

# Polymer Chemistry

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## Polymer Chemistry

## ARTICLE

## Synthesis and Characterization of Silica Nanoparticles Functionalized with Multiple TEMPO Groups and Investigation on Their Oxidation Activity

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Series of novel silica nanoparticles functionalized with multiple TEMPO groups were synthesized using a novel, efficient and versatile protocol. First, the amino-functionalized silica nanoparticles (SN-NH<sub>2</sub>) were obtained using an improved one-pot hydrolysis and co-condensation procedure of APTES and TEOS agent, and further modified with 2-bromoisobutyryl bromide for macro-initiator (SN-Br) by amidation reaction. Then, the polymer grafted silica nanoparticles (SN-*g*-PGMA) with a dense shell layer of PGMA side-chains were realized via the surface-initiated atom transfer radical polymerization (SI-ATRP) procedure in a controlled manner. Subsequently, the azido groups were introduced onto PGMA side-chains by the quantitative ring-opening reaction of epoxide with sodium azide agent, and the TEMPO groups were further attached by efficient "Click" chemistry with Propargyl-TEMPO for the target SN-*g*-(PGMA-TEMPO). The evidences for the successful synthesis of target polymers and intermediates were sufficiently provided by FT-IR, EPR, XPS, TEM, <sup>1</sup>H NMR, and TGA measurements. As an important task, the catalytic activity of the synthesized SN-*g*-(PGMA-TEMPO) was evaluated by the oxidation of benzylic alcohols according to the Anelli protocol, as well as the excellent efficiency, stability and recyclability of the catalyst were also confirmed.

### Introduction

The stable radicals, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and its derivatives, with numerous applications in material science, organic chemistry, biochemistry and polymer chemistry have been well documented in several reviews.<sup>1-5</sup> Originally, in 1964, Rozantsev<sup>6</sup> had reported that the stable nitroxide radical on TEMPO has the ability to scavenge alkyl radicals at a near diffusion-controlled rate ( $R=10^7$  to  $10^9$  M<sup>-1</sup>S<sup>-1</sup>) to give stable alkoxyamine products. In fact, almost all the functions and applications of the stable nitroxide radicals are related to this rapid capturing reaction.

Typically, on the one hand, the stable nitroxide radical on TEMPO can be oxidized into oxoammonium cation, which is corresponded to *p*-type redox reaction. On the other hand, the nitroxides radical can also be reduced to the aminoxy anion, which ascribed to *n*-type doping of materials.<sup>7</sup> The most important feature of nitroxide radical is its remarkably rapid and reversible one-electron transfer in the oxidation process. Thus, as a promising application, the TEMPO and its derivatives make themselves an excellent candidate for electrode material.<sup>2</sup> Alternatively, for the application in biochemistry

field, the TEMPO and its analogues are usually used as spin labels,<sup>8-10</sup> which can provide dynamic information of target biological molecules by spin labelling Electron Paramagnetic Resonance (EPR) technique. Also, in polymer chemistry field, the TEMPO and the derived alkoxyamines are also widely used as mediators in nitroxide-mediated radical polymerization (NMRP) mechanism<sup>11-13</sup> or as reactants in nitroxide radical coupling (NRC) reaction.<sup>14-16</sup>

Recently, the nitroxide radical on TEMPO is also found its important role in organic chemistry. That is, the TEMPO and its derivatives have been widely studied as redox mediators / catalysts for the oxidation reaction of alcohols into carbonyl groups, which are among the most important functional groups in organic synthesis.<sup>17-20</sup> Usually, the metal compounds based on ruthenium,<sup>21</sup> palladium,<sup>22, 23</sup> molybdenum,<sup>24</sup> wolfram,<sup>25</sup> cobalt,<sup>26</sup> copper<sup>27-31</sup> are dominantly used as catalyst, and the TEMPO or its derivatives are always accompanied as common catalysts. Especially, the combination of copper salt [such as Cu<sup>I</sup>Cl, Cu<sup>II</sup>Br<sub>2</sub>, Cu<sup>I</sup>OTf, Cu<sup>II</sup>(OTf)<sub>2</sub>] with TEMPO agent is the most versatile catalytic system. However, the small molecules of TEMPO and its derivatives are always difficult to be separated from the target oxidized products, which largely limited the application of the TEMPO agent in industry. In order to overcome this drawback, some researchers attempted to attach the TEMPO groups onto certain main chains or matrix. For example, the PolyTEMPO based on poly(methacrylate)<sup>32</sup> and poly(acrylate)<sup>33</sup> main-chain can be realized by the classical radical polymerization of

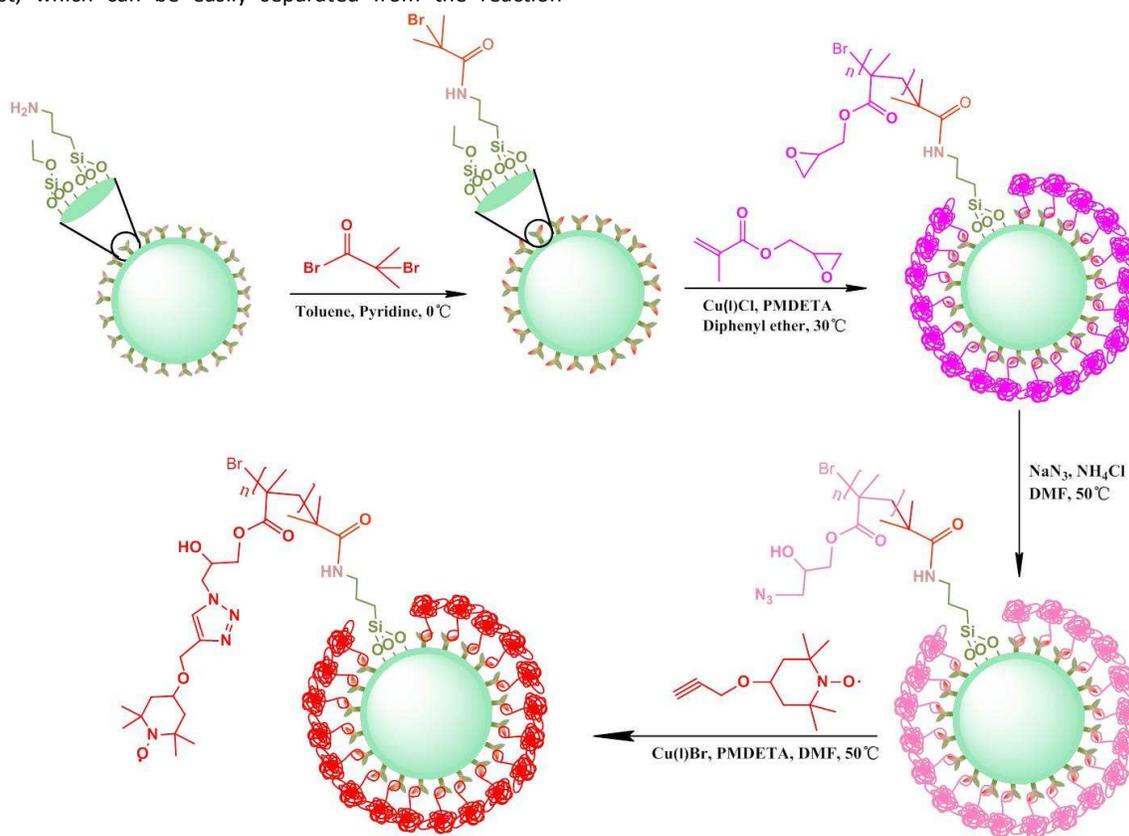
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2,2,6,6-tetramethylpiperidine (meth)acrylate monomers and the following modification procedure. The PolyTEMPO based on poly(vinyl ether)<sup>34</sup> and poly(allene)<sup>35</sup> main-chain can be obtained by cationic polymerization of the corresponding TEMPO-contained monomer. The PolyTEMPO based on poly(ether)<sup>36</sup> main-chain can be obtained by anionic ring-opening polymerization of epoxides bearing TEMPO groups, such as 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO). The PolyTEMPO based on poly(norbornene)<sup>37</sup> main-chain can be prepared by ring-opening metathesis polymerization (ROMP) of norbornene bearing TEMPO groups. Similarly, the PolyTEMPO based on poly(styrene)<sup>38</sup> and poly(acetylene)<sup>39</sup> main-chain are also realized. Obviously, these polymers also have some solubility in certain solvent because of the linear structure of main-chain and are still difficult to be removed from the reaction system when the oxidation reaction is finished.

