Removal of the Copper Catalyst from Atom Transfer Radical Polymerization Mixtures by Chemical Reduction with Zinc Powder

FATMA CANTURK, BUNYAMIN KARAGOZ, NIYAZI BICAK

Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 34469, Turkey

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ABSTRACT: Simple mixing of an atom transfer radical polymerization (ATRP) mixture with zinc powder was demonstrated to result in rapid decolorizing of the solution and precipitation of elemental copper, using small amounts of silica gel as seeding material. The experiments revealed that the chemical reduction of copper by wetted zinc powder (i.e., 0.325 g/mmol copper) is fast and completed within less than 5 min. UV spectra of the filtered polymer solution showed no any trace of copper. Terminal bromoalkyl groups of the polymers in the ATRP solution were determined to be unchanged by short-term contact with zinc powder at room temperature and a nearly complete reductive dehalogenation takes place only after 24 h of interaction, as evidenced by reaction of elemental zinc with a model compound, ethyl bromoacetate. Indeed, poly(methyl methacrylate) (PMMA) sample (M_n : 7900, polydispersity index: 1.09) isolated from ATRP mixture after the copper removal a by short contact with zinc powder (i.e., 15 min) was determined "still living" as confirmed by chain extension with styrene, ethyl acrylate, and *t*-butyl acrylate monomers to give block copolymers. The presence of acetic acid was demonstrated to accelerate reductive dehalogenation of PMMA end-groups by zinc and yields nonliving polymer within 2 h. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3536–3542, 2011

KEYWORDS: atom transfer radical polymerization (ATRP); block copolymer; chemical reduction; copper catalyst; copper removal; separation of polymers

INTRODUCTION Copper mediated atom transfer radical polymerization (ATRP) has been widely used for creating numerous polymer architectures such as block, multiblock, star-block, and graft copolymers with well-defined structures, from styrenic and acrylic monomers.¹ Comparing with other controlled/living polymerization techniques such as reversible addition fragmentation chain transfer (RAFT) and nitroxy mediated polymerization (NMP) operating with chain transfer mechanism, ATRP is much more efficient in grafting from solid surfaces and provides better chain growth control.² Despite its great versatility, ATRP has not found extensive use in mass production of polymers. This is largely due to greenish color of the polymer products arising from the copper complex contaminants.

Removal of the copper from laboratory-scale samples can be achieved by flash chromatography using alumina or silica gel columns.³ However, this is not practical for industrial processes. Considerable efforts aiming at preparing copper-free polymers by ATRP have been proceeded in two directions:⁴ (i) design of solid supported or special ligands forming easily isolable copper complexes and (ii) removal of the copper complexes from ordinary ATRP mixtures by chemical or physical means.

The use of solid supported copper catalyst has been considered as convenient way because of easy recovery of the catalyst by filtration. Copper complexes of physically adsorbed ligands on silica supports were determined to be effective and able to reduce the copper concentrations down to 35– 40 ppm levels. However, molecular weight distributions of the polymers were broad, owing to heterogeneity of the process.⁵ Haddleton's group reported a Schiff base ligand covalently linked to silica support⁶ yielding copper-free polymers with relatively high polydispersities [polydispersity index (PDI): 1.4–1.6]. Shen et al. introduced amine ligands covalently attached to silica gel support through oligoethyleneoxide spacer chains.⁷ Moderate chain length of the spacer group was demonstrated to provide better control of the molecular weights and low polydispersities as low as 1.2.

Shen's group also reported an ATRP catalyst supported on magnetic nanoparticles (20–30 nm) easily recoverable by a magnetic bar from the reaction medium.⁸ Although narrow molecular weight distributions (PDI < 1.2) were attained, significant activity loss of the recycled catalyst was the main drawback. Honigfort and Brittain described copper complex of an amine functionalized Janda-gel resin as recoverable catalyst.⁹ However, the polydispersities were relatively high (PDI: 1.40–1.85).

