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Immobilized copper catalyst for atom transfer radical addition and polymerization

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A novel multidentate amine grafted on silica gel and magnetic microsphere was prepared. Its chemical structure was confirmed by C^{13} NMR, XPS and FTIR, and the nitrogen content was determined by elemental analysis. It was also used as a ligand for CuCl and successfully catalyzed the atom transfer radical addition of both carbon tetrachloride (CCl_4) to methyl methacrylate and methyl trichloroacetate to styrene, repeatedly. The conversion and purity of the product were determined through gas chromatography and ^1H NMR, respectively. The immobilized copper catalyst complex was also used in atom transfer radical polymerization of styrene initiated by 1,1,1,3-tetrachloro-3-phenylpropane and methyl methacrylate initiated by methyl 2-methyl-2,4,4,4-tetrachlorobutyrate, respectively. Although the polymerization took place successfully, it did not proceed in a controlled fashion. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: ATRA; ATRP; copper catalysts; immobilization

Introduction

In recent years, transition-metal-catalyzed Kharasch addition reaction (atom transfer radical addition, ATRA) has been extensively investigated, especially since ATRA was successfully extended to a controlled radical polymerization, atom transfer radical polymerization (ATRP), in 1995.[1,2] A wide range of metal catalysts have been reported in ATRA, such as copper,[3,4] nickel,[5] iron[6,7] and ruthenium[8–10] complexes. Verpoort *et al*.[11] reported an immobilized multifunctional Schiff bases containing ruthenium complexes on MCM-41 and used them for ATRA. Compared with the homogeneous catalysts, the use of heterogeneous catalysts offers several advantages such as simplification of reaction procedures, easy separation of products, repeated use and the possibility of designing continuous flow processes.[12–15] Recently, Clark *et al*.[16] used solid-supported copper catalyst for atom transfer radical cyclizations. Solid-supported copper catalysts for ATRP were also reported. Haddleton and co-workers showed that ATRP of methyl methacrylate (MMA) and styrene (St) were feasible by supporting cuprous bromide (CuBr) using a Schiff base ligand to amino-functionalized silica gel and crosslinked polystyrene.[17] However, the polymerizations by these catalysts showed poor living characteristics. The molecular weights were significantly higher than those predicted, and the polydispersities were high. Matyjaszewski *et al*.[18] reported the use of surface-modified silica gel particles with immobilized multidentate amine donor ligands for copper-mediated ATRP, but the catalyst immobilized by multidentate amine-functionalized silica gel did not mediate a living polymerization of MMA, methyl acrylate (MA) and St. Zhu *et al*.[19] investigated the spacer effect by using silica gels grafted with tetraethyldiethylenetriamine or di(2-picolyl)amine via poly(ethylene glycol) spacers of different lengths for MMA polymerizations. In the recent literature[20–22] there are also some examples of successful immobilization of catalysts that maintain their activity on a solid support. Matyjaszewski *et al*.[23] reported a new two-component catalyst system consisting of an immobilized catalyst and a soluble catalyst in ppm quantities and applied this system in ATRP successfully. A high monomer conversion ($>$90%) was achieved with a predetermined molecular weight and narrow molecular weight distribution (M_w/M_n 1.1–1.3) in the ATRP of MMA and MA.

In this study, we first prepared a novel multidentate amine-modified silica gel, then used it as a ligand for CuCl in ATRA of CCl_4 with MMA and methyl trichloroacetate (MTCA) with St, and finally used it in ATRP of St initiated by 1,1,1,3-tetrachloro-3-phenylpropane (TCPP) and MMA initiated by methyl 2-methyl-2,4,4,4-tetrachlorobutyrate (MMTCB).

We also prepared a multidentate amine-modified magnetic microsphere and evaluated its efficiency as a ligand for CuCl in ATRA and ATRP. Multidentate amine-modified magnetic microspheres not only had the same advantages as multidentate amine-modified silica gel, but also could be separated very fast and easily by the use of a magnet.

Experimental

Materials

γ-Aminopropyl trimethoxy silane (γ-APS, Zhangjiagang Guotai-Huarong Chemical New Materials Co.) and trihydroxymethyl propyl triacrylate (TMPTA, Tianjinshi Tianjiao Chemical Co.) were used without further purification. St (Polymerization grade, Yanshan Petrochemical Co.), MMA (99%, Beijing Chemical Reagent Company) and butyl acrylate (BA, Analytical grade, Beijing Chemical Plant) were dried over anhydrous $MgSO_4$, then distilled under reduced pressure, and stored at $-15\,^{\circ}C$ in a freezer.