Alternatively, the cross-linked polymers or silica particles bearing TEMPO groups were synthesized and even commercialized by direct modification of the surfaces with certain TEMPO-contained agent.<sup>40-47</sup> The large sizes of the cross-linked polymers or silica particles largely simplify the operation of catalyst, which can be easily separated from the reaction

system by centrifugation and recycled by several times. However, there were still some problems that these commercialized catalysts always kept their heterogeneous catalytic properties and were not effective because of the limited amount of TEMPO groups modified on surfaces of particles.<sup>4</sup>

Herein, considered the above limitations on TEMPO-based catalyst, we attempt to synthesize series of novel silica nanoparticles functionalized with multiple TEMPO groups [SN-*g*-(PGMA-TEMPO)] by developing a novel, efficient and versatile protocol. During the synthetic procedure, the silica nanoparticles functionalized with high density of amino groups (SN-NH<sub>2</sub>), macro-initiator (SN-Br) with high density of grafting sites and the polymer grafted silica nanoparticles (SN-*g*-PGMA) with a shell layer of dense side-chains were sequentially modified and prepared. And then, the azido groups were introduced onto PGMA side-chains and the TEMPO groups were further attached for the target SN-*g*-(PGMA-TEMPO) (Scheme 1). Finally, the catalytic activity of the SN-*g*-(PGMA-TEMPO) was evaluated by the oxidation of benzyl alcohols.



**Scheme 1** The synthetic procedure for polymer grafted silica nanoparticles SN-*g*-(PGMA-TEMPO).

## Experimental Part

### Materials

Tetraethoxysilane (TEOS, Lingfeng Chemical Industrial Co. Ltd, 99 %), 3-aminopropyltriethoxysilane (APTES, Aldrich, 99 %), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (HO-TEMPO, J&K, 98 %), 2-bromoisobutyryl bromide (Aldrich, 99 %),

N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99 %), sodium azide (NaN<sub>3</sub>, Alfa Aesar, 99 %), diphenyl ether (Aladdin, 98 %), N,N-dimethylformamide (DMF, Sinopharm Chemical Reagent Co. (SCR)), toluene (SCR, 99 %) and hydrofluoric acid (HF, SCR, 40 %), ethylenediaminetetraacetic acid disodium salt (EDTA salt, 98 %, SCR) were all used as received. Pyridine (SCR, 99 %) was refluxed and distilled from potassium solution. Glycidyl methacrylate (GMA, Aldrich, 99 %) and propargyl bromide (Aladdin, 98 %) were distilled under reduced pressure prior to use. Copper(I) bromide (Cu(I)Br, SCR, 95 %) and cuprous(I) chloride (Cu(I)Cl, SCR, 97%) were stirred overnight in acetic acid, filtered, then washed with ethanol and ethyl ether successively, and dried in a vacuum. 4-propargyl-2,2,6,6-tetramethylpiperidine-1-oxyl (Propargyl-TEMPO) was synthesized by nucleophilic substitution reaction between HO-TEMPO and propargyl bromide according to our previous work<sup>48</sup> and purified by recrystallization from cyclohexane to give the orange powder, and the calculated purity was 99.9 %. All other reagents and solvents were purchased from SCR and used as received except for special declaration.

### Characterization

The thermal gravimetric analysis (TGA) curves were obtained using a Perkin Elmer Pyris 1 at a heating rate of 10 °C/min from 120 °C to 800 °C. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a NEXUS 470 FT-IR spectrometer by KBr disk method in the range 400-4000 cm<sup>-1</sup> with a spectral resolution of 4 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra were recorded on a Bruker (400 MHz) spectrometer in CDCl<sub>3</sub> with tetramethylsilane (TMS) as the internal reference at 298 K. Dynamic light scattering (DLS) experiments were carried out at 25 °C on a Malvern particle size analyser (Zetasizer Nano ZS90) by dispersing nanoparticles (0.01 mg) into ethanol (1.0 mL). A He-Ne laser (633 nm, 4 mW) was used to detect the intensity of light scattering, and the detection angle was 90°. Transmission electron microscopy (TEM) images of particles were obtained by using a Tecnai G2 F20 S-Twin electron microscope. The samples were prepared by placing 10 µL of silica suspension on copper grids. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMX-8/2.7 at room temperature in solid state. X-ray photoelectron spectroscopy (XPS) experiments were carried out with a RBD 147 upgraded PerkinElmer PHI 5000C ESCA system equipped with a hemispherical electron energy analyzer. The Mg Kα ( $h\nu=1253.6$  eV) anode was operated at 14 kV and 20 mA. The spectra were recorded in the constant pass energy mode with a value of 46.95 eV, and all binding energies were calibrated using the carbonaceous C 1s line at 284.6 eV as reference.

