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Recyclable polymerization catalysts: methyl methacrylate polymerization with silica-supported CuBr–bipyridine atom transfer radical polymerization catalysts

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Abstract

CuBr/Bipyridine (Bpy) atom transfer radical polymerization (ATRP) catalysts are physisorbed and covalently tethered to nonporous fumed silica and are characterized by elemental analysis, thermogravimetric analysis, and UV/vis spectroscopy. The supported catalysts are used for the polymerization of methyl methacrylate (MMA), promoting the polymerization to moderate conversions with good control, with molecular weights similar to theoretical values and low polydispersity indices (PDIs). The used, Cu(II)-containing catalysts are subjected to a regeneration process with AIBN as a reductant, producing increased concentrations of Cu(I) species on the surface for the tethered system. Leaching experiments indicate that the tethered systems result in no detectable soluble copper species and that the majority of the catalytic transformations occur with sites tethered to the surface. In contrast, use of the physisorbed catalyst results in a substantial amount of leached copper species, and the soluble species are capable of controlling the polymerization in the absence of the solid, although with extremely low polymerization rates.

Keywords: ATRP; Immobilized catalyst; Catalyst regeneration; Metal complex leaching; Copper complex; Tether

1. Introduction

Polymerization catalysts are perhaps the only class of catalysts that are not routinely recovered and recycled on a large scale. Because catalyst recovery and separation from the product polymer are difficult, most polymerization catalysts are single-use entities, and, in many cases, such as Ziegler–Natta catalysts for olefin polymerization, the catalyst is so highly active it can economically be left in the final polymer product [1]. Despite the widespread application of single-use heterogeneous catalysts for olefin polymerization, there are many unique polymers that can be made with less active transition-metal-based catalysts where catalyst disposal with the product is not cost effective. In other cases, there are reasons why removal of any catalyst residues from the final polymer product can be critically important—for example, in polymers for biomedical applications [2–4].

Recently we immobilized a Zn-β-diiminate (BDI) complex [5] that is active for lactide polymerization and epoxide/CO_2 copolymerizations on various silica supports [6,7]. We showed that these tethered complexes effectively produced the intended polymers and that the solid catalyst could be simply recovered from the liquid polymerization medium. However, the recovered catalysts were only moderately effective in recycle experiments, and significant amounts of polymer remained associated with the solid catalysts after use [8]. Washing with acidic methanol to quench the polymerization, thereby breaking the covalent bond between the metal center and the growing polymer chain, allowed for effective recovery of most of the polymer that was associated with the solid after use. However, this treatment also resulted in loss of Zn species from the solid catalyst [8], highlighting a difficulty with attempted recycling with metal complex cat-

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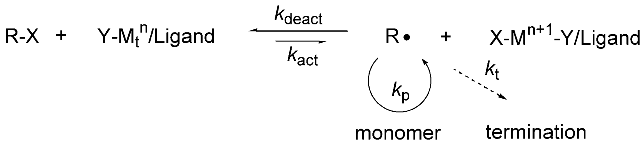
alysts that operate by a coordination-insertion mechanism. Indeed, with catalysts of this type, the final reaction quench, whereby the polymer chains are cleaved from the catalyst, can become quite problematic.

In contrast, effective recovery of polymerization catalysts that never contain a covalent bond between the catalyst and the growing polymer chains would be much easier, as no problematic quenching step would be necessary. Indeed, such a system exists in controlled radical polymerizations (CRPs) such as atom transfer radical polymerization (ATRP), where catalyst recovery is critical.

In the past decade, rapid growth in the development and understanding of new CRP methods has occurred. Currently there are three CRP systems that seem to be most successful; they include CRP mediated by nitroxides [9] (e.g., TEMPO), CRP mediated by degenerative transfer by dithioesters [10] and xanthates [11,12] (so-called RAFT and MADIX process, reversible addition fragmentation chain transfer, and macromolecular design via the interchange of xanthates, respectively) and by transition-metal complex-catalyzed atom transfer radical polymerization (ATRP) [13–15].[1] All of these methods are based on establishing a rapid, dynamic equilibration between a small amount of growing free radicals and a large majority of the dormant species.

ATRP was first discovered in 1995 independently by Matyjaszewski [13,14] and Sawamoto [15], who used Cu(I)X/bipyridines (X = Cl, Br) and $RuCl_2(PPH_3)_3$ as the transfer agents, respectively. In this type of polymerization, a monomeric or polymeric alkyl halide (R–X or P_n–X) transfers its halogen atom reversibly to a transition-metal complex (M_t^n–Y/ligand), forming an organic radical ($P_n^{\bullet}$) and a higher oxidation state transition-metal complex (X–M_t^{n+1}–Y/ligand), shown in Scheme 1. The equilibrium between the M_t^n–Y/ligand and X–M_t^{n+1}–Y/ligand species is strongly shifted toward M_t^n–Y/ligand complex ($k_{deact} \gg k_{act}$); therefore the radical concentration is kept low, allowing for the controlled addition of monomer with reduced termination (propagation is first-order in radical concentration; termination is second-order). Successful, controlled ATRP involves only a very small amount of chain termination coupled with uniform growth of all other polymer chains. This behavior allows for the controlled preparation of unique polymer architectures, such as block copolymers, graft copolymers, star (multi-arm) polymers, etc. [16].



Scheme 1.

A major challenge that could limit the potential commercial application of ATRP is the removal of the transition-metal complex from the final polymer product and recycling of the recovered catalyst [16,17]. In a typical ATRP recipe, the initiator-to-catalyst ratio is usually 1:1 (typically 0.1–1.0% w/w), which is one catalyst molecule mediating one polymer chain, although in some catalyst systems, catalyst concentrations can be as low as 10 mol% relative to initiator [18–20].[2] Even so, this accounts for a large amount of metal needed to mediate a controlled polymerization.

There are several approaches that have been evaluated for catalyst removal; such approaches include treatment with ion-exchange resin [21], use of fluorous biphasic systems [22], use of ionic liquids [23–25], and use of precipitins [26]. All of these methods require post-treatment of polymerization solution. Another method that provides a convenient way to recover the catalyst is catalyst immobilization. Immobilization of the catalysts on organic or inorganic support materials is the most attractive method for recovery because the catalyst can be recovered easily and potentially recycled.

