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Combination of Living Radical Polymerization and Click Chemistry for Surface Modification

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ABSTRACT: A novel reversible addition fragmentation technique chain transfer agent (RAFT CTA) was synthesized which permits the possibility of using RAFT polymerization and click chemistry together for surface modification. Using this RAFT CTA, the surface of silica nanoparticles was modified with polystyrene and polyacrylamide brushes via the "grafting to" approach. A click reaction was used to attach polymers onto the surface which produced relatively high grafting density. Both tethered polystyrene and polyacrylamide chains were found in the brush regime. The combination of ATRP and click chemistry was also explored for surface modification. To our knowledge, this is first report of RAFT polymerization and click chemistry together for surface modification.

Introduction

The development of controlled free radical polymerization is among the most important advances in polymer chemistry.[1] Living polymerization techniques afford control over molecular weight, molecular weight distribution, architecture, and functionalities of the resulting polymer.[2] Three commonly used controlled free radical polymerizations include nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation techniques (RAFT). Sharpless et al.[3] popularized the 1,3-dipolar cycloaddition of azides and terminal alkynes, catalyzed by copper(I), in organic synthesis. These reactions have a very high thermodynamic driving force which makes them one of the most efficient reactions available. Such reactions were proven to be very practical because they can be performed in high yield, in multiple solvents (including water), and in the presence of many other functional groups. Moreover, the 1,2,3-triazole product is chemically very stable. Because of their efficiency and simplicity, these cycloadditions were classified as ‘‘click” reactions.

Combining the chain-end functionality control of living free radical polymerization and the efficiency of click chemistry is attractive. Postpolymerization modification remains a viable means of incorporating functionality into a polymer that is potentially incompatible with synthetic, characterization, or processing conditions.[4] A drawback of this method of functionalization is relatively low yields and side reactions with other groups within the polymer. Highly efficient and specific click reactions are suitable for successful postpolymerization modification.

Lutz et al.[5] used click chemistry to prepare an end-functionalized ATRP polymer. The bromine chain ends of the polymer were first transformed into an azide end group and subsequently reacted with terminal alkynes to create different functional end groups. van Hest et al.[6] prepared terminal azide and alkyne functionalized ATRP polymers to modularly synthesize block copolymers. Matyjaszewski et al.[7] synthesized an alkyne-terminated ATRP initiator to polymerize well-defined α-alkyne-ω-bromo-terminated polystyrene (PS). These polymers prepared by ATRP were coupled via a step growth mechanism using click coupling to yield PS containing triazole linkages in the repeat units. Matyjaszewski et al.[8,9] also synthesized α,ω-dihydroxypolystyrene and star polymers via ATRP and click chemistry. Macrocyclic polymer, neoglycopolymer, and first-generation dendritic copolymers have also been synthesized by combination of ATRP and click chemistry.[10−12]

RAFT polymerization has received increasing attention in recent years. Among available controlled free radical polymerization techniques, RAFT has arguably the most important commercial significance because it works with the greatest range of vinyl monomers and under a wide variety of experimental conditions.[13] Little work has been done on combination of RAFT polymerization and the click reaction. Hawker, Wooley and coworkers[14] used RAFT polymerization to synthesize alkyne-functionalized block copolymers. Sumerlin et al.[15] synthesized functional telechelic polymers using this approach. Davis, Barner-Kowollik, and co-workers[16] synthesized block copolymers via RAFT polymerization and click chemistry.

The target of the present work was to illustrate that a one-step process can be used to make alkyne end-functional polymers via RAFT polymerization that can be used in a multitude of postpolymerization processes. These alkyne-functionalized polymers can participate in different kinds of end functionalization reactions using versatile click chemistry. The reports of RAFT to prepare polymer grafted solid substrates are low compared with RAFT polymerization in solution.[17] Alkyne-terminated RAFT polymers can be potentially useful for click coupling to solid substrates having an azide group. Meldal et al.[18] found that click coupling worked well on solid supports. Combined use of click and RAFT can be used for surface modification by both "grafting to" and "grafting from" approaches. Surface modification using the "grafting to" approach is more challenging in achieving higher grafting densities and thus represents a potentially useful application of a combined RAFT and click chemistry. In this report, we have used the combination of RAFT and click chemistry to graft polymers to silica nanoparticles.

