Macromolecules **2006,** *39,* 6399−6405

Magnetic Nanoparticle Supported Catalyst for Atom Transfer Radical Polymerization

Shijie Ding,[†] Yangchuan Xing,[‡] Maciej Radosz,[†] and Youqing Shen*,[†]

Department of Chemical and Petroleum Engineering, University of Wyoming,
Laramie, Wyoming 82071, and Department of Chemical and Biological Engineering,
University of Missouri—Rolla, Rolla, Missouri 65409

Received May 11, 2006; Revised Manuscript Received July 16, 2006

ABSTRACT: Magnetic nanoparticles were used to support an ATRP catalyst for the polymerization of methyl methacrylate (MMA) for minimized adverse effect of catalyst support and easy catalyst separation. The nanoparticle-supported catalyst mediated a living/controlled radical polymerization of MMA as effectively as unsupported catalysts. With the addition of 22 mol % of $CuBr_2$, the polymer molecular weights were well-controlled with an initiator efficiency of 0.85 and polydispersity lower than 1.2. The supported catalysts could be easily separated/isolated using an external magnetic field and reused with slightly decreased activity but further improved control. The activity of the recycled catalyst was regenerated by copper metal or in-situ regeneration using reducing agents such as alkylamine or tin(II) compounds. Block copolymerization using PEG macroinitiator and chain extension were conducted to confirm the livingness. Block copolymers with controlled molecular weights and low polydispersity were obtained using the fresh or reused supported catalysts. It was concluded that nanosized supports had reduced adverse effects on catalysis.

Introduction

ATRP represents one of the most versatile synthetic tools for preparing new polymer materials with well-controlled molecular weights and well-defined structures.[1,2] However, one remaining challenge of ATRP is the difficulty to effectively separate the homogeneous ATRP catalysts from their products. Many purification methods[3] such as postpurification[4,5] and liquid−liquid biphasic separation[6−10] have been developed for the removal of catalysts from polymers.

Immobilization of catalysts on solids via chemical bonding is more versatile for catalyst separation. Catalysts tethered on solid surfaces such as silica gel, polystyrene beads, and Janda Jel resins have been explored for catalyst removal and reuse in ATRP.[11−21] It has the advantages of easy separation of the catalysts from their products and the possibility to reuse the catalysts for cost-saving. However, the control level of the polymerization by these covalently solid-supported systems is generally lower than that by unsupported catalyst. This is mainly due to that the deactivation rate constant by the immobilized catalysts is reduced to the diffusion limit, ca. 10^5 L mol^{-1} s^{-1}, which is much lower than that of the homogeneous systems (10^9 L mol^{-1} s^{-1}).[22] Diffusion effects thereby significantly lower the overall rate of deactivation in an immobilized catalyst system. Another adverse effect of the catalyst immobilization is that the catalyst on the surface may not be able to reach inside the polymer coils for deactivation, especially for the solids with porous structures.[3,19−21] One approach to improve the control is the addition of the soluble deactivators or free soluble ligand.[22−24] Also, some new catalyst systems, which combine the advantages of both heterogeneous and homogeneous catalysis, have been developed to ameliorate this problem.[25−30]

The solids used for immobilization of catalysts are generally on the order of micrometers in diameter. We envisioned that a catalyst support with smaller sizes (on the order of nanometers) would lead to a less reduction in catalyst diffusivity and minimize the steric effect from the support. Such a supported catalyst would act similarly to homogeneous catalysts and can be considered as “quasi-soluble”. We thus expected that this “quasi-soluble” supported catalyst system would effectively improve the control over polymerization compared to heterogeneous catalysts. Nanoparticles, however, are difficult to be separated from solutions. We thus used magnetic nanoparticles as the support, which have been used for inorganic and organic synthesis and can be easily separated by a magnetic field.[31−34]

In this paper, we used regular shaped Fe_3O_4 magnetic nanoparticles (20−30 nm) to support the catalyst for ATRP. The ATRP catalyst was tethered onto the magnetic nanoparticles (Scheme 1). The supported catalyst could mediate ATRP with a control over polymerization unattainable by heterogeneous catalysts. The separation of nanosized magnetic supports could be easily achieved by applying a magnetic field.

Experimental Section

Chemicals. Acryloyl chloride (Lancaster, 96%), methyl α-bromophenylacetate (Aldrich, 97%, MBP), 3-aminopropyltrimethoxysilane (Aldrich, 97%), *N,N,N″,N″*-tetraethyldiethylenetriamine (Aldrich, tech. 90%, TEDETA), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (Aldrich, 99%, PMDETA), triethylamine (TEA, Aldrich, 98%), tin(II) 2-ethylhexanoate ($Sn(EH)_2$, Aldrich, 95%), nitric acid (EM, A.C.S.), and Fe_3O_4 powder (APS 20−30 nm, Nanostructured & Amorphous Materials Inc., Houston, TX) were used directly without further purification. Toluene (Baker) and methyl methacrylate (Aldrich, 99%, MMA) were distilled before use. Copper(I) bromide (Aldrich, 98%) was stirred with glacial acetic acid, filtered, washed with ethanol, and dried.