### Synthesis of Silica Nanoparticles Modified with ATRP Initiator (SN-Br)

The monodisperse amino-functionalized silica nanoparticles (SN-NH<sub>2</sub>) were firstly synthesized according to the Stöber method by hydrolysis and condensation of TEOS and APTES in absolute ethanol (EtOH) and water (H<sub>2</sub>O) solvents using ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O) as catalyst. For example, into

a 500 mL round bottomed flask, TEOS (9.2 mL, 41.3 mmol), APTES (9.6 mL, 41.3 mmol), H<sub>2</sub>O (2.8 mL) and ethanol (180 mL) were sequentially added, the system was vigorously stirred and an emulsion was formed. Subsequently, NH<sub>3</sub>·H<sub>2</sub>O (20 mL) was added into the emulsion (pH=11.5), and the reaction system was kept at room temperature for 24 h. After the homogeneous colloidal dispersion was obtained, the dispersion was centrifuged and the resulting precipitate was sequentially washed three times by ethanol and water. The obtained SN-NH<sub>2</sub> was dried under vacuum at 50 °C for 12 h till to a constant weight, and SN1-NH<sub>2</sub> nanoparticles with average diameter ( $D_{DLS}$ ) of 321 nm was obtained. Similarly, by changing the volume ratio of EtOH to TEOS and APTES as 180 / 4.2 / 4.4, the silica nanoparticles with  $D_{DLS}$  of 226 nm can be prepared (SN2-NH<sub>2</sub>). In the following procedure, the derivation of silica nanoparticles with  $D_{DLS}$  of 321 nm (SN1-NH<sub>2</sub>) was used as example.

The silica nanoparticles modified with ATRP initiator (SN-Br) were prepared by amidation of NH<sub>2</sub> groups on SN-NH<sub>2</sub> with 2-bromoisobutyryl bromide. Typically, SN1-NH<sub>2</sub> (2.0 g, 12.4 mmol -NH<sub>2</sub> groups, which was calculated by the TGA result assuming that all the weight loss was contributed by the introduced 3-aminopropyl functionalities), nanoparticles dried by azeotropic distillation with toluene were dispersed in 50 mL anhydrous pyridine in a 150 mL round bottomed flask, and then 2-bromoisobutyryl bromide (2.0 mL, 16.0 mmol) was dropwise added at 0 °C within 30 min. After the reaction system was continued for 48 h, the nanoparticles were centrifuged and sequentially washed three times with THF and ethanol, and the obtained SN1-Br was then dried under vacuum at 50 °C for 12 h till to a constant weight.

### Synthesis of Silica Nanoparticles Grafted with Poly (glycidyl methacrylate) Side-chains (SN-g-PGMA)

Polymer grafted silica nanoparticles SN-g-PGMA was prepared by SI-ATRP of GMA monomers using SN-Br as macro-initiator and Cu(I)Cl / PMDETA as catalyst. Typically, SN1-Br (2.0 g, 1.14 mmol bromoisobutyryl groups, which was calculated by Formula (1) according to the TGA result), GMA (17.04 g, 1.20 mmol), PMDETA (208 mg, 1.20 mmol), Cu(I)Cl (118.8 mg, 1.20 mmol), and 20 mL anisole were sequentially charged into a 200 mL ampoule. The mixture was degassed by three freeze-thaw cycles and backfilled with nitrogen, and then immersed into a 30 °C oil bath. After the polymerization was proceeded for 12 h, the ampoule was dipped into liquid nitrogen to stop the polymerization. Finally, the crude products were separated by centrifugation, sequentially washed three times with DMF and ethanol, and the obtained SN1-g-PGMA1 was then dried under vacuum at 50 °C for 12 h. Similarly, by varying the polymerization time as 24 h, the polymer grafted silica nanoparticles SN1-g-PGMA2 with different length of side-chains can be produced.

Further, in order to give the information of PGMA side-chains, according to literature,<sup>49</sup> the silica core of polymer grafted silica nanoparticles SN-g-PGMA was removed by a hydrolysis procedure. Typically, into a 50 mL round bottomed

flask, SN1-*g*-PGMA1 (0.30 g) was added into 24 % HF aqueous solution (2.0 mL) and stirred at room temperature for 2.0 h. The mixtures were extracted three times by CH<sub>2</sub>Cl<sub>2</sub> and water, and the CH<sub>2</sub>Cl<sub>2</sub> layer was then concentrated under reduced pressure. The obtained PGMA homopolymer was finally dried under vacuum at 50 °C for 12 h.  $M_{n, GPC}=21,000$  g/mol, PDI=1.69.

#### Synthesis of Silica Nanoparticles Functionalized with Azido Groups [SN-*g*-(PGMA-N<sub>3</sub>)]

The SN-*g*-(PGMA-N<sub>3</sub>) was synthesized by ring-opening reaction of pendent epoxide groups on PGMA segments with NaN<sub>3</sub> agent. The typical procedure employed for the preparation was as the following. To a stirred solution of SN1-*g*-PGMA1 (2.5 g, 10.96 mmol epoxide groups, which was calculated by Formula (2) according to the TGA result) in 100 mL DMF in a 250 mL round bottomed flask, NaN<sub>3</sub> (1.0 g, 15.35 mmol) and ammonium chloride (0.85 g, 15.65 mmol) were added. The mixture was stirred at 50 °C for 24 h and the remained salts were removed by filtration. The crude products were sequentially washed with water, and the obtained SN1-*g*-(PGMA1-N<sub>3</sub>) was then dried under vacuum at 50 °C for 12 h.

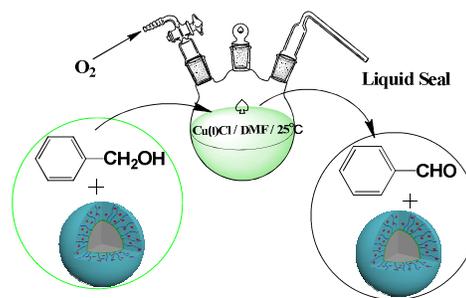
#### Synthesis of Silica Nanoparticles Functionalized with TEMPO Groups [SN-*g*-(PGMA-TEMPO)]

Using the classical “Click” chemistry, the TEMPO groups were further introduced onto polymer grafted silica nanoparticless. In a typical example, DMF (20.0 mL), Cu(I)Br (1.44 g, 10.0 mmol), PMDETA (2.08 mL, 10.0 mmol), and SN1-*g*-(PGMA1-N<sub>3</sub>) (2.0 g, 8.8 mmol of azido groups, assuming that all the epoxide moieties were transformed into azido groups) were mixed in a 100 mL ampoule, and degassed by three freeze-thaw cycles and backfilled with nitrogen. Subsequently, 6.0 mL degassed solution of Propargyl-TEMPO (3.15 g, 15.0 mmol of propargyl groups) in DMF was introduced into the ampoule using a syringe. The system was then immersed into a 90 °C oil bath and proceeded for 48 h. After the crude products were sequentially washed three times with DMF and saturated aqueous EDTA solution to remove the copper catalysts, the final SN1-*g*-(PGMA1-TEMPO) was obtained and dried under vacuum at 50 °C for 12 h.