Surface modification of silica nanoparticles has attracted considerable attention in recent years.[19] Acrylamide (AAm) polymers are an important class of materials because of applications such as coatings, flocculants, paper making, mining, electrophoresis, and biology. Demchenko et al.[20] used conven-

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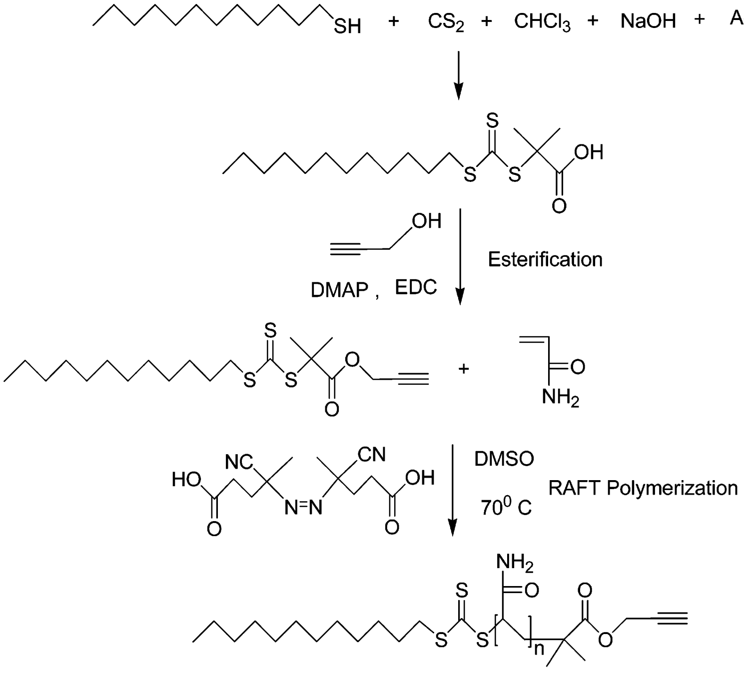
Scheme 1. Synthesis of Alkyne-Terminated Polyacrylamide



tional radical polymerization to graft AAm onto silica nanoparticles using redox initiation with ceric ions. Jang and Park[21] used a sol−gel process to make polyAAm−silica nanocomposites. The cooperative system of hydrogen bonds between the silica surface and polyacrylamide (PAAm) forms a dense polymer shell. The unification of the sorption ability of a colloidal particle surface and the binding properties of PAAm grafted silica produces a strong flocculative capability. Although the use of PAAm has increased, there have not been many reports on the preparation of silica−PAAm hybrid nanoparticles. The solubility of PAAm is limited and presents an experimental challenge in the preparation of silica−PAAm hybrid nanoparticles. We combined RAFT and click coupling to graft PAAm onto the surface of silica nanoparticles.

Experimental Section

Materials. Colloidal silica (D = 75−100 nm) as a 30 wt % dispersion in isopropanol was provided by Nissan Chemical. *N*-(3-(Dimethylamino)propyl)-*N*′-ethylcarbodiimide hydrochloride (EDC), 4-(*N*,*N*-dimethylamino)pyridine (DMAP), 4,4′-azobis(4-cyanovaleric acid) (VA 501), azobis(isobutyronitrile) (AIBN), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), acrylamide (electrophoresis grade), methanol, sodium azide, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%), copper sulfate, and sodium ascorbate were purchased from Aldrich. Styrene was purchased from Aldrich Chemical and was purified by passage through a column of chemically activated alumina (Aldrich, 150 mesh). CuBr (Aldrich, 98%) was purified as described in the literature.[22] 3-Bromopropyltrichlorosilane was purchased from Gelest Inc. Unless otherwise specified, all the chemicals were used as received.

