles were redispersed into 30 ml acetone, and then reprecipitated from 300 ml hexane. The GPS-anchored silica particles were dispersed into 50 ml MIBK to afford a solution. Into this solution, the BDB (1.0 g) was added. After the reaction was carried out at 95 °C for 12 h, the reaction mixture was cooled to room temperature. The modified silica nanoparticles were precipitated from 500 ml hexane and then collected by centrifugation at 4000 rpm for 10 min. The final product was purified by redispersing in THF (30 ml) − centrifugated at 13,000 rpm for 20 min for five cycles. The BDB anchored silica nanoparticles (2.6 g) were obtained as red powder after drying in vacuum oven at 50 °C for 24 h. FT-IR (KBr, $\mathrm{cm}^{-1}$): 2950 (C−H), 1730 (C=O).

The amount of grafted initiators was determined by TGA and was calculated by the similar method (Eq. (1)) reported by Bartholome et al. [16,17]

$$\text{Grafting amount }(\mu\text{mol/g}) = \frac{\left(\frac{W_{60-600}}{100-W_{60-600}}\right)\times 100 - W_{\text{silica-epoxy}}}{M\times 100}\times 10^{6} \qquad (1)$$

where $W_{60-600}$, is the weight loss data measured between 60 and 600 °C, and $M$ is the molecular weight of BDB, $W_{\text{silica-epoxy}}$ is the weight loss of GPS grafted-silica.

### 2.6. *RAFT polymerization of styrene using BDB anchored silica as RAFT agent*

RAFT agent anchored silica nanoparticles (0.10 g), styrene (1.04 g) and THF (1.04 g) were added into a 5 ml glass tube, followed by ultrasonication for 1 min. After degassing by three freeze−evacuate−thaw cycles, the glass tube was sealed in vacuo. The polymerization was carried out at 110 °C for a prescribed time, and then the polymerization mixture diluted with THF was poured into excess of methanol, the polymer coated silica was precipitated. The product contaminated with polystyrene (PS) was collected by filtration, and dried in a vacuum oven at 60 °C for 12 h.

The purification of PS-grafted silica was as follows. The crude product (80 mg) was homogeneously dispersed in THF (10 ml). The suspension was centrifugated at 13,000 rpm for 30 min. The upper clean liquid was collected, and the fresh THF (10 ml) was added into the residue. This procedure was repeated five times until no polymer was in THF. All the upper clean liquids were combined and the solvent was removed under reduced pressure. The PS was precipitated from methanol, and collected by filtration. The PS-grafted silica and the PS obtained were dried at 60 °C in a vacuum oven for 12 h.

### 2.7. *Cleavage of the grafted PS from the PS grafted silica nanoparticles*

Cleavage of the PS from the PS-grafted silica was carried out according to the procedure described in Ref. [33]. In a polyethylene (PE) tube, the PS-grafted silica (40 mg) was dissolved in 5 ml THF. Into the solution, aqueous HF (48 wt%, 0.3 ml) was added, and the reaction mixture was stirred at room temperature for 12 h. The polymer was precipitated by adding the polymer solution into 10-fold excess of methanol in a PE beaker, and then the precipitate was collected by filtration. The PS obtained was dried in a vacuum oven at 60 °C overnight. The recovered PS was then subjected to GPC analysis.

## 3. Results and discussion

In the preparation of star-shaped polymers by RAFT polymerization, two types of multifunctional RAFT agents have been employed in the RAFT process: those involving the reaction of the linear chains with the functional core (core is a part of Z-group) and those involving an outward growth of arms from the core (core is a part of R-group), following ‘‘arm-first’’ and ‘‘core-first’’ approaches, respectively. These two approaches are complementary with their respective merits and drawbacks [35−37]. For synthesis of dithiobenzoate-anchored silica nanoparticles, the same two types of RAFT agents can be prepared. The shielding effect in the arm-first approach will decrease the grafting density of cores [36], thus a ‘‘core-first’’ RAFT approach was selected and the RAFT agent was connected to silica nanoparticles via R group.

