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Communications to the Editor

Use of Precipitons for Copper Removal in Atom Transfer Radical Polymerization

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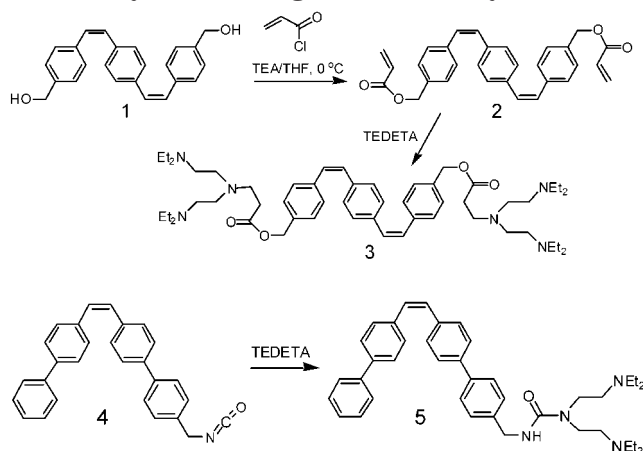
Atom transfer radical polymerization (ATRP) methods have been improved in recent years and provide a promising set of tools for the controlled synthesis of polymers.¹ One drawback of ATRP, arising when standard homogeneous catalysts are used, is contamination of the polymer by the ligand/metal complex. The colored catalyst complex is typically removed by passing through a column of alumina, followed by precipitation of the polymer. Post-polymerization processing to remove catalyst increases the cost of polymer production. Methods that generate a clean polymer solution after reaction and allow for catalyst recycling are desirable.

Surface-immobilized catalysts offer a convenient method for catalyst recovery and have been applied to ATRP.^{2–4} The catalyst is removed by simple filtration or decantation, but comparison of these methods to traditional ATRP conditions shows the surface-immobilized catalysts often provide products with higher molecular weights than predicted and broader molecular weight distributions, and sometimes have longer reaction times. It has been hypothesized that the sluggish reaction rates seen with surface-immobilized catalysts may be due to retarded diffusion of the polymer chain to the silica or polystyrene bead surface. We have investigated polyethylene-bound ATRP ligands because this strategy allows polymerization to be conducted under homogeneous reaction conditions and offers an

easier approach to catalyst removal.⁵ Zhu and co-workers have reported the use of polyethylene–poly(ethylene glycol)-bound ligands.⁶ They also report an improvement in the use of silica-supported multidentate amine ligands in ATRP, affording polymers with low polydispersity, good molecular weight control, and high conversion for methyl methacrylate (MMA) reactions.⁷ Use of silica supported ligands with a poly(ethylene glycol) spacer has been investigated by Zhu et al.,⁸ demonstrating that the length of the spacer affects the rate of polymerization and molecular weight control.

Here we report an investigation using precipitons for copper catalyst removal in ATRP. Precipitons were developed to provide a convenient method for isolating solutes from homogeneous reaction media. These isomerizable compounds are attached to a reactant and after a reaction is complete they can be isomerized to cause precipitation of the attached product.^{9–11} The *cis*-form of the stilbene is soluble whereas the *trans*-form is insoluble in common organic solvents. The precipitated product can be isolated by filtration or centrifugation. To test the usefulness of this strategy when applied to the removal of catalysts in ATRP, nitrogen ligands bearing precipitons were prepared and used to mediate ATRP. This strategy enables homogeneous reaction conditions to be combined with a facile method for removal of the copper catalyst. We expected that after the polymerization was complete, the polymer solution could be exposed to UV light to induce precipitation of the precipiton ligand/CuBr complex. The ATRP ligands **3** and **5** were synthesized starting from the bis-OH **1** and isocyanate **4** precipitons, respectively.

Bis-OH precipiton **1** was prepared as described in the literature⁷ and was reacted with acryloyl chloride. The resultant bis-acrylate underwent a Michael reaction with *N,N,N,N*-tetraethyldiethylenetriamine (TEDETA) to afford ligand **3** in 65% yield (Scheme 1). The isocyanate functional precipiton **4** was prepared as described in the literature.¹² Ligand **5** was synthesized in a one-step reaction of compound **4** with TEDETA (Scheme 1) to afford **5** quantitatively.