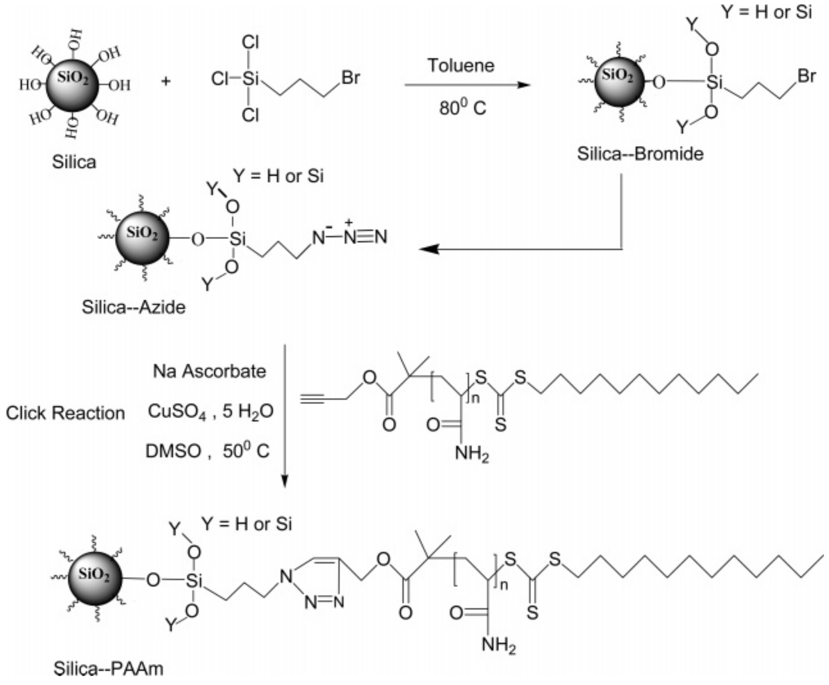
Measurements. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker Tensor 27 FT-IR spectrometer using a diffuse reflection apparatus (Cricket, Harrick Scientific). Thermogravimetric analysis (TGA) was performed on a TA 2950 instrument at a scan rate of 20 °C/min under a nitrogen atmosphere. The molecular weights of polystyrene were measured in THF (at 35 °C with a flow rate of 1 mL/min) by gel permeation chromatography (GPC) using a Waters 501 pump, Waters HR4 and HR2 Styragel columns, a Waters 410 differential refractometer, and a Viscotek 760A dual light scattering and viscosity detector. Matrix-assisted laser desorption/ionization (MALDI) spectra were acquired using a Bruker Reflex III MALDI−TOF mass spectrometer. Elemental analyses were obtained from Galbraith Labs in Knoxville, TN.

Deposition of 3-Bromopropyltrichlorosilane on Silica Nanoparticles. Into a Schlenk flask, 6 g of dried silica and 45 mL of anhydrous toluene were added under an inert atmosphere. This flask was sonicated for 30 min and then placed into an oil bath preset at 80 °C. 5.5 mL of 3-bromopropyltrichlorosilane in 15 mL of toluene was added dropwise, and the solution was maintained at 80 °C for 18 h. The particles were recovered by centrifugation at 3000 rpm for 30 min. These particles were redispersed in toluene and centrifuged. This cycle was repeated six times to get the final product. After drying, these modified nanoparticles were characterized by IR, TGA, and elemental analysis. Using elemental analysis of bromine, the grafting density of bromopropyl group introduced onto the particle surface was determined as 3.68 groups/nm^2.

Synthesis of Azide-Modified Silica Nanoparticle. 5 g of 3-bromopropyl-modified silica nanoparticles and 2 g of NaN_3 in 100 mL of DMF were combined under an inert atmosphere. This solution was stirred at 80 °C for 18 h. The particles were recovered by centrifugation at 3000 rpm for 30 min. The cycle of centrifugation and redispersion in water was repeated three times. Obtained particles were characterized by IR, TGA, and elemental analysis. Elemental analysis indicated that the modified nanoparticles contained, on average, 3.45 azide groups per nm^2 on the surface.

Esterification Reaction of *S*-1-Dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate. The synthesis of *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate chain transfer agent (trithiocarbonate CTA) was carried out according to a previously reported method in the literature.[23] Trithiocarbonate CTA (1 g, 2.73 mmol), EDC (0.783 g, 4.095 mmol), DMAP (0.5 g, 4.095 mmol), and 10 mL of dichloromethane were added to a round-bottomed flask and stirred for few minutes under an inert atmosphere. 0.5 mL (8.9 mmol) of propargyl alcohol was added, and the mixture was stirred overnight at room temperature. The product was washed with acidic water, water, and brine several times and dried under reduced pressure. Without further purification product was obtained and collected as a dark yellow viscous liquid (at room temperature). The yield was 80%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.87 (t, $-\mathrm{CH_2C}H_3$, 3H), 1.2−1.4 (m, $-\mathrm{C}H_2\mathrm{CH_2}$, 20H), 1.65 (s, $-\mathrm{C(C}H_3)-\mathrm{C}H_3$, 6H), 2.5 (s, $-\mathrm{C}H\equiv\mathrm{C}$, 1H), 3.25 (t, $-\mathrm{C}H_2\mathrm{S}$, 2H), 4.7 (s, $-\mathrm{C}H_2\mathrm{C}$, 2H). ^{13}C NMR (300 MHz, $CDCl_3$, δ): 17

Scheme 2. Modification of Silica Nanoparticle



($CH_2{-}CH_3$), 22 ($CH_2(CH_3){-}CH_2$), 24.5 (2C, $CH_3{-}C$), 26−32 (9C, $CH_2(CH_2){-}CH_2$), 37 ($CH_2(CH_2){-}S$), 53 ($C(CH_3){-}CH_3$), 55 (CH_2-(C)−O), 76 ($CH{\equiv}C$), 77 ($C(CH_2)\equiv CH$), 173 (C═O), 222 (C═S).