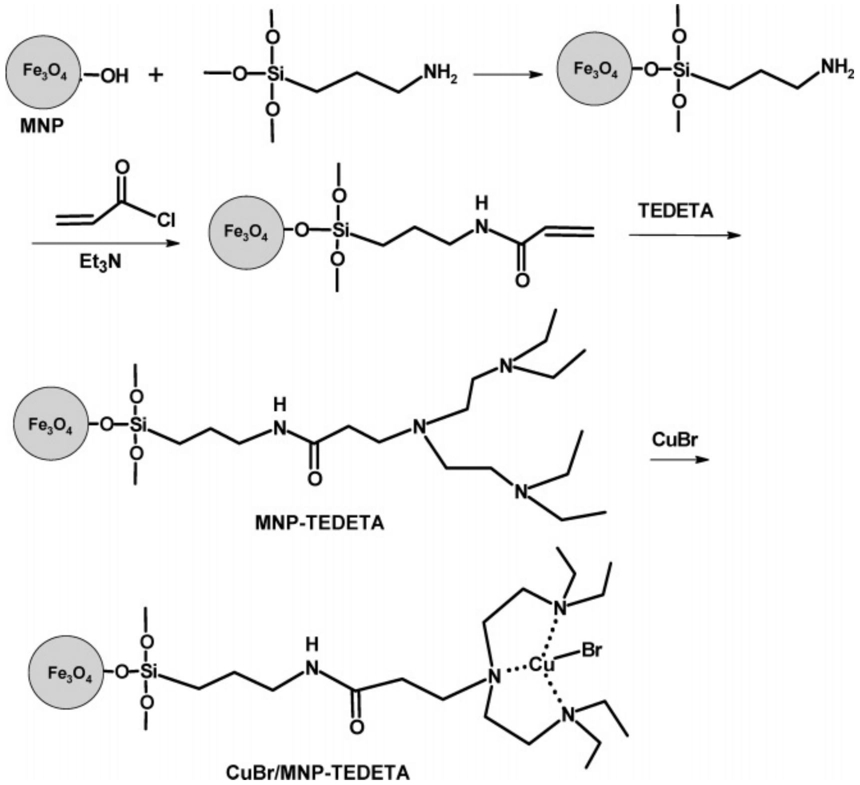
Characterization. Gel permeation chromatography (GPC) was used to determine polymer molecular weights and molecular weight distributions (PDI) using polystyrene standards (Polysciences Corp.) to generate a universal calibration curve for poly(methyl methacrylate) (PMMA). The measurements were operated on a Waters SEC equipped with a Waters 2414 refractive index detector and two 300 mm Solvent-Saving GPC columns (molecular weight ranges: 1×10^2−5×10^3, 5×10^3−5×10^5) at a flow rate of

---

[†] University of Wyoming.
[‡] University of Missouri—Rolla.

10.1021/ma061062y CCC: \$33.50

Scheme 1. Immobilization of the Ligand *N*,*N*,*N*″,*N*″-Tetraethyldiethylenetriamine (TEDETA) and the Catalyst onto Fe_3O_4 Magnetic Nanoparticles



0.30 mL/min using tetrahydrofuran (THF) as solvent at 30 °C. Data were recorded and processed using Waters software package. ^1H NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer using $CDCl_3$ as solvent. Chemical shifts were reported downfield from 0.00 ppm using tetramethylsilane (TMS) as internal reference.

The X-ray photoelectron spectroscopy (XPS) measurements were conducted in University of Missouri—Rolla using a Kratos Axis 165 X-ray photoelectron spectrometer with a Mg Kα anode operated at 15 kV. The base pressure of the chamber was $\sim 1 \times 10^{-9}$ Torr. The catalyst particles were packed as pellets for testing. The transmission electron microscopy (TEM) images were recorded on a Hitachi H-7000 at an accelerating voltage of 75 kV. The magnetic nanoparticles or modified nanoparticles were dispersed in toluene. One drop of the suspension (1000 ppm) was applied on a carbon-coated copper grid and dried under ambient conditions. Elemental analysis was conducted by Midwest Microlab, LLC, Indianapolis, IN. A CHNOS elemental analyzer was used for the nitrogen determination. The weighed sample was combusted at 1000 °C under ultrapure oxygen, and the nitrogen gases were read via a detector measuring the electrical heat conductivity. The method was calibrated using a chemical standard cyclohexanone—2,4-dinitrophenylhydrazone.

The residual copper concentration in crude polymer products was measured by inductively coupled plasma mass spectrometry (ICP-MS) at the Department of Geology of the University of Wyoming. The polymer solution separated from the catalyst particles was dried under vacuum, and then the polymer powder (50.0 mg) was dissolved in nitric acid with heating. The solution was then diluted to 25.0 mL for ICP-MS analysis.

Grafting TEDETA Ligand onto Fe_3O_4 Magnetic Nanoparticles (MNP-TEDETA). As shown in Scheme 1, Fe_3O_4 magnetic nanoparticles (5.0 g, 25 nm) were refluxed with 3-aminopropyltrimethoxysilane (20 mL, 0.113 mol) in dry toluene (30.0 mL) for 4 days. The solids were separated by applying an external magnetic field and washed with 4 × 100 mL of dry toluene and then 2 × 100 mL of dry acetone. The resulting product was dried under vacuum for 12 h. The nitrogen content analyzed by elemental analysis was 0.61 wt %.

The resulting solids were dispersed in 50 mL of dry dichloromethane, and the flask was cooled in an ice—water bath. Triethylamine (16.0 mL, 0.113 mol) was added and stirred for 30 min. Then acryloyl chloride (4.0 mL, 49.2 mmol) was added dropwise over 30 min. The mixture was stirred at room temperature for 48 h. It was successively washed with acetone (3 × 100 mL), DI H_2O (3 × 100 mL), and again acetone (2 × 100 mL). The resulting product was dried under vacuum for 5 h, then dispersed in methanol (30.0 mL), and stirred with TEDETA (5.0 mL, 19.4 mmol) at room temperature for 1 week. The solids were separated by a magnetic field and washed with acetone 5 × 100 mL. The resulting product was dried under vacuum for 12 h. The nitrogen content analyzed by elemental analysis was 1.87 wt %.

Preparation of Poly(ethylene glycol) Macroinitiator (Ini-PEG). PEG_{45}-OH (20.0 g, 0.010 mol) was dissolved in 300 mL of toluene in a 500 mL flask. Then triethylamine (2.78 mL, 0.020 mol) was added, and the solution was cooled to 0 °C. 2-Bromoisobutyryl bromide (2.47 mL, 0.020 mol) was added dropwise via a syringe over 1 h. The reaction mixture was stirred overnight at room temperature. The solution was filtered and the solvent was removed in a vacuum. The crude polymer was dissolved in water at pH 8.5 and extracted with dichloromethane. The organic layer was collected, dried over $CaCl_2$, and purified under vacuum to remove the residual solvent. A 10-fold excess of diethyl ether was added to precipitate the PEG initiator (Ini-PEG). The product was dried under high vacuum overnight. Yield: 79.0%. ^1H NMR (D_2O, 400 MHz) δ (ppm): 3.57 (s, 191H, CH_2CH_2O), 3.25 (s, 3H, CH_3), 1.82 (s, 6H, $CBr(CH_3)_2$).

