Closer to the "Ideal Recoverable Catalyst" for Atom Transfer Radical Polymerization Using a Molecular Non-Fluorous Thermomorphic System

Guillaume Barré,[†] Daniel Taton,[‡] Dominique Lastécouères,*,[†] and Jean-Marc Vincent*,[†]

Laboratoire de Chimie Organique et Organométallique (UMR-CNRS 5802), Université Bordeaux 1, 351 cours de la Libération, 33405 Talence Cedex, France, Laboratoire de Chimie des Polymères Organiques, 16 Avenue Pey-Berland, 33607 Talence Cedex, France

Received April 2, 2004; E-mail: jm.vincent@lcoo.u-bordeaux1.fr

The search for recoverable catalysts is a major concern of modern chemistry.[1] The "ideal recoverable catalyst" as outlined by Gladysz would satisfy an exacting set of criteria related to its preparation (low cost, easy synthesis and handling, being nontoxic and hazard-free), its reactivity (no activation, gives 100% product yield, fast kinetics at ambient temperature, low loading) and its recovery (quantitative by filtration).[2]

Atom transfer radical polymerization (ATRP) is a versatile transition-metal-mediated "controlled/living" polymerization allowing the synthesis of end-functionalized polymers with controlled molar masses and low polydispersity.[3] Nonetheless, there is still a need to develop catalytic systems that can meet the aforementioned criteria for a large-scale production of polymeric materials. Indeed, one of the limitations of ATRP for its industrial development is the presence of residual transition metal catalyst in the final polymer which may cause environmental problems. Different purification methods were proposed in the recent literature, among which the most developed is the immobilization of the ATRP catalyst onto organic or inorganic polymeric supports. While efficient copper removal of the final polymer was achieved with the simpler heterogeneous systems, they typically exhibit moderate control of the polymer molar masses and polydispersities along with moderate recyclabiblity.[4] More efficient purely heterogeneous,[5a−c] two-component heterogeneous/homogeneous,[5d−f] or macromolecular thermoresponsive catalysts[6] were recently reported. However, their rather tedious preparation and/or recovery procedures might limit the applicability of these methods at the industrial scale.

We previously reported the first example of a molecular recyclable catalyst for ATRA that was based on the thermomorphic behavior of a fluorous biphasic system (FBS).[7] CuCl−fluorous polyamine catalysts were efficiently recycled by hydrocarbon/perfluorocarbon extraction, leading to low copper contamination of the final lactone products. This FBS also proved to be effective for catalyst recovery in ATRP, but its prohibitive cost and its low efficiency in controlling the molar masses of the polymers renders it nonapplicable in industrial processes.[8]

Recently, Gladysz and co-workers introduced the solubility-based thermomorphic properties of heavy fluorous catalysts in organic solvents as a new and rather general strategy to perform homogeneous fluorous catalysis without fluorous solvent.[9] Catalyst recovery was achieved by a simple liquid-/solid-phase separation. Inspired by this seminal work, we wondered whether this approach could not be extended, for particular cases, to catalysts in which the perfluoroalkylated chains could be replaced by cheaper, long alkyl chains. Herein we report the simple, molecular thermoresponsive CuBr/**1**-dioxane catalytic system for ATRP exhibiting both the

advantages of simple recovery by filtration and optimal reactivity due to its homogeneous character at high temperature.

The hexasubstituted tetramine ligand **1** (white powder, mp 58 °C) was prepared in 85% yield by refluxing tris(2-aminoethyl)-amine, 1-iodooctadecane, and potassium carbonate in acetonitrile for 2 days (see Supporting Information).
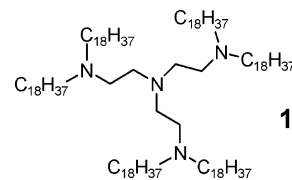
Compound **1** was fully soluble at ambient temperature in solvents of low to moderate polarity such as *n*-alkanes, chlorinated solvents, and toluene. In contrast, a much lower solubility was observed in highly polar and/or protic solvents including acetonitrile, ethanol, methanol, and 1,4-dioxane. The latter solvent was chosen to develop a catalytic thermomorphic catalytic system. An exceptionally large temperature-dependent solubility in 1,4-dioxane was observed for **1**, its solubility increasing ca. $\sim 10^4$-fold between 23 and 50 °C.[10] For comparison, the strongly thermomorphic fluorous phosphine $P((CH_2)_2(CF_2)_7CF_3)_3$ exhibits a 600-fold solubility increase in *n*-octane between a much larger temperature range, ca. −20 to 80 °C.[9] Even more important, the very low concentration level measured for **1** in 1,4-dioxane at 10 °C ($<5 \times 10^{-5}$ M) should allow the efficient recycling of the catalyst at this temperature.[11]

The complex CuBr/**1** was prepared by heating (60 °C) equimolar quantities of CuBr and **1** in degassed 1,4-dioxane for 6 h. After cooling to room temperature, the complex was easily isolated as a fine, faint-greenish powder in 95% yield by filtration on a scintered glass frit under ambient conditions.[12] While the copper(I)−polyamine complexes are known to be very sensitive to molecular oxygen, the CuBr/**1** complex was conveniently handled in air without significant decomposition. For long periods (several days) storage under inert atmosphere would be preferable.