Synthesis of new special ligands forming isolable and soluble complexes has been alternative pathway to attain homogeneity and better control of the chain growth in ATRP. In the following studies, Honigfort et al. reported amine ligands bearing stilbene

Correspondence to: N. Bicak (E-mail: bicak@itu.edu.tr)

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units.¹⁰ Copper complexes of those ligands become soluble or insoluble according to the *cis-trans* isomerization of the stilbene moieties upon irradiation with UV lamp for 2 h. An intersting ligand, perluoro alkylated diethylenetriamine ($-C_8F_{17}$) has been exploited together with a fluorous solvent immisciple with toluene at room temperature. Copper complex of the ligand in the mixed solvent provides nearly homogeneous ATRP at 90 °C. A phase separation occurs upon cooling, the copper complex being retained in the fluorous phase.¹¹

Postpurification of ATRP mixtures by chemical or physical sorption of the copper catalyst is another pathway to copper-free polymers. Commercial ion exchange resin in acid or Na⁺ forms has been demonstrated to be useful in the copper removal, but the process is rather slow and greatly affects from solvent polarity.¹² Hydrated clay has also been used to remove copper catalyst by physical sorption.¹³ Ding et al. reported a reversibly immobilized catalyst system, in which a thymine anchored silica reversibly binds the ligand via hydrogen bonding with amido groups of the multiamine functional ligand.¹⁴ Direct electro-deposition of the copper catalyst from ATRP mixtures using tetrabutylammonium hydroxide as supporting electrolyte has been used for preparing colorless polymers.¹⁵

Despite those significant contributions, there is yet no practical solution for the copper removal from ATRP mixtures.

Herein, we describe a simple and quick method of the copper removal from ATRP mixtures, based on chemical reduction of the copper by zinc powder. The standard redox potential of Cu/Zn couple is,

$$Cu^0 - Zn^0 = 0.337 V - (-0.763 V) = 1.1 Volt$$

The spontaneous electron transfer from zinc metal to Cu (II) in aqueous medium furnishes well-known "Daniel Battery," which has been widely studied in electrochemistry.

Commercial zinc powder contains oxide film on its surface. Activation of the zinc powder by removal of the oxide layer is especially crucial in organometallic reactions.

In this work, commercial zinc powder was activated by concentrated NaOH solution before use in the copper removal. The chemical reduction of the copper complex was followed by disappearance of the color of ATRP mixtures containing some common ligands and effects of contact time, and the ingredients were studied.

EXPERIMENTAL

Materials

Methyl methacrylate (Aldrich), styrene (E. Merck), ethyl bromoacetate (Fluka), and toluene (E. Merck) were redistilled before use. Cuprous bromide was freshly prepared by the method given in the literature.¹⁶ The ligand, hexacis-1,1,4,7,10,10-hexyl-1,4,7,10-tetraaza decane, forming entirely soluble copper complexes was prepared by action of 1-bromo hexane on triethylene tetramine (TETA) as reported before.¹⁷ Zinc powder (J.T. Baker), silica gel (E. Merck), pentamethylated diethylene triamine (PMDETA, Merck), 2,2'-Bipyridine (J.T. Baker), and all the other chemicals were used as purchased.

Activation of Zinc Powder

Commercial zinc powder (2 g) was treated with 10 mL NaOH solution (30%) for 5 min to dissolve the oxide layer at the particle surfaces, and the aqueous phase was decanted. This process was repeated twice, and the residue was washed several times with distilled water (5×30 mL). The activated zinc powder was obtained after successive washings with methanol (2×10 mL), and diethyl ether (2×10 mL). The resulting active powder was stored in a tightly closed bottle, without further drying. Vapor of the residual ether provides protective atmosphere against air oxygen. This is useful to avoid rapid oxidation of the activated zinc powder, while handling.

