Soluble and Recoverable Support for Copper Bromide-Mediated Living Radical Polymerization

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Received November 14, 2000

ABSTRACT: Transition-metal-mediated living radical polymerizations (atom transfer radical polymerization, ATRP) have many potential applications, but the high concentration of residual catalyst colors their products. Supporting catalyst on insoluble solids has been used to reduce the content of residual catalyst and to reuse the catalyst, but the ability of the supported catalyst to mediate a polymerization is substantially reduced due to heterogeneity. Here we report a soluble but recoverable catalyst support for ATRP. Poly(ethylene)-*block*-poly(ethylene glycol) (PE-PEG) was soluble in toluene above 70 °C but insoluble at room temperature. CuBr supported on PE-PEG via tetraethyldiethylenetriamine thus mediated living polymerizations of methyl methacrylate, 2-(dimethylamino)ethyl methacrylate, and styrene as homogeneous catalyst at 80 or 100 °C, producing polymers with well-controlled molecular weight and very low polydispersity. The catalyst recycled at ambient temperature retained high activity and still mediated living polymerizations as well as the fresh catalyst. Subsequent block copolymerization confirmed its living nature.

Introduction

The transition-metal-mediated living polymerization (also named atom transfer radical polymerization, ATRP) is versatile for various vinyl monomers in the syntheses of polymers with controlled molecular weights and low polydispersities[1−5] as well as end-functionalized polymers.[6−8] It also provides an effective approach to novel polymer architectures such as star polymers,[9,10] polymer brushes,[11] nanoparticle hybrids,[12] and polymer monolayers.[13] The obvious advantages of ATRP are its mild reaction conditions and tolerance to water and other protonic species.

The main challenge for ATRP is minimizing the amount of residual catalyst in the resulting polymers. The residual catalyst (typically 0.1−1% w/w) deeply colors the product (e.g., deep green using copper bromide−aliphatic amine). Even though the residue can be removed from the product by silica gel or resin[14] or by reprecipitation,[15] this postpurification is not only costly but also wastes catalyst. Supported catalysts on insoluble particles[16−18] have been developed to reduce the catalyst residue and to reuse the catalysts. However, the heterogeneous nature causes some problems. The ability of supported catalysts to mediate ATRP was much lower than that of their homogeneous counterparts.[16−18] The polydispersity of resulting polymer was broad ($M_w/M_n \sim 1.5$[18] or higher[16,17]), and the initiator efficiency was generally low. This negative effect of the catalyst support on the polymerization has been attributed to the limited catalyst diffusion caused by heterogeneity.[16−18] Unlike a small molecule, a polymer chain generally adopts random coil conformation in solution. The active ($P^\bullet$, radical) or dormant (P−Br) polymer ends embodied in the coils may experience difficulty in accessing the catalyst sites on the solid. A homogeneous support is thus preferred for ATRP.

Thermoresponsive polymer supports based on temperature-dependent solubility have been developed for small molecule reactions to achieve homogeneity under reaction conditions but catalyst separation under workup conditions.[19−22] Polyethylene oligmer is soluble in toluene but precipitates at room temperature. Catalyst bound on polyethylene thus dissolves in solution at high temperature for reaction but precipitates at ambient temperature for separation and recycling. Very recently, Brittain et al.[23] used polyethylene as a support for ATRP of MMA. However, the activity of the supported catalyst was very low even at 100 °C, and the polymerization underwent some terminations. The polydispersities of resulting PMMA were in the range 1.4−1.5.

Here we report copper bromide supported on poly(ethylene) via a poly(ethylene glycol) (PEG) spacer. PEG is soluble in common solvents, and its flexibility renders the catalyst more mobile at low temperature, which favors complexation of copper bromide with the ligand at ambient temperature and catalyst diffusion at higher reaction temperatures.

Experimental Section

Materials. Styrene (St, 99%), methyl methacrylate (MMA, 99%), and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%) from Aldrich were distilled under vacuum and stored at −15 °C. *N*,*N*,*N*′,*N*′-Tetraethyldiethylenetriamine (TEDETA, 90%), CuBr (99.99%), and methyl α-bromophenylacetate (MBP, 98%) were used as received from Aldrich. Poly(ethylene)-*block*-poly(ethylene glycol) ($M_n = 875$, PE-PEG-OH, 21 wt % ethylene glycol) (Aldrich) was characterized by NMR, and its structure was agreeable with reported. Toluene from Aldrich was distilled.