The ATRP of methyl methacrylate (MMA) was carried out in 1,4-dioxane at 70 °C using ethyl 2-bromoisobutyrate as initiator and CuBr/**1** as the catalyst (see Supporting Information). At this temperature the preformed molecular CuBr/**1** complex dissolved in a few seconds, allowing precise control of the amount of catalyst present in solution at the early stage of the reaction to ensure an efficient initiation step.

The polymerization proceeded efficiently at 70 °C (86% conversion in 7 h) with first-order kinetics with respect to monomer concentration (Figure 1). Good control of both polymer polydispersities ($M_w/M_n \approx 1.3$) and molar masses of the polymers was obtained (Figure 2). Cooling down the solution to 10 °C after

---

[†] Laboratoire de Chimie Organique et Organométallique.
[‡] Laboratoire de Chimie des Polymères Organiques.
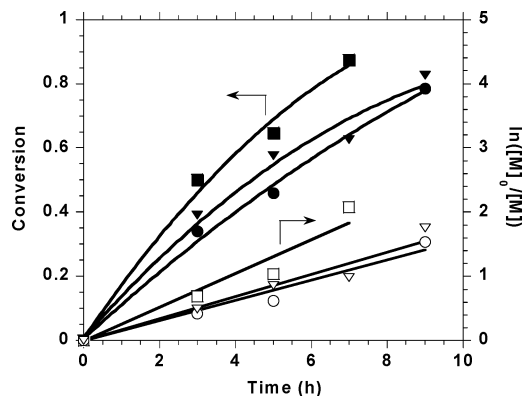
Figure 1. ATRP of MMA at 70 °C in 1,4-dioxane (3 mL) with fresh and recycled catalysts. CuBr/**1** = initiator = 5×10^{-2} mmol, MMA = 5 mmol. Fresh catalyst (■,□), first recycled catalyst (●,○), second recycled catalyst (▼,▽).
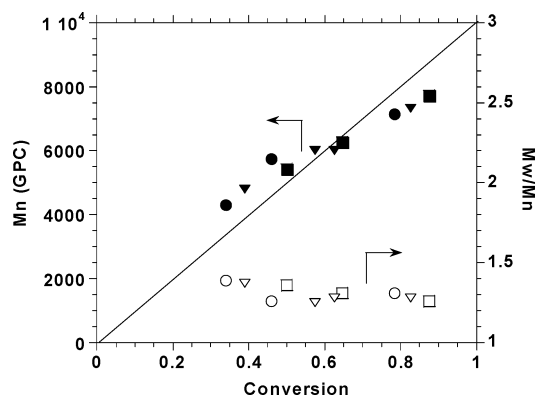
Figure 2. Evolution of molar masses and polydispersities of PMMA as a function of conversion in MMA polymerization with fresh and recycled catalysts. Fresh catalyst (■,□), first recycled catalyst (●,○), second recycled catalyst (▼,▽), theoretical M_n (—).

polymerization provoked the precipitation of the catalyst while the polymer remained soluble in 1,4-dioxane. The catalyst was then simply recovered by filtration followed by two successive washings with cold dioxane (~95% yield). After evaporation of the volatiles, PMMA was obtained from the filtrate as a yellowish, glassy solid. Inductive coupled plasma (ICP) analysis revealed a low amount of residual copper in the polymers ca. ~200 ppm (polymerizations with 70–90% conversions) as opposed to ~8000 ppm expected if all the catalyst remained in the polymer. Notice that the value of 200 ppm is very close to the theoretical value of 210 ppm expected at 90% MMA conversion and a complex recovery of 97%. Interestingly, we found that a simple treatment of the polymer on activated carbon in 1,4-dioxane led to a colorless PMMA with a copper content <50 ppm.