There are several reports in the literature that describe methods for the immobilization of ATRP catalysts on various supports [17]. Three types of catalysts have generally been employed: (1) catalyst physically adsorbed (physisorbed) on silica [27–30], (2) catalyst covalently immobilized (tethered) on silica [31–42] and polymers [34,43–47], and (3) a dual immobilized catalyst/soluble deactivator system [32,48–52]. Catalysts of type 1 are easily prepared, but catalyst leaching often occurs because the catalyst complex is not firmly bonded to the support surface. Tethered catalysts of type 2 are generally harder to prepare but allow for facile catalyst recovery and recycle. The downside to these systems is that the surface-tethered complexes can be less accessible to the growing polymer chains than are leached or homogeneous complexes. In this system, these transport limitations manifest themselves as increased polymerization rates (due to decreased deactivation events), higher molecular weights, and broad polymer polydispersities. To circumvent these problems, catalysts of type 3 described above were developed. Type 3 catalyst systems have shown some of the best polymerizations results, where a soluble deactivating catalyst is introduced in very small quantities to help improve the deactivation process and acts as a molecular shuttle between the growing polymer chains and the

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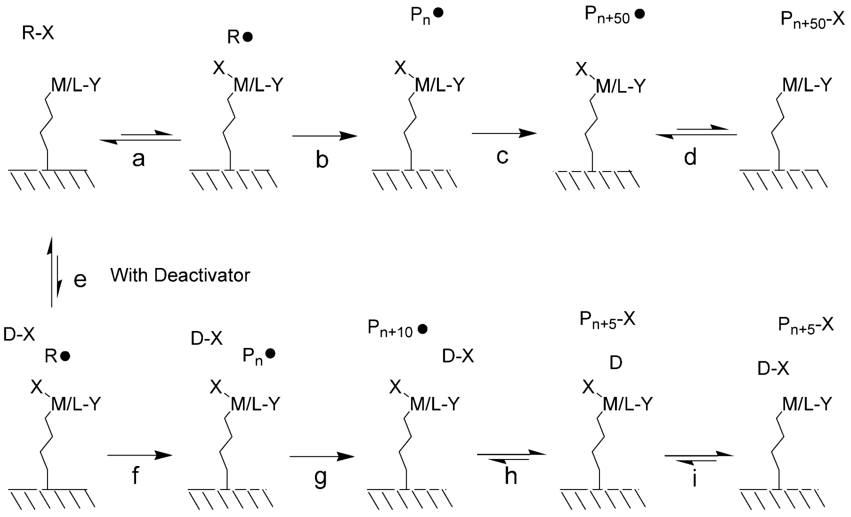
[1] CRP possesses the majority of the characteristics of “living” polymerization; however, a small amount of chain termination, chain transfer, and side reactions does occur (< 5%). Consequently, it does not meet the strict definition of “living” polymerization; therefore it is denoted here as controlled radical polymerization (CRP).

[2] At first glance, ATRP “catalysts” may not seem to meet the strict definition of a catalyst. ATRP is a transition-metal-mediated polymerization that is stoichiometric in metal for most polymerization recipes (i.e., one catalyst complex mediating the growth of one polymer chain). In this regard, it can be best viewed as a chain transfer agent. However, since in the absence of the catalyst polymerization is not initiated and since each complex mediates multiple activation and deactivation steps (turnovers), the complexes are commonly referred to as catalysts.



Scheme 2.

surface-tethered complexes (Scheme 2). Without the deactivator, many monomer units can be added to the growing polymer chain before the growing radical is deactivated by reaction with a deactivator complex (Scheme 2, b–d). In contrast, with the deactivator, only a small number of monomer units are added before the soluble deactivator caps the growing polymer chains (Scheme 2, g–i). Although this method works well, there are several drawbacks to this system. Because of the presence of some homogeneous species, there will be metal contaminants in the product polymer that will need to be removed. Furthermore, these immobilized/soluble hybrid systems have only been successful for polymer supports [32,48–52], which can be more expensive than silica supports.

A final catalyst immobilization method that does not fit into the above categories is the reversibly hydrogen-bonded catalyst recently reported by Shen and co-workers. They utilized a multipoint hydrogen bonding interaction to immobilize a CuBr/ligand complex to its complementary hydrogen bonding pair, which was covalently immobilized on silica [53] or a polymer resin [54]. When the polymerization reaches reaction temperature, the hydrogen bonds dissociate and release the catalysts from the solid support and the polymerization proceeds in the liquid phase. After the polymerization is complete, the temperature is lowered and the catalysts reattach to the support via hydrogen bonds. Some catalyst is eventually lost because of entanglement in the polymer (up to 2%).

To date, most reports of solid catalysts for ATRP have focused primarily on the production of well-defined polymer with efficient catalyst recovery. However, less attention has been focused on the optimization of catalyst regeneration and recycling. Indeed, in most cases, the polymerization rate decreases after the first use, and there has been speculation in the literature about why this is observed. Essentially two potential reasons for this have been proposed [55]. First, for copper-containing catalysts, Cu(I)/ligand species are immobilized for the first catalyst use, but because of chain termination and/or the stability of the copper–ligand complex in the Cu(II) oxidation state, Cu(II) species accumulate on the support surface after the polymerization. As a result, when these catalysts are recycled, they display decreased polymerization rates, as chains are only initiated by Cu(I) species. To recover the catalyst activity, the catalyst must be "regenerated," that is, the Cu(II) sites must be reduced back to the Cu(I) oxidation state. Various regeneration methods have been utilized, but the extent of Cu(I) regeneration has not been directly probed [32,36,41]. The second proposed reason for decreased rates upon recycling is the loss of immobilized catalyst due to leaching—fewer polymerization-initiation sites remain on the solid support.

We recently reported a silica-tethered CuBr/bipyridine (Bpy) ATRP catalyst [41]. The CuBr/Bpy complex was covalently immobilized by a preassembled complex approach on various silica supports of different structures and porosities. A battery of characterization techniques revealed that the immobilized species likely consist of copper species coordinated by one or two Bpys, uncoordinated Bpys, and in some cases physisorbed CuBr on silica. Catalysts immobilized on controlled pore glass with a 240-Å pore diameter (CPG-240) and nonporous Cabosil EH5 exhibited the best polymerization results, with moderate conversions, PDIs as low as 1.25, and low residual copper content in the final polymer [41].

In this work, we probe the CuBr/Bpy system with three key issues as foci. First, we evaluate both silica-tethered and physisorbed CuBr/Bpy systems (Scheme 3)[3] in the controlled polymerization of methyl methacrylate, with a focus on the role of the immobilization method in catalytic

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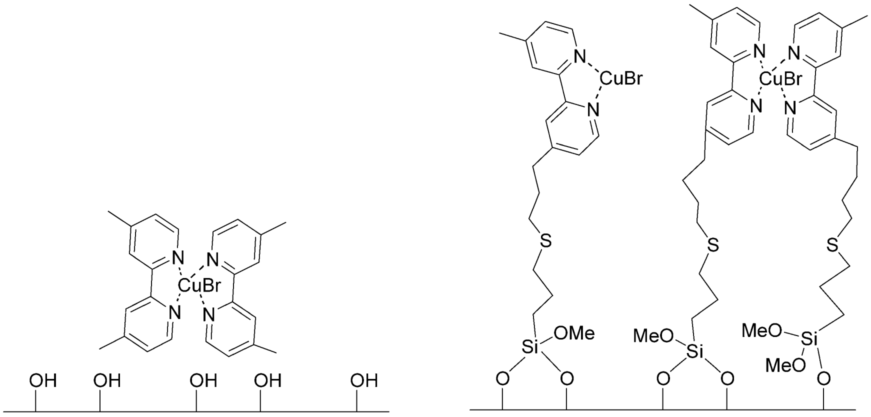
[3] Scheme 3 represents hypothetical, idealized surface structures for physisorbed and tethered complexes. For both catalysts, a distribution of types of sites likely exists on the surface, with at least some of the copper species utilizing the silica surface as a ligand.