Measurements. (a) Nuclear Magnetic Resonance (NMR) Spectroscopy. Proton (^{1}H) NMR spectra were recorded on a Bruker ARX-200 spectrometer at 200 or 300 MHz. ^{1}H NMR chemical shifts in $CDCl_3$ were reported downfield from 0.00 ppm using TMS an internal reference.

(b) UV spectra were recorded on Hewlett Packard 8452A diode array spectrophotometer. After each polymerization finished, the mixture was centrifuged and the upper layer solution was taken out by syringe to measure the UV spectra. A catalyst solution (0.0113 mol/L) was prepared by mixing the same amount of CuBr, tetraethyldiethylenetriamine, MMA, MBP, and toluene as used in polymerization.

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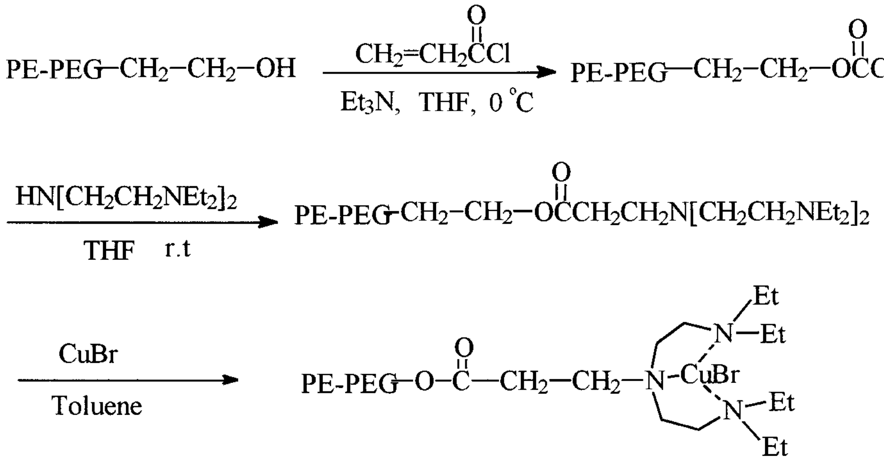
10.1021/ma001948g CCC: $20.00

Scheme 1. Supporting the Catalyst onto Polyethylene via Tetraethyldiethylenetriamine (TEDETA)



(c) Molecular Weight Measurements. Number- and weight-average molecular weights (M_n and M_w, respectively) were determined by gel permeation chromatography (pore size: 500, 1500, and 10 000 Å) using THF−2% (v/v) triethylamine as solvent at a flow rate of 1.0 mL/min at 25 °C with a RI detector. Narrow polystyrene standards (Polysciences) and Mark−Houwink−Sakurada constants ($K_{PS} = 0.000\,128$, $\alpha_{PS} = 0.712$; $K_{PMMA} = 0.000\,128$, $\alpha_{PMMA} = 0.69$) were used to generate a universal calibration curve. Data were recorded and manipulated using the Windows-based Millennium software package.

Ligand Synthesis. The catalyst supporting procedure is shown in Scheme 1. Polyethylene-*block*-poly(ethylene glycol) (PE-PEG-OH) was end-capped with an acrylate group by reaction of the terminal hydroxyl group with acryloyl chloride. The Michael reaction of the acrylate group with tetraethyldiethylenetriamine (TEDETA) attached the ligand onto the support (PE-PEG-TEDETA).