The recovered complex was then reused under the same conditions for a second and a third run for ATRP of MMA. As shown in Figure 1 the first and second recycled catalysts displayed almost the same catalytic activity, approximately 80% of the activity of the fresh catalyst, a decrease in activity that can be ascribed to the presence of a low amount of copper(II) in the first recycled catalyst.[6,13] The polymerization kinetics with recycled catalysts were still first-order with respect to the monomer producing polymers of low polydispersity ($M_w/M_n \approx 1.3$) and molar masses close to the theoretical values (Figure 2). These results clearly demonstrated

that the molecular CuBr/**1** catalyst is efficiently recycled using a straightforward filtration in air, in contrast to the rather tedious recycling procedures described to date that often required catalyst separation by centrifugation,[5a,c,f,6] strictly anaerobic conditions and washing with degassed solvents,[5a−c,f,6,8] or catalyst regeneration using reducing agents.[5a,e]

Finally, a block copolymer consisting of MMA units as the first block and benzyl methacrylate (BzMA) as the second block was successfully prepared by chain-extending a PMMA precursor. A block copolymer of P(MMA-*b*-BzMA) was isolated with $M_n = 26000$ ($M_{n\,theor} = 24600$) and PDi = 1.45 (see Supporting Information). This further demonstrates the living character of the CuBr/**1** catalytic system.

In conclusion, the low cost, the easiness of preparation and handling, the efficiency of both polymerization and complex recovery by simple filtration in air, and the very low content of transition metal in the final polymer make the molecular CuBr/**1** complex closer to the "ideal recoverable catalyst" for living radical polymerization of MMA. Additionally, these results show that for catalytic reactions performed in highly polar solvents, introduction of very long alkyl chains ($C_{18}H_{37}$) on the catalyst might be considered as a valuable strategy to achieve its recovery by simple liquid-/solid-phase separation.

Supporting Information Available: Detailed preparation for **1** and procedures for the polymerizations, recycling, and block copolymerization experiments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For reviews on catalyst recycling see the *Chem. Rev.* issue entitled Recoverable Catalysts and Reagents. Gladysz, J. A., Guest Ed. *Chem. Rev.* **2002**, *102*, 3215−3892.
(2) For an essay on the "ideal recoverable catalyst", see: Gladysz, J. A. *Pure Appl. Chem.* **2001**, *73*, 1319−1324.
(3) For recent reviews, see: (a) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990. (b) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3746.
(4) (a) Haddleton, D. M.; Kukulj, D.; Radigue, A. P. *Chem. Commun.* **1999**, 99−100. (b) Kickelbick, G.; Paik, H.-J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2941−2947. (c) Haddleton, D. M.; Duncalf, D. J.; Kukulj, D.; Radigue, A. P. *Macromolecules* **1999**, *32*, 4769−4775.
(5) (a) Nguyen, J. V.; Jones, C. W. *Macromolecules* **2004**, *37*, 1190−1203. (b) Shen, Y.; Zhu, S.; Zeng, F.; Pelton, R. H. *Macromolecules* **2000**, *33*, 5427−5431. (c) Shen, Y.; Zhu, S.; Pelton, R. *Macromolecules* **2001**, *34*, 5812−5818. (d) Hong, S. C.; Paik, H.-J.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 5099−5102. (e) Hong, S. C.; Matyjaszewski, K. *Macromolecules* **2002**, 35, 7592−7605. (f) Yang, J.; Ding, S.; Radosz, M.; Shen, Y. *Macromolecules* **2004**, *37*, 1728−1734.
(6) Shen, Y.; Zhu, S.; Pelton, R. *Macromolecules* **2001**, *34*, 3182−3185.
(7) De Campo, F.; Lastécouères, D.; Vincent, J.-M.; Verlhac, J.-B. *J. Org. Chem.* **1999**, *64*, 4969−4971.
(8) Haddleton, D. M.; Jakson, S. G.; Bon, S. A. F. *J. Am. Chem. Soc.* **2000**, *122*, 1542−1543.
(9) (a) Wende, M.; Meier, R.; Gladysz, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 11490−11491. (b) Wende, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 5861−5872.
(10) The temperature-dependent solubility was estimated by the recrystallization method. A 10^{-4} M solution of **1** in 1,4-dioxane was heated at 50 °C, and the solution was allowed to cool. Recrystallization of **1** was reproducibly observed when the temperature reached 23 °C. On the other hand, a 1 M solution of **1** in 1,4-dioxane was obtained when the temperature reached 50 °C.
(11) Recrystallization of **1** from a 5×10^{-5} M solution in 1,4-dioxane was observed in less than 24 h at 10 °C.
(12) Anal. Calcd for $C_{114}H_{234}N_4BrCu \cdot C_4H_8O_2$: C, 74.9; H, 12.8; N, 3.0; Cu, 3.4. Found: C, 74.0; H, 12.7; N, 2.9; Cu, 3.4.
(13) Shen, Y.; Zhu, S.; Zeng, F.; Pelton, R. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1051−1059.

JA048096A