Communications to the Editor

Facile and Effective Purification of Polymers Produced by Atom Transfer Radical Polymerization via Simple Catalyst Precipitation and Microfiltration

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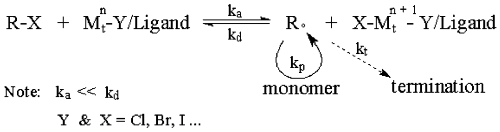
Atom transfer radical polymerization (ATRP) is one of the many recently discovered mechanisms capable of producing living and well-controlled polymers.[1,2] Its tolerance of impurities, mild reaction conditions, and catalytic nature make the process desirable for industrial production of polymers. ATRP mediates the growth of the polymer chain using a catalyst, unlike other living free radical polymerization methods. This catalyst activates and deactivates the growing polymer chains, as shown in Scheme 1.[1,2] Unfortunately, ATRP catalyst activities are low, requiring large amounts be used to drive the polymerization at acceptable rates. The cost of the catalyst and the need to remove it from the polymer product have, however, limited ATRP's use primarily to the laboratory.

Several catalyst−polymer separation and recovery strategies have been applied to overcome the low catalytic activities in ATRP and reduce catalyst residue in the polymer product. Soluble/recoverable, biphasic, and solid supported catalysts have been designed to achieve these ends.[3−16] They have generally been successful for catalyst recovery and recycling, but further reductions of residual catalyst concentrations in polymer are sought.

Physically adsorbed catalysts on silica supports are found to be recyclable and are effective at reducing the residual metal concentration in polymer.[3,4] Jones reports residual copper concentrations in polymer solution of 37 ppm when using catalyst adsorbed to Cab-O-Sil.[3] On the basis of the provided conversion data, catalyst-to-monomer ratios, and monomer concentration, we calculate an equivalent copper concentration in polymer of 250 ppm. For a similar system developed by Zhu consisting of CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine physically adsorbed to silica gel, we measure 110 ppm of copper in the polymerization solution, which equates to 360 ppm of copper in polymer.[4] An improvement to simple physical adsorption of the catalyst is reversible self-assembly on catalyst sponges as developed by Shen.[5] Using this method, residual copper concentration in polymer is reported to be as low as 0.38% of the total copper used in the first polymerization. This translates to 39 ppm of copper in polymer.

Scheme 1. Atom Transfer Radical Polymerization Mechanism



Comparable results are achieved with catalysts chemically grafted to the underlying support.[3,6−10] Haddleton reports 1000 ppm of residual ruthenium in polymer using 3-aminopropyl silica complexed with $RuCl_2(PPh_3)_3$.[6] Matyjaszewski uses catalyst tethered to commercial Merrifield resins to yield polymer containing residual copper concentrations of 3% of the initial amount of copper loaded.[7] This equates to 120 ppm of copper in polymer. Matyjaszewski also uses a dual immobilized/soluble hybrid catalyst system to reduce these concentrations to 15 ppm of copper in polymer.[8] Brittain utilizes JandaJel-supported catalysts and reports residual copper concentrations in polymer to be 5−7% of the original copper loaded for the polymerization.[9] The equivalent concentrations are 331−463 ppm of copper in polymer per our calculations. Dubois achieves residual nickel concentrations of 34 ppm in polymer following precipitation of the polymerization solution in heptane.[10] More recently, Jones used catalyst chemically tethered to Cab-O-Sil to produce polymer solutions containing less than 1 ppm of copper.[3] This equates to copper concentrations in polymer of less than 3 ppm as calculated from the given data.

Biphasic systems are also successful at reducing residual copper concentrations in polymer.[11,12] Haddleton uses a fluorous biphasic catalyst and reports a residual copper concentration in polymer of 880 ppm.[11] Vincent et al. studied a nonfluorous biphasic catalyst and report a residual copper concentration in polymer of 200 ppm.[12] Further reductions to less than 50 ppm are attainable if the product is further treated with activated carbon in 1,4-dioxane.

Soluble and recoverable catalysts yield similar results.[13−15] Zhu uses poly(ethylene-*b*-ethylene glycol) supported catalyst and reports polymerization solutions containing as little as 0.51% of the original copper loaded. This translates to 33 ppm of copper in polymer. Refrigeration of the polymerized solution to 0 °C prior to catalyst product separation is necessary to achieve these lower values.[13] Brooks uses catalyst supported onto polyglycidol and reports copper concentration in polymer of 100 ppm following precipitation and filtration of 10 g of polymeric solution in 1 L of methanol.[14] Weberskirch uses a bipyridine-functionalized block copolymer support and reports residual copper concentrations as low as 100 ppm in polymer following precipitation and two washing steps in ice cold methanol.[15] Brittain uses a precipiton tethered catalyst and reports residual copper concentrations in polymer of less than 1% of the copper used.[16] This equates to less than 70 ppm of copper in polymer per our calculations.