Silica(CuBr/dMBpy)
Physisorbed
(a)

Silica-CuBr/SdMBpy
Covalently tethered
(b)

Scheme 3.

performance. Second, we evaluate the effectiveness of a unique catalyst regeneration procedure that we developed, with spectroscopic characterization of the state of the copper species before and after reaction and regeneration. Third, we elucidate the role of leached copper species in the course of the polymerization in both the tethered and physisorbed systems. Ultimately, the results indicate that the tethered CuBr/Bpy system is superior to the physisorbed system with regard to polymerization performance, catalyst recyclability, and copper loss.

2. Experimental

2.1. Materials and instrumentation

2-Bromopropionitrile (BPN) (Aldrich; 97%) was dried over 4-Å molecular sieves and stored under dry nitrogen. Copper (II) bromide ($CuBr_2$) (Aldrich; 99%), 4,4′-dimethyl-2,2′-dipyridyl (dMBpy) (Aldrich; 99%), and 2,2′-azobis(2-methylpropionitrile) (AIBN) (Aldrich; 99%) were used as received and stored under dry nitrogen. Copper (I) bromide (CuBr) (Acros; 98%) was purified with stirring in glacial acetic acid for 5 h, washed with absolute ethanol and anhydrous diethyl ether, dried under vacuum for 12 h at room temperature, and stored under dry nitrogen. Methyl methacrylate (MMA) (Aldrich; 99%) was passed three times through an inhibitor removal column (Aldrich-311332), distilled once under reduced pressure, degassed by three freeze/pump/thaw cycles, and stored under dry nitrogen at $-22\,^{\circ}C$. Toluene for polymerization (Acros; 99.8%) was distilled under reduced pressure over sodium/benzophenone, degassed by three freeze/thaw cycles, and stored under dry nitrogen. 2-Bromopropionitrile was stored in a 0.46 M stock solution in dry toluene under dry nitrogen. Tetrahydrofuran (Aldrich; HPLC-grade, inhibitor-free, $>99\%$) was used as received for the eluent in GPC analysis. Cabosil EH5 (Cabot) was dried under vacuum for 12 h at $200\,^{\circ}C$ and stored under dry nitrogen. Cabosil is a fumed, nonporous silica with multiparticle aggregates with a length of 0.2–0.3 µm (individual particles have nanosized features), a surface area of 335 m^2/g, and 2.7 $mmol_{OH}/g_{solid}$, determined by dinitrogen physisorption and TGA analyses, respectively. Hexanes (Aldrich; $>99\%$), methylene chloride (CH_2Cl_2; Aldrich; $>99\%$), and tetrahydrofuran (THF) (Aldrich; $>99\%$) were dried and deoxygenated with a purification system and stored under dry nitrogen [56]. 4′-{4-[3-(Trimethoxy-silanyl)-propylsulfanyl]-butyl}-4-methyl-[2,2′]bipyridinyl (SdMBpyTMS) was synthesized according to methods described in the literature [41]. We prepared powders of CuBr/dMBpy and $CuBr_2$/dMBpy complexes used for UV/vis spectroscopy by mixing the ligand with metal salt (2:1 ratio) in THF. The complexes were recovered by filtration and dried under vacuum for analysis. All reactions and polymerizations were carried out under a dry nitrogen/argon atmosphere in a MBraun UniLab 2000 drybox and/or with standard Schlenk line techniques.

Silica pore diameters and surface areas were determined from dinitrogen physisorption data obtained with a Micromeritics ASAP 2000 system. The surface areas were analyzed by the BET method, and the pore size distribution was determined with the BJH method applied to the adsorption branch of the isotherm. ^1H NMR (300 MHz) spectra were determined on a Mercury VX instrument. A Netzsch Thermoanalyzer (STA409) was used for simultaneous thermal analysis combining thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), with a heating rate of $20\,^{\circ}C/min$ and an air flow of 30 ml/min. Diffuse–reflectance ultraviolet–visible (UV/vis) spectroscopy was performed on solid materials in a dry glovebox with an Ocean Optics USB2000 fiber optic spectrometer, with the use of a PTFE diffuse reflectance standard. Copper and silicon elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN) or Chemisar Laboratories, (Guelph, Canada) with ICP-AES. Carbon, hydrogen, and nitrogen contents were determined via CHN analysis by

Galbraith Laboratories, Inc. Gas chromatographic analyses were performed on a Shimadzu GC 14-A gas chromatograph equipped with a flame ionization detector and an HP-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 µm). The temperature program for GC analysis was heating from 50 to 140 °C at 30 K/min and from 140 to 300 °C at 40 K/min under constant pressure, with inlet and detector temperatures set constant at 330 °C. The molecular weight and molecular weight distributions were determined by gel permeation chromatography (GPC), with the use of American Polymer Standards columns (10^5, 10^3, and 10^2 Å) equipped with a Waters 510 pump and a Waters 410 differential refractometer. THF was used as an eluent at a flow rate of 1 ml/min. Nine linear PMMA standards (700–2100 K) were used for calibration of methyl methacrylate polymers.

2.2. Catalyst synthesis

2.2.1. Preparation of Cabosil(CuBr/dMBpy) physisorbed catalyst

In a 100-ml flask, a solution of 1.00 g of dMBpy (5.45 mmol) and 5 ml of dry toluene was slowly added to a stirring mixture of 0.391 g of CuBr (2.73 mmol) in 50 ml of dry toluene at 70 °C in a nitrogen glovebox. The resulting light brown mixture was then stirred at 70 °C for 30 min under nitrogen or until the reaction mixture became a dark, reddish brown, homogeneous solution. Then the mixture was added to a 250-ml flask containing 3.00 g of Cab-O-Sil EH5 and 100 ml of dry toluene; the flask was sealed with a valve and removed from the nitrogen glovebox. Then the reaction mixture was stirred at 110 °C for 48 h under argon. The reaction flask was transferred into the nitrogen glovebox after three freeze/pump/thaw cycles, and the solid product was recovered and washed, once with 100 ml of dry toluene and once with copious amounts of dry hexanes until the solvent that filtered out was clear. The dark reddish brown powder was dried under vacuum at room temperature for 12 h and stored under dry nitrogen in a glovebox. CHN, Si, and Cu analyses showed 0.92 $\text{mmol}_{\text{dMBpy}}/\text{g}_{\text{cat}}$ and 0.53 $\text{mmol}_{\text{Cu}}/\text{g}_{\text{cat}}$.