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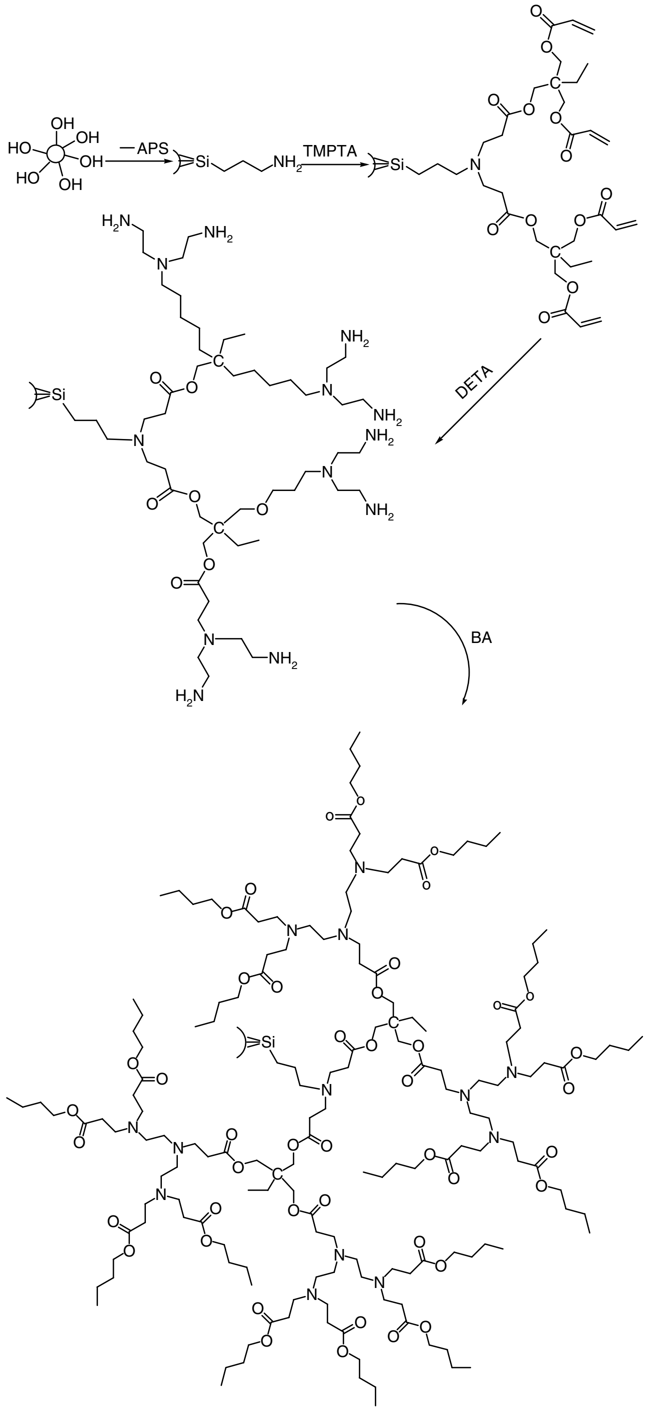
Diethylenetriamine (DETA) was obtained from Beijing Chemical Reagent Company. TCPP and MMTCB were synthesized in our laboratory. Toluene and tetrahydrofuran (THF) were redistilled under normal pressure before use. Silica gel (chromatographic grade, Qingdao Haiyang Chemical Plant) was treated with nitric acid ($HNO_3 : H_2O = 1:1$) at refluxing temperature for 3 h, 18% hydrochloric acid at room temperature for 6 h, and then calcined in a muffle at 200 °C for 10 h, finally being dried in vacuum at 110 °C for 48 h before use. All other chemicals were analytical reagents and were used as received. All water was doubly distilled.

Preparation of Multidentate Amine-modified Silica Gel

Multidentate amine-modified silica gel was synthesized through the following steps as shown in Scheme 1. Firstly, the introduction of amino groups onto the silica surface was achieved by treating the surface silanol groups with γ-APS. A suspension of 50.0 g of silica gel and 50 ml of γ-APS was stirred at 70 °C in 150 ml of toluene solution for 6 h. The product was then filtered and transferred to a Soxhlet extraction apparatus for refluxing extraction in toluene and methanol for 10 h, respectively. The product was dried under vacuum at 50 °C over 48 h. Secondly, a mixture of 35 g of γ-APS-modified silica gel (52 mmol amino groups) and 46.2g (156 mmol) of TMPTA was added to a 500 ml flask with 250 ml of methanol as solvent. The mixture was stirred at 25 °C for 4 days in order to react sufficiently. The solid product was then filtered and transferred to a Soxhlet extraction apparatus for refluxing extraction in methanol and tetrahydrofuran for 24 h. After extracting, it was dried under vacuum at 50 °C over 48 h, and TMPTA-modified silica gel was obtained. Thirdly, a suspension of 30.0 g of TMPTA-modified silica gel (about 90 mmol of double bonds) and 27.8 g (270 mmol) of DETA was stirred at 25 °C in a flask with 250 ml of methanol as solvent for 4 days. The obtained DETA-modified silica gel was purified in the same way as γ-APS-modified silica gel. Finally, 30.0 g of DETA-modified silica gels (about 360.0 mmol of amino groups) was treated with 83.2 g (720 mmol) of BA in 250 ml of methanol for 6 days at 25 °C, and multidentate amine-modified silica gel was obtained. It was also purified in the same way as γ-APS-modified silica gel. All the above reactions were carried out under nitrogen atmosphere.

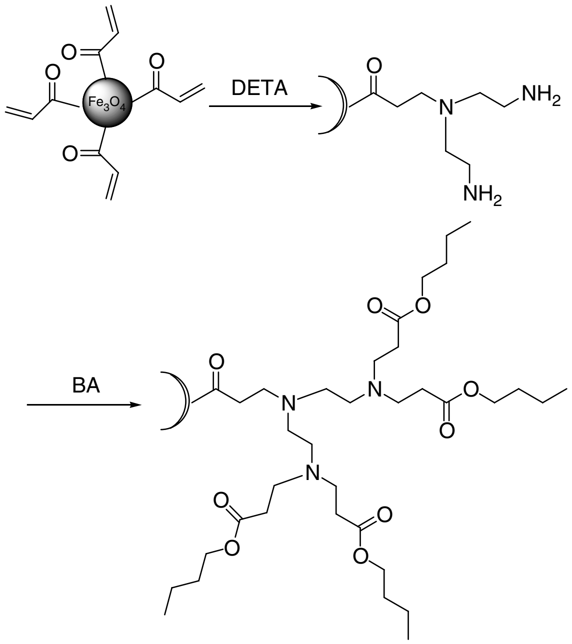
Preparation Fe_3O_4 Ferrofluid and its Surface Modification