Polymerization by Magnetic Nanoparticle-Supported Catalyst CuBr/MNP-TEDETA. A typical procedure for the polymerization with the supported catalyst is as follows: CuBr (0.0135 g, 0.0941 mmol), MNP-TEDETA (0.2864 g, equivalent TEDETA 0.0956 mmol), and a stirring bar were put into a reaction tube. The tube was tightly sealed and degassed by 10 vacuum/nitrogen cycles. Degassed toluene (3.0 mL) was added via a degassed syringe. The mixture was stirred and bubbled with nitrogen for 5 min. The sealed tube was sonicated at room temperature for 10 min. Degassed MMA (0.943 g, 9.41 mmol) was added, and then the mixture was degassed again for 2 min. The tube was immersed in an oil bath preset at the polymerization temperature. Finally, the initiator (MBP, 15.0 μL, 0.0955 mmol) was added to the mixture with stirring. Samples (0.050 mL) were withdrawn from the tube using nitrogen-purged syringes at timed intervals and dissolved in $CDCl_3$. Conversions were measured by ^{1}H NMR spectroscopy (Figure 3) and the molecular weights and polydispersity of the polymers were measured by GPC (Figure 4).

Polymerization by Unsupported Catalyst CuBr/PMDETA or CuBr/TEDETA. A polymerization of MMA with unsupported catalyst is as follows: CuBr (0.0135 g, 0.0941 mmol) and a stirring bar were put into a reactor. The reactor was tightly sealed. Degassed toluene (3.0 mL) was added and degassed for 5 min. Then PMDETA (20.0 μL, 0.0957 mmol) was added and degassed for another 3 min. The degassed MMA (0.943 g, 9.41 mmol) was introduced with a syringe, and the reaction mixture was degassed for 2 min more. The reactor was immersed in an oil bath (70 °C), and the initiator (MBP, 15.0 μL, 0.0955 mmol) was added to the mixture with stirring. Some precipitation was produced immediately. Samples (0.050 mL) were withdrawn at different time intervals to analyze the conversion (by NMR) and molecular weight (GPC) (Figures 3 and 4).

Catalyst Recycling and Reuse. A procedure for catalyst recycling is as follows: CuBr (0.0108 g, 0.0753 mmol), $CuBr_2$ (0.00480 g, 0.0215 mmol), MNP-TEDETA (0.2906 g, TEDETA 0.0970 mmol), and a stirring bar were put into a reaction tube. The tube was tightly sealed and degassed by 10 vacuum/nitrogen cycles. Degassed toluene (3.0 mL) was added via a degassed syringe. The mixture was stirred and bubbled with nitrogen for 5 min. Degassed MMA (0.943 g, 9.41 mmol) was added, and then the mixture was degassed again for 2 min. The tube was immersed in an oil bath (70 °C). Finally, the initiator (MBP, 15.0 μL, 0.0955 mmol) was added to the mixture with stirring.

After the polymerization was complete, the reactor tube was cooled to room temperature and placed on a magnetic bar. The catalyst was attracted to the bottom of the reactor by the external magnetic bar. The polymer solution was taken out, and the residual solid was washed by 3 × 3.0 mL degassed toluene under nitrogen. This isolated catalyst is referred to as the reused catalyst. Then degassed MMA, toluene, and initiator were charged to the tube, and the second polymerization run was conducted following the same procedure as the first polymerization run. The catalyst isolated after the second run of polymerization is referred to as the second-reused catalyst (Figures 8 and 9).

Catalyst Extraction and Polymerization. CuBr (0.0108 g, 0.0753 mmol), $CuBr_2$ (0.00480 g, 0.0215 mmol), MNP-TEDETA (0.2906 g, TEDETA 0.0970 mmol), toluene (3.0 mL), and MMA (0.943 g, 9.41 mmol) were mixed and degassed following the typical polymerization procedure and stirred at 70 °C for 30 min. While at this temperature, the stirring was stopped, and the catalyst particles were attracted down to the bottom of the reactor using a magnetic bar. The upper layer clear solution was transferred to another degassed tube, and the initiator MBP was then added. The reaction mixture was heated at 70 °C for 18 h. Both NMR and GPC analysis showed no polymerization occurred.

Regeneration of the Recycled Catalyst with Copper Metal. After the second-reused catalyst was isolated, about 1 g of copper metal beads (~1 mm diameter) and 3.0 mL of toluene were added and stirred with the catalyst at 40 °C overnight. The resulting reactivated catalyst was separated from the copper beads and transferred into a degassed, tightly sealed tube. Then degassed MMA, toluene, and initiator were added, and the polymerization was performed following the same procedure as the first polymerization run (Figures 8 and 9).

In-Situ Regeneration of the Recycled Catalyst Using Triethylamine. The reused catalyst was isolated. Then degassed MMA (0.943 g, 9.41 mmol), toluene (3.0 mL), and triethylamine (13.2 μL, 0.0947 mmol) were added and degassed for 5 min. The mixture was stirred at 25 °C for 1 h, and the tube was immersed in an oil bath at 70 °C. The initiator MBP (15.0 μL, 0.0955 mmol) was added. The polymerization was performed following the same procedure as the first polymerization run (Figures 10 and 11).

In-Situ Regeneration of the Recycled Catalyst Using $Sn(EH)_2$. The reused catalyst was isolated. Degassed MMA (0.943 g. 9.41 mmol) and the degassed $Sn(EH)_2$ (3.81 mg, 9.40×10^{-3} mmol) in toluene (3.0 mL) were added and degassed for 5 min. The mixture was stirred at 25 °C for 1 h and then put into an oil bath (70 °C). MBP (15.0 μL, 0.0955 mmol) was added, and the polymerization was performed following the same procedure as the first polymerization run (Figures 10 and 11).

Chain Extension in ATRP of MMA Using the Fresh Catalyst. CuBr (0.0108 g, 0.0753 mmol), $CuBr_2$ (0.00480 g, 0.0215 mmol), MNP-TEDETA (0.2906 g, TEDETA 0.0970 mmol), and a stirring bar were put into a reaction tube. The tube was tightly sealed and purged by 10 vacuum/nitrogen cycles. Degassed toluene (3.0 mL) was added, and the mixture was stirred and bubbled with nitrogen for 5 min. Degassed MMA (0.943 g, 9.41 mmol) was added, and then the mixture was degassed again for 2 min. The tube was immersed in an oil bath (70 °C). Finally, the initiator (MBP, 15.0 μL, 0.0955 mmol) was added to the mixture with stirring. After the polymerization reached 91% conversion analyzed by NMR, a second portion of degassed MMA (0.943 g) was added into the reactor with a degassed syringe. The polymerization was monitored with NMR (conversion) and GPC (molecular weight and molecular weight distribution) (Figure 13).