RAFT Polymerization of Acrylamide. 0.4 g (0.958 mmol) of alkyne-terminated chain transfer agent, 8.0 g (0.112 mol) of acrylamide, 70 mL of DMSO, and 0.01 g (0.035 mmol) of azo-initiator (VA501) were combined in a Schlenk flask. The flask was subjected to three freeze−pump−thaw cycles to remove oxygen. The mixture was heated to 70 °C for 3−4 h under an inert atmosphere. The polymerization was stopped by quenching the flask in ice water, and PAAm was obtained after precipitation in cold methanol. Two independent analytical techniques were used, MALDI-TOF mass spectroscopy and ^{1}H NMR spectroscopy, in order to characterize the low molecular weight PAAm. A good agreement was observed between calculated molecular weight ($M_n = 4500$ g/mol) by both techniques. ^{13}C NMR was used to confirm the presence of the alkyne end group.

Click Coupling between Polyacrylamide and Silica Nanoparticle. 3 g (0.66 mmol) of PAAm and 15 mL of DMSO were combined in a round-bottomed flask and stirred until the PAAm dissolved; 1 g of azide modified silica nanoparticle was added, and the mixture was sonicated for 30 min. A solution of 0.005 g (0.031 mmol) of $CuSO_4$ in 1 mL of water was added to the mixture followed by addition of a freshly prepared solution of 0.015 g (0.75 mmol) of sodium ascorbate in 1 mL. The mixture was heated in an oil bath at 50 °C overnight. The particles were recovered by centrifugation at 3000 rpm for 30 min. The particles were 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 water for 18 h.

RAFT Polymerization of Styrene. 0.4 g (1.00 mmol) of alkyne-terminated chain transfer agent, 24 mL (0.21 mol) of styrene, 25 mL of toluene, and 0.01 g (0.06 mmol) of AIBN were combined in a Schlenk flask. The flask was subjected to three freeze−pump−thaw cycles to remove oxygen, and the mixture was heated at 90 °C for 18 h under an inert atmosphere. The polymerization was stopped by quenching the flask in ice water, and polystyrene was obtained after precipitation in cold methanol. GPC was used to calculate molecular weight ($M_n = 9000$ g/mol) and polydispersity (1.09). Monomer conversion was 41%. ^{13}C NMR was used to confirm the alkyne functionality in PS.

ATRP of Styrene. The synthesis of alkyne-terminated ATRP initiator propargyl 2-bromoisobutyrate was carried out according to a previously reported method in the literature.[24] Now 0.3 mg (1.47 mmol) of propargyl 2-bromoisobutyrate, 0.225 g (1.56 mmol) of CuBr, 0.6 mL (3.12 mmol) of PMDETA, 22 mL (0.19 mol) of styrene, and 19 mL of toluene were combined in a Schlenk flask. The flask was subjected to three freeze−pump−thaw cycles, and polymerization was performed under an inert atmosphere at 90 °C for 9 h. The polymerization was stopped by quenching the flask in ice water. The polymer solution was passed though an alumina column three times to remove any trace of copper. The purified solution was precipitated in cold methanol to afford the polymer. The polystyrene was characterized by GPC, ^{1}H NMR, and ^{13}C NMR. The molecular weight of polystyrene was calculated to be 6000 g/mol (PDI = 1.1) with 47% monomer conversion.

Click Coupling between Polystyrene and Silica Nanoparticles. 3 g (0.33 mmol) of polystyrene, 1.3 g of azide-modified silica, and 40 mL of DMF were combined in a round-bottomed flask, and the solution was stirred for 5 min. 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 for 18 h. The particles were recovered by centrifugation at 3000 rpm for 30 min. These particles were redispersed in solvent and centrifuged; this cycle was repeated four times in toluene, one time in water, and then one time in toluene. The modified silica particles were obtained after drying at reduced pressure.