PE-PEG-OH (20 g, 0.0228 mol) was dissolved in toluene (200 mL) at 90 °C under nitrogen atmosphere. The solution was cooled slowly to room temperature. Precipitated PE-PEG-OH was centrifuged. The solid was dispersed in 200 mL of THF−Et_3N (5/1 in v/v) at ambient temperature. Acryloyl chloride (3.6 mL, 0.0442 mol) diluted in 10 mL of THF was dropwise added to this mixture. The mixture was stirred for overnight and then centrifuged. The solid was washed successively seven times with THF, 10 times with water (to wash out formed $Et_3N{\cdot}HCl$ salt), and twice with THF. The solid was then dispersed in 25 mL of TEDETA and stirred for 48 h (Michael reaction) at ambient temperature. The solid was separated by centrifugation, washed with THF 10 times, and dried under vacuum at 30 °C. ^{1}H NMR in $CDCl_3$ (60 °C, 300 MHz): CH_3-$(CH_2{-}CH_2)_x(OCH_2CH_2)_yCH_2CH_2OC(O)CH_2CH_2N[CH_2CH_2N(CH_2CH_3)_2]_2$ 1.27 (CH_2 in PE segments, 88H), 3.65 (CH_2 in PEG segment, 12H), 4.20 (COOCH_2, 1H), 2.85 (OC(O)CH_2, 1H), 2.50−2.7 (NCH_2, 7H), 1.0 (NCH$_2$CH_3, 5H), 0.87 (CH_3 at the PE end, 3H). About 42% PE-PEO chains were capped with TEDETA ligand.

Polymerizations. In a typical polymerization run, CuBr (0.011 g, 0.0764 mmol), PE-PEG-TEDETA (0.3 g), and toluene (5 g) were charged to a Schlenk flask and degassed with several vacuum/nitrogen cycles. Then degassed MMA (1.0 g, 10 mmol) was introduced by syringe and stirred. After the PE-PEG-TEDETA support was thoroughly dispersed, degassed methyl α-bromophenylacetate (12 μL, 0.0757 mmol) was dropwise added to the mixture with stirring. The slightly yellow solution immediately turned green. The mixture was further stirred at room temperature for 30 min. Then the flask was immersed in an oil bath (80 °C) for polymerization. The polymerization solution (0.05−0.1 mL) was withdrawn at different intervals to analyze the conversion (by NMR) (see Figure 1) and molecular weight (GPC) (see Figure 2). For styrene polymerization a small amount of γ-butyrolactone was added as internal reference for ^{1}H NMR for conversion calculation (see Table 1).

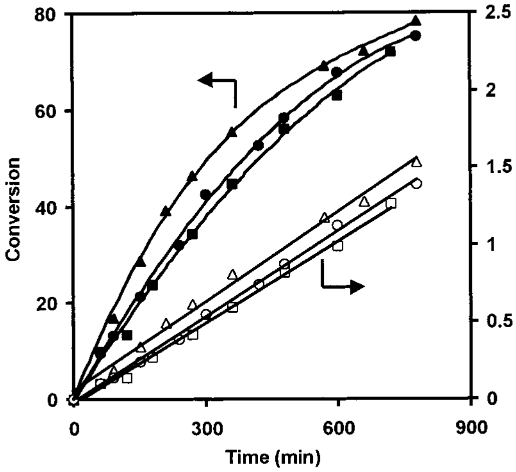


Figure 1. MMA polymerization with fresh and recycled catalysts. [CuBr] = [MBP] = 0.0115 mol/L, PE-PEG-TEDETA/CuBr = 1.5, [MMA] = 1.5 mol/L, 80 °C. Fresh catalyst (▲, △), first recycled catalyst (●, ○), second recycled catalyst (■, □).

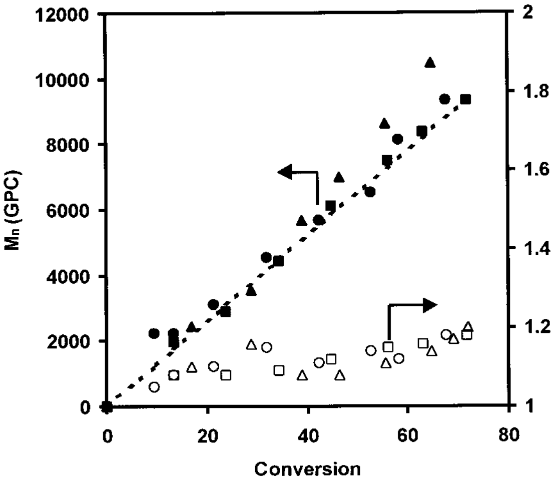


Figure 2. Molecular weight and polydispersity of PMMA as a function of conversion in MMA polymerization with fresh and recycled catalysts. Fresh catalyst (▲, △), first recycled catalyst (●, ○), second recycled catalyst (■, □), theoretical M_n (- - -). See Figure 1 for experimental conditions.