#### Evaluation on the Catalytic Activity of SN-*g*-(PGMA-TEMPO) Nanoparticles

Using SN-*g*-(PGMA-TEMPO) as catalyst, a model oxidation of benzyl alcohol to aldehyde was monitored (Scheme 2). Typically, into a three-necked bottle, benzyl alcohol (1.04 mL, 10.0 mmol), SN1-*g*-(PGMA1-TEMPO) (1.34 g, 1.0 mmol TEMPO groups, which was calculated by Formula (3) according to TGA results), and Cu(I)Cl (0.10 g, 1.0 mmol) were mixed into 25 mL DMF solvent, and the oxygen was simultaneously bubbled into the system. After the system was stirred at 25 °C for a certain time, the filtrate was separated and the solvent was removed under reduced pressure. The SN1-*g*-(PGMA1-TEMPO) in filtrate was recovered by washing with water, and the final oxidized product derived from DMF solution was examined by <sup>1</sup>H NMR analysis. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 4.61 (s, -

C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH), 7.38-7.47 (s, -C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH), 7.64-7.89 (s, -C<sub>6</sub>H<sub>5</sub>CHO), 10.03 (s, -PhCHO).



**Scheme 2** The illustration of apparatus for oxidation reaction of benzyl alcohol catalysed by SN-*g*-(PGMA-TEMPO).

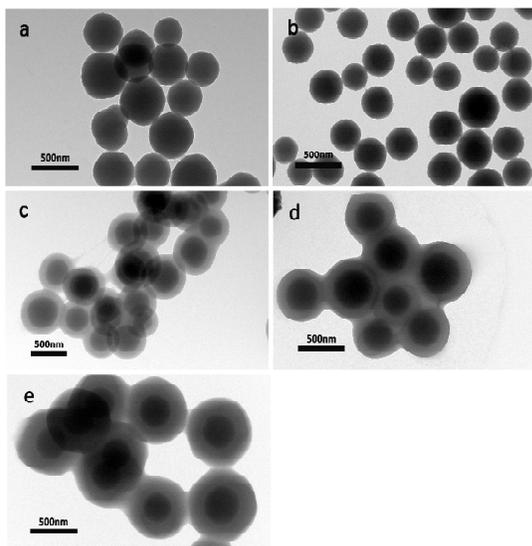
## Results and Discussion

The novel polymer grafted silica nanoparticles SN-*g*-(PGMA-TEMPO) functionalized with multiple TEMPO groups were realized by a novel, efficient and versatile protocol (Scheme 1): (a) the amino groups were introduced onto silica nanoparticles by an improved one-pot Stöber method for SN-NH<sub>2</sub> and the bromoisobutyryl groups were modified onto silica nanoparticles by amidation reaction for macro-initiator SN-Br, and the following surface-initiated atom transfer radical polymerization (SI-ATRP) procedure was carried out for polymer grafted silica nanoparticles SN-*g*-PGMA; (b) the azido groups were introduced onto PGMA segments by the quantitative ring-opening reaction between epoxide and NaN<sub>3</sub> agents for SN-*g*-(PGMA-N<sub>3</sub>), and the TEMPO groups were then attached by efficient “Click” chemistry for SN-*g*-(PGMA-TEMPO). Finally, aiming to develop an efficient catalyst for oxidation reaction, the catalytic activity, stability and recyclability of polymer grafted silica nanoparticles SN-*g*-(PGMA-TEMPO) were also evaluated.

#### Synthesis and Characterization of the Silica Nanoparticles SN-*g*-PGMA

Different from the literature<sup>50</sup> for typical graft polymers with silica nanoparticles as the matrix, in which the silica matrix was firstly produced by hydrolysis and condensation of TEOS, and certain functional groups were then introduced. In this contribution, a facile, improved one-step synthetic approach for silica nanoparticles was adopted: the TEOS and APTES agents (with a molar ratio of 1:1) were simultaneously mixed into ethanol, water, and NH<sub>3</sub>·H<sub>2</sub>O catalyst and co-condensed, and a constant stirring speed was kept. By this method, as much as possible NH<sub>2</sub> groups can be introduced onto the surface of silica nanoparticles, which might lead to a high grafting density in the following procedure. After the formed silica nanoparticles was washed three times by successive ethanol and water, the obtained SN-NH<sub>2</sub> can be dried under vacuum to powder, easily re-dispersed into

solvents to give the colloidal suspension and kept stable for several weeks without any aggregates or precipitation. From the TEM image (Fig. 1a), we can observe that the average sizes and homogeneity of the silica nanoparticles SN1-NH<sub>2</sub> (360 nm) can be well controlled. Subsequently, using the efficient amidation reaction between -NH<sub>2</sub> and 2-bromoisobutyryl bromide, the ATRP initiator was successfully introduced onto the surface of silica nanoparticles (SN1-Br). In order to guarantee a completion consumption of -NH<sub>2</sub> groups on the surface of SN1-NH<sub>2</sub>, the excessive (1.3 folds) 2-bromoisobutyryl bromide was fed and a prolonged amidation time (48 h) was proceeded. Additionally, the high reactivity between -NH<sub>2</sub> groups and acyl bromide was also well known. Thus, the quantitative efficiency of amidation on the surface of SN1-NH<sub>2</sub> can be actually guaranteed. Fig. 1b gave the similar distribution and sizes of SN1-Br (367 nm) silica nanoparticles as that of SN1-NH<sub>2</sub>, which actually confirmed that the only modification of certain groups on surface of silica nanoparticles would not lead to obvious change in their morphology.

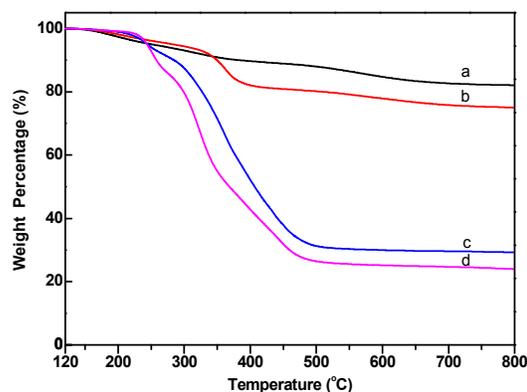


**Fig. 1** The TEM images of SN1-NH<sub>2</sub> (a), SN1-Br (b), SN1-g-PGMA1 (c), SN1-g-(PGMA1-N<sub>3</sub>) (d), and SN1-g-(PGMA1-TEMPO) (e).