After the polymerization was completed, the reused catalyst was isolated. Then degassed MMA (0.943 g, 9.41 mmol), toluene (3.0 mL), and triethylamine (13.2 μL, 0.0947 mmol) were added and degassed for 5 min. The mixture was stirred at 25 °C for 1 h, and the tube was immersed in an oil bath at 70 °C. The initiator MBP (15.0 μL, 0.0955 mmol) was added. The polymerization was performed following the same procedure as the first polymerization run (Figure 14).

Results and Discussion

The ATRP catalyst immobilization is shown in Scheme 1. Fe_3O_4 magnetic nanoparticles were refluxed with 3-aminopropyltrimethoxysilane in dry toluene to anchor amine groups onto their surface using silane chemistry.[35] Acryloxyl groups were introduced by the reaction of the amine groups with acryloyl chloride. The Michael reaction of the acryloxyl groups with tetraethyldiethylenetriamine (TEDETA) attached the ligand onto the support, as we used previously with a conversion of about 86.6%.[29] According to the elemental analysis, the loading of TEDETA on the surface was 7.19 wt %. The nanoparticles grafted with TEDETA (MNP-TEDETA) were easily dispersed in organic solvents compared with the nonmodified nanoparticles (Figure 1). The complexation of CuBr with TEDETA on the nanoparticles was also confirmed by XPS. Figure 2 is the XPS survey scan spectra of six samples, including two references of the CuBr and magnetite nanoparticles. Elements of interest were identified on the XPS. The elements of nitrogen and carbon were present in MNP-TEDETA besides Fe and O. Elements of copper, iron, oxygen, nitrogen, carbon, and bromine showed up in the fresh and reused CuBr/MNP-TEDETA samples.

The ATRP of MMA was carried out in toluene at 70 °C using methyl α-bromophenylacetate (MBP) as initiator and CuBr/MNP-TEDETA as the catalyst. The polymerizations catalyzed by unsupported CuBr/TEDETA or CuBr/PMDETA were also conducted under identical conditions for comparison. Figure 3 shows that all of the three polymerizations exhibited first-order kinetics, and the polymerization rates were very close, indicating that the supported catalyst had a similar activity to the unsupported catalysts (CuBr/TEDETA or CuBr/PMDETA). The measured molecular weights of PMMA increased linearly as MMA conversion increased with polydispersity less than 1.23 (Figure 4). Although the initiator efficiency was only about 50%, it was higher than that of the polymerizations with unsupported

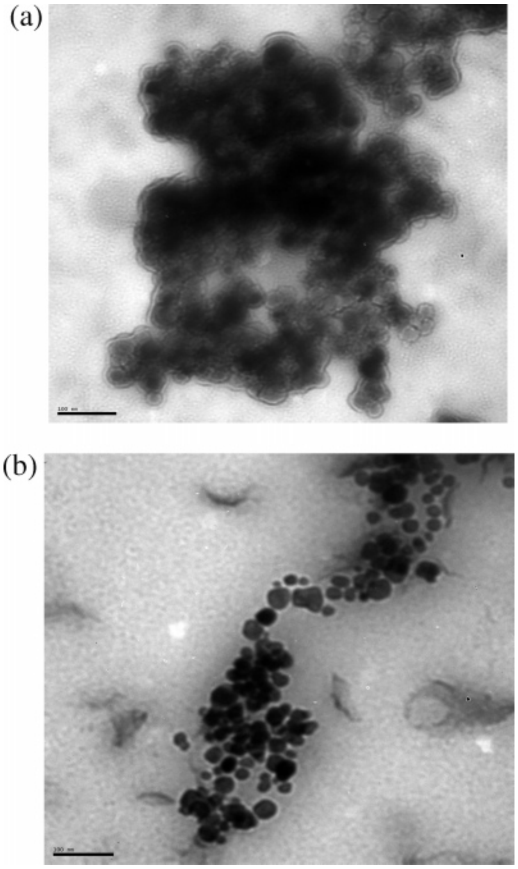


Figure 1. Transmission electron microscopy (TEM) images of unmodified magnetic nanoparticles (a) and the *N*,*N*,*N*″,*N*″-tetraethyldiethylenetriamine (TEDETA) modified magnetic nanoparticles (MNP-TEDETA) (b).

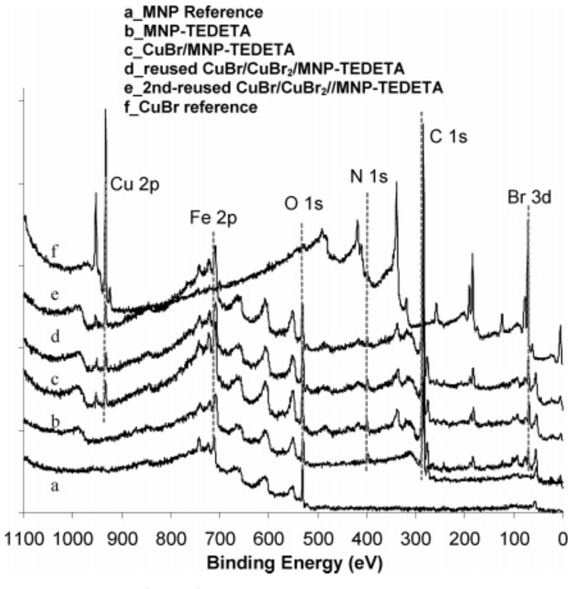


Figure 2. X-ray photoelectron spectroscopy (XPS) survey scans of magnetic nanoparticles (MNP reference) (a), *N*,*N*,*N*″,*N*″-tetraethyldiethylenetriamine-modified magnetic nanoparticles (MNP-TEDETA) (b), supported catalyst CuBr/MNP-TEDETA (c), reused CuBr/CuBr$_2$/MNP-TEDETA supported catalyst (d), second-reused CuBr/CuBr$_2$//MNP-TEDETA catalyst (e), and CuBr reference (f).

CuBr/TEDETA or CuBr/PMDETA. The less control over polymerization by the unsupported catalysts may be due to their low solubility in toluene. This indicates that the relatively low initiator efficiency was due to the nature of CuBr/TEDETA catalyst rather than the effect of the nanosized support. Thus, the supported catalyst could mediate ATRP as effectively as the unsupported catalyst.