Results and Discussion

Synthesis and Application of Alkyne-Terminated RAFT Chain Transfer Agent. A carboxyl-terminated trithiocarbonate RAFT CTA was prepared by a previously reported one-step procedure.[23] This CTA is readily used to obtain carboxyl-functionalized polymer. For the application of this type of CTA in click chemistry, we converted the terminal carboxyl group of CTA to an alkyne group via esterification with propargyl alcohol (Scheme 1). The esterification reaction was done in the presence of EDC coupling agent and DMAP base. The product structure was confirmed by ^{1}H and ^{13}C NMR. ^{1}H NMR displayed a peak at 4.7 ppm ($CH_2(O){-}C{\equiv}CH$) and 2.5 ppm ($CH{\equiv}C$) which confirmed the attachment of propargyl group to CTA. ^{13}C NMR also showed alkyne resonances at 75 and 77 ppm.

The alkyne-terminated CTA can be directly clicked to silica nanoparticles. These CTA immobilized silica particles can be modified by a "grafting from" approach using surface-mediated RAFT polymerization. That will be the subject of a future publication. In this report, we use this CTA to prepare alkyne-terminated polymers which are "grafted to" azide-functionalized silica nanoparticles.

The alkyne bond is susceptible to addition reactions as well as polymerization. The trimethylsilyl group has been used as a protecting group for alkyne functionality during ATRP[6,11] and anionic polymerization.[25] Opsteen and van Hest[6] used a protective group to circumvent complexation of the alkyne group with the copper catalyst during polymerization. In anionic polymerization, the proton of the alkyne bond is acidic and reacts with the initiator. Matyjaszewski et al.[7] have polymerized styrene at 90 °C using an alkyne-terminated ATRP initiator without using any protecting group. With milder conditions and absence of copper atom in RAFT polymerization, we expect little interference from the alkyne group.

Synthesis of Alkyne-Terminated Polystyrene. RAFT polymerization of styrene using the alkyne-terminated CTA was performed at 90 °C (6% initiator) for 18 h. Well-defined PS with polydispersity of 1.09 and $M_n = 9000$ g/mol was obtained. The presence of the alkyne group was confirmed by ^{13}C NMR which showed alkyne resonances at 75 and 77 ppm.

Synthesis of Alkyne-Terminated Polyacrylamide. Well-controlled RAFT polymerization of acrylamide has been difficult due to CTA degradation which is a result of the amide hydrolysis of the acrylamide monomers.[26] Even a small amount of monomer hydrolysis could produce enough ammonia to convert all dithioesters in solution to thiols. So appropriate choices of CTA and reaction conditions are very important for achieving well-controlled RAFT polymerization of acrylamide. McCormick et al.[27] studied the kinetics and molecular weight control of the RAFT polymerization of acrylamide in order to determine reaction conditions which would provide controlled polymerization. Because of less stabilized intermediate radicals, trithiocarbonate CTA affords much faster polymerization rates which is necessary for controlled polymerization of acrylamide. McCormick and co-workers established that RAFT polymerizations of acrylamide in DMSO mediated by the trithiocarbonate CTA in the presence of VA 501 free initiator at 70 °C provides good control of molecular weight and polydispersity for PAAm.

We employed exactly the same experimental conditions with our trithiocarbonate CTA to polymerize acrylamide. In 3.5−4 h of polymerization, 50−60% conversion was achieved which indicated a faster rate of polymerization. Our goal was to prepare low molecular weight PAAm to facilitate characterization (end-group analysis). We synthesized low molecular weight (M_n = 4000−5000 g/mol) PAAm with a terminal alkyne group. ^{1}H NMR displayed a peak at 4.6 ppm ($CH_2(O)-C{\equiv}CH$), and ^{13}C NMR revealed peaks at 75 and 78 ppm which correspond to an alkyne. The molecular weight analysis of PAAm was determined by ^{1}H NMR and MALDI. By comparing the peak obtained by terminal H (CH_3-CH_2, 0.87 ppm) and H of repeating units (1.8 and 2.4 ppm), the M_n was calculated. Via NMR, the calculated molecular weight was $M_n = 4500$ g/mol. MALDI analysis confirmed the molecular weight (see Supporting Information).

Synthesis of Azide-Modified Silica Nanoparticles. Two step synthetic routes were used to modify the surface of a silica nanoparticle with azide functionality (Scheme 2).[28] In the first step, 3-bromopropyltrichlorosilane was used to introduce a bromide group on the surface of a silica nanoparticle. IR analysis of the bromide-modified silica nanoparticle (Figure 1d) revealed an absorption at 2900 cm^{-1} corresponding to C−H stretching. Elemental analysis also confirmed the presence of bromine (1.53%) which corresponds to a surface grafting density of 3.65 groups/nm^2.