Catalyst Reuse. After the polymerization was complete, the flask was lifted from the oil bath and centrifuged. The supernatant was carefully removed with a cannula under nitrogen pressure. The remaining green solid in the flask was washed three times with degassed toluene (total 20 mL) under

Table 1. DMAEMA and Styrene Polymerization with CuBr/PE-PEG-TEDETA[a]

monomer	time (h)	conv (%)	$M_n \times 10^{-3}$ (calcd)	$M_n \times 10^{-3}$ (GPC)	M_w/M_n
DMAEMA[b]	1	18	3.64	3.70	1.16
	3	46	9.36	11.3	1.14
	6.6	74	15.1	16.6	1.20
styrene[c]	11	31	4.20	4.30	1.11
	22	47	6.40	8.00	1.14
	74	70	9.50	12.1	1.21

[a] [CuBr] = [MBP] = 0.0113 mol/L, PE-PEG-TEDETA/CuBr = 1.5, [monomer] = 1.5 mol/L. [b] 80 °C. [c] 100 °C.

nitrogen. The same amounts of degassed MMA, toluene, and initiator as in the first run were added to the flask and reheated to 80 °C. The same procedure as the first run was repeated (see Figures 1 and 2).

Block Copolymerization. CuBr (0.011 g, 0.0764 mmol), PE-PEG-TEDETA (0.3 g), and toluene (2.5 g) were added to a Schlenk flask and degassed as described above. Degassed MMA (0.60 g, 6.0 mmol) and methyl α-bromophenylacetate (12 μL, 0.0757 mmol) were added. The mixture was immersed in an 80 °C oil bath for 10 h. A small amount of this mixture (0.05 mL) was withdrawn to analyze the conversion by NMR (conversion, 90%) and molecular weight by GPC (M_n = 8500, M_w/M_n = 1.09). Then the flask was connected to vacuum to remove the volatiles. Degassed DMAEMA (1.26 g, 8.0 mmol) and toluene (2.5 mL) were charged to the flask and stirred for 10 min. Then the flask was reheated at 80 °C for 10 h (conversion, 79%; M_n = 21 000, M_w/M_n = 1.26).

Results and Discussion

PE-PEG-TEDETA was easily dispersed in toluene at ambient temperature. It formed a yellow-green complex with CuBr. This complex turned green once methyl α-bromophenylacetate (MBP, initiator) was added. The green complex settled to the bottom of the flask if the stirring was stopped and left a colorless upper layer. Heating at 70 or 80 °C resulted in a homogeneous solution. Figure 1 shows that MMA polymerization mediated by CuBr on this soluble support was a typical first-order reaction with respect to monomer. The molecular weights of the produced polymers increased linearly with conversion and were very close to the theoretical values (Figure 2). The polydispersities were less than 1.2, similar to those from homogeneous ATRP,[24] and much narrower than those from heterogeneous ATRP of MMA.[16-18] This suggests that this soluble catalyst mediated the ATRP of MMA as effectively as homogeneous catalyst with small molecule ligand.[24]

After polymerization, the mixture was cooled to ambient temperature and centrifuged. The deep green solid was on the bottom of the flask while the upper layer solution was colorless. The copper concentration in the solution measured by UV (Figure 3) was less than 2−3% of the catalyst used. The PMMA isolated from the solution was colorless. The exact residual catalyst concentration in the polymer is being studied currently. The remaining catalyst was washed with degassed toluene. The same amounts of monomer, initiator, and solvent as in the first run were recharged to the catalyst, and the mixture was reheated at 80 °C. The recycled catalysts still mediated a first-order polymerization as well as the fresh catalyst (Figure 1). The first recycled catalyst retained 90% activity (slope ratio in Figure 1) of fresh catalyst, while the second recycled catalyst had almost the same activity as the first recycled catalyst (97% activity). This activity retention was much higher than those of silica gel supported CuBr.[16-18] The slight reduction in activity of recycled catalyst has been ascribed to the presence of Cu(II) in the recycled catalyst, which could significantly decrease the polymerization rate even in the presence of a small amount.[18] Most significantly, the recycled catalyst still had excellent control over the molecular weight development. The molecular weights were very close to those predicated, and the polydispersities remained very narrow. These results indicate that the PE-PEG-TEDETA supported CuBr is recoverable and reusable.