For the silica nanoparticles modified with different functionalities, the TGA measurement could actually give more reliable information. For example, in Fig. 2a, the TGA curve of SN1-NH<sub>2</sub> gave a weight loss percentage of 18.0 % between 120 and 800 °C, while the weight loss percentage of SN1-Br was increased up to 25.0 % (Fig. 2b). By discriminating the weight loss percentage between SN1-NH<sub>2</sub> and SN1-Br nanoparticles, the content of 2-bromoisobutyryl groups ( $C_{Br}$ ) modified onto SN1-Br could be derived as  $5.69 \times 10^{-4}$  mol/g according to the Formula:

$$C_{Br} = \left( \frac{W\%_{SN-Br} - W\%_{SN-NH_2}}{1 - W\%_{SN-NH_2}} \right) / 150 \text{ (mol / g)} \quad (1)$$

Where  $W\%_{SN-Br}$  and  $W\%_{SN-NH_2}$  were the weight loss percentage of SN-Br and SN-NH<sub>2</sub> nanoparticles at 800 °C, respectively. The value of 150 was the molar mass of the introduced 2-bromoisobutyryl group. Similarly, the  $C_{Br}$  for SN2-Br could be derived as  $8.13 \times 10^{-4}$  mol/g. Further, based on the measured specific surface areas ( $S_{Surface}$ , which were 17.45 and 49.39 m<sup>2</sup>/g for SN1-NH<sub>2</sub> and SN2-NH<sub>2</sub>, respectively) of silica nanoparticles, the content of 2-bromoisobutyryl groups could also be derived as 19.62 and 9.91 groups/nm<sup>2</sup>, respectively.

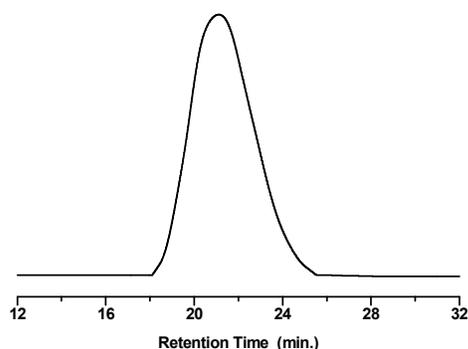


**Fig. 2** The TGA curves of SN1-NH<sub>2</sub> (a), SN1-Br (b), SN1-g-PGMA1 (c), and SN1-g-(PGMA1-TEMPO) (d).

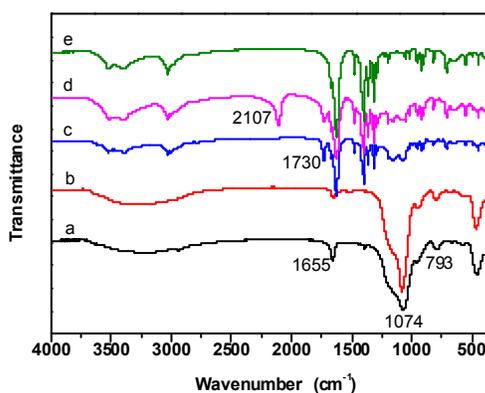
Subsequently, using SN-Br as macro-initiator, the PGMA side-chains were grafted onto silica nanoparticles by a SI-ATRP procedure for polymer grafted silica nanoparticles SN-g-PGMA. Based on the controllability of ATRP mechanism, the PGMA side-chains with different length on silica nanoparticles can be well tuned by changing the reaction time, and each initiating sites might grow a PGMA side chain. By etching the silica core, the grafted side-chains of PGMA can be released and its molecular weight can be derived by GPC measurement (Fig. 3). From the TEM image of SN1-g-PGMA1 (Fig. 1c), an obvious core-shell structure can be observed, and there was an increase of 208 nm of shell layer in diameters from SN1-Br (367 nm) to SN1-g-PGMA1 (575 nm). Additionally, the thickness of the PGMA shell was also dependent upon the length (or molecular weight) of the grafted PGMA side chains (Table 2). Again, the TGA curve further gave the information that the weight loss percentage of SN1-g-PGMA1 reached 71.7 % (Fig. 2c). By comparing the TGA data of SN1-Br and SN1-g-PGMA1, the introduced amount of GMA units ( $C_{GMA}$ ) can be calculated as  $4.38 \times 10^{-3}$  mol/g using the Formula:

$$C_{GMA} = \left( \frac{W\%_{SN-g-PGMA} - W\%_{SN-Br}}{1 - W\%_{SN-Br}} \right) / 142 \text{ (mol / g)} \quad (2)$$

Where  $W\%_{SN-Br}$  and  $W\%_{SN-g-PGMA}$  were the weight loss percentage of SN-Br and SN1-g-PGMA1 nanoparticles at 800 °C, respectively. The value of 142 was the molar mass of GMA unit.



**Fig. 3** The GPC trace of the released PGMA side-chains on SN1-*g*-PGMA1 ( $M_{n,GPC}=2.1 \times 10^4$  g/mol, PDI=1.69).



**Fig. 4** FT-IR spectra of SN1-NH<sub>2</sub> (a), SN1-Br (b), SN1-*g*-PGMA1 (c), SN1-*g*-(PGMA1-N<sub>3</sub>) (d), SN1-*g*-(PGMA1-TEMPO) (e).

Furthermore, the derivations from SN-NH<sub>2</sub> to graft polymer SN-*g*-PGMA were also evidenced by FT-IR, XPS and DLS measurements, respectively. From the FT-IR spectra (Fig. 4) of SN1-NH<sub>2</sub> and SN1-Br, the band at 1655 cm<sup>-1</sup> was assigned to the signal of N-H bond, and two characteristic bands at 1074 and 793 cm<sup>-1</sup> were assigned to the signals of Si-O-C<sub>2</sub>H<sub>5</sub> bonds.