For safety reasons, however, storage of large amounts of activated powder is not advisable owing to its potential flammability, especially when contacting with paper.

Preparation of ATRP Stock Solution of PMMA

Methylmethacrylate (MMA) (40 mL, 0.4 mol) was polymerized by ATRP method in toluene (60 mL), using ethyl bromoacetate (1.34 g, 8 mmol) as initiator, CuBr (1.148 g, 8 mmol) and one of the ligands selected from PMDETA, 2,2'-Bipyridine, and HTETA. The initial composition of the polymerization mixtures was chosen as [MMA]/[R-Br]/[CuBr]/[Ligand]: 25/1/1/1 molar ratio, and the polymerizations were conducted for 3 h at 70 °C. The resulting viscous solution was cooled and stored as stock solution for the copper removal experiments.

The Copper Removal Experiments

A sample of ATRP solution (10.0 mL) containing 0.8 mmol copper complex was thoroughly mixed with 0.26 g of activated zinc powder, 0.2 g of silica gel, and 0.1 g of water, without dilution. The mixture was stirred until disappearance of the color of ATRP solution and filtered. The colorless polymer in filtrate was isolated by precipitation in methanol-acetic acid mixture (95/5, v/v).

Test for the Reductive Dehalogenation of Ethyl Bromoacetate by Zinc Powder

To inspect reductive dehalogenating effect of wetted zinc powder on polymers in the ATRP mixtures, a model compound, ethyl bromoacetate (EBA) was reacted with toluene in the absence of the copper complex. For this purpose, activated zinc powder (3 g), water (0.9 g, 0.05 mol), toluene (20 mL), and ethyl bromoacetate (5.6 g, 0.04 mol) were mixed in a canonical flask and stirred at room temperature for 24 h. Progress of the reductive dehalogenation was simply monitored by ¹H-NMR spectra of the aliquots taken at various time intervals (15, 30, 60, 100 min, and 24 h) from the mixtures. Debromination of EBA was assayed by decreasing integral of the singlet of $-CH_2Br$ group at 3.4 ppm.

Chain Extension Test by ATRP for the Presence of Terminal Bromines in PMMA

To investigate dehalogenating effect of zinc powder on the polymers, an ATRP solution of PMMA was prepared by

similar procedure described above, using initial composition with [MMA]/[Ethyl-2-bromoisobutyrate]/[CuBr]/[PMDETA]: 50/1/1/1 molar ratio. The reaction was conducted in toluene (1/1) for 1 h. Forty milliliters of this solution was freed from copper by immediate zinc powder treatment as described above. Gel permeation chromatogram (GPC) traces of the isolated polymer by precipitation in 150 mL methanol-acetic acid mixture (9/1) revealed a molecular weight of M_n : 7.900 (PDI: 1.09).

To inspect the presence of bromine end groups in the polymer, it was subjected to chain extension with styrene, ethyl acrylate, and *t*-butyl acrylate by ATRP method. In these reactions, the molar composition, [monomer]/[R-Br]/[CuBr]/ [PMDETA]: 300/1/1/1, was kept constant. A typical procedure is as follows: PMMA sample (0.5 g) was dissolved in a mixture of 4.4 mL toluene–styrene (1/1) under nitrogen atmosphere. PMDETA (11 mg, 6.3×10^{-5} mol) and CuBr (9 mg, 6.3×10^{-5} mol)

The reaction was conducted at 90 °C for 24 h, and the product was isolated as described above. This procedure was repeated for the chain extensions with ethyl acrylate and *t*-butyl acrylate monomers, except the polymerization temperature was 80 °C. The polymers isolated similarly after copper removal by treating with zinc powder. The GPC traces of the resulting polymers obtained by chain extension with styrene, ethyl acrylate, and *t*-butyl acrylate revealed number average molecular weights of M_n : 35.900 (PDI: 1.07), 47.800 (PDI: 1.15), and 21.400 (PDI: 1.03), respectively.