A 150 ml aliquot of $FeCl_3 \cdot 6H_2O$ aqueous solution (0.5 M) and 75 ml of $FeSO_4$ aqueous solution (0.5 M) were put into a 250 ml four-necked flask equipped with a stirrer, a condenser, a thermometer and an N_2 inlet. A 20 ml aliquot of 25% $NH_3 \cdot H_2O$ solution was added under stirring at 30 °C until pH reached 9.0, and the reaction was allowed to proceed for 30 min. The resulting colloidal particles were washed with water until neutrality was achieved. Finally, the magnetite content was adjusted to 10% (w/v) using the mixture of ethanol and water (volume ratio 1 : 5). The dispersed Fe_3O_4 was stirred at 60 °C under an atmosphere of N_2 and 3.0 ml of oleic acid was added dropwise. The temperature was raised to 85 °C, and the reaction was allowed to proceed for 30 min and then was cooled. Finally, 1.0 g of sodium dodecyl sulfonate (SAS) was added and stirred for 30 min and obtained the magnetic fluid with good dispersivity and stability.



Scheme 1. The synthetic route of immobilized multidentate amine ligand on silica gel.

A 10 ml aliquot of dispersed Fe_3O_4 obtained above 0.1 g of SAS, 0.04 g of potassium persulfate, 2 ml of MMA, 0.2 ml of TMPTA and 140 ml of mixed solvent of ethanol and water (volume ratio 1 : 5) was added to a 250 ml four-necked flask equipped with a stirrer, a condenser, a thermometer and an N_2 inlet. After pre-emulsion treatment by sonicating for 30 min, the temperature was raised to 70 °C, and a mixture of 8 ml of MMA and 0.8 ml of TMPTA was added dropwise in 30 min. The polymerization was allowed to proceed for 8 h. The obtained brown magnetic polymer microspheres were collected by putting a magnet under a beaker bottom, then washed with deionized water and ethanol repeatedly, and finally dried under vacuum at 50 °C.



Scheme 2. The preparation route of immobilized multidentate amine ligand on magnetic microspheres.

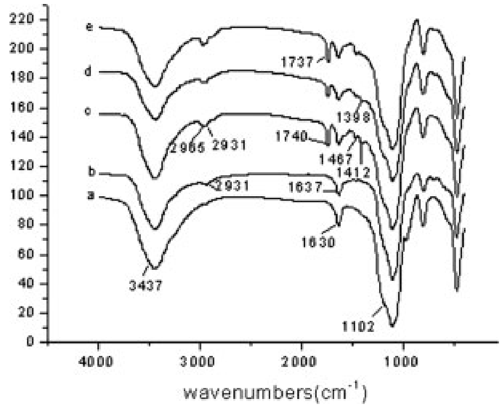


Figure 1. FTIR spectra of silica gel and modified silica gel obtained at different steps. (a) Silica gel; (b) γ-APS-modified silica gel; (c) TMPTA-modified silica gel; (d) DETA-modified silica gel; (e) multidentate amine-modified silica gel.

Preparation of Multidentate Amine-modified Magnetic Microspheres

Multidentate amine-modified magnetic microspheres were prepared through the following steps, as shown in Scheme 2. Firstly, a suspension of 2.0 g of magnetic microspheres with the double bonds on the surface obtained above and excess DETA was stirred at 25 °C for 4 days with 250 ml of methanol as solvent. DETA-modified magnetic microspheres with the amino groups on the surface were collected using a magnet and washed with methanol repeatedly and finally dried at 50 °C under vacuum. Secondly, 2.0 g of DETA-modified magnetic microspheres reacted with excess BA in 250 ml of methanol. The mixture was stirred at 25 °C for 6 days, and multidentate amine-modified magnetic microspheres were collected using a magnet and washed with methanol repeatedly and finally dried 50 °C under vacuum.

Use of Multidentate Amine-modified Silica Gel or Magnetic Microspheres as Ligand for CuCl in ATRA

In a typical experiment, 30 mmol of MMA, 50 mmol of CCl_4, 1 mmol of CuCl, 0.4 g of multidentate amine-modified silica gel and 30 ml of toluene were added to a 100 ml dried round-bottom flask equipped with a magnetic stirrer. After the flask was sealed with a rubber septum, it was degassed by three freeze–pump–thaw cycles and subsequently purged under argon atmosphere, and then immersed in an oil bath thermostated at 85 °C. At definite time intervals, portions of the sample were withdrawn from the flask using argon-filled gas-tight syringes to determine monomer conversions by GC and yields by ^1H NMR. The final crude product was distilled at 30 °C under reduced pressure to remove toluene and unreacted CCl_4.

Use of Multidentate Amine-modified Silica Gel or Magnetic Microspheres as Ligand for CuCl in ATRP

In a typical experiment, 96 mmol of St, 1 mmol of TCPP, 1 mmol of CuCl, 0.4 g multidentate amine-modified silica gel and 10 g of xylene were added to a 100 ml dried round-bottom flask equipped with a magnetic stirrer. After the flask was sealed with a rubber septum, it was degassed by three freeze–pump–thaw cycles and subsequently purged under argon atmosphere, and then immersed in an oil bath thermostated at 110 °C. At definite time intervals, portions of the sample were withdrawn from the flask using argon-filled gas-tight syringes to determine monomer conversions and molecular weights.