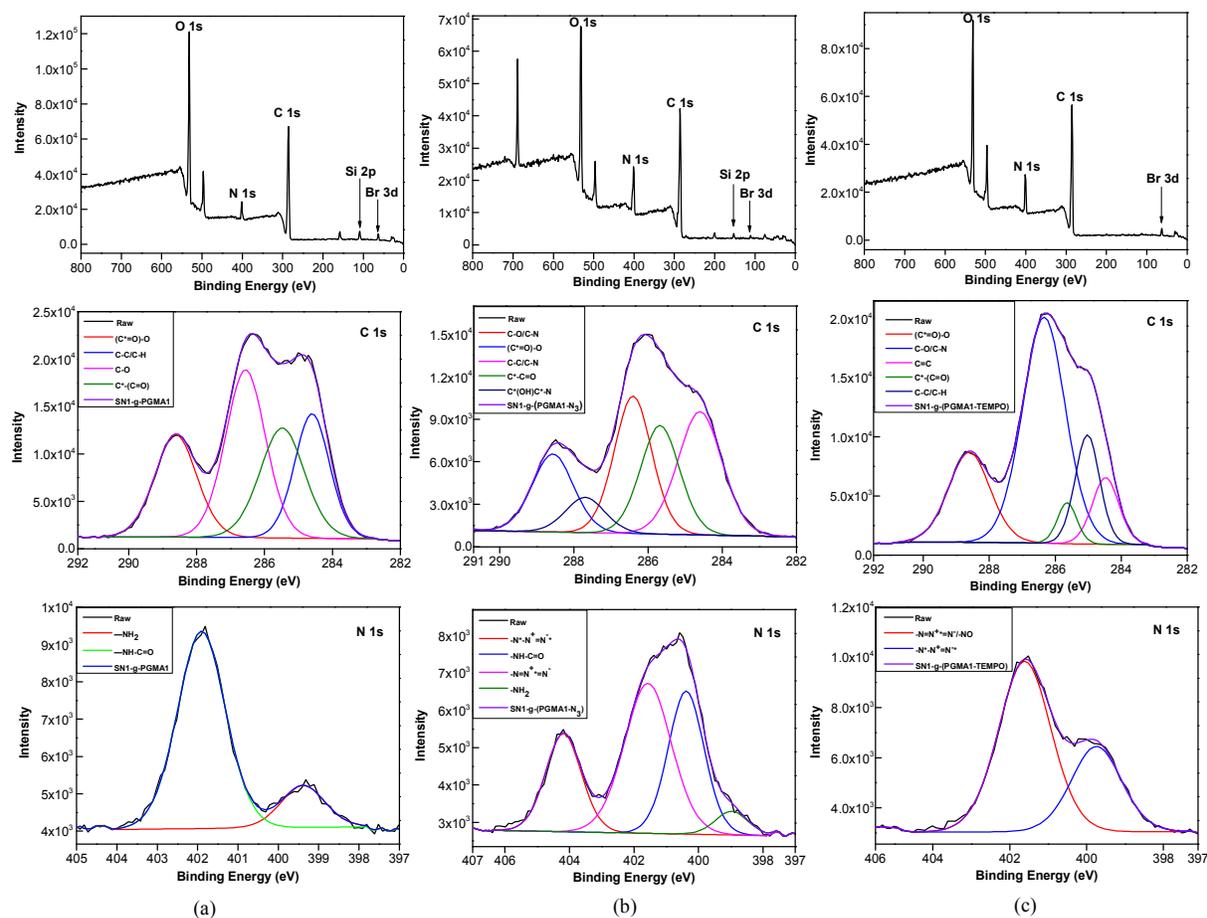
For polymer grafted silica nanoparticles SN1-*g*-PGMA1, the signal for stretch of the ester group (C=O bond) appeared at 1730 cm<sup>-1</sup>, and the presence of the epoxide group was confirmed by the band appearing at 909 cm<sup>-1</sup>. Also, in XPS survey spectrum for SN1-*g*-PGMA1, the deconvolution of the high-resolution C 1s spectrum gave four peaks located at binding energies of 284.6, 285.6, 286.6, and 288.6 eV (Fig. 5a, C 1s), which were corresponded to C-C/C-H, C\*(=O), C-O, and O-C\*=O functional groups, respectively. The deconvolution of the N 1s peaks at 399.4 and 401.9 eV gave a 4:21 ratio (Fig. 5a, N 1s), which were corresponded to partial unreacted NH<sub>2</sub> and -NH-C=O groups after the amidation reaction. From the XPS results, the atomic concentration of introduced N, O, C and Br elements can also be well calculated (Table 1). Obvious changes of all these four atomic concentration after each modification can be well discriminated, which confirmed that the successful proceeding of each modification reactions. Additionally, the derivation procedure can be well discriminated by DLS measurement (Table 2). Obviously, there were some regular changes in the diameters of silica nanoparticles from SN-Br to polymer grafted silica nanoparticles SN-*g*-PGMA, as well as the graft polymers with different length of side-chains. Thus, all the information from the above measurements actually confirmed that the polymer grafted silica nanoparticles SN-*g*-PGMA with a high dense shell layer have been successfully synthesized.

**Table 1** XPS atomic concentration of elements on silica nanoparticles.

Samples	XPS Atomic Concentration of Elements (%)				
	[C]	[N]	[O]	[Si]	[Br]
SN1-NH <sub>2</sub>	54.08	3.69	30.67	11.56	
SN1-Br	57.63	2.97	28.01	10.27	1.23
SN1- <i>g</i> -PGMA1	64.87	2.87	27.03	3.97	0.14
SN1- <i>g</i> -(PGMA1-N <sub>3</sub> )	65.68	4.86	23.37	4.88	0.02
SN1- <i>g</i> -(PGMA1-TEMPO)	68.12	5.08	23.23	1.61	0.05

**Table 2** The parameters for the synthesized silica nanoparticles.

Samples	D <sub>DLS</sub> (nm)	PDI	Samples	D <sub>DLS</sub> (nm)	PDI
SN1-NH <sub>2</sub>	321	0.083	SN2-NH <sub>2</sub>	226	0.014
SN1-Br	347	0.056	SN2-Br	262	0.067
SN1- <i>g</i> -PGMA1	613	0.547	SN2- <i>g</i> -PGMA1	449	0.525
SN1- <i>g</i> -(PGMA1-N <sub>3</sub> )	635	0.582	SN2- <i>g</i> -(PGMA1-N <sub>3</sub> )	549	0.674
SN1- <i>g</i> -(PGMA1-TEMPO)	882	0.174	SN2- <i>g</i> -(PGMA1-TEMPO)	701	0.170
SN1- <i>g</i> -PGMA2	835	0.258	SN2- <i>g</i> -PGMA2	547	0.275
SN1- <i>g</i> -(PGMA2-N <sub>3</sub> )	901	0.245	SN2- <i>g</i> -(PGMA2-N <sub>3</sub> )	713	0.273
SN1- <i>g</i> -(PGMA2-TEMPO)	1042	0.473	SN2- <i>g</i> -(PGMA2-TEMPO)	1146	0.058



**Fig. 5** XPS survey spectra and high-resolution C 1s, and N 1s spectra for SN1-g-PGMA1 (a), SN1-g-(PGMA1-N<sub>3</sub>) (b), and SN1-g-(PGMA1-TEMPO) (c).