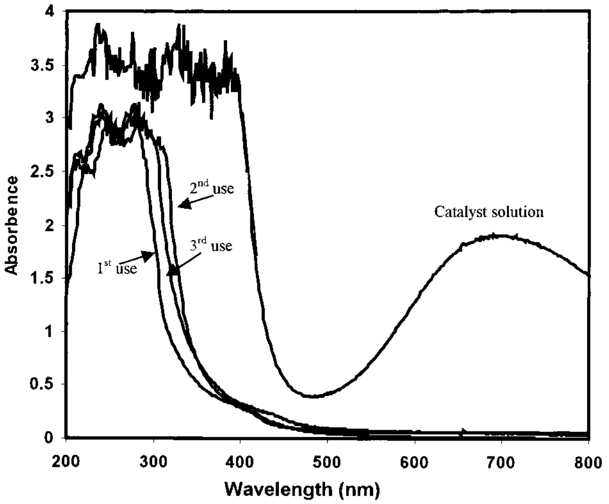


Figure 3. UV spectra of the polymerization solution after the catalyst precipitated. First use: reaction solution after first run polymerization; second use: reaction solution after second run polymerization; third use: reaction solution after third run polymerization. Catalyst solution: 0.011 g of CuBr, 0.041 g of tetraethyldiethylenetriamine, 5.0 g of toluene, 1.0 g of MMA, and 12 μL of MBP (as used in polymerization) were mixed and degassed.

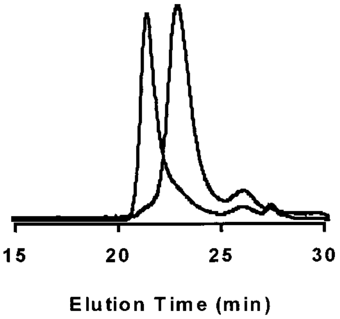


Figure 4. GPC traces of the PMMA-*b*-PDMAEMA (A) and PMMA prepolymer (B). [CuBr] = [MBP] = 0.021 mol/L, PE-PEG-TEDETA/CuBr = 1.5, [MMA] = 1.71 mol/L, 80 °C. Toluene as solvent.

The PE-PEG-TEDETA-supported CuBr also catalyzed the polymerizations of styrene and 2-(dimethylamino)ethyl methacrylate (DMAEMA), as shown in Table 1. DMAEMA polymerization was faster than that of MMA, but the polymerization of styrene was much slower. The molecular weights of the polymers were also close to those predicated with low polydispersities. The polydispersities increased slightly at high conversion, which may be caused by reduced diffusivity of the catalyst as the solution became viscous.

Block Copolymerization. The block copolymer of MMA with DMAEMA was prepared by the reinitiation method. MMA (MMA/MBP = 80) was first polymerized for 10 h, yielding PMMA of M_n = 8500 with M_w/M_n =

1.09 (M_n(theor) = 7200). After the volatiles (toluene and unpolymerized MMA) were removed by vacuum, degassed toluene and DMAEMA were combined with the remaining solid and reheated at 80 °C for 10 h. A block copolymer of P(MMA-*b*-DMAEMA) was isolated with M_n = 21 100 (M_n(theor) = 21 000) and polydispersity of 1.26 (Figure 4). This further demonstrates that the reaction by this soluble-supported CuBr occurred in a living polymerization process.

In conclusion, PE-PEG-TEDETA is a soluble but recoverable support for CuBr in ATRP. It allowed not only easy separation of the catalyst from the product and the ability to reuse the catalyst but also ATRP under homogeneous conditions, which is much better than in heterogeneous solutions. The study of the effects of the spacer and ligand is currently under way.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada (NSERC) for financial support.

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