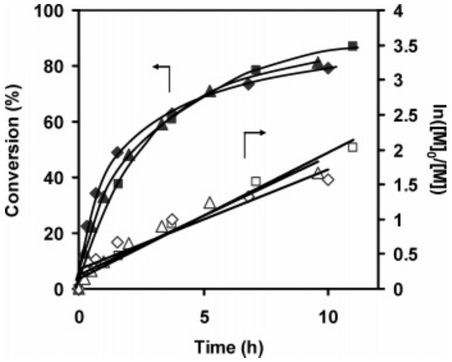


Figure 3. Methyl methacrylate (MMA) polymerization with the magnetic nanoparticle supported catalyst CuBr/MNP-TEDETA and the polymerization catalyzed by unsupported catalyst CuBr/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), CuBr/*N*,*N*,*N*″,*N*″-tetraethyldiethylenetriamine (TEDETA) in toluene. 70 °C, $[\mathrm{MMA}]_0 = 2.35$ mol/L, $[\mathrm{CuBr}]_0 = [\mathrm{TEDETA\ or\ PMDETA}]_0 =$ [methyl α-bromophenylacetate $(\mathrm{MBP})]_0 = 0.0235$ mol/L. CuBr/PMDETA (▲, △), CuBr/TEDETA (◆, ◇), and CuBr/MNP-TEDETA (■, □).

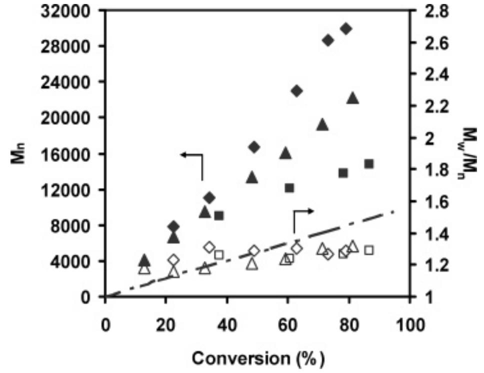


Figure 4. Dependence of poly(methyl methacrylate) (PMMA) molecular weights and polydispersities on conversion in the polymerization of methyl methacrylate (MMA) with magnetic nanoparticle supported catalyst CuBr/MNP-TEDETA and the polymerization catalyzed by unsupported catalyst CuBr/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) and CuBr/*N*,*N*,*N*″,*N*″-tetraethyldiethylenetriamine (TEDETA) in toluene. See Figure 3 for experimental conditions. CuBr/PMDETA (▲, △), CuBr/TEDETA (◆, ◇), and CuBr/MNP-TEDETA (■, □); PMMA theoretical molecular weights (– · –).

The initiator efficiency of the polymerization by the supported catalyst could be substantially increased by adding 22 mol % Cu(II)Br$_2$ relative to the total catalyst (i.e., 22 mol % CuBr$_2$ and 78 mol % CuBr). Figure 5 showed that with the addition of CuBr$_2$ the rate of polymerization was only slightly decreased (conversion reached 80% in 10 h). The polydispersity of PMMA was decreased to less than 1.2, and the initiator efficiency was increased from 0.5 to 0.85 (Figure 6). This is in contrast to the catalysts grafted on micron-sized supports, in which the addition of Cu(II)Br$_2$ could not improve the level of control over polymerization.[14] The needed concentration of CuBr$_2$ in this heterogeneous system was higher, which was needed for radical deactivation. The excess of CuBr$_2$, however, caused an induction period.

After the polymerization was complete, the solution was cooled to room temperature. The catalyst particles were easily attracted on the bottom of the reactor using a magnetic stirring bar (Figure 7). The upper layer of polymer solution could be removed with a degassed syringe. ICP-MS analysis showed that the concentration of copper bromide in the colorless solution was 6 ppm. The isolated catalysts were washed with toluene

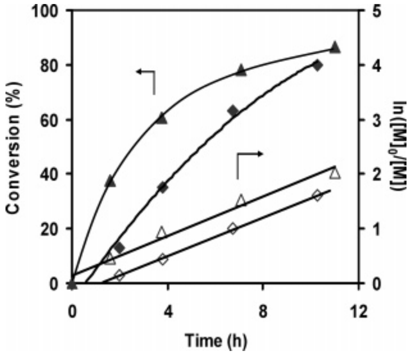


Figure 5. Methyl methacrylate (MMA) polymerization with magnetic nanoparticle supported catalyst CuBr/MNP-TEDETA in toluene with the addition of Cu(II)Br$_2$. 70 °C, [MMA]$_0$ = 2.35 mol/L, [CuBr + CuBr$_2$]$_0$ = [MNP-TEDETA]$_0$ = [methyl α-bromophenylacetate (MBP)]$_0$ = 0.0235 mol/L. CuBr$_2$ relative to the total catalyst: 0 mol %(▲, △), 22 mol % (◆, ◇).

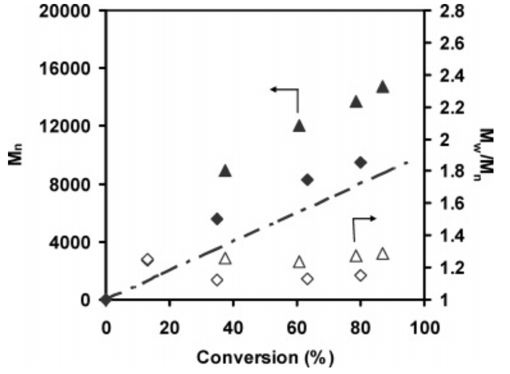


Figure 6. Dependence of poly(methyl methacrylate) (PMMA) molecular weights and polydispersities on conversion in the polymerization of methyl methacrylate (MMA) with magnetic nanoparticle supported catalyst CuBr/MNP-TEDETAin toluene with the addition of Cu(II)Br$_2$. See Figure 5 for experimental conditions. CuBr$_2$ relative to the total catalyst: 0 mol % (▲, △), 22 mol % (◆, ◇); PMMA theoretical molecular weights (− • −).

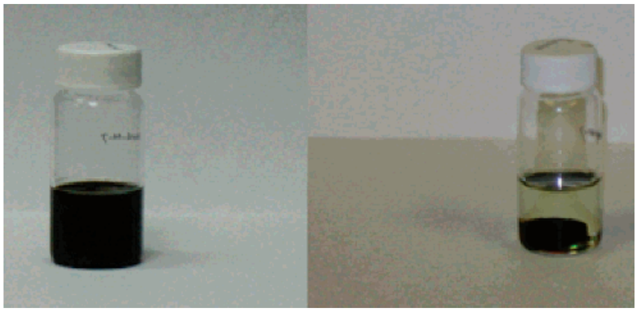


Figure 7. Dispersing and isolating the nanoparticle-supported catalyst.