### Synthesis and Characterization of the Silica Nanoparticles SN-g-(PGMA-TEMPO)

The introduction of PGMA side-chains on silica nanoparticles could bring a versatile application of the obtained polymers because that the epoxide groups on GMA units are a kind of very useful functionalities with special activity.<sup>51, 52</sup> For example, the epoxide groups can be attacked by some nucleophile to realize certain post-modification of PGMA segment. Herein, NaN<sub>3</sub> agent was the preferred nucleophile, not only because of its high nucleophilicity and conversion efficiency, but also because of the usefulness of the formed azido group as a chemical platform for introducing countless other substituents via the efficient “Click” chemistry.<sup>53-55</sup> In a typical modification procedure, the reaction between epoxide groups and NaN<sub>3</sub> agent was conducted in the presence of NH<sub>4</sub>Cl to protonate the alkoxides formed during the ring-opening reaction,<sup>56</sup> which can prevent the possible side reactions. In order to obtain a quantitative transformation of epoxides groups, the excessive (1.4 folds) NaN<sub>3</sub> was used.

Subsequently, by means of the efficient “Click” chemistry between Propargyl-TEMPO and the introduced azido groups, the functionalized polymer grafted silica nanoparticles SN-g-(PGMA-TEMPO) were obtained.

From Fig. 1, as the observed core-shell structure for SN1-g-PGMA1 (575 nm), the SN1-g-(PGMA1-N<sub>3</sub>) and SN1-g-(PGMA1-TEMPO) also gave the similar core-shell morphologies with the average sizes of 581 and 689 nm, respectively, which also have the similar increasing tendency as that derived from the DLS results (Table 2). Obviously, the thickness of the nanoparticles have a slightly increase from SN1-g-PGMA1 (101 nm) to SN1-g-(PGMA1-N<sub>3</sub>) (109 nm) and SN1-g-(PGMA1-TEMPO) (175 nm), which might due to the introduction of plenty of functional azido and TEMPO groups. Also, by comparing the TGA data, there was an increase of weight loss percentage from SN1-g-PGMA1 to SN1-g-(PGMA1-TEMPO), and the introduced amount of TEMPO groups ( $C_{\text{TEMPO}}$ ) can be calculated as  $7.46 \times 10^{-4}$  mol/g using the Formula:

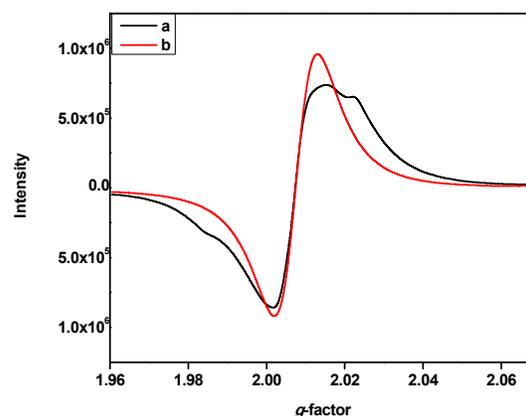
$$C_{\text{TEMPO}} = \left( \frac{W\%_{\text{SN-g-PGMA-TEMPO}} - W\%_{\text{SN-g-PGMA}}}{1 - W\%_{\text{SN-g-PGMA}}} \right) / 252 \text{ (mol/g)} \quad (3)$$

Where  $W\%_{\text{SN-g-PGMA-TEMPO}}$  and  $W\%_{\text{SN-g-PGMA}}$  were the weight loss percentage of SN1-*g*-(PGMA1-TEMPO) to SN1-*g*-(PGMA1-TEMPO) at 800 °C, respectively. The value of 252 was the molar mass of the introduced TEMPO unit.

Again, the introduction of azido and TEMPO groups onto silica nanoparticles was also confirmed by FT-IR and XPS results. From FT-IR spectra, the presence of the azido group in SN1-*g*-(PGMA1-N<sub>3</sub>) was confirmed by the signal observed at 2107 cm<sup>-1</sup> (Fig. 4d). After the “Click” chemistry, the characteristic and asymmetric stretch of the azido group observed at 2107 cm<sup>-1</sup> was completely disappeared in spectrum for SN1-*g*-(PGMA1-TEMPO) (Fig. 4e). Alternatively, the XPS measurement further gave some defined information of the transformation of polymer grafted silica nanoparticles. From the XPS spectrum for SN1-*g*-(PGMA1-N<sub>3</sub>), the deconvolution of the high-resolution C 1s spectrum gave five peaks located at binding energies of 284.6, 285.7, 286.4, 287.7, and 288.6 eV (Fig. 5b, C 1s), which were corresponded to C-C/H, C\*(C=O), C-O/C-N, -C\*(OH) and O-C\*=O groups, respectively. The deconvolution of N 1s peaks at 404.2 and 401.5 eV gave a 1:2 ratio (Fig. 5b, N 1s) as expected for an azido group having a much electron-poorer central N compared with the other two nitrogen atoms. For sample SN1-*g*-(PGMA1-TEMPO), the most notable in the high resolution C 1s spectrum was the appearance of a component at 284.5 eV (Fig. 5c, C 1s), which was assigned to the C\* in C=C of the triazole moiety. The high-resolution N 1s spectrum (Fig. 5c, N 1s) showed a broad peak, which can be resolved into two components centred at 399.7 and 401.9 eV with a ratio of 1:2. The deviation to the ratio of 2:1 as expected for an azido group having a much electron-poorer central N compared with the other two nitrogen atoms can be attributed to the introduction of -NO· on TEMPO group, which increased the area at 401.9 eV and resulted to a broad band. These binding energies were also rather agreed with the previous reports on the triazole functionality.<sup>57</sup> At the same time, the high-energy peak at 404.2 eV assigned to the electron deficient central N of azido group in SN1-*g*-(PGMA1-N<sub>3</sub>) was completely disappeared, which underlined the nearly 100 % efficiency of “Click” chemistry. Also, the derivation procedures could further be confirmed by the calculated atomic concentration of elements (Table 1).

Furthermore, the introduced TEMPO groups on PGMA side-chains were measured and confirmed by EPR measurement, which was a typical method for the paramagnetic compound. As shown in Fig. 6a, the *g*-factor of SN1-*g*-(PGMA1-TEMPO) nanoparticles was observed as 2.0067, which was rather corresponded to a typical N-O· radical on TEMPO reported in reference.<sup>58</sup> Obviously, all the results gave the strong evidence that the polymer grafted silica

nanoparticles SN-*g*-(PGMA-TEMPO) functionalized with multiple TEMPO groups had been actually realized.