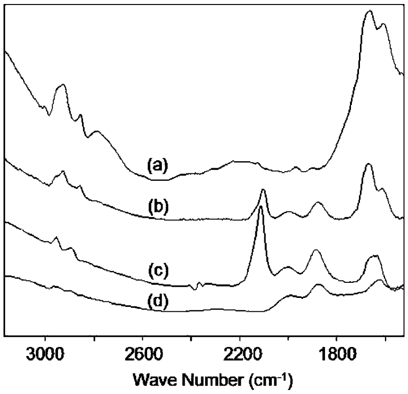


Figure 1. IR spectra of (a) PAAm, (b) silica−PAAm nanoparticles, (c) silica−azide nanoparticles, and (d) silica−bromide nanoparticles.

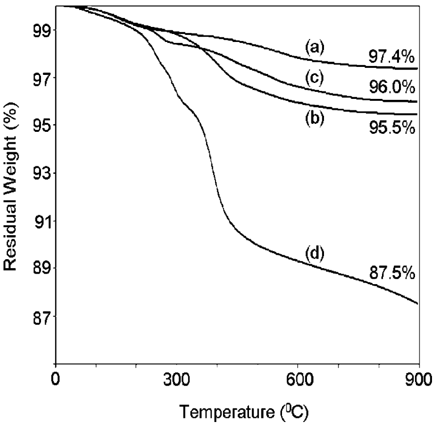
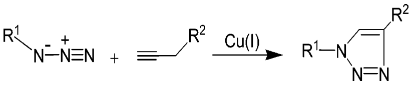


Figure 2. Thermogravimetric analysis (TGA) of (a) bare silica nanoparticles, (b) silica−bromide nanoparticles, (c) silica−azide nanoparticles, and (d) silica−PAAm nanoparticles.

Scheme 3. Model Click Reaction



This bromide was substituted with azide by reaction with sodium azide. An azide group was verified by an IR adsorption at 2110 cm^{-1} (Figure 1c). Elemental analysis also showed the presence of nitrogen (0.76%) which corresponds to a surface grafting density of 3.47 groups/nm^2. Using TGA, we observed a weight loss of 1.9% (Figure 2b) for the bromide-modified nanoparticle and 1.6% weight loss for the azide-modified nanoparticle (Figure 2c), which is consistent with the difference in atomic masses of the functional groups.

Click Coupling between Azide-Modified Silica Nanoparticle and Alkyne Terminated PAAm. The click reaction commonly corresponds to the Cu$^{\mathrm{I}}$-catalyzed reaction of the Huisgen 1,3-dipolar cycloaddition of azides and alkynes to afford 1,2,3-triazoles (Scheme 3).[29] We first tried this coupling reaction with alkyne-terminated PS and azide-modified silica particles. PS-coated silica nanoparticles with a relatively high grafting density of 0.37 groups/nm^2 were obtained, which corresponds to a distance between grafting sites of 1.85 nm.[30] The Flory radius of PS ($M_n = 9000$ g/mol) was calculated as 6 nm (for Θ solvent).[31,32] Thus, the diameter of the coils was larger than the distance between grafting points. On the basis of the

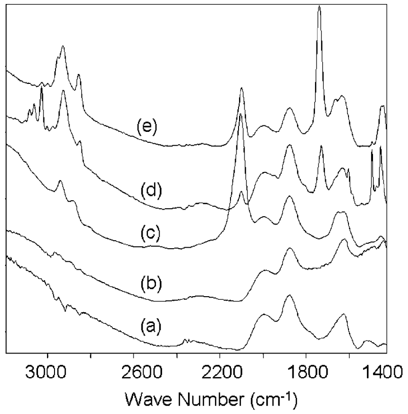


Figure 3. IR spectra of (a) bare silica nanoparticles, (b) silica−bromide, (c) silica−azide, (d) silica−PS (by ATRP), and (e) silica−PMA (by ATRP).

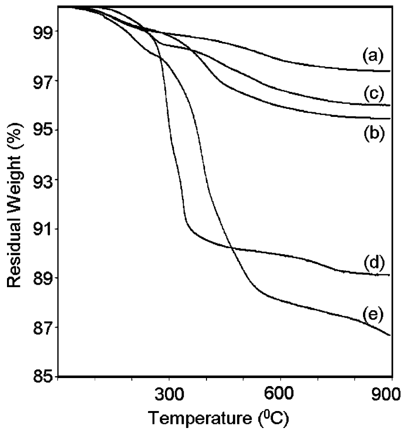


Figure 4. Thermogravimetric analysis (TGA) of (a) bare silica nanoparticles, (b) silica−bromide, (c) silica−azide, (d) silica−PS (by ATRP), and (e) silica−PMA (by ATRP).