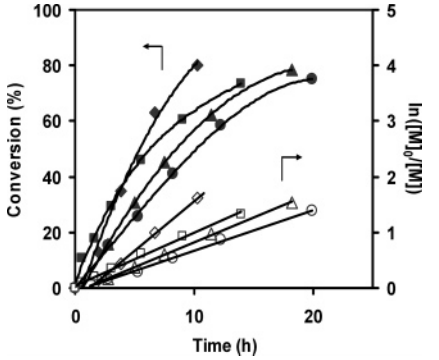


Figure 8. Methyl methacrylate (MMA) polymerization in toluene with fresh, recycled, and regenerated magnetic nanoparticle supported catalyst (MNP-TEDETA). 70 °C, [MMA]$_0$ = 2.35 mol/L, [78 mol % CuBr + 22 mol % CuBr$_2$]$_0$ = [MNP-TEDETA]$_0$ = [methyl α-bromophenylacetate (MBP)]$_0$ = 0.0235 mol/L. Fresh catalyst (◆, ◇); reused catalyst (▲, △), second-reused (●, ○) and second-reused catalyst regenerated by copper metal (■, □).

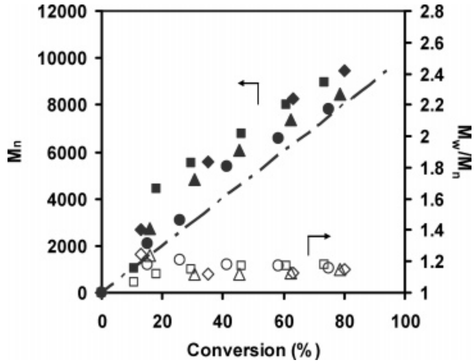


Figure 9. Poly(methyl methacrylate) (PMMA) molecular weights and polydispersity as a function of conversion in the polymerizations of methyl methacrylate (MMA) using fresh catalyst (◆, ◇), reused catalyst (▲, △), second-reused (●, ○), and second-reused catalyst regenerated with copper metal (■, □); PMMA theoretical molecular weights (− • −). See Figure 8 for reaction conditions.

and then used for the second and third runs of polymerization (Figures 8 and 9). The reused catalyst has a lower catalytic activity than the fresh catalyst, but the activity of the second-reused catalyst was only reduced slightly further. The molecular weights of PMMA by the reused catalysts were closer to their theoretical values than those obtained from the fresh catalyst, indicating an improved control over polymerization. The polydispersity of the polymers from these three polymerization runs were similar, all less than 1.2 (Figure 9).

It was suggested that in the supported ATRP it was the catalyst leached from the support that catalyzed the ATRP.[36] To examine this hypothesis, we tested whether the polymerization could be conducted by the catalyst that had leached into the solution. A sample of the degassed catalyst was stirred in a MMA−toluene polymerization solution at 70 °C for 30 min. The supported catalyst was separated with a magnetic bar, and then MBP was added into the clear solution, which was taken out and put into another sealed, degassed tube. The clear solution isolated from the supported catalyst could not be polymerized at 70 °C even after 18 h. This confirms that the copper catalyst in the solution cannot catalyze the polymerization. Therefore, the reduced activity of the recycled catalysts was not due to the loss of the catalyst during catalyst recovery, but rather the presence of more Cu(II) species produced by persistent radical effect[1] during the prior polymerization.

The activity of the recycled catalyst could be regenerated by stirring with copper metal to reduce Cu(II)Br$_2$ to CuBr.[16,37] The second-reused catalyst was stirred with copper beads under nitrogen at 40 °C in toluene for 12 h. The regenerated catalyst was used for a new polymerization run. Figure 8 showed that the activity of the regenerated catalyst was lower than the fresh catalyst, which could be shown by the apparent polymerization rate constant k_p^*, defined by $R_p = k_p[R^\bullet][M] = k_p^*[M]$ ($k_p^* = 0.1761$ h^{-1} for fresh catalyst vs 0.0947 h^{-1} for regenerated catalyst). This suggests that the reaction of Cu(0) with the Cu(II) immobilized on the nanoparticles was slow due to solid-semi-homogeneous reaction. However, it was higher than the recycled catalyst (k_p^* was 0.0889 h^{-1} for reused catalyst and 0.0730 h^{-1} for second-reused catalyst). The control of polymerization was similar to that of the fresh catalyst (Figure 9). This also confirms that the decrease in activity of the recycled

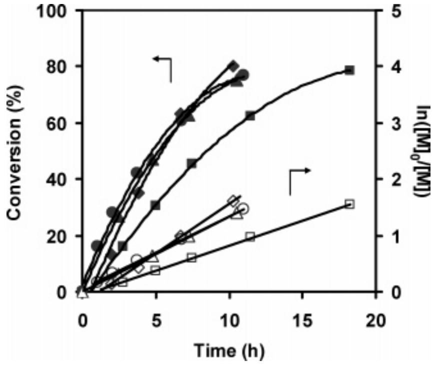


Figure 10. Methyl methacrylate (MMA) polymerization in toluene with fresh, recycled and in-situ regenerated magnetic nanoparticle supported catalyst (MNP-TEDETA). 70 °C, $[MMA]_0 = 2.35$ mol/L, $[78 \text{ mol \% } CuBr + 22 \text{ mol \% } CuBr_2]_0 = [\text{MNP-TEDETA}]_0 =$ [methyl α-bromophenylacetate (MBP)]$_0$ = 0.0235 mol/L. Fresh catalyst (◆, ◇); reused catalyst (■, □), reused catalyst in the presence of triethylamine (0.0235 mol/L) (▲, △), reused catalyst in the presence of tin(II) 2-ethylhexanoate (Sn(EH)$_2$)(0.00235 mol/L) (●, ○).