The remaining portion of the ATRP mixture (~10 mL) was stirred with 0.52 g (10 mmol), 0.1 g H₂O, and 0.2 g silica gel for 24 h. The resulting polymer was isolated in conventional manner. A sample of this product (0.5 g) was subjected to chain extension with styrene using exactly the same procedure given above, to inspect the presence of reactivable bromine terminal groups. However, no mass increase was observed in this case. Its GPC trace did not show significant increase in the molecular weight (M_n : 8100) in comparison with that of the prepolymer (M_n : 7900).

Accelerated Dehalogenation of PMMA Chain-Ends by Zinc and Acetic Acid

To obtain dehalogenated polymer, the copper removal experiment described above was repeated in the same conditions, except acetic acid was used instead of water. For this purpose, 0.4 g (~ 6 mmol) zinc powder, 0.2 g silica gel, and 1 mL acetic acid were added to 5 mL of colored ATRP solution of PMMA and stirred for 2 h at room temperature. The green color the ATRP mixture disappeared in 2-3 min and gray zinc particles turned to white within 10 min, because of oxidation of elemental zinc. After stirring for additional 1 h, the polymer sample (M_n : 7.900, PDI: 1.09) in the mixture was subjected to chain extension with ATRP of styrene (8h) and isolated by precipitation in methanol-acetic acid mixture (95/5, v/v) and dried overnight at 40 °C under vacuum). ¹H-NMR spectrum of the polymer did not show the presence of the polystyrene block, indicating a complete dehalogenation of the prepolymer, PMMA by zinc and acetic acid.

$$CuBr_2 \cdot L + Zn(0) \longrightarrow Cu(0) + ZnBr_2 \cdot L$$

SCHEME 1 Chemical reduction of the copper complex by zero-valent zinc.

Characterization and Analysis of the Polymer Solutions

¹H-NMR spectra of the polymers were recorded by a Bruker 250 MHz NMR spectrometer, using CDCl₃ as solvent.

GPCs were taken in tetrahydrofuran (THF) solutions with a flow rate of 0.3 mL/min using Agillant 1100 series instrument consisting of a pump, a refractive index-detector, and Waters Styrogel (HR4, HR3, and HR2) columns. Polystyrene was used as standard.

UV-visible spectra were obtained by a Chebios Optimum-One UV-visible spectrophotometer.

Atomic absorption spectrometer (AAS) was used for analyses of zinc and copper ions in the polymer solutions, using a High-resolution continuum source atomic absorption spectrometer (HR-CS AAS; ContrAA 700) comprising a flame and a graphite furnace in tandem.

RESULTS AND DISCUSSION

Chemical Reduction of the Copper Complex

Addition of small amounts of wetted zinc powder (0.325 g/ mmol copper) to ATRP solution and stirring for 5 min resulted in disappearance of the greenish color of the solution, indicating removal of the copper catalyst by chemical reduction.

Without trace water, however, the time for the disappearance of the color was about 1 h. Most probably, the role of water in this process is to facilitate the electron transfer in the organic medium. Stoichiometric equation of the chemical reduction of the copper (Scheme 1) suggests 1 mol of elemental zinc per 1 mol of copper complex in ATRP mixture.

However, the use of equimolar zinc powder did not result in colorless solution, and no copper precipitate was observed in the ATRP mixture of PMMA. Considering with the use of 3- to 5-fold excess of activated zinc in organic reactions, that is, Reformatsky reaction,¹⁶ only small portion of zinc (20–30%) is estimated to involve in the reactions. The rest part remains unreacted.