Characterization

FTIR spectra were recorded at room temperature on a Nicolet Nexus-670 spectrometer using KBr tablets. ^1H NMR spectra were recorded on a Bruker AV 600 MHz spectrometer with $CDCl_3$ as solvent at room temperature. The yields were determined by ^1H NMR spectroscopy. ^{13}C NMR spectra were recorded on a Bruker AV 300 MHz spectrometer. The nitrogen content was measured by an HP-MOD/106 elemental analysis instrument. Conversion in ATRA was determined using a GC-7800-A gas chromatograph equipped with a FID detector and an PEG-20M column (30 m × 0.25 mm).

Results and Discussion

Preparation of Multidentate Amine-modified Silica Gel

The attachment of amino groups onto silica gel was based on the reaction of silicon alkoxides of γ-APS with silanol groups on the particle surface. Therefore, the content of silanol groups would affect the content of amino groups introduced onto the particle surface. For this purpose, the silica gel was treated with 32% (wt) nitric acid at refluxing temperature for 3 h, 18% (wt) hydrochloric acid at room temperature for 6 h, calcined in muffle at 200 °C for 10 h, and finally dried in vacuum at 110 °C for 48 h before use. The strong absorption peak appeared at about 3437 cm^{-1} in Figure 1a demonstrated that the treatment was successful. Furthermore, it should be noted that silica gel untreated by nitric acid had pale yellow color after calcined in muffle, while that treated with nitric acid had a white color. This phenomenon indicated that nitric acid not only activated the silanol group, but also removed the impurities adsorbed on the silica gel surface. The amount of γ-APS grafted onto silica gel was determined by HP-MOD/106 elemental analysis apparatus. The calculated amount of γ-APS

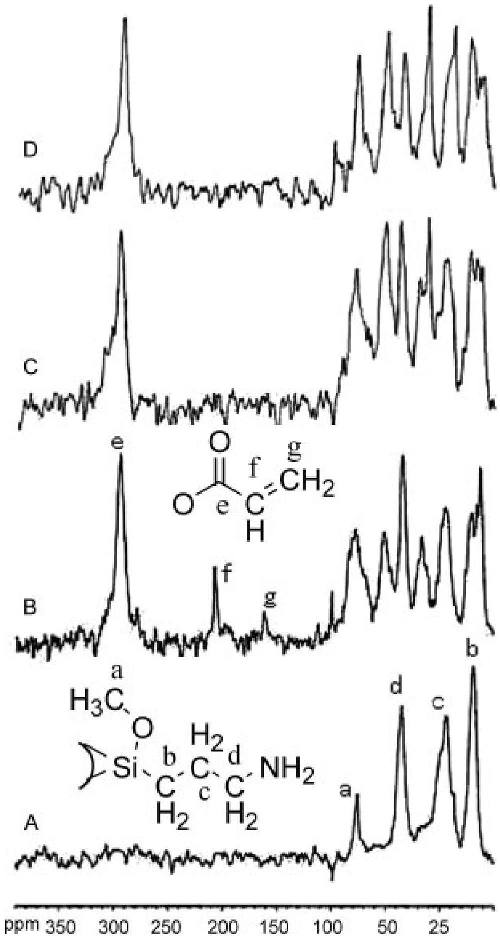


Figure 2. ^{13}C NMR spectra of modified silica gel obtained at different steps. (A) γ-APS-modified silica gel; (B) TMPTA-modified silica gel; (C) DETA-modified silica gel; (D) multidentate amine-modified silica gel.

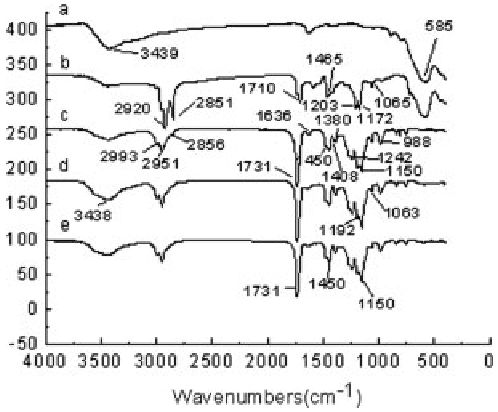


Figure 3. FTIR spectra of unmodified Fe_3O_4 and modified Fe_3O_4 obtained at different steps. (a) Fe_3O_4; (b) Fe_3O_4 nanoparticles modified with oleic acid and sodium dodecyl sulfonate; (c) magnetic microspheres; (d) DETA-modified magnetic microspheres; (e) multidentate amine-modified magnetic microspheres.

was 1.486 mmol g^{-1} of silica gel. Comparing the FTIR spectrum (Fig. 1b) of γ-APS-modified silica gel with that of silica gel (Fig. 1a), the absorption at 1630 cm^{-1} shifted to 1637 cm^{-1}, which was the characteristic absorption of amino groups, and a new absorption appeared at 2931 cm^{-1}, which was the characteristic absorption of the asymmetric stretching vibration of CH_2 bands. Figure 2(a) shows the ^{13}C NMR spectrum of γ-APS-modified silica gel. We can observe that the methylene carbon atom adjacent to Si atom resonated at 9.8 ppm, the middle methylene carbon atom resonated in the region of 18.7–22.1 ppm, and the methylene carbon atom adjacent to amino groups resonated at 42.5 ppm. The two methyl carbon atoms of the methoxy group resonated at 63.0 ppm. The above results show that γ-APS-modified silica gel was obtained.