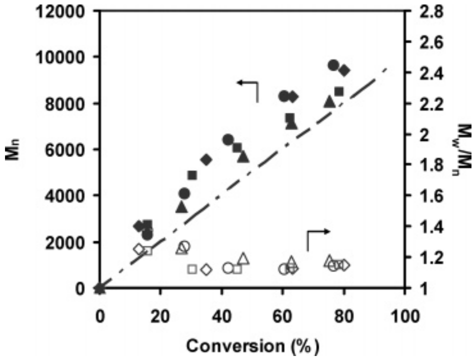


Figure 11. Poly(methyl methacrylate) (PMMA) molecular weights and polydispersity as a function of conversion in the polymerizations of methyl methacrylate (MMA) using fresh, recycled, and in-situ regenerated magnetic nanoparticle supported catalyst (MNP-TEDETA). Fresh catalyst (◆, ◇); reused catalyst (■, □), reused catalyst in the presence of triethylamine (0.0235 mol/L) (▲, △), reused catalyst in the presence of tin(II) 2-ethylhexanoate (0.002 35 mol/L) (●, ○); PMMA theoretical molecular weights (− • −). See Figure 10 for experimental conditions.

catalyst was due to the presence of an increased level of Cu(II) species.

We also developed an in-situ catalyst regeneration method using soluble reducing agents. For example, we recently demonstrated that triethylamine (TEA) could reduce Cu(II) complexes to Cu(I) complexes.[38] Figure 10 shows that in the presence of a low concentration of TEA (1/1 molar ratio of TEA/Cu) the reused catalysts had a activity similar to the fresh catalyst ($k_p^* \sim 0.1364$ h^{-1}) and much higher than the reused catalyst without regeneration (0.0889 h^{-1}). The molecular weights of the resulting PMMA were very close to theoretical values, and its polydispersity was still less than 1.2 (Figure 11). Similarly, with the addition of 10.0 mol % of tin(II) 2-ethylhexanoate (Sn(EH)$_2$), which was the reducing agent used in AGET ATRP,[39] the activity of reused catalyst was very close to that of the reused catalyst with TEA. And it had similar control over polymerization as the fresh catalyst. Thus, the in-situ regeneration of the recycled catalysts using triethylamine or Sn(EH)$_2$ restored the activity while maintaining a good control over the polymerization. This in-situ regeneration is advantageous over the regeneration using Cu(0) metal, which requires separation.

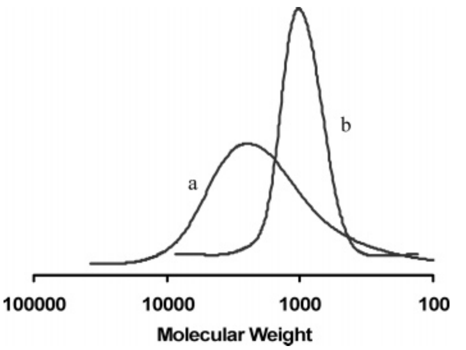


Figure 12. GPC traces of (a) PEG-*b*-PMMA block copolymer and (b) PEG macroinitiator. 70 °C, $[MMA]_0 = 2.35$ mol/L, $[Cu(I)Br]_0 = 0.0183$ mol/L, $[Cu(II)Br_2]_0 = 0.00520$ mol/L, $[\text{MNP-TEDETA}]_0 = [\text{Ini-PEG}]_0 = 0.0235$ mol/L.

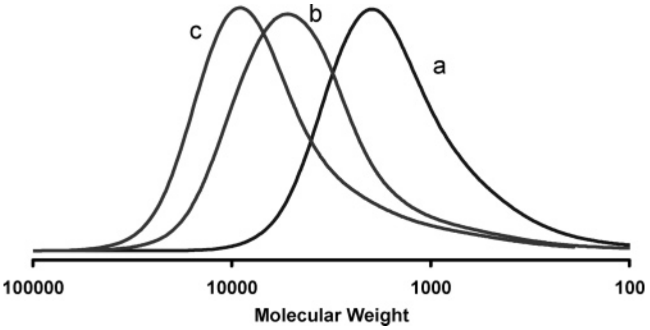


Figure 13. GPC traces of PMMA-*b*-MMA catalyzed by magnetic nanoparticle supported catalyst: 70 °C, $[MMA]_0 = 2.35$ mol/L, $[Cu(I)Br]_0 = 0.0183$ mol/L, $[Cu(II)Br_2]_0 = 0.00520$ mol/L, $[\text{MNP-TEDETA}]_0 = 0.0235$ mol/L. (a) The first MMA polymerization at 91.30% conversion, $M_n = 12\,000$ g/mol, $M_w/M_n = 1.21$; (b) 9.3 h after adding the second portion of MMA, the conversion of the second portion MMA = 71.01%, PMMA-*b*-PMMA $M_n = 20\,600$ g/mol, $M_w/M_n = 1.23$; (c) 19.8 h after the second addition of MMA, the conversion of the second portion of MMA = 82.55%, PMMA-*b*-MMA $M_n = 25\,200$ g/mol, $M_w/M_n = 1.25$.

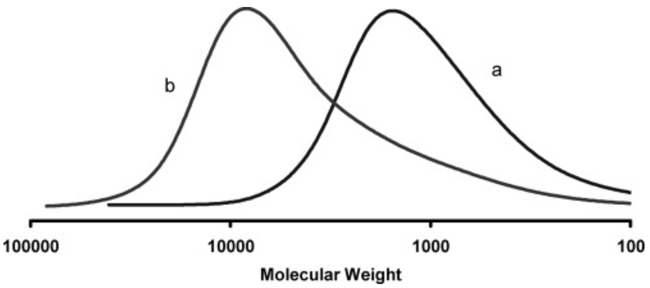


Figure 14. GPC traces of PMMA-*b*-MMA catalyzed by reused magnetic nanoparticle supported catalyst with the addition of TEA: 70 °C, $[MMA]_0 = 2.35$ mol/L, reused catalyst $[Cu(I)Br]_0 = 0.0183$ mol/L, $[Cu(II)Br_2]_0 = 0.00520$ mol/L, $[\text{MNP-TEDETA}]_0 = [TEA]_0 = 0.0235$ mol/L. (a) The first MMA polymerization at 91.30% conversion, $M_n = 9800$ g/mol, $M_w/M_n = 1.25$; (b) 20.0 h after the second addition of MMA, MMA conversion = 93.55%, $M_n = 21\,100$ g/mol, $M_w/M_n = 1.34$.