2.2.2. Preparation of covalently immobilized Cabosil-CuBr/dMBpy catalyst

Catalyst preparation was done according to procedures described in the literature [41]. In a 100-ml flask, 1.00 g of SdMBpyTMS (2.37 mmol) and 5 ml of dry toluene were slowly added to a stirring mixture of 0.17 g of CuBr (1.19 mmol) in 50 ml of dry toluene at 70 °C in a nitrogen glovebox. The resulting light brown mixture was then stirred at 70 °C for 30 min under nitrogen or until the reaction mixture became a dark, reddish brown, homogeneous solution. Then the mixture was added to a 250-ml flask containing 2.00 g of Cab-O-Sil EH5 and 100 ml of dry toluene; the flask was sealed with a valve and removed from the nitrogen glovebox. Then the reaction mixture was stirred at 110 °C for 48 h under argon. The reaction flask was transferred into the nitrogen glovebox after three freeze/pump/thaw cycles, and the solid product was recovered and washed, once with 100 ml of dry toluene, once with 100 ml of dry hexanes, and once with a copious amount of dry dichloromethane until the solvent that filtered out was clear. The dark reddish brown powder was dried under vacuum at room temperature for 12 h and stored under dry nitrogen in a glovebox. CHN, Si, and Cu analyses showed 0.46 $\text{mmol}_{\text{SdMBpy}}/\text{g}_{\text{cat}}$ and 0.34 $\text{mmol}_{\text{Cu}}/\text{g}_{\text{cat}}$.

2.3. Polymerization catalysis

2.3.1. Homogeneous

For homogeneous polymerization of MMA with CuBr/dMBpy, the following conditions were typical: [MMA]/[dMBpy]/[Cu]/[BPN] = X:2:1:1 in Y% by v/v MMA in toluene ($X = 300$, $Y = 50$ or $X = 100$, $Y = 25$). For example ($X = 100$, $Y = 25$ in toluene), in a 10-ml flask with a sidearm valve, 0.94 g of MMA (9.42 mmol, 1 ml), 34.7 mg of dMBpy (0.188 mmol), 13.5 g of CuBr (0.094 mmol), and 204 µl of BPN initiator stock solution (0.094 mmol) were added to 2.60 g of toluene (3 ml) under nitrogen. The polymerization vessel was immersed in an oil bath preset to 90 °C. At set time intervals, 0.1-ml aliquots of polymerization solution were removed via syringe and placed in a vial. The vials were immediately quenched in a dry ice/acetone bath. Subsequently, 25 µl of sample was added to 1.5 ml of acetone for GC analysis to monitor MMA conversion. The remaining sample was dried, re-dissolved in HPLC-grade THF to 8.0 mg/ml, and filtered through a Gelman Acrodisc PTFE filter (0.2 µm) for GPC analysis to determine the polymer molecular weight and molecular weight distribution. After the polymerization, the catalyst was recovered from the remaining polymerization solution by centrifugation. The polymerization solutions were analyzed for trace amounts of copper.

2.3.2. Heterogeneous

2.3.2.1. Polymerization with physisorbed CuBr/Bpy catalyst on Cabosil For heterogeneous polymerization of MMA with CuBr/Bpy physisorbed on silica, the following conditions were typical: [MMA]/[Cu]/[BPN] = X:1:1 in Y% by v/v MMA in toluene at 90 °C ($X = 300$, $Y = 50$ or $X = 100$, $Y = 25$). For instance ($X = 100$, $Y = 25$), in a 10-ml Schlenk tube with a sidearm valve, 0.15 g of Cabosil-CuBr/SdMBpy (5.00×10^{-2} mmol of Cu, 0.34 $\text{mmol}_{\text{Cu}}/\text{g}_{\text{cat}}$), 0.48 g of MMA (5.00 mmol), and 97 µl of initiator stock solution BPN (5.00×10^{-2} mmol) were added to 1.25 g of toluene under nitrogen. The polymerization vessel was immersed in an oil bath preset to 90 °C. Samples were taken at preset times and quenched by the procedure described above. Kinetic analysis and polymer characterization were carried out in a manner similar to that described for the homogeneous polymerization. After the polymerization, the catalyst was recovered from the remaining polymerization solution by centrifugation. The polymerization solutions were analyzed for trace amounts of copper. Cabosil-CuBr/SdMBpy catalyst was washed with copious amounts of dry DCM, and Cabosil(CuBr/dMBpy) was washed with copious amounts of dry toluene. The catalysts were vacuum dried and stored under nitrogen for further characterization and reuse.

2.3.2.2. One-pot polymerization with CuBr/dMBpy and Cabosil For one-pot polymerization of MMA with CuBr/dMBpy and Cabosil, the following condition was typical: [MMA]/[dMBpy]/[Cu]/[BPN] = $X/2/1/1$ in Y% by v/v MMA in toluene and 0.10 g of Cabosil ($X = 300$, $Y = 50$ or $X = 100$, $Y = 25$). For example ($X = 100$, $Y = 25$ in toluene), in a 10-ml flask with a sidearm valve, 0.94 g of MMA (9.42 mmol, 1 ml), 34.7 mg of dMBpy (0.188 mmol), 13.5 g of CuBr (0.094 mmol), 0.10 g of Cabosil, and 204 µl of BPN initiator stock solution (0.094 mmol) were added to 2.60 g of toluene (3 ml) under nitrogen. The polymerization vessel was immersed in an oil bath preset to 90 °C. Samples were taken at preset times and quenched by the procedure described above. Kinetic analysis and polymer characterization were carried out in a manner similar to that described for the homogeneous polymerization. After the polymerization, the catalyst was recovered from the remaining polymerization solution by centrifugation. The polymerization solutions were analyzed for trace amounts of copper.

2.4. Catalyst regeneration

The spent immobilized Cabosil-CuBr/SdMBpy or Cabosil(CuBr/dMBpy) catalyst was regenerated with AIBN by our literature procedure [41]. The used catalysts were recovered from the polymerization solution by centrifugation and washed with copious amounts of DCM and then toluene. The catalyst was transferred to a vial (i.e., 0.15 g of Cabosil-CuBr/SdMBpy, 0.050 mmol of Cu). Then 3.00 g of toluene and an equivalent of AIBN to Cu (0.050 mmol or 9 mg of AIBN) were added to the vial. The sealed vial was placed in a preheated oil bath at 90 °C. The mixture was stirred for a predetermined time. The catalyst was then recovered by filtration and washed with copious amounts of toluene and dichloromethane. The catalyst was dried under vacuum for 12 h and stored under dry nitrogen in a glovebox for further characterization and reuse. (Note: Physisorbed catalysts were only washed with toluene.)