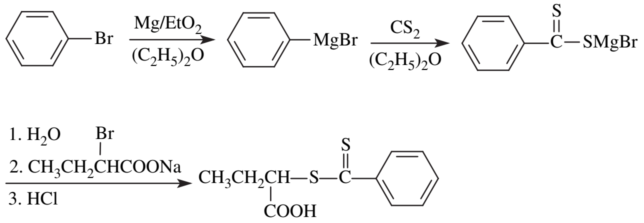
### 3.1. *Preparation of dithiobenzoate-anchored silica nanoparticles*

To anchor the dithiobenzoate group onto the surface of silica nanoparticles with epoxy group, the reaction of carboxylic acid with epoxy group was selected. Thus the 2-butyric acid dithiobenzoate (BDB) was used as intermediate for this purpose, and it was usually synthesized by the reaction of 2-bromobutyric acid with dithiobenzoate magnesium bromide in THF or diethyl ether. The resultant product, BDB was obtained generally in fairly low yield (~12%) after purifying by column chromatography because of side reactions. So, a new method was used to prepare BDB by the reaction of the dithiobenzoate magnesium bromide (which was filtered and washed with diethyl ether to remove by-products) with sodium 2-bromobutyrate in aqueous solution under alkali condition, and the reaction was performed at room temperature to afford the target product in 41% yield (Scheme 1).

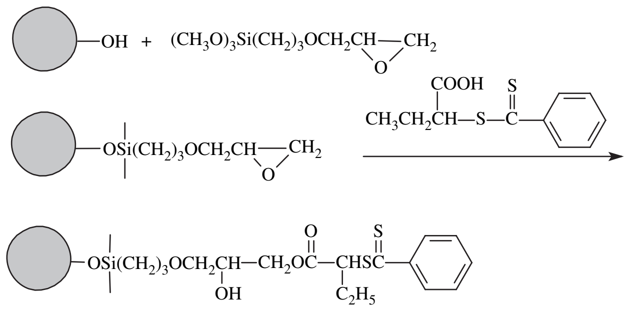
Spherical silica nanoparticles with narrow size distribution were prepared by Stober method [38,39]. Their average diameter prepared in this study is 78 nm, which was measured by DLS. As mentioned in Section 1, based on our knowledge, only three articles reported the attachment of dithiobenzoate onto silica particles [33,34]. Here, we report a novel and simple method for preparation of dithiobenzoate-anchored silica nanoparticles. As shown in Scheme 2, the first step is treatment of silica nanoparticles with GPS, and the second step is the ring-opening reaction of the epoxy of GPS with carboxylic acid of BDB. The FT-IR spectra of the reaction products confirmed complete reaction of the epoxy groups on the silica with BDB.

Fig. 1 shows the FT-IR spectra of the bare silica (Fig. 1a) and the dithiobenzoate-anchored silica (Fig. 1b). Although the characteristic bands of thiocarbonyl around 1050 cm$^{-1}$ overlapped with the strong absorption of the bare silica (Fig. 1b), the alkyl C−H stretching vibration band at 2948 cm$^{-1}$ and the carbonyl vibration band at 1730 cm$^{-1}$ are clearly visible. This indicates that the dithiobenzoate group is covalently bound to the surface of the silica particles.

The amount of RAFT agent anchored on the silica nanoparticles was determined by TGA using a similar method reported by Bartholome et al. [16,17]. Calculation based on TGA shows that the content of dithiobenzoate group on the particles is 36 μmol/g, corresponding to 0.60 RAFT agent/nm$^2$.



Scheme 1. Synthesis of α-butyric acid dithiobenzoate (BDB).



Scheme 2. Synthesis of BDB anchored silica nanoparticles.