Recently, we studied the solubility and kinetics of heterogeneous ATRPs using the catalyst complexes of Cu^IBr and $Cu^{II}Br_2$ with *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA (**1**)), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA (**2**)), and *N*,*N*,*N*′,*N*″,*N*‴,*N*⁗,*N*⁗′,*N*⁗′-octamethylpentaethylene−hexamine (OMPEHA (**3**)).[17] The complexes of $Cu^{II}Br_2$ with PMDETA and HMTETA at metal salt to ligand

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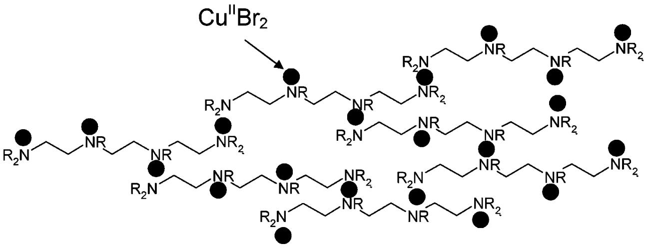
Scheme 2. Ligand−Metal Salt Network Complex



molar ratios of 4 are found to have no detectable solubility in toluene as measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES).[17] While the reason for this insolubility remains unclear, we believe it results from the formation of a network-like complex between the metal center and the multidentate amine ligand, as shown in Scheme 2. On the basis of the results of the solubility study, the structure of this network is expected to be of the form $[(Cu^{II}Br_2)_{3\text{ or }4}(L)]_n$. A similar mechanism has been proposed to explain the solubility behavior of copper(II) in the presence of plant polyphenols.[18] We hypothesized that the formation of this insoluble network could be used to generate a new method for catalyst−polymer purification post-ATRP. We hoped that the addition of excess $Cu^{II}Br_2$ at the end of the polymerization would precipitate out the soluble catalyst and allow the product to be siphoned off catalyst free.

ATRPs of methyl methacrylate (MMA) (33 wt %) in toluene at 90 °C were completed using the three ligands. The catalyst complexes consisted of $Cu^{I}Br$ coordinated with PMDETA, HMTETA, or OMPEHA in a one-to-one molar ratio. Methyl α-bromophenylacetate (MBP) was used as the initiator. Molar ratios were fixed to MMA/MBP/$Cu^{I}Br$/ligand = 100/1/1/1. Following 315 min of polymerization time a small sample of the polymerizing solution was hot filtered (90 °C) through a 0.1 μm PTFE membrane. The solvent and residual monomer, in this control sample, were evaporated under vacuum, leaving a green polymer (see Figure 1). This polymer was then digested for subsequent copper analysis using ICP-AES.

Following the removal of the control sample, $Cu^{II}Br_2$ (3 equiv to the original $Cu^{I}Br$ loaded) was added to the polymerizing solution under a nitrogen atmosphere. The reaction flask was then left to stir at 90 °C for 3 h under a nitrogen atmosphere. Over this period the originally green translucent polymeric solution turned dark brown and opaque for all three catalyst types. Unfortunately, the precipitate formed did not settle freely even when centrifuged. The formation of the precipitate increased the viscosity of the polymer solution. This high viscosity explains the lack of settling.

To overcome this challenge, microfiltration of the product was attempted. Following the 3 h complexing period, a sample of the polymer solution was withdrawn under a nitrogen atmosphere and passed through 0.1 μm syringe filter. This filtered sample was colorless compared to the green control sample previously collected. Thus, the copper−ligand precipitate appeared to be effectively retained by the filter while the polymer passed through it freely. The collected filtrates (post- and pre-$Cu^{II}Br_2$ addition) following drying overnight in a vacuum oven are shown in Figure 1. The clear polymer was digested and subsequently assayed for copper using ICP-AES.

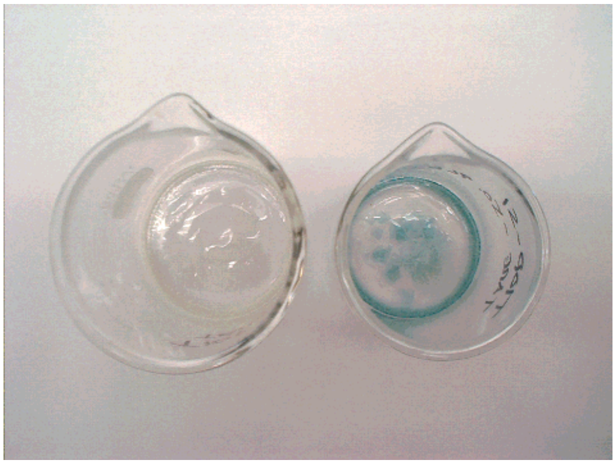


Figure 1. Poly(methyl methacrylate) produced by microfiltration and drying of a treated (left) and untreated (right) ATRP polymer solution. Polymerization conditions: toluene/MMA = 2 (w/w), [MMA]/[initiator]/[$Cu^{I}Br$]/[ligand] = 100:1:1:1 (molar), 90 °C, stirred. Treatment conditions: to the polymerized solution add $Cu^{II}Br_2$, 3 equiv to the initial $Cu^{I}Br$ loaded for the ATRP, and stir at 90 °C.