The γ-APS-modified silica gel then reacted with excess TMPTA via the Michael addition reaction. Figure 1(c) shows the FTIR spectrum of TMPTA-modified silica gel. The new absorption at 1740 cm^{-1} was ascribed to the stretching vibration of ester bond. The absorptions at 2965 and 2931 cm^{-1} were the characteristic absorption of the asymmetric stretching vibration of CH_3 and CH_2 bonds. The absorptions at 1412, 1467 and 1398 cm^{-1} were the characteristic absorptions of the bending vibration of CH_3 and CH_2 bonds, and the absorption at 1412 cm^{-1} was ascribed to the CH_2 bond adjacent to ester group. The stretching vibration of C–O–C and Si–O–Si was overlapped at 1102 cm^{-1}. The absorption at 1637 cm^{-1} was ascribed to the characteristic absorption of amino groups and it was overlapped with the absorption of double bond of TMPTA. Figure 2(b) is the ^{13}C NMR spectrum of TMPTA-modified silica gel. The carbon atom of carbonyl group resonated at 172 ppm, and the carbon atoms of double bond resonated at 105.9 and 128.4 ppm.

The DETA-modified silica gel was obtained by the reaction of TMPTA-modified silica gel with a great excess of DETA. Figure 2(c) shows its ^{13}C NMR spectrum. Comparing Fig. 2(b) with the ^{13}C NMR spectrum of TMPTA-modified silica gel, the resonances at 105.9 and 128.4 ppm due to the two carbon atoms of the double bond disappeared completely, indicating the formation of DETA-modified silica gel.

The multidentate amine-modified silica gel was finally obtained by the reaction of amino groups on the surface of DETA-modified silica gel with double bond of BA. Figure 2(d) shows its ^{13}C NMR spectrum. The change in absorption was less compared with Fig. 2(c). The absorptions of all the carbon atoms overlapped each other at 5.2–74.3 and at 172 ppm. However, comparing the relative contents of carbonyl group at 1740 cm^{-1} with that of amino groups at 1637 cm^{-1} from Fig. 1(d,e), it was observed that the relative proportion of the C=O carbonyl group increased. The nitrogen content of the multidentate amine-modified silica gel was 2.5 mmol g^{-1}.

Preparation of Multidentate Amine-modified Magnetic Microspheres

Fe_3O_4 magnetic nanoparticles were prepared by the classical chemical co-precipitation procedure. The diameter of Fe_3O_4 particles was about 15 nm. Figure 3(a) shows the FTIR spectrum of unmodified Fe_3O_4 nanoparticles. The characteristic absorption band of Fe_3O_4 appeared at 585 cm^{-1}. The absorption at 3430 cm^{-1} was ascribed to the characteristic absorption of surface hydroxyl group of $Fe(OH)_2$ or $Fe(OH)_3$. The absorptions at 1450–1650 cm^{-1} were the characteristic absorptions of the symmetrical stretching vibration of $CO_3{}^{2-}$, which formed due to the combination of Fe_3O_4 and CO_2 absorbed from air.

The Fe_3O_4 magnetic nanoparticles were modified by oleic acid and sodium dodecyl sulfonate bilayer surfactants. The stability of the magnetic fluid was very good and could be dispersed well in polar solvent. Figure 3(b) shows the FTIR spectrum of modified

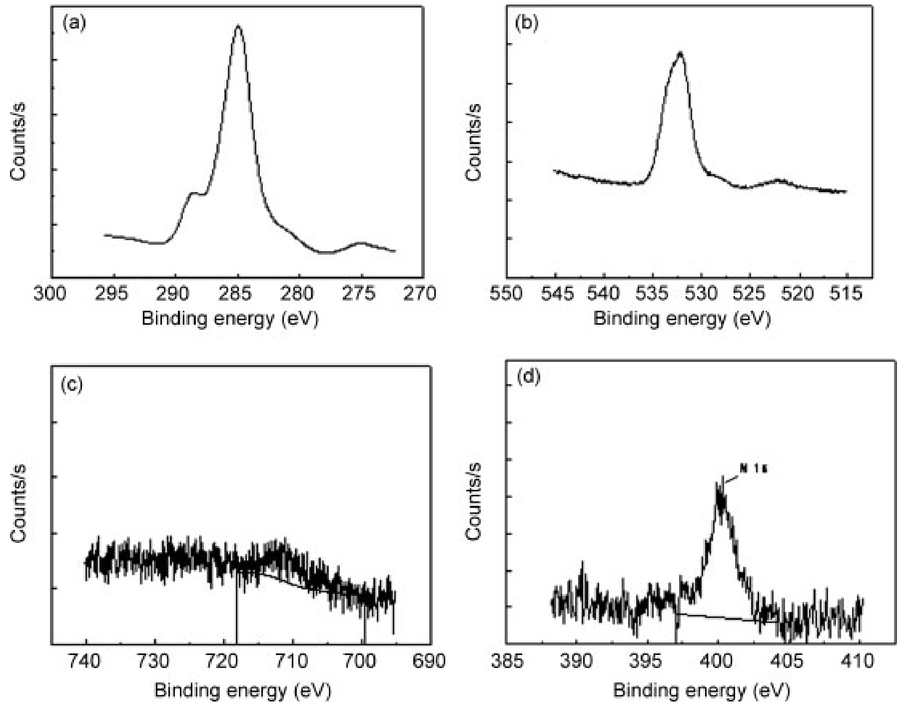


Figure 4. XPS of magnetic microspheres and DETA modified magnetic microspheres: (a) C1s core-level spectrum of the magnetic microspheres; (b) O1s core-level spectrum of the magnetic microspheres; (c) Fe 2p core-level spectrum of the magnetic microspheres; (d) N1s core-level spectrum of the DETA modified magnetic microspheres.