To verify the controlled/living nature of the magnetic nanoparticle-supported catalyst, two experiments were conducted for the block copolymerization of MMA. One was using poly(ethylene glycol) (Ini-PEG) as macroinitiator. The block polymer had a M_n of 16 000 and a polydispersity of 1.44 at a 92.2% MMA conversion (Figure 12). The second was to use "chain-extension" experiment. After the polymerization catalyzed by the supported catalyst reached 91.30% conversion ($M_n = 12\,000$ g/mol, $M_w/M_n = 1.21$), the second portion of MMA was added into the polymerization reactor. Figure 13 shows that the GPC curves continued to shift forward to the higher molecular weight region. The polydispersities were still less than 1.3. The reused catalyst with the addition of TEA mediated a similar "block" copolymerization (Figure 14). This further proves the living character of the polymerization mediated by the supported catalysts. ICP-MS analysis shows that the copper content in the copolymerization solution was the same as that in the homopolymerization.

Conclusions

In conclusion, we have demonstrated that by reducing the size of the solid support to ~25 nm, the adverse effects of solid supports on the immobilized ATRP catalyst could be minimized. In contrast to the catalysts immobilized on large particles, whose resulting polymers had uncontrolled molecular weights and high polydispersity even in the presence of an excess amount of $CuBr_2$,[14] the catalyst supported on the nanoparticles effectively mediated ATRP in a manner similar to homogeneous catalysts. The supported catalyst could be easily dispersed in the reaction media and separated from the solution by applying an external magnetic field. The recycled catalysts maintained similar activity and excellent control over polymerization compared to the fresh catalyst after in-situ regenerated using triethylamine or tin(II) 2-ethylhexanoate. The fresh and reused supported catalyst effectively mediated the chain extension of MMA, once again exemplifying the controlled/living nature of the polymerization. This supported catalyst does not need free deactivator or ligands, and thus the resulting residual catalyst concentration in the resulting polymer is low.

Acknowledgment. We thank National Science Foundation (CTS 0352812) for financial support.

References and Notes

(1) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.
(2) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3746.
(3) Shen, Y.; Tang, H.; Ding, S. *Prog. Polym. Sci.* **2004**, *29*, 1053−1078.
(4) Kasko, A. M.; Heintz, A. M.; Pugh, C. *Macromolecules* **1998**, *31*, 256−271.
(5) Matyjaszewski, K.; Pintauer, T.; Gaynor, S. *Macromolecules* **2000**, *33*, 1476−1478.
(6) Haddleton, D. M.; Jackson, S. G.; Bon, S. A. F. *J. Am. Chem. Soc.* **2000**, *122*, 1542−1543.
(7) Xia, J.; Johnson, T.; Gaynor, S. G.; Matyjaszewski, K.; DeSimone, J. *Macromolecules* **1999**, *32*, 4802−4805.
(8) Carmichael, A. J.; Haddleton, D. M.; Bon, S. A. F.; Seddon, K. R. *Chem. Commun.* **2000**, 1237−1238.
(9) Sarbu, T.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2001**, *202*, 3379−3391.
(10) Ding, S.; Radosz, M.; Shen, Y. *Macromolecules* **2005**, *38*, 5921−5928.
(11) Haddleton, D. M.; Duncalf, D. J.; Kukulj, D.; Radigue, A. P. *Macromolecules* **1999**, *32*, 4769−4775.
(12) Shen, Y.; Zhu, S.; Zeng, F.; Pelton, R. *Macromolecules* **2000**, *33*, 5427−5431.
(13) Shen, Y.; Zhu, S.; Pelton, R. *Macromol. Rapid Commun.* **2000**, *21*, 956−959.
(14) Kickelbick, G.; Paik, H.-j; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2941−2947.
(15) Haddleton, D. M.; Kukulj, D.; Radigue, A. P. *Chem. Commun.* **1999**, 99.
(16) Shen, Y.; Zhu, S.; Zeng, F.; Pelton, R. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1051−1059.
(17) Shen, Y.; Zhu, S.; Pelton, R. *Macromolecules* **2001**, *34*, 5812−5818.
(18) Honigfort, M. E.; Brittain, W. J. *Macromolecules* **2003**, *36*, 3111−3114.
(19) Nguyen, J. V.; Jones, C. W. *Macromolecules* **2004**, *37*, 1190−1203.
(20) Nguyen, J. V.; Jones, C. W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1384−1399.
(21) Nguyen, J. V.; Jones, C. W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1367−1383.
(22) Hong, S. C.; Matyjaszewski, K. *Macromolecules* **2002**, *35*, 7592−7605.
(23) Hong, S. C.; Neugebauer, D.; Inoue, Y.; Lutz, J.-F.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 27−35.
(24) Duquesne, E.; Degee, Ph.; Habimana, J.; Dubois, Ph. *Chem. Commun.* **2004**, *6*, 640−641.
(25) Liou, S.; Rademacher, J. T.; Malaba, D.; Pallack, M. E.; Brittain, W. J. *Macromolecules* **2000**, *33*, 4295−4296.
(26) Shen, Y.; Zhu, S.; Pelton, R. *Macromolecules* **2001**, *34*, 3182−3185.
(27) Shen, Y.; Zhu, S. *Macromolecules* **2001**, *34*, 8603−8609.
(28) Barre, G.; Taton, D.; Lastecoueres, D.; Vincent, J.-M. *J. Am. Chem. Soc.* **2004**, *126*, 7764−7765.
(29) Yang, J.; Ding, S.; Radosz, M.; Shen, Y. *Macromolecules* **2004**, *37*, 1728−1734.
(30) Ding, S.; Yang, J.; Radosz, M.; Shen, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, 42, 22−30.
(31) Phan, N. T. S.; Jones, C. W. *J. Mol. Catal.. A: Chem.* **2006**, *253*, 123−131.
(32) Abu-Reziq, R.; Alper, H.; Wang, D.; Post, M. L. *J. Am. Chem. Soc.* **2006**, *128*, 5279−5282.
(33) Zheng, Y.; Stevens, P. D.; Gao, Y. *J. Organomet. Chem.* **2006**, *71*, 537−542.
(34) Stevens, P. D.; Li, G.; Fan, J.; Yen, M.; Gao, Y. *Chem. Commun.* **2005**, *35*, 4435−4437.
(35) Pan, B.; Gao, F.; Gu, H. *J. Colloid Interface Sci.* **2005**, *284*, 1−6.
(36) Faucher, S.; Zhu, S. *Macromol. Rapid Commun.* **2004**, *25*, 991−994.
(37) Nguyen, J. V.; Jones, C. W. *J. Catal.* **2005**, *232*, 276−294.
(38) Tang, H.; Radosz, M.; Shen, Y. *Macromol. Rapid Commun.* **2006**, *27*, 1127−1131.
(39) Jakubowski, W.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 4139−4146.

MA061062Y