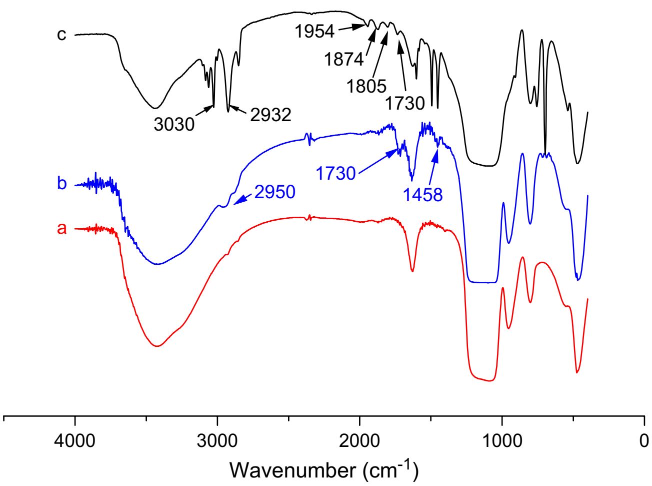


Fig. 1. FT-IR spectra of bare silica nanoparticles (a), dithiobenzoate-anchored silica particles (b) and PS-grafted silica particles (c).

### 3.2. RAFT polymerization of St using dithiobenzoate-anchored silica as RAFT agent

The PS-graft silica nanoparticles were prepared by RAFT polymerization of St in the presence of dithiobenzoate-anchored silica particles. The polymerization was carried out in THF at 110 °C without free radical initiator. The conversion of St was determined by gravimetric method. The pseudo-first-order kinetic plot is shown in Fig. 2 for the surface RAFT polymerization of St using PhC(S)S-anchored silica nanoparticles as RAFT agent. This indicates a constant free radical concentration during the polymerization. But the straight line didn't pass through the original point, indicating the existence of a slight induction period, which was observed in our previous work using a dendritic RAFT agent to synthesize star polymer and also in the Li's work [34]. The inhibition might be attributed to slow fragmentation and/or slow reinitiation

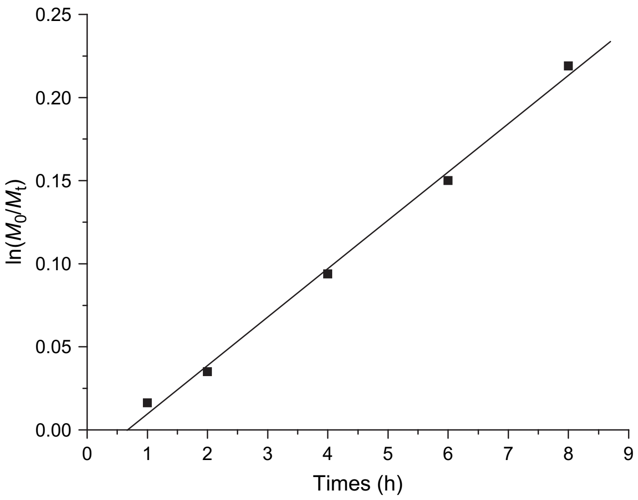


Fig. 2. Pseudo-first-order kinetic plot for the RAFT polymerization of St at 110 °C in THF using dithiobenzoate-anchored silica nanoparticles as RAFT agent.

of the leaving group in the early stage of polymerization [37,40–42].