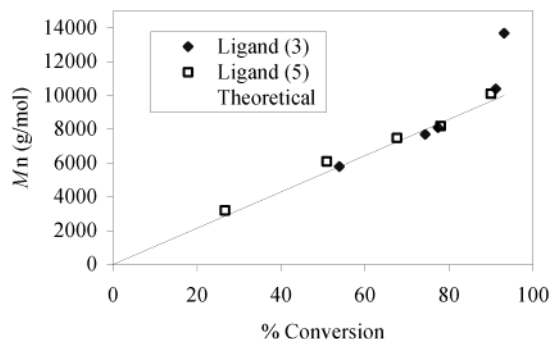
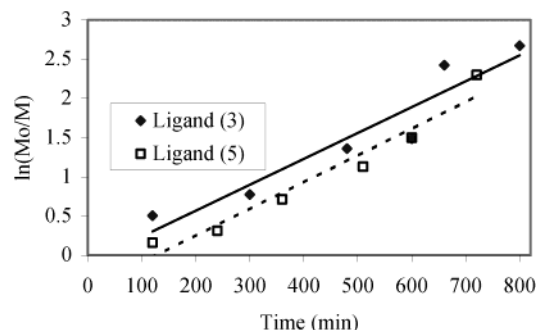
Scheme 1. Synthesis of Ligand 3 Starting from Diol 1 and Synthesis of Ligand 5 from Isocyanate 4**Table 1. Results for Polymerization of MMA at 90 °C in 50% (v/v) Toluene Using Ligands 3 and 5 ([MMA]:[Ethyl 2-Bromoisobutyrate]:[Ligand] = 100:1:1.5)**

ligand	time (min)	conv (%)	$M_n(\text{exptl})$	$M_n(\text{theor})$	PDI
3	120	40	4600	4000	1.45
3	300	54	5800	5400	1.45
3	480	74	7700	7400	1.44
3	600	78	8100	7800	1.42
3	660	91	10 400	9100	1.42
3	800	93	13 700	9300	1.40
5	120	15		1500	
5	240	27	3200	2700	1.22
5	360	51	6100	5100	1.20
5	510	68	7500	6800	1.20
5	600	78	8200	7800	1.19
5	720	90	10 100	9000	1.19

Ligands **3** and **5** were successfully used for ATRP of MMA mediated by CuBr, using toluene as the solvent and ethyl 2-bromoisobutyrate as the initiator. Upon completion of the polymerization, the solution was cooled and exposed to UV radiation for 2 h. The precipiton ligand precipitated and remained complexed with the Cu catalyst. The precipitated product can be isolated by decantation, filtration, or centrifugation. Copper content of the polymer solution was determined by UV spectroscopy and indicated no detectable copper based on the lack of absorbance at 680 nm. ICP analysis for copper content indicates <1% of original copper in the PMMA obtained using both ligands **3** and **5**. The PMMA from this reaction required no purification other than simple decantation.

Compared to the various heterogeneous copper removal techniques, this system offered somewhat better control of molecular weight and molecular weight distribution in reasonable reaction times. The results are summarized in Table 1 for the reactions using ligands **3** and **5**. The plot of M_n vs monomer conversion (Figure 2) shows that $M_n(\text{exptl})$ is in good agreement with $M_n(\text{theor})$ until high conversion. At high conversions, $M_n(\text{exptl})$ is greater than expected, indicating possible radical-radical termination. The reaction followed pseudo-first-order kinetics (Figure 2) and achieved 90–93% conversion in 12 h while polydispersity narrowed over the course of the reaction. Better control over polydispersity was obtained using ligand **5**.

The precipiton-bound ligands successfully mediated the ATRP of MMA and allowed for easy and fast removal of the copper catalyst by exposure of the solution to a UV light source. The present inability to

**Figure 1.** M_n vs percent monomer conversion for ATRP of MMA.**Figure 2.** Kinetic plot for ATRP of MMA using precipiton ligands.

reuse or recycle the ligand in this catalyst system is an undesirable feature. In other supported catalyst systems, the ligand can be recovered and used again, but the precipitons in our experiments cannot be recycled. If ongoing efforts to develop recyclable precipitons are successful, this system will provide a general and economically attractive way to remove metals from ATRP systems.

Experimental Section. Materials. Reagents were purchased from Aldrich and used as received unless otherwise noted. *N,N,N,N*-Tetraethyldiethylenetriamine (TEDETA, 90%) and acryloyl chloride (96%) were vacuum distilled. Methyl methacrylate (MMA) was passed through a basic alumina column then vacuum distilled from CaH₂. CuBr (98%) was purified by the method described by Keller and Wycoff.¹³

Characterization. ¹H NMR spectra were recorded on a Varian Gemini-300 spectrometer. Molecular weight analysis was performed by gel permeation chromatography (GPC) using a Waters 501 pump, guard column, Waters HR2 and HR4 Styragel columns, a Waters 410 differential refractometer, and a Viscotek T60A dual light scattering and viscosity detector. The eluent was THF and flow rate was 1.0 mL/min. M_n and M_w were determined using universal calibration. UV spectroscopy was performed on a HP 8453 UV–visible spectrophotometer. ICP analysis for copper was performed by Galbraith Laboratories.