Taking this into account, nearly 4-fold excess of activated zinc (0.325 g/mmol of the copper complex) was used for the copper removal in this study. This procedure resulted in disappearance of the green color of the ATRP solution in less than 5 min. It is noteworthy that, when zinc powder-ATRP mixture was left to stand for 1 h without agitation, surfaces of the zinc powder turned to reddish-brown indicating accumulation of elemental copper, and the mixture was still colored. Further stirring did not give a colorless solution. This is evidence for the fact that, surfaces of the zinc powder are covered by zero-valent copper and not able to reduce the cupric ions any more. To avoid this problem, small amount of silica gel (0.2 g) was introduced together with zinc powder to create seeding centers for the precipitation



FIGURE 1 UV-visible spectrum of diluted (1/250) ATRP mixture of PMMA in toluene, before (a) and after (b) copper removal with zinc powder.

of elemental copper. This was helpful to reduce the copper complex in short times by moderate stirring.

UV-visible spectrum of the colorless filtrate (Fig. 1) does not show absorption bands of the original ATRP solution, located at 330 and 780 nm.

A weak band appeared at 315 nm might be attributed to residual copper complex. However, this band having a maximum at 315 nm was also observed in UV spectrum of toluene solution of ZnCl_2 -ligand mixture (10^{-4} M of each). Therefore, this band must be due to zinc complex formed. AAS of the filtrate revealed 4.1 ppm of zinc, but no detectible copper. Considering the detection limit of the AAS apparatus, final copper concentration of the solution must be lower than 0.25 ppm.

The polymer, PMMA isolated by precipitation in methanol with 5% acetic acid was colorless, and AAS of its toluene solution, however, did not show any detectible zinc or copper. Most probably, the zinc impurities in the previous solution have been retained in the methanol solution as acetate salt.

The Side Reaction

Simplicity of the wetted-zinc powder process is very attractive to obtain copper-free polymers in ATRP. However, a possible side reaction, dehalogenation of halo alkyl end-groups of ATRP growth-polymers can be considered as important limitation of this procedure. The reaction of activated zinc with alkyl halides is well documented in organic chemistry. In the presence of proton donors such as acids and water,¹⁸ the reaction results in replacement of halogen with hydrogen atom, and the process is termed as "reductive dehalogenation." The reaction of zinc with alkyl halides in neutral or basic conditions results in Wurtz-type of coupling to alkyl dimers alongside with the reductive dehalogenation.¹⁹ Such a side reaction of zinc metal with the haloalkyl end-groups of the polymers prepared by ATRP may destroy their bromoalkyl end groups as well.

Extent of possible reductive dehalogenation with zinc powder while removing the copper catalyst was investigated using ethyl bromoacetate (EBA) as model compound. This was carried out by action of 3 g of zinc powder on ethyl bromoacetate solution (5.6 g, 0.04 mol) in toluene (20 mL) in the absence of copper complex.

By adding trace amount water (0.9 g, 0.05 mol), the mixture was stirred for 24 h at room temperature. ¹H-NMR spectrum of the filtered solution [Fig. 2(b)] did not show typical singlet of $-CH_2$ —Br group at 3.9 ppm.



FIGURE 2 ¹H-NMR spectrum of ethyl bromoacetate-toluene mixtures before (a) and after (b) treatment with zinc powder.



SCHEME 2 Reductive dehalogenation of the model compound, EBA with zinc powder.

Instead, a new singlet emerged at 2.2 ppm revealed a quantitative reductive dehalogenation of the bromomethyl group (Scheme 2). Except those of toluene solvent, the three peaks in the ¹H-NMR spectrum of the resulting mixture [Fig. 3(b)] well match with those of simple ethyl acetate.

Rapid disappearance of the greenish color of the ATRP solution implies a fast copper reduction in comparison with the reductive dehalogenation. To compare the reaction rates, the model reaction was repeated also for 15, 30, 60, and 100 min. Time depended dehalogenation yields of EBA were simply estimated based on ¹H-NMR spectra, using the following relationship.