2.5. Catalyst recycling

Regenerated catalyst was recycled by the addition of a fresh charge of monomer, solvent, and initiator. For example, the following condition was typical: [MMA]/[Cu]/[BPN] = 100:1:1 in 25% by v/v MMA in toluene at 90 °C. In a 10-ml Schlenk tube with a sidearm valve, 0.15 g of Cabosil-CuBr/SdMBpy (5.00×10^{-2} mmol of Cu, 0.335 $\text{mmol}_{\text{Cu}}/\text{g}_{\text{cat}}$), 0.48 g of MMA (5.00 mmol), and 97 µl of initiator stock solution BPN (5.00×10^{-2} mmol) were added to 1.25 g of toluene under nitrogen. The polymerization vessel was immersed in an oil bath preset to 90 °C. MMA conversion and polymer characterization were carried out in a manner similar to that described for homogeneous polymerizations.

2.6. Evaluation of catalyst leaching

An air-free swivel medium frit filter was used to hot-filter the catalyst to test for catalyst leaching [57]. For example, the following conditions were typical: [MMA]/[Cu]/[BPN] = 100:1:1 in 25% by v/v MMA in toluene at 90 °C. In a 10-ml Schlenk tube with a sidearm valve, 0.30 g of Cabosil-CuBr/SdMBpy (10.00×10^{-2} mmol of Cu, 0.335 $\text{mmol}_{\text{Cu}}/\text{g}_{\text{cat}}$), 0.96 g of MMA (10.00 mmol), and 195 µl of initiator stock solution BPN (10.00×10^{-2} mmol) were added to 2.50 g of toluene under nitrogen, and then the 10-ml flask was attached to one end of the swivel frit. An empty 15-ml receiving flask with a stir bar was attached to the other end. The complete apparatus was sealed and attached to the Schlenk line. The flask containing the polymerization mixture was then immersed in a 90 °C oil bath. At 15 min the oil bath was removed, and a 0.2-ml sample was taken through the side arm under positive argon pressure. The swivel frit apparatus was then rotated 180°, and the polymerization solution was filtered through the frit with a partial static vacuum to remove the Cabosil-CuBr/SdMBpy catalyst and collected it in the 15-ml receiving flask. The oil bath was returned, and the polymerization solution continued to react for 24 h. The final polymerization solution was then analyzed for conversion, molecular weight, polydispersity, and residual copper content.

3. Results and discussion

3.1. Catalyst synthesis and characterization

Two types of catalysts are reported in this work, designated with the following notation. Silica-tethered CuBr/Bpy complexes are designated as Cabosil-CuBr/SdMBpyTMS [40], where the dash indicates a covalent tether. Catalysts with CuBr/Bpy complexes physically adsorbed to silica supports are labeled Cabosil(CuBr/SdMBpyTMS).

The covalent immobilization of CuBr/SdMBpyTMS complex on Cabosil was previously reported in our laboratory [41]. A battery of characterization techniques showed that a mixture of mono- and bis copper coordinated Bpy complexes and uncoordinated Bpys was covalently attached to the silica surface. ^{13}C CPMAS NMR showed the successful covalent immobilization of Bpy ligands on the silica support (Fig. 1) [41]. The combination of FT-Raman spectroscopy and elemental analysis revealed a potential for several different immobilized Bpy species (i.e., immobilized CuBr(Bpy), CuBr(Bpy)_2, and Bpy). However, the oxidation state of the immobilized complex was not directly

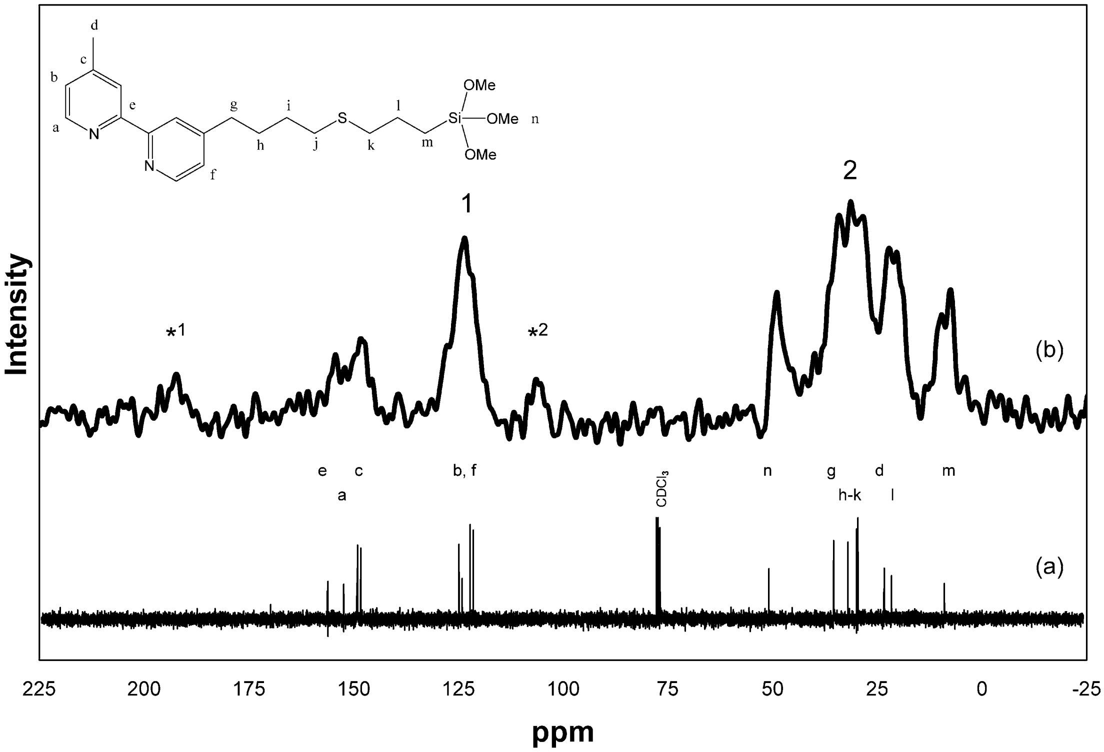


Fig. 1. ^{13}C Solution and solid state NMR spectra of (a) SdMBpyTMS and (b) silica-supported SdMBpy by CP-MAS. Figure adapted from our previous work [41].