Table 1. Elemental Analysis of Modified Silica Nanoparticle

sample	elemental analysis	result (%)	surface grafting density (groups/nm^2)
silica−bromide	bromine	1.53	3.68
silica−azide	carbon	0.98	3.45
	nitrogen	0.76	
silica−PAAm	carbon	3.84	0.31
	nitrogen	1.52	
silica−PS	carbon	12	0.37

conventional interpretation of polymer brushes, these tethered PS chains exist in the brush regime. These PS modified particles were characterized by IR, TGA, and elemental analysis.

This 1,3-dipolar cycloaddition reactions are often performed in water for faster reaction times and to alleviate the requirement for additional base. Aqueous solutions of polyacrylamide are usually viscous. Therefore, we utilized a mixture of water and DMSO (1:7.5, v/v) as a medium for the click reaction between alkyne-terminated PAAm and azide-modified silica nanoparticles (Scheme 2).

Grafting of polyacrylamide onto silica nanoparticles was characterized by IR (Figure 1b) where a reduction of azide peak at 2110 cm^{-1} was observed concomitant with an increase in the alkyl peak at 2900−3000 cm^{-1} and appearance of carbonyl peak at 1735 cm^{-1} that corresponds to the amide group. The polyacrylamide was degrafted from the silica by cleavage in HF; ^{1}H NMR indicated the disappearance of the alkyne group and the presence of the triazole group. TGA also confirmed the presence of polyacrylamide on the silica nanoparticle as evidenced by an additional 8% weight loss corresponding to the grafted polyacrylamide (Figure 2d). Using elemental analysis, we confirmed the presence of polyacrylamide on the surface of silica nanoparticle.[33] There was increase in carbon and nitrogen weight percentage on silica particle after click coupling (Table 1). The ratio of carbon (3.84%) and nitrogen (1.52%) (2.52:1) on silica−PAAm matched with relative atomic mass of carbon (36 amu) and nitrogen (14 amu) in the repeating units. Elemental analysis results were used to calculate the surface grafting density. We calculated that 0.31 polyacrylamide chains were present on 1 nm^2 surface area of silica, which corresponds to a 2.02 nm distance between grafting sites.[30] The diameter of polyacrylamide coils ($M_n = 4500$ g/mol, $R_g = 26$ nm) is larger than the distance between grafting sites. Thus, grafted polyacrylamide was also in the brush regime. The grafting density of polyacrylamide indicates that roughly 10% azide groups were converted during the click reaction with the alkyne-functionalized polyacrylamide. This grafting density is lower compared to polystyrene coupling (0.37 chains/nm^2) which we predicted on the basis of the larger steric hindrance (greater R_g) involved in the polyacrylamide coupling reaction.

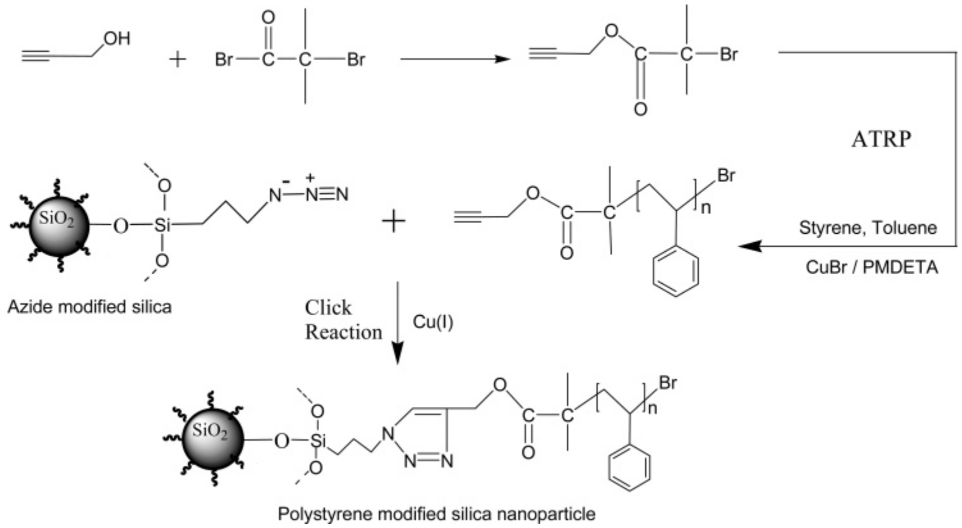
There have been few reports on the modification of silica nanoparticles by a RAFT polymer. Benicewicz et al.[17,34] deposited RAFT CTA on silica nanoparticles with grafting densities of 0.15−0.54 RAFT agents/nm^2. This was the surface density of RAFT CTA prior to surface-mediated polymerization. Guo et al.[35] immobilized a lactose-containing polymer onto silica gel particles with grafting densities 0.035−0.178 groups/nm^2. In contrast the surface grafting density obtained with an ATRP initiator was 2−5 groups/nm^2.[36] Comparing the grafting densities of a RAFT CTA and ATRP initiator, lower grafting densities are obtained with the RAFT CTA. This is likely due to the attachment of a more bulky RAFT CTA onto silica using the silanization reaction.