ATRP Procedure. A Schlenk flask was charged with CuBr (1 equiv, 0.17 mmol, 0.02 g) and precipiton ligand (for ligand **3**, 0.5 equiv, 0.085 mmol, 0.075 g; for ligand **5**, 1 equiv, 0.17 mmol, 0.10 g) and degassed with three vacuum/argon cycles. Via syringe, deoxygenated toluene (2 mL) and MMA (100 equiv, 0.017 mol, 1.7 g) were added. The solution was heated in an oil bath at 90 °C. Ethyl 2-bromoisobutyrate (1 equiv, 0.17 mmol, 25 μ L) was added and the solution heated for 12 h. Aliquots were removed to determine conversion by ¹H NMR and

molecular weight. After cooling, the polymer solution was transferred to a quartz tube and irradiated with ultraviolet light from a xenon arc lamp (UV output = 2.8 W) for 2 h. The polymer solution was decanted from the solid ligand/CuBr complex, collected by removal of solvent in vacuo and analyzed by UV spectroscopy. Copper content of the polymer without further purification was determined by ICP analysis.

Synthesis and NMR Data for Precipiton Acrylate 2. Bis-OH precipiton **1** was prepared as described in the literature.⁷ The precipiton (1 equiv) was dissolved in anhydrous THF and cooled to 0 °C. Triethylamine (1.5 equiv) was added followed by dropwise addition of acryloyl chloride (1.5 equiv), and the mixture was stirred overnight. Volatiles were removed in vacuo and the precipiton ligand was washed 10 times with water, collected by centrifugation, and dried in vacuo to afford yellow solid (65%). ¹H NMR (CDCl₃): δ 5.2 (s, 4 H), 5.9 (d, 2 H), 6.1–6.4 (q, 2 H), 6.5 (d, 2 H), 6.6 (s, 4 H), 7.1 (s, 4 H), 7.2 (s, 8 H). ¹³C NMR (CDCl₃): δ 164.1, 137.5, 136.2, 134.9, 130.5, 129.2, 129.0, 128.5, 126.9.

Synthesis and NMR Data for Precipiton Ligand 3. Bis-acrylate precipiton **2** was dissolved in excess TEDETA and stirred overnight. TEDETA was removed via Kugelrohr distillation to afford a brownish solid (quantitative). ¹H NMR (CDCl₃): δ 0.9–1.0 (t, 24 H), 2.4–2.6 (m, 36 H), 2.8 (t, 4 H), 5.1 (s, 4 H), 6.6 (s, 4 H), 7.1 (s, 4 H), 7.2 (s, 12 H). ¹³C NMR (CDCl₃): δ 137.5, 136.2, 134.9, 130.5, 129.2, 128.5, 126.9, 52.9, 52.5, 48.0, 47.3, 12.0.

Synthesis and NMR Data for Precipiton Ligand 5. Isocyanate **4** was placed in a Schlenk flask and purged with argon. THF (anhydrous) was added to dissolve the solids. TEDETA was added dropwise and the reaction was stirred overnight. THF was removed in vacuo, and TEDETA was removed via Kugelrohr distillation to afford a yellow powder (quantitative). ¹H

NMR (CDCl₃): δ 0.9–1.0 (t, 12 H), 2.4–2.6 (m, 12 H), 3.3 (t, 4H), 4.3 (d, 2H), 6.6 (s, 2H), 7.0–7.6 (m, 17 H), 8.4 (s, 1 H). ¹³C NMR (CDCl₃): δ 140.6, 140.4, 139.8, 139.0, 136.6, 130.2, 129.9, 129.6, 128.9, 127.4, 127.3, 127.2, 127.0, 126.9, 126.8, 52.9, 52.5, 48.0, 47.3, 12.0.

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Supporting Information Available: Text giving experimental details and characterization data and a figure showing a UV spectral comparison of the PMMA/toluene solution compared with a Cu-containing standard solution.. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Matyjaszewski, K. *Controlled Radical Polymerization*; American Chemical Society: Washington, DC, 1998; Vol. 685.
- (2) Kickelbick, G.; Paik, H.-j.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2941–2947.
- (3) Haddleton, D. M.; Kukulj, D.; Radigue, A. P. *Chem. Commun.* **1999**, 99.
- (4) Haddleton, D. M.; Duncalf, D. J.; Kukulj, D.; Radigue, A. P. *Macromolecules* **1999**, *32*, 4769.
- (5) Liou, S.; Rademacher, J. T.; Malaba, D.; Pallack, M. E.; Brittain, W. J. *Macromolecules* **2000**, *33*, 4295.
- (6) Shen, Y.; Zhu, S.; Zeng, F.; Pelton, R. H. *Macromolecules* **2000**, *33*, 5427.
- (7) Shen, Y.; Zhu, S.; Pelton, R. H. *Macromolecules* **2001**, *34*, 3182.
- (8) Shen, Y.; Zhu, S.; Pelton, R. H. *Macromolecules* **2001**, *34*, 5812.
- (9) Bosanac, T.; Yang, J.; Wilcox, C. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1875.
- (10) Bosanac, T.; Wilcox, C. S. *Chem. Commun.* **2001**, 1618.
- (11) Bosanac, T.; Wilcox, C. S. *Tetrahedron Lett.* **2001**, 4309.
- (12) Bosanac, T.; Wilcox, C. S. *J. Am. Chem. Soc.* **2002**, *124*, 4194.
- (13) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1947**, *2*, 1.

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