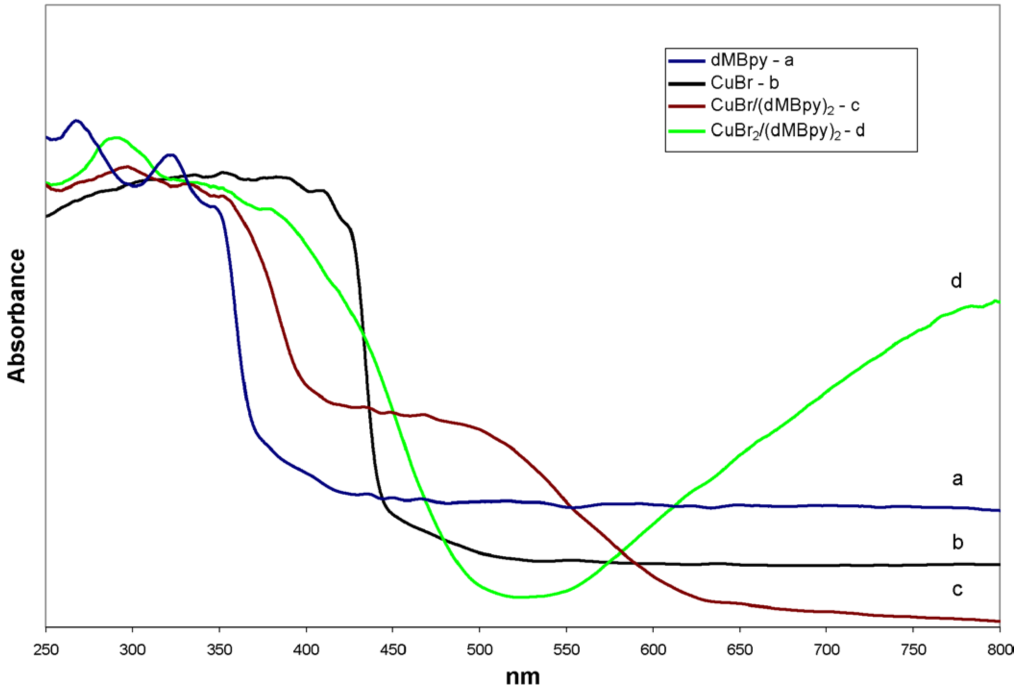


Fig. 2. UV/vis spectra (vs PTFE) of reference compounds (a) dMBpy, (b) CuBr, (c) CuBr/(dMBpy)$_2$, and (d) CuBr$_2$/(dMBpy)$_2$.

probed. For this work, diffuse–reflectance ultraviolet–visible (UV/vis) spectroscopy was used to determine the oxidation state of the immobilized complexes. For reference, UV/vis spectra were obtained for homogeneous reference compounds and complexes in the solid state to determine the transitions for the ligand and copper complexes. Fig. 2 shows UV/vis spectra for CuBr, dimethylbipyridine (dMBpy), CuBr/dMBpy, and CuBr$_2$/dMBpy. The π–π^* transition of the uncomplexed dMBpy (Fig. 2a) appears between 250 and 350 nm. After complexation of both Cu(I) and Cu(II)

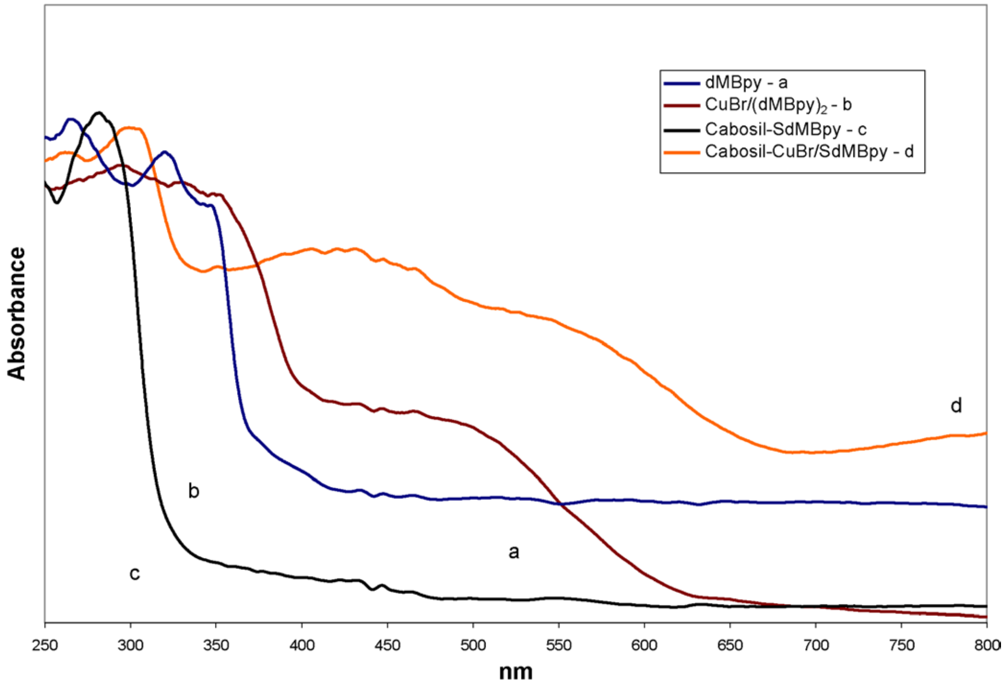


Fig. 3. Immobilization of Cabosil-CuBr/SdMBpy followed by UV/vis spectroscopy. UV/vis spectra (vs PTFE) of (a) dMBpy, (b) CuBr/(dMBpy)$_2$, (c) Cabosil-SdMBpy, and (d) Cabosil-CuBr/SdMBpy.

bromide species, the breadth of the transition shifts to 400 and 450 nm, respectively (Fig. 2, c and d, respectively). The metal-to-ligand charge-transfer band (MLCT) (t_{2g}–π^*) for the CuBr/dMBpy complex appears between 400 and 600 nm, consistent with a Cu(I) oxidation state. The d–d transition for the $CuBr_2$/dMBpy complex has a broad band between 600 and 800 nm, indicative of a Cu(II) oxidation state. The π–π^*, MLCT, and d–d transitions were similar to those reported for solution-phase UV/vis spectra for similar CuX_n/Bpy species [58–61]. Fig. 3 shows UV/vis spectra for various components of CuBr/SdMBpyTMS on Cabosil. The π–π^* transition of the immobilized uncomplexed dMBpy ligand appears between 260 and 310 nm. The immobilized CuBr/SdMBpy complex has a π–π^* transition at 270–340 nm and a MLCT band between 350 and 650 nm. The broadness of the MLCT transition may be indicative of several different symmetries on the surface of the immobilized CuBr/SdMBpy complex (i.e., distorted tetrahedral geometry, CuBr(Bpy), $CuBr(Bpy)_2$, and free CuBr) [62], which is consistent with our previous results [41]. There also appears to be a transition beyond 600 nm, which was attributed to a low concentration of Cu(II) species on the surface. Nevertheless, it appears by UV/vis spectroscopy that the Cabosil-CuBr/SdMBpy catalyst surface is dominated by a much higher concentration of Cu(I)/SdMBpy complexes, as was intended. The catalyst loading, determined by CHN, Cu, and Si microanalysis, was 0.46 $\text{mmol}_{\text{SdMBpy}}/\text{g}_{\text{cat}}$ and 0.34 $\text{mmol}_{\text{Cu}}/\text{g}_{\text{cat}}$. The ligand/metal ratio was 1.35 (a L/M ratio of 2 was targeted for the catalyst synthesis). The presence of excess metal relative to the ligand indicates that some free CuBr or some monocoordinated Bpy ligands exist on the surface. Although the difference between mono- and bis-coordinated Bpy ligands cannot be discerned by FT-Raman or UV/vis spectroscopy, previous FT-Raman studies do provide evidence for a small population of unligated Bpy ligands [41].