The copper assay results are presented in Table 1 along with details of the polymer produced in the ATRPs. The copper assays corroborate the visual observations. Microfiltration on its own only removes, on average, 95.7% of the heterogeneous catalyst as part of it, the active catalyst, remains soluble.[17,19] Average concentrations of residual copper in polymer were measured to be 310 ppm post-filtration. Following the addition of $Cu^{II}Br_2$, however, average residual copper concentrations in the filtered polymer drop to 30 ppm, representing an average removal of 99.6% of the catalyst loaded. In the case of the HMTETA-based catalyst, the addition of $Cu^{II}Br_2$ results in 99.9% of the catalyst being removed. Residual copper concentrations in polymer following filtration drop from 470 to 10 ppm when the precipitating agent ($Cu^{II}Br_2$) is used.

The precipitation and microfiltration method reported here provides a practical means of purifying polymers produced by ATRP. The residual copper concentrations in polymer it produces are lower than most other methods thus far developed.[3−16] Little catalyst synthesis and preparation work is necessary to yield polymer with very low residual copper concentrations as compared to chemically grafted catalysts.[3,6−16] While catalyst adsorption onto silica gel also offers a simple

Table 1. Residual Copper Concentrations Pre- and Post-Treatment with $Cu^{II}Br_2$ in Filtered Poly(methyl methacrylate) Synthesized by Atom Transfer Radical Polymerization Using Various Catalysts

	copper in poly(methyl methacrylate) (ppm)						
		filtered[c]		monomer conversion (%)[d]		polymer characteristics[d,f]	
catalyst used[a]	theor[b]	pre-$Cu^{II}Br_2$[d]	post-$Cu^{II}Br_2$[e]	pre-$Cu^{II}Br_2$[d]	post-$Cu^{II}Br_2$[e]	M_N (g/mol)	M_W/M_N
$Cu^{I}Br$/PMDETA	7650	240	30	83	83	15 400	1.29
$Cu^{I}Br$/HMTETA	6900	470	10	92	92	14 600	1.25
$Cu^{I}Br$/OMPEHA	6830	210	50	93	95	15 800	1.34

[a] PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine; HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine; OMPEHA = *N*,*N*,*N*′,*N*″,*N*‴,*N*′′′′,*N*′′′′′,*N*′′′′′-octamethylpentaethylene−hexamine. [b] Theoretical calculated as follows: (copper(I) added for catalysis/(monomer weight × conversion reached)) × 1 × 10^6. [c] Measured by ICP-AES, filtered using a 0.1 μm PTFE filter. [d] Following 315 min of polymerization time. [e] 180 min after the addition of $Cu^{II}Br_2$ at 315 min. [f] M_N = number-average molecular weight, and M_W = weight-average molecular weight, measured by gel permeation chromatography.

route to purifying the polymer, the residual catalyst concentrations in polymer are higher to those reported here by an order of magnitude.[3,4] The precipitation process uses reagents and procedures that can be easily procured and applied in common laboratories or industrially. Furthermore, the ligands used to form the ATRP catalyst (PMDETA and HMTETA) and to which the method applies are inexpensive, widely used, provide good control of polymer architecture, and form highly active catalysts.[20,21] Finally, the method described provides an opportunity to recover the catalyst in the filter cake and recycle it following its reduction back to its active $\mathrm{Cu^I}$ form—an option presently being investigated along with optimization of the process and polishing using precipitation with nonsolvents.

In conclusion, we have discovered a simple and highly effective method of purifying polymers produced by ATRP using catalyst precipitation and microfiltration. The method relies on the precipitation of the $\mathrm{Cu^IBr}$/ligand catalyst complex using the addition of $\mathrm{Cu^{II}Br_2}$. The precipitate thus formed is effectively retained by a 0.1 μm PTFE filter, resulting in up to 99.9% of the catalyst being removed from the polymer. The resulting clear polymer filtrate contains little residual copper, down to 10 ppm. Optimization of this purification process is ongoing; its simplicity makes it very appealing to laboratory and industrial application.

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Supporting Information Available: Ligand structures, polymerization, microfiltration, and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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