Fe$_3$O$_4$ nanoparticles with oleic acid and sodium dodecyl sulfonate. The absorptions at 1710, 1600–1560 and 1420–1300 cm^{-1} were the characteristic absorptions of COO$^-$; the absorptions at 3007, 1700–1600 and 970 cm^{-1} were ascribed to the $-$C=C- bond of oleic acid. The characteristic absorptions of the sulfonic group were observed at 1203, 1172, 1086 and 1065 cm^{-1}; the absorptions at 2920, 2851, 1380 and 1465 cm^{-1} were the characteristic absorptions of -CH$_3$ and -CH$_2$-; and the characteristic absorptions band of Fe$_3$O$_4$ appeared at 585 and 3439 cm^{-1}. The above results showed that modified Fe$_3$O$_4$ was obtained by oleic acid and sodium dodecyl sulfonate.

Fe$_3$O$_4$ magnetic nanoparticles were covered with polyacrylate polymer via emulsion copolymerization of MMA and TMPTA in order to introduce a double bond on the surface. Figure 3(c) shows the FTIR spectrum of magnetic poly(MMA-co-TMPTA) microspheres. The strong absorption peak at 1731 cm^{-1} was ascribed to the stretching vibration of the carbonyl group. The absorption at 1636 cm^{-1} was the characteristic absorption of the stretching vibration of unreacted double bonds of TMPTA on the surface, and the absorptions at 1408 and 900–750 cm^{-1} were the characteristic absorptions of the bending vibration of unreacted double bonds. The stretching vibration of C–O–C was at 1268, 1240, 1192, 1150, 1063 and 988 cm^{-1}, and the absorptions at 2993, 2951 and 2856 cm^{-1} were the characteristic absorptions of -CH$_3$ and -CH$_2$-. The absorptions at 1450 and 1388 cm^{-1} were the characteristic absorptions of the bending vibration of -CH$_3$ and -CH$_2$- bonds. The absorption peak at 3439 cm^{-1} was the characteristic absorption of surface hydroxyl group of Fe$_3$O$_4$, which was not wrapped completely.

Figure 4(a) shows the X-ray photoelectron spectroscopy (XPS) C1s core-level spectrum of the magnetic microspheres surfaces. The C1s core-level spectrum of the magnetic microspheres surface can be curve fitted into two peak components with binding energies (BEs) of about 285.04 and 288.7 eV attributable to the overlapped C–H/C–C/C–O and O=C–O species, respectively. The corresponding O1s (at a BE of about 532.23 eV) core-level spectrum is shown in Fig. 4(b). Fe2p (at a BE of about 712.23 eV) signals appeared on the magnetic microspheres surfaces. The corresponding Fe2p core-level spectrum is shown in Fig. 4(c). When the magnetic microspheres were treated with HCl (1 mmol l^{-1}), the characteristic peak of Fe2p disappeared, suggesting that the characteristic peak of Fe2p was caused by incompletely wraped Fe$_3$O$_4$. The above results showed that magnetic poly(MMA-co-TMPTA) microspheres were obtained.

The DETA-modified magnetic microspheres were obtained by reacting double bonds on the surface of magnetic microspheres with a great excess of DETA via the Michael addition reaction. Figure 3(d) shows FTIR spectrum of DETA-modified magnetic microspheres. The absorptions of bending vibration of double bonds on magnetic microspheres surface at 1408 cm^{-1} disappeared, and a new absorption at 1637 cm^{-1} appeared, which was ascribed to the characteristic absorption of amino groups of DETA-modified magnetic microspheres. The absorption peak at 3439 cm^{-1} was the overlapped characteristic absorption of amino groups and surface hydroxyl group on Fe$_3$O$_4$ which was not wrapped completely. Figure 4(d) shows the X-ray photoelectron spectroscopy N1s core-level spectrum of the magnetic microspheres surfaces. Besides the characteristic peaks of C1s (C–H/C–C/C–O and O=C–O) and O1s at BE 285.04 and BE 532.23 eV in Fig. 4(a,b), new N1s (at a BE of about 399.70 eV) signals, a characteristic peak of covalently bonded nitrogen, appeared on the surface of magnetic microspheres. This shows that DETA-modified magnetic microspheres were obtained.

The multidentate amine-modified magnetic microspheres were finally obtained by the reaction of amino groups on the surface

Table 1. Results for ATRA of CCl_4 to MMA and MTCA to St catalyzed by CuCl and CuCl/multidentate amine modified silica gel respectively

	(a) CCl_4 to MMA				(b) MTCA to St	
	Run(s)	Time (h)	Conversion (%)	Yield (%)	Conversion (%)	Yield (%)
CuCl/multidentate amine modified silica gel	1	20	55	–	77	–
		40	80	–	80	–
		60	87	85	82	81
	2	20	52	–	62	–
		40	62	–	65	–
		60	75	73	68	66
	3	20	47	–	55	–
		40	55	–	58	–
		60	65	–	65	–
	4	20	43	–	43	–
		40	51	–	50	–
		60	59	–	62	–
	5	20	40	–	37	–
		40	46	–	40	–
		60	53	–	46	–
	6	20	33	–	33	–
		40	42	–	37	–
		60	48	–	41	–
	7	20	21	–	22	–
		40	29	–	23	–
		60	38	35	25	22
CuCl	1	20	0	0	0	0
		40	0	0	0	0
		60	0	0	0	0

Conditions: (a) 30 mmol (3.0 g) of MMA, 50 mmol (7.7 g) of CCl_4, 1 mmol (0.0989 g) of CuCl, 0.4 g of multidentate amine modified silica gel and 30 ml of toluene were added to a 100 ml round-bottom flask equipped with a magnetic stirrer. The reaction was carried out at 85 °C under argon atmosphere. (b) 30 mmol (3.1 g) of St, 40 mmol (7.1 g) of MTCA, 1 mmol (0.0989 g)of CuCl, 0.4 g of multidentate amine modified silica gel and 30 ml of toluene were added to a 100 ml round-bottom flask equipped with a magnetic stirrer. The reaction was carried out at 80 °C under argon atmosphere.