CuBr/dMBpy complex was physisorbed on the Cabosil support in a manner similar to the covalent immobilization to give Cabosil(CuBr/dMBpy). However, polar solvents were not used to wash the catalyst, because the solvent will strip the physisorbed complex from the silica surface [39]. UV/vis spectroscopy was again used to determine the nature of the immobilized species. Fig. 4 shows a comparison of the UV/vis spectrum for the CuBr/dMBpy complex and immobilized Cabosil-CuBr/SdMBpy and Cabosil(CuBr/dMBpy) catalyst. The two immobilized catalysts have similar UV/vis spectra; however, the Cabosil(CuBr/dMBpy) catalyst does not appear to have the Cu(II) transition beyond 600 nm. The Cabosil(CuBr/dMBpy) catalyst loading was 0.92 $\text{mmol}_{\text{dMBpy}}/\text{g}_{\text{cat}}$ and 0.53 $\text{mmol}_{\text{Cu}}/\text{g}_{\text{cat}}$. The 1.73 ligand/metal ratio was much closer to the target value than it was in the tethered case.

3.2. Polymerization of MMA

The solid catalysts were used for the heterogeneous polymerization of methyl methacrylate (MMA). In addition to both the covalent and physisorbed catalysts, a heterogeneous one-pot polymerization technique and homogeneous polymerization were used to compare the effect of immobilization of the CuBr/Bpy complex on silica. The one-pot polymerization was similar to a homogeneous polymeriza-

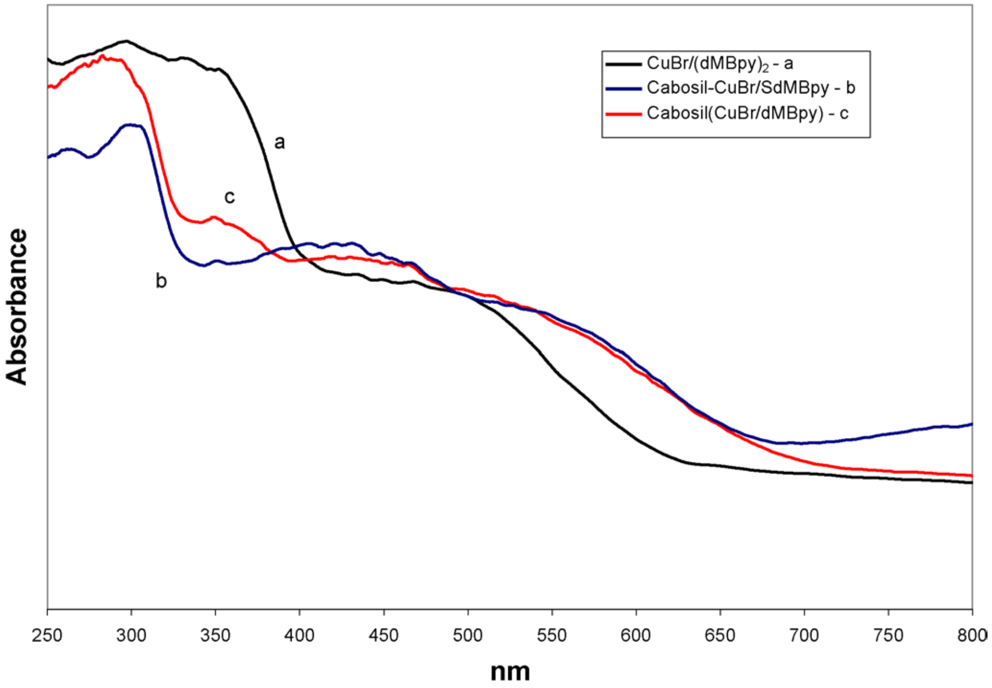


Fig. 4. UV/vis comparison of non-immobilized and immobilized CuBr/dMBpy complexes. UV/vis spectra (vs PTFE) of (a) CuBr/$(dMBpy)_2$, (b) covalent Cabosil-CuBr/SdMBpy, and (c) physisorbed Cabosil(CuBr/dMBpy).

tion; however, bare Cabosil silica was added to the homogeneous complex in solution at the start of the polymerization. This represents a system for testing whether bare silica can effectively adsorb the free complex in situ and whether this will have any affect on the polymerization. Two different monomer/initiator ratios ([MMA]/[BPN] = 100 and 300) were investigated to determine the effect the polymer molecular weight and the silica support structure have on the MMA conversion and final polydispersity of the polymer. Finally, the catalysts were removed by centrifugation, and the polymerization solutions were analyzed for residual or leached copper. It was speculated in our previous report [40,41] that ppm levels of leached copper species can help mediate the controlled polymerization in a manner similar to that of the immobilized/soluble hybrid catalyst system (PS8-dMBpy/CuBr:$CuBr_2$/Tris-(2-(dimethylamino)ethyl)amine (or Me_6TREN)) of Matyjaszewski et al. [32] and the physisorbed hexamethyltriethylenetetramine (or HMTETA)/CuBr/Silica system of Zhu et al. [55]. The nature and location of the catalyst active site for covalent and physisorbed CuBr/dMBpy-immobilized catalysts on Cabosil are discussed in a later section.

Table 1 summarizes the results of the polymerizations. Fig. 5 shows the kinetic plots, the evolution of M_n, and polydispersity index (PDI) versus conversion plots for [MMA]/[BPN] = 100. The homogeneous polymerization reached 73% conversion, $M_n = 10000$, and PDI = 1.22. The covalent Cabosil-CuBr/SdMBpy catalyst was the only catalyst to perform similarly to the homogeneous catalyst; however, the molecular weight distribution was slightly broader (PDI = 1.31). Both the physisorbed Cabosil(CuBr/dMBpy) and one-pot polymerizations performed poorly compared with the homogeneous polymerization, with conversions reaching only 56% and PDI > 1.30. The severity of chain termination in these two polymerizations was much greater, as seen in the significant curvature in the pseudo-first-order plots (ln[Mo]/[Mt] versus time plots) and low reactivity after 2 h. The poor results could be the result of the short catalyst distance from the solid support, if most of the sites remain adsorbed under reaction conditions. Since the CuBr/dMBpy catalysts are physisorbed to the support, unlike the covalently tethered, potentially more accessible CuBr/SdMBpy catalysts, it could be difficult for the growing polymer chain to interact with immobilized catalyst because of steric constraints. As the polymer molecular weight increases, this case could be exacerbated even more. In the case of the tethered CuBr/SdMBpy catalysts, the active site

Table 1
Polymerization results[a]

X	Catalyst condition	Conversion (final)	$M_{n,\mathrm{Th}}$	$M_{n,\mathrm{Ex}}$	PDI	R_{Cu}
100	Homogeneous	73	7300	10000	1.22	2193
	Covalent	73	7300	10000	1.31	< 1
	Physisorbed	56	5600	9300	1.39	37
	One-pot	56	5600	8600	1.31	68
300	Homogeneous	80	24000	24900	1.30	2031
	Covalent	76	22800	27700	1.51	< 1
	Physisorbed	89	26700	33100	1.57	115
	One-pot	61	18300	27500	1.56	219

[a] Polymerization conditions [MMA]/[Cu]/[BPN] = $X/1/1$ in Y% MMA in toluene at 90 °C for 24 h ($X = 100$, $Y = 25$; $X = 300$, $Y = 50$). Only the final conversion was determined in these polymerizations.