One interesting phenomenon for the dithiobenzoate-anchored silica mediated RAFT polymerization of St is the existence of linear PS in the polymerization system, variation of the polymerization conditions, such as concentration and temperature, did not avoid the formation of linear PS completely. The linear PS (unimmobilized PS) and PS-anchored silica particles were separated by centrifugation of the product solution in THF, and the linear PS was obtained from the upper clean solution. Its GPC curve is shown in Fig. 3b. The GPC curve of the PS obtained from hydrolysis of PS-anchored silica particles is shown in Fig. 3a. The two GPC curves demonstrate that both PSs have the similar molecular weights and PDIs. If the unhomogeneous distribution of PhC(S)S-terminated PS in the polymerization solution restricted the reaction rate between chain radicals formed in solution and RAFT agent on the surface of silica, resulted in termination of chain radicals, the molecular weight of the PS formed in solution and on the surface of silica should not be the same. Therefore, the possible reason for these phenomena is shown in Scheme 3. The chain radicals formed by thermal initiation of St in solution react with PhC(S)S groups on the surface of silica particles quickly, after fragmentation, the PhC(S)S-terminated polymer chains will be released into the solution, and the chain radicals on the surface initiate the polymerization of monomer to form PS-anchored silica. The chain radical **4** in solution or **1** on the surface of silica react with RAFT agent **3** on the surface or **2** in solution will release one linear chain into the solution. Thus complete disappearance of linear PS in the final product is impossible. For the similar molecular weights and narrow PDI of both the linear PSs in solution and on the surface of the silica, the probable reason is the fast equilibrium between chain radical **1** (**4**) and dormant chain **3** (**2**) as shown in Scheme 3, and the PS chains in the solution and on the surface of silica have the same possibility to propagate. However, when the polymerization was carried out up to high conversion, the gelation occurred, which indicates the occurrence of combination termination reactions between chain radicals on the surface of two silica particles. In addition, RAFT process may occur on surface of the same silica particle and in solution [43]. For estimating the effect of these complicate reactions on the controlled characteristics, the molecular weight of the linear PS obtained from hydrolysis of the PS-anchored silica at various conversions were measured, the plots of molecular weights and molecular weight distribution against conversions are shown in Fig. 4. Linear evolution of molecular weight with conversion and narrow molecular weight distribution (less than 1.10) shown in Fig. 4, as well as first-order-kinetics in Fig. 2 confirm the living nature of the surface RAFT polymerization.

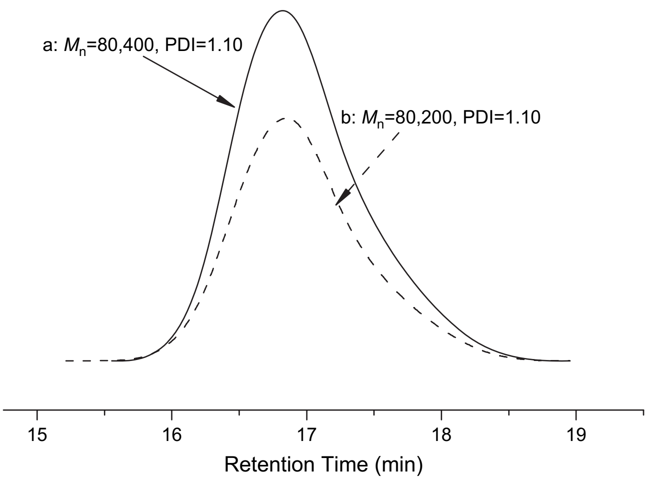
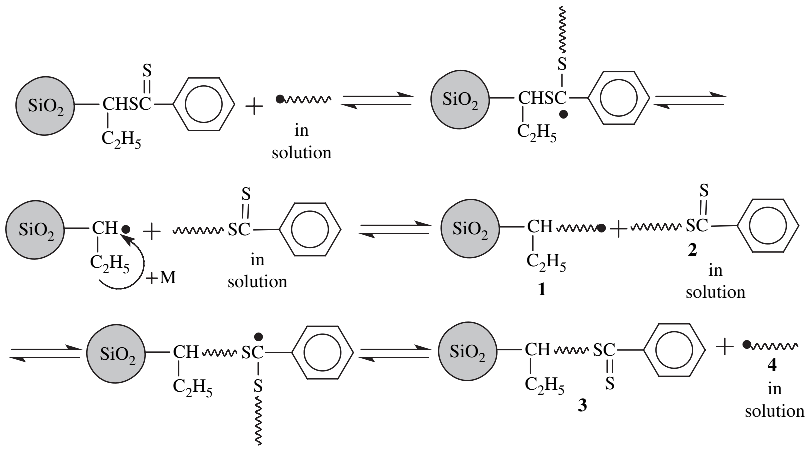


Fig. 3. GPC curves of a: PS cleaved from PS-anchored silica nanoparticles and b: unimmobilized PS obtained from polymerization at 19.7% conversion.