Percentage debromination yield =
$$\frac{\left(I_1^0/I_2^0\right) - \left(I_1/I_2\right)}{\left(I_1^0/I_2^0\right)} \times 100$$

where I_1 and I_2 represent integrals of the proton signals of $-CH_2$ -Br and $-OCH_2$ - groups, respectively. The superscript zero denotes initial values of the corresponding peak integrals. The results showed that debromination of EBA within 30 min is almost zero and stirring for longer than 1 h causes to significant rise in the debromination as shown in Table 1.

This result revealed possible loss of the bromine atom at the chain ends of ATRP-growth polymers and disposal of terminal bromoalkyl groups by long-term interaction with zinc powder.

Apparently, reduction of copper in ATRP solution by zinc powder is reasonably fast in comparison with the reductive debromination of the polymer end-groups.



FIGURE 3 GPC traces of PMMA isolated from ATRP solution after removal of the copper by zinc powder treatment for 15 min and the polymers obtained by chain extension of this polymer with styrene, ethyl acrylate, and *t*-butyl acrylate using ATRP method.

To examine whether the bromo end groups of PMMA in the mixture were affected within short periods, 40 mL of ATRP solution was freed from copper by zinc powder treatment (for 15 min), and the polymer isolated from the colorless solution by precipitation in methanol-acetic acid mixture (9/1) was subjected to chain extension with styrene, ethyl acrylate, and *t*-butyl acrylate monomers by ATRP method (see "Experimental" section).

GPC traces of the resulting products (Fig. 3) showed significant mass increases in the molecular weights. Thus, number average molecular weights and polydispersity indexes of the chain extension products were M_n : 35.900 (PDI: 1.07), 47.800 (PDI: 1.15), and 21.400 (PDI: 1.03) for styrene, ethyl acrylate, and *t*-butyl acrylate, respectively. These results imply formation of the block copolymers, PMMA-*b*-PS, PMMA-*b*-PEA and PMMA-*b*-P(*t*-BA), and the presence of bromoalkyl end groups of the prepolymer used in the chain extension as well. The narrow molecular weight distributions and unimodal curves in their GPC traces can be ascribed to the absence of dead end in PMMA used in the chain extensions performed by ATRP.

¹H-NMR spectrum of the product obtained by chain extension with styrene (Fig. 4) exhibits aromatic proton signals of the polystyrene block in 7.2–7.4 ppm range in addition to the typical signals of PMMA block. The strong signal at 1.6 ppm is associated with CH_2 protons of this block. A weak singlet arising from OCH_3 of PMMA block appears at 3.58 ppm. Weakness of PMMA proton signals is due to low percentage of this block.

¹H-NMR spectrum of the block copolymer with PEA shows OCH₂ signals at 4.1 ppm. New peaks appearing at 2.27 and 1.62 ppm are associated with CH—CO and CH₂ protons of PEA, respectively. The ¹H-NMR spectrum of the block copolymer with *t*-BA exhibits characteristic methyl protons of *t*-butyl group of P(*t*-BA) component at 1.42 ppm as a sharp singlet.

TABLE 1 Reductive Debromination of EBA with Zinc Powder at

 Room Temperature

[Zn]/[EBA]	Reaction Time	Debromination ^a (%)
1.37	15 min	0
1.37	30 min	0
1.37	60 min	<1
1.37	100 min	~3.4
1.37	24 h	~100

^a Assigned by ¹H-NMR.



FIGURE 4 ¹H-NMR spectrum of the block copolymers, PMMA*b*-PS, PMMA-*b*-PEA, and PMMA-*b*-P(*t*-BA) obtained by chain extension of PMMA isolated from ATRP solution, freed from copper by zinc powder treatment for 15 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

All these results are clear evidences for the formation of block copolymers and retaining of bromoalkyl groups of the precursor polymer, PMMA isolated after short-term zinc treatment. By contrast, GPC trace of the polymer isolated from the ATRP mixture treated with zinc powder for 24 h did not show a significant increase in molecular mass $(M_n = 8.100)$.