of DETA-modified magnetic microspheres with the double bond of BA. Figure 3(e) shows FTIR spectrum of BA-modified magnetic microspheres. The absorption at 1637 cm^{-1} was ascribed to the characteristic absorption of unreacted amino groups. By comparing the relative contents of the carbonyl group at 1731 cm^{-1} with that of amino groups at 1637 cm^{-1} from Fig. 3(d,e), we observed that relative proportion of carbonyl group increased. The nitrogen content of the multidentate amine-modified magnetic microspheres determined by elemental analysis was 1.0 mmol g^{-1}. The BA-modified magnetic microspheres were measured using XPS. Comparing the relative contents of C1s (C–H/C–C/C–O and O=C–O) at BE 285.04 eV and the N1s at 399.7 eV between DETA-modified magnetic microspheres and BA-modified magnetic microspheres, we know that the relative proportion of nitrogen content of BA-modified magnetic microspheres decreased. The results show that BA-modified magnetic microspheres were obtained.

ATRA of CCl_4 to MMA and MTCA to St Using Multidentate Amine-modified Silica Gel or Magnetic Microspheres as Ligand for CuCl

The multidentate amines immobilized on silica gel or magnetic microspheres were used as ligands for CuCl in ATRA of both CCl_4 to MMA and MTCA to St. When multidentate amine-modified silica gel or magnetic particles were added to the CuCl, MMA/St, toluene solution, it immediately became blue. Without stirring, the blue particles quickly settled to the bottom of the flask, and the upper layer solution became colorless. This indicated that the multidentate amine-modified silica gel (or magnetic particles)–CuCl complex was formed. The blue particles immediately turned green upon adding the initiator and the solution gradually became a red/brown color throughout the reaction. Once agitation was ceased, the supported catalyst settled to the bottom of the flask, leaving a light red/brown-colored solution which could be easily separated from the catalyst by filtration, decanting, etc., in a glovebox.

ATRA of CCl_4 to MMA and MTCA to St produced MMTCB and methyl 2,2,4-trichloro-4-phenylbutyrate (MTCPB), respectively. From Tables 1 and 2, it can be seen that, when the multidentate amine immobilized on silica gel as the ligand of CuCl was used for the first time, the conversion of MMA to MMTCB reached 55% in 20 h, 80% in 40 h and 87% in 60 h, yielding 53% in 20 h, 78% in 40 h and 85% in 60 h, respectively. When the multidentate amine immobilized on magnetic microspheres was used as the ligand of CuCl for the first time, the conversion of MMA to MMTCB reached 60% in 20 h, 80% in 40 h and 90% in 60 h, yielding 60% in 20 h, 79% in 40 h and 89% in 60 h, respectively. In a control experiment, where no multidentate amine-modified silica gel or

Table 2. Results for ATRA of CCl_4 to MMA and MTCA to St catalyzed by CuCl and CuCl/multidentate amine modified magnetic microspheres respectively

		(a) CCl_4 to MMA			(b) MTCA to St	
	Run(s)	Time (h)	Conversion (%)	Yield (%)	Conversion (%)	Yield (%)
CuCl/multidentate amine modified magnetic microspheres	1	20	60		65	–
		40	80		83	–
		60	90	89	92	91
	2	20	54		60	–
		40	65		67	–
		60	78	77	72	70
	3	20	49		58	–
		40	57		60	–
		60	69		65	–
	4	20	45		47	–
		40	51		53	–
		60	60		62	–
	5	20	28		29	–
		40	35		35	–
		60	39	37	40	38
CuCl	1	20	0	0	0	0
		40	0	0	0	0
		60	0	0	0	0

Conditions: (a) 30 mmol (3.0 g) of MMA, 50 mmol (7.7 g) of CCl_4, 1 mmol (0.0989 g) of CuCl, 1 g of multidentate amine modified magnetic microspheres and 30 ml of toluene were added to a 100 ml round-bottom flask equipped with a magnetic stirrer. The reaction was carried out at 85 °C under argon atmosphere. (b) 30 mmol (3.1 g) of St, 40 mmol (7.1 g) of MTCA, 1 mmol (0.0989 g)of CuCl, 1 g of multidentate amine modified magnetic microspheres and 30 ml of toluene were added to a 100 ml round-bottom flask equipped with a magnetic stirrer. The reaction was carried out at 80 °C under argon atmosphere.

magnetic microspheres were added to the reaction system, no MMTCB could be detected in the mixture, even for a long enough reaction time.

The reuse of the immobilized CuCl catalyst was examined. After the first reaction, the reactor containing multidentate amine-modified silica gel/CuCl was transferred into a glovebox where the catalyst was recovered by filtration and washed with a large amount of toluene. The reactor contained magnetic microspheres/CuCl was transferred into a glovebox where the catalyst was adsorpted by a magnetic separator and the upper layer solution was decanted and washed with a large amount of toluene. The catalysts were then dried under vacuum for 12 h and stored under dry nitrogen for further use. As shown in Tables 1 and 2, the activity of the supported silica gel catalyst remained about 90% relative to its initial activity in the second use, 85% in the third use and even 40% in the seventh use. The activity of the supported magnetic microspheres catalyst also remained about 90% in the second use, 80% in the third use and 30% in the fifth use. The reduction in catalytic activity may be due to the oxidation of part of Cu(I) to Cu(II) during the recycling and reaction; this could be demonstrated by the phenomenon that, with increasing frequency of reuse, the supported catalyst gradually became more green. The Cu(II) is produced during the reaction process by a side reaction of combination or disproportionation between two radicals, which happens commonly in ATRA. These side reactions not only decrease the yield in the desired addition products but also induce the accumulation of Cu^{2+}, affecting the $Cu^{+}/[Cu^{2+}]$ ratio and finally causing the reduction of the catalytic activity of the catalysts.[24]