**Fig. 6** The EPR spectra of SN1-*g*-(PGMA1-TEMPO) before (a) and after (b) the oxidation of benzyl alcohol.

#### Evaluation on Catalytic Activity of the Silica Nanoparticles SN-*g*-(PGMA-TEMPO)

Following the above section, the silica nanoparticles SN-*g*-(PGMA-TEMPO) attached with multiple TEMPO groups have been successfully synthesized and confirmed. Additionally, this material might find its application in oxidation reaction. Following a typical protocol for the Anelli oxidation of alcohols to aldehydes and ketones, the catalytic activity of SN-*g*-(PGMA-TEMPO) was also investigated in this contribution. The catalyst reaction was proceeded in the presence of Cu(I)Cl and our SN-*g*-(PGMA-TEMPO) in DMF solvent, and the high catalytic efficiencies (almost 100 %) were always traced and confirmed by the <sup>1</sup>H NMR measurement.

As described in INTRODUCTION section, there were several catalysts functionalized with TEMPO groups have been commercialized.<sup>59</sup> However, these catalysts were always synthesized by direct modification the surface of cross-linked polymer and silica particles, and only limited TEMPO groups can be modified on the solid matrix.<sup>60</sup> Thus, the catalytic activity was also always limited because of the heterogeneity between the catalyst and reaction solution, and some significant loss of catalytic activity for the recycled analogous was also always accompanied.<sup>61</sup> In our SN-*g*-(PGMA-TEMPO), the dense and stretched PGMA segment, on the one hand, provided a possibility to introduce plenty of TEMPO groups; on the other hand, brought an excellent solubility of the catalyst in reaction solution. Ultimately, the prominent catalytic activity in oxidation reaction can be realized.

Additionally, using the silica nanoparticles as catalyst, an important advantage is its recyclability. As expected, in model reaction, the SN-*g*-(PGMA-TEMPO) can be easily and quantitatively recovered from the reaction system by a mechanical centrifugation method. Also, the high stability is another important character endowed on our SN-*g*-(PGMA-TEMPO). In order to confirm this versatility, the catalyst SN-*g*-(PGMA-TEMPO) was subjected to 4 runs of oxidation reaction-

recovery procedures. The results promisingly demonstrated that silica nanoparticles functionalized with multiple TEMPO groups can retain their pronounced efficiency (100 %) even after 4 runs of cycles. Also, in Fig. 6, almost no obvious difference can be discriminated on the ESR spectra of SN1-*g*-(PGMA1-TEMPO) before and after 4 runs of cycles, which gave another solid evidence for the high stability of the catalyst. The high stability of SN-*g*-(PGMA-TEMPO) can be attributed to the stable connection between PGMA side-chains and TEMPO groups, and the possible loss of TEMPO groups from the silica nanoparticles can be largely avoided.

## Conclusions

In this contribution, we have successfully synthesized series of novel silica nanoparticles SN-*g*-(PGMA-TEMPO) functionalized with multiple TEMPO groups by SI-ATRP technique and efficient "Click" chemistry. Based on the controllability on the sizes of silica nanoparticles, the functionalities of amino and bromoisobutyryl groups, the SI-ATRP mechanism and modification procedure, the attached numbers of TEMPO groups can all be well tuned, which actually confirmed as a novel, efficient and versatile protocol. Also, in this contribution, the synthesized SN-*g*-(PGMA-TEMPO) was found with promisingly application in classical oxidation reaction of alcohols with perfect catalytic activity, efficiency, stability and recyclability. Comparing with the present commercialized analogues, the special advantages of SN-*g*-(PGMA-TEMPO) can be attributed to the excellent homogeneity and plenty of the attached TEMPO groups brought by the PGMA side-chains. Thus, the synthesized SN-*g*-(PGMA-TEMPO) is hoped to find its potential application in industry in the near future.

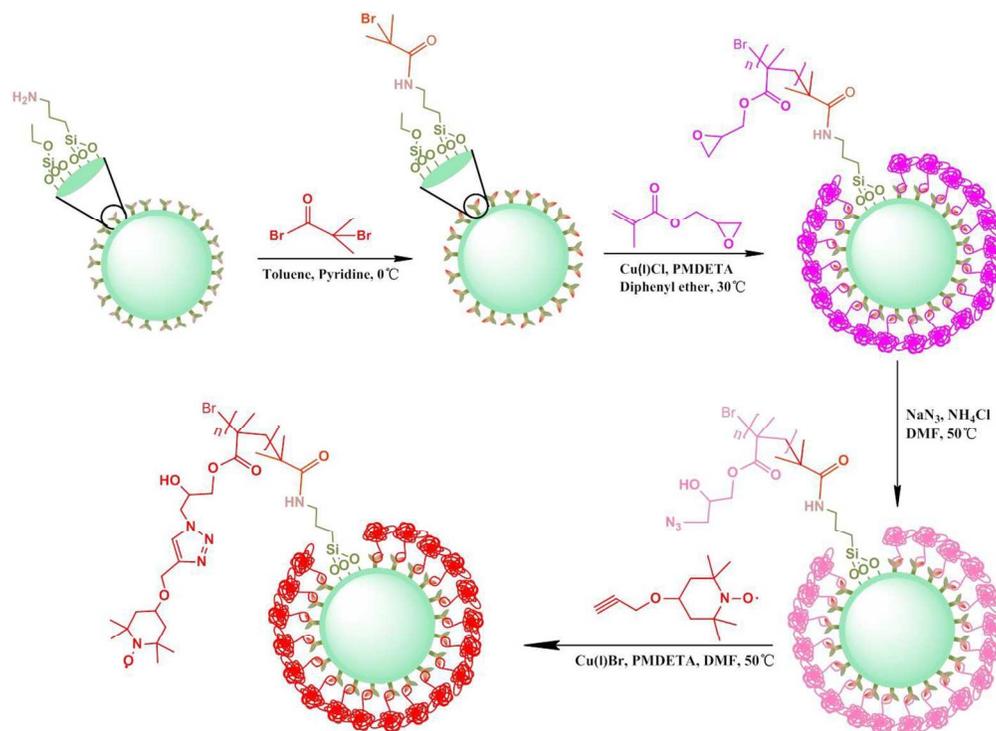
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Series of novel silica nanoparticles functionalized with multiple TEMPO groups were synthesized using a novel, efficient and versatile protocol. The catalytic activity of the synthesized SN-g-(PGMA-TEMPO) was evaluated by the oxidation of benzylic alcohols according to the Anelli protocol, as well as the excellent efficiency, stability and recyclability of the catalyst were also confirmed.

239x175mm (150 x 150 DPI)