### 3.3. Characterization of the PS-anchored silica nanoparticles

FT-IR, TEM and TGA were used to characterize the PS-anchored silica nanoparticles. As we discussed, the free PS chains existed in the polymerization system consistently. The pure PS-anchored silica particles were obtained by repeated centrifugation–redispersion procedure until no free polymer was detected in the THF solution. Fig. 1c shows the FT-IR



Scheme 3. Chain growth on the surface of silica particles and in solution.

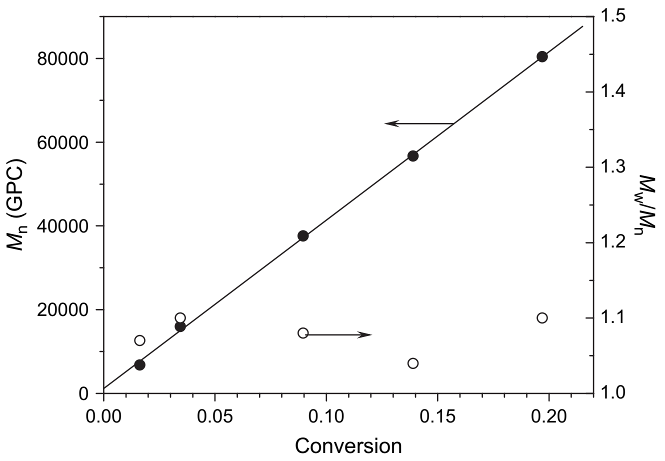


Fig. 4. Evolution of the molecular weight and PDIs with conversion for the RAFT polymerization of styrene at 110 °C in tetrahydrofuran in the presence of PhCS(S)-anchored silica nanoparticles.

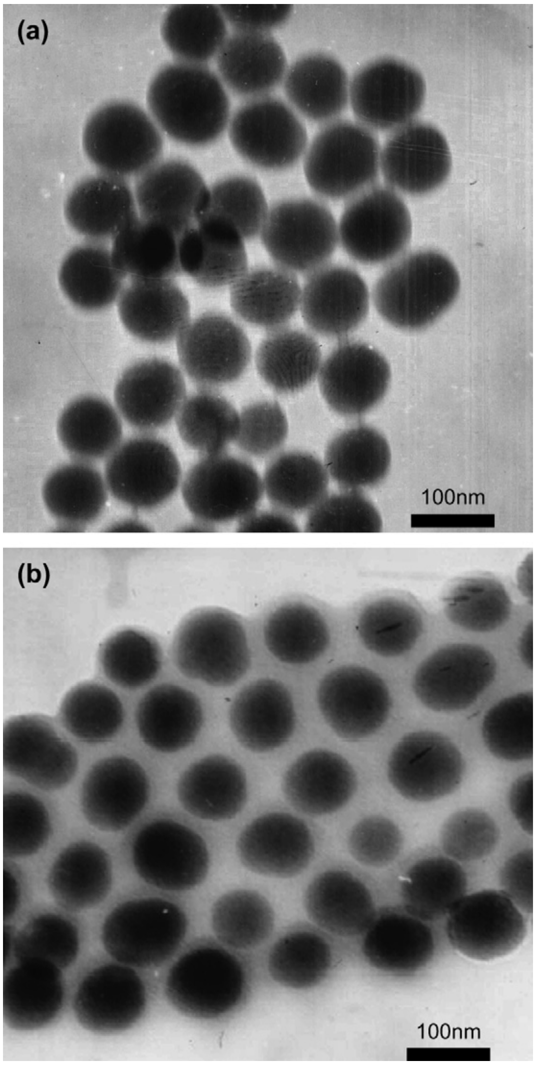


Fig. 5. TEM images of a: RAFT agent anchored silica and b: PS-grafted silica nanoparticles obtained at 13.9% conversion.

spectrum of the purified PS grafted silica nanoparticles. In comparison with the IR spectra in Fig. 1b and c, the characteristic absorption bands of PS in the range of 2900–3100, 1800–2000 and 1450–1650 $cm^{-1}$ were found. This proved qualitatively that the PS was chemically bound to the silica nanoparticles.