As for the ATRA of MTCA to St, similar results were obtained. This is also shown in Tables 1 and 2. The reaction filtrates of MMTCB and MTCPB were diluted in ether. The solutions were successively washed with a 10 wt% HCl solution, a saturated solution of sodium carbonate and neutral water. They were then dried over $MgSO_4$ and filtered. The residual monomer and volatiles were then evaporated under vacuum. The products were then purified by distillation and were isolated. The chemical structures of MMTCB [$CCl_3CH_2CCl(CH_3)COOCH_3$] and MTCPB ($CCl_3CH_2CHClPh$) were confirmed by ^1H NMR and ^{13}C NMR.

$CCl_3CH_2CCl(CH_3)COOCH_3$: ^1H NMR ($CDCl_3$, ppm) δ 2.00 (3H, s, CH_3), 3.45 (1H, d, CH_2), 3.80 (3H, s), 4.00 (1H, d, CH_2). ^{13}C NMR ($CDCl_3$, ppm) δ 26.2 (1C, CH_3), 53.6 (1C, OCH_3), 62.2(1C, CH_2), 64.6 (1C, CCl), 96.4 (1C, CCl_3), 170.0 (1C, CO).

$CCl_3CH_2CHClPh$: ^1H NMR ($CDCl_3$, ppm) δ 3.10–3.40 (2H, m, CH_2), 5.15 (1H, t, CH), 7.20–7.50 (5H, m, phenyl). ^{13}C NMR ($CDCl_3$, ppm) δ 59.1 (1C, CH), 62.7 (1C, CH_2), 97.0 (1C, CCl_3), 128.1–141.0 (6C, phenyl). The result shows that MMTCB and MTCPB was synthesized successfully.

ATRP of MMA was carried out with CuCl supported on multidentate amine-modified silica gel as catalyst and MMTCB as initiator. Figure 5 shows GPC traces of polymers obtained at different monomer conversions. The number average molecular weights were much higher than those predicted based on the assumption that one initiator molecule generated one polymer chain, for instance, at 8% conversion with 1% initiator, a PMMA M_n of 800 is expected, while an M_n of 47,000 was measured by GPC. The polydispersities (M_w/M_n) were low enough ($M_w/M_n < 2$). These results indicated that ATRP of MMA catalyzed by CuCl supported

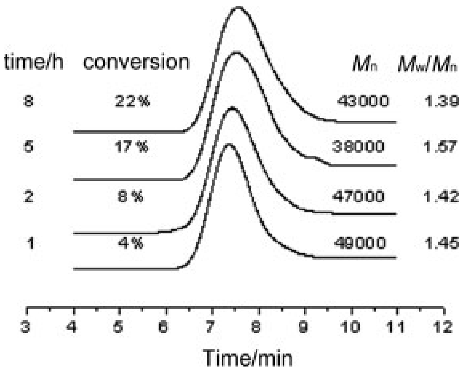


Figure 5. GPC traces of PMMAs obtained at different monomer conversions. Conditions: MMA 100 mmol (10 g), MMTCB 1 mmol (0.254 g), CuCl 1 mmol (0.0989 g), multidentate amine-modified silica gel 0.4 g (1 mmol nitrogen atom), xylene 30 ml. Temperature 70 °C.

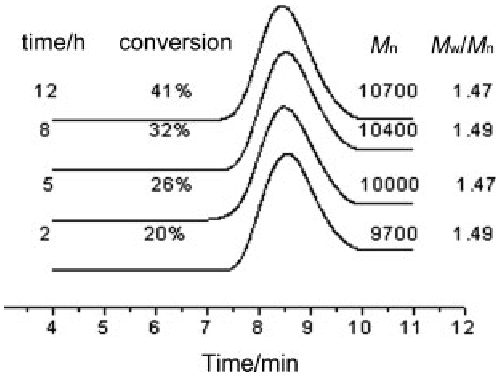


Figure 6. GPC traces of PSts obtained at different monomer conversions. Conditions: St 96 mmol (10 g), TCPP 1 mmol (0.258 g), CuCl 1 mmol (0.0989 g), multidentate amine-modified silica gel 0.4 g (1 mmol nitrogen atom), xylene 20 ml. Temperature 110 °C.

on multidentate amine-modified silica gel did not proceed in a controlled fashion. This may be due to the mobility of the catalyst molecules being substantially reduced when they were bound to the large (relative to small soluble molecules) insoluble particles, and thus the deactivation reaction may become slower, resulting in a less controlled ATRP. In a control experiment of ATRP, no PMMA could be obtained with only CuCl as catalyst, even for a long enough reaction time.

ATRP of styrene was also carried out with CuCl supported on multidentate amine-modified silica gel as catalyst and TCPP as initiator. Similar results, shown in Fig. 6, were obtained.

In conclusion, a novel multidentate amine grafted on silica gel or magnetic microsphere was prepared successfully. It could be used as a ligand for CuCl in ATRA of both CCl_4 to MMA and MTCA to St. Furthermore, the immobilized CuCl catalyst could be reused at least five times with 30% reactivity retained. These immobilized copper catalysts could also be used in ATRP of St initiated by TCPP and MMA initiated by MMTCB. Although the polymerization took place successfully, it did not proceed in a controlled fashion.

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