¹H-NMR spectrum of this product did not show any aromatic signal, indicating the absence of polystyrene segments and debromination of the prepolymer PMMA by zinc powder in 24 h. In another words, stirring with zinc powder for 24 h results in almost quantitative removal of the bromine at the chain ends, and the resulting polymer is no longer living.

To investigate ligand effect on the copper reduction, ATRP solutions with PMDETA and bipyridyl ligands were treated with zinc powder similarly. The reaction was even faster than before, so that colors of the solutions fade within 1.5

and 3.3 min, for the cases of PMDETA and bipyridyl ligand, respectively (Table 2). Obviously the difference is due to greater hydrophilicity of those ligands comparing with that of HTETA. Although THF and acetone are not common solvents in ATRP, we have studied effects of these solvents on the copper removal with zinc powder.

Colors of the solutions diluted with equal volumes of THF and acetone disappeared within 10.2 and 13.1 min, respectively. Most probably these water-miscible solvents cause to partial precipitation of the polymer on the wet particle surfaces, thereby the copper reduction by zinc particles becomes slow (Table 2). Slightly shorter time (8.8 min) to fade the color of ATRP solution diluted with MMA must be due to its immiscibility with water.

Dehalogenation of the Polymer by Zinc Powder and Acetic Acid

Replacement of terminal halogen atoms of the polymers produced by ATRP might be of interest in some applications, as reported by Coessens and Matyjaszewski.²⁰

Taking this into account, the last part of the study was addressed to replacement of the haloalkyl end groups of PMMA in ATRP solution, while removing the copper. To accelerate the reductive dehalogenation, acetic acid was chosen as proton donor, because of its miscibility with organic solvents. Addition of 1 mL acetic acid to the zinc powder-ATRP mixture gave white precipitate of zinc acetate within 10-15 min. The stirring was continued for 2 h at room temperature. To prove the absence of the bromoalkyl groups at the chain ends, isolated PMMA (Mn: 7.900, PDI: 1.09) was subjected to chain extension by ARTP of styrene at 90 $^\circ$ C similarly (see "Experimental" section). ¹H-NMR spectrum of the resulting product did not show aromatic proton signals of poly(styrene), indicating a complete reduction of the terminal bromoalkyl groups of PMMA by zinc powder treatment in the presence of acetic acid. It was found that preactivation of zinc powder is not necessary for the dehalogenation, because the oxide layer on the particle surfaces is readily removed by action acetic acid.

Entry ^a	[Zn]/[Cu] (mol/mol)	Ligand	Solvent	Contact Time for Decolorization with Zn Powder (min)
1	5	HTETA	Toluene	3.5
2	5	PMDETA	Toluene	1.5
3	5	Bipyridyl	Toluene	3.3
4	5	HTETA	$Toluene + THF^b$	10.2
5	5	HTETA	${\sf Toluene} + {\sf acetone}^{\sf b}$	13.1
6	5	HTETA	$Toluene + MMA^b$	8.8

TABL	.E 2	2 Ligand	and	Solvent	Effects	on the	Chemi	ical R	eduction	of (Copper	by	Zinc	Powde	r in	ATRP	Solution

^a *Conditions*: A mixture of 7.5 mL ATRP solution with 0.133 M copper complex, 0.3 g activated zinc powder, 0.2 g silica gel, 0.1 g water was stirred until disappearance of the color.

^b The solutions were diluted by equal volume of the solvents.

CONCLUSIONS

The wetted zinc powder process presented offers an easy access to copper-free ATRP solutions within minutes, while retaining the bromoalkyl end-groups of the polymers. Also, the process can be used for dehalogenation of the polymers, using small amounts of acetic acid. Considering with 10^{-3} M average copper concentration of typical ATRP solutions, zinc powder to be used for the chemical reduction of copper in 1 L solution is around 3 g, together with 2 g of silica gel. Recovery of the copper in elemental form may be considered as beneficial for large-scale processing of ATRP mixtures.

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