The “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. In the “grafting to” approach reported here, the grafting density was relatively high and even comparable with the “grafting from” approach. We speculate this is attributable to the facile nature of click chemistry. Thus, we predict that the use of click chemistry for “grafting-to” modification of nanoparticles will play an increasingly important role.

This click reaction was done in presence of excess polymer. After the click reaction silica particles could be easily collected by centrifugation. The excess polymer can be precipitated in cold methanol to recover the alkyne-terminated polymer which can be used in subsequent nanoparticle modifications.

This approach was also used to attach alkyne-terminated diblock copolymer to the surface of silica nanoparticles. Using alkyne-terminated RAFT CTA, PS-*b*-PMA block copolymers were synthesized through a two-step sequential RAFT polymerizations (see Supporting Information). Polymerization of styrene was performed at 90 °C using AIBN as a radical initiator to synthesize well-defined PS ($M_n = 3000$ g/mol, PDI = 1.05). PS was then employed as macro-RAFT CTA for the subsequent growth of PMA to form the final diblock copolymer PS-*b*-PMA ($M_n = 6000$ g/mol, PDI = 1.06). Alkyne-terminated PS-*b*-PMA was grafted onto azide-modified silica nanoparticle using click coupling reaction. Diblock brushes modified particles act as responsive materials as they have the ability to alter their surface chemistry in response to different environments.

Scheme 4. Surface Modification Using ARTP and Click Chemistry



Combination of ATRP and Click Chemistry for Surface Modification. This approach was easily extended to ATRP (Scheme 4). Alkyne-terminated ATRP initiator propargyl 2-bromoisobutyrate was prepared by reacting α-bromoisobutyric acid with propargyl alcohol in the presence of triethylamine.[24] Using this functionalized initiator, ATRP of styrene was done at 90 °C for 9 h to obtain alkyne-terminated PS ($M_n = 6000$ g/mol, PDI = 1.1). The presence of the alkyne group was confirmed by ^{13}C NMR. This alkyne-functionalized PS was click coupled to azide-modified silica nanoparticles in DMF/water mixture to create PS silica hybrid nanoparticles. These modified silica nanoparticles were thoroughly washed to remove any physisorbed polymers. Dried nanoparticles were characterized by IR and TGA. IR analysis of PS-modified particles showed new aromatic peaks at 1450−1500 and 3000−3100 cm^{-1}, which confirmed the presence of polystyrene on the surface of the particles (Figure 3d). TGA showed additional weight loss corresponding to attached polystyrene (Figure 4d). Methyl acrylate (MA) was also polymerized using propargyl 2-bromoisobutyrate ATRP initiator to synthesize alkyne-terminated PMA ($M_n = 8000$ g/mol, PDI = 1.14) which was then click coupled to azide-modified silica nanoparticles to make PMA silica hybrid nanoparticles (Figures 3 and 4).

Summary

A novel alkyne-terminated trithiocarbonate CTA was synthesized which permitted the combination of RAFT polymerization and click chemistry. Using this CTA, alkyne-terminated RAFT polymers were synthesized. Protecting groups were unnecessary for the RAFT polymerization. Click chemistry was used to graft polymer brushes on azide-modified silica nanoparticles. To the best of our knowledge, we report the highest surface grafting density for the attachment of a RAFT polymer via the "grafting to" approach. We exploited this method to prepare homopolymer (PAAm, PS, PMA) and diblock copolymer (PS-*b*-PMA) modified silica nanoparticles. This is the first example of synthesis of polyacrylamide−silica hybrid nanoparticles via any living free radical polymerization method. We have determined that the attached polymers exist in the brush regime.

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Supporting Information Available: Experimental procedure for the synthesis of diblock copolymer via RAFT polymerization, ATRP of MA, MALDI spectra of PAAm, and IR spectra and TGA of PS modified particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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