Fig. 5a and b show the TEM images of the RAFT agent and PS-anchored silica nanoparticles respectively. Aggregates of several particles can be observed in Fig. 5a, which is similar to the result obtained during GPS grafted on silica [13]. The gray surface layer of the silica particles in Fig. 5b is visible clearly, which can be ascribed to the PS formed on their surface. The PS-anchored nanoparticles exhibit regular array on the copper grid, and this agrees with the Auroy's conclusion that colloid spheres tethered with high molar mass and low polydispersity polymer should be packed crystalline [44]. The distance between PS-anchored nanoparticles increased compared with their precursors, the PhC(S)S-anchored nanoparticles in Fig. 5a. This may demonstrate that the PS chains are chemically bound to the silica nanoparticles.

The relative amount of free linear PS and the PS-anchored silica particles in the products can be estimated by TGA method. Fig. 6 shows the TGA curves of the products obtained at 3.4% and 19.7% conversions before and after purification. The decomposition temperature range is 300–460 °C for all the four TGA curves shown in Fig. 6. Assuming that the PS is decomposed completely, when styrene conversion increased from 3.4 to 19.7%, the relative amounts of PS before purification varied from 29 to 73 wt%, while after purification varied from 25 to 51 wt%. Although the amount of the grafted PS increased with conversion, the graft efficiency, which is defined as the weight ratio of the polymer anchored on the silica to the total polymer formed, decreased from 81 to 70%.

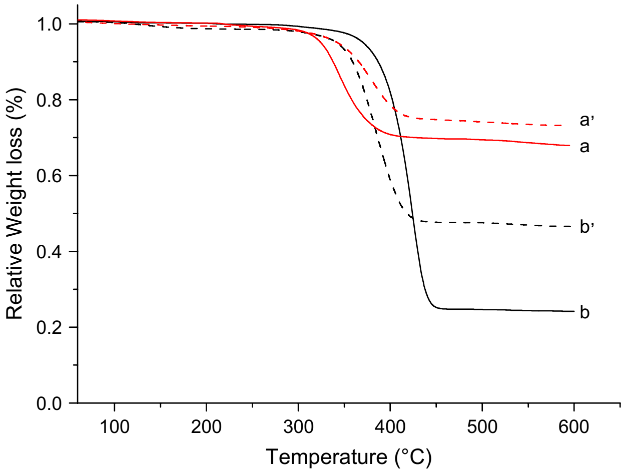


Fig. 6. TGA analysis of a: crude product obtained at 3.4% conversion before purification ($M_{n,GPC} = 6800$); a′: PS-anchored silica nanoparticles obtained after purification of the sample in a; b: crude product obtained at 19.7% conversion before purification ($M_{n,GPC} = 80,400$); b′: PS-anchored silica particles obtained after purification of the sample in b.

## 4. Conclusion

The RAFT agent BDB with higher purity was synthesized in aqueous phase. The dithiobenzoate-anchored silica nanoparticles could be successfully prepared in a simple way via the reaction of commercially available silane coupling agent GPS with silica, following reacted with BDB. The PhC(S)S-anchored silica mediated surface RAFT polymerization of St displayed living nature. Similar to the results obtained from RAFT polymerization using dendritic RAFT agent, the linear polymer exists always in the polymerization system, which is determined by RAFT polymerization mechanism. TEM image of the PS-anchored silica nanoparticles shows regular array on the copper grid.

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