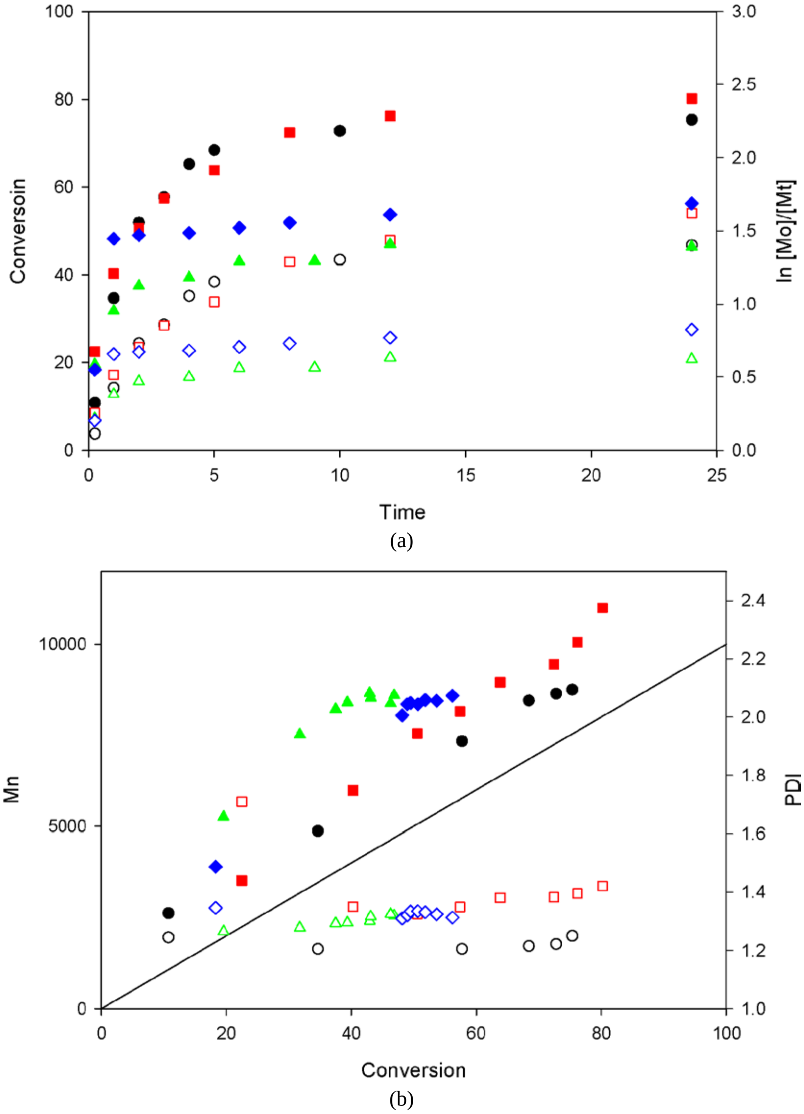
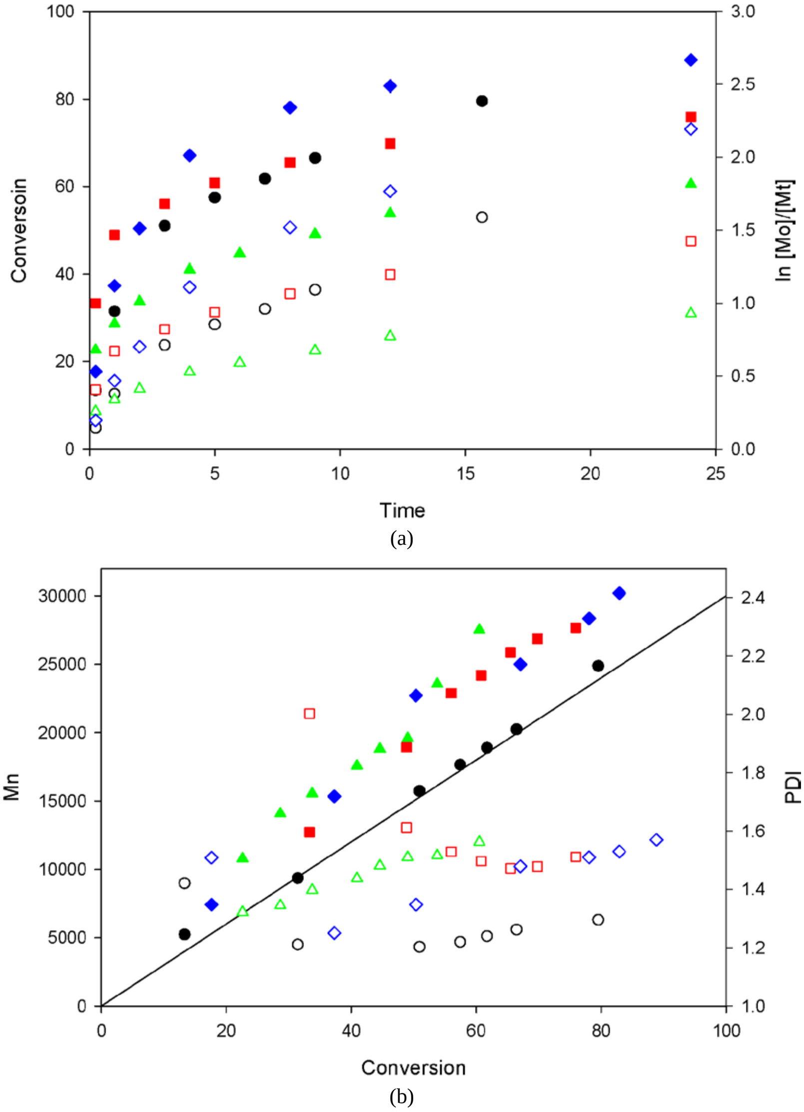


Fig. 5. (a) Kinetic plots and (b) evolution of M_n and PDI vs % conversion of MMA plots for polymerizations with (●, ○) homogeneous CuBr/dMBpy, (■, □) covalent Cabosil-CuBr/SdMBpy, (◆, ◇) physisorbed Cabosil(CuBr/dMBpy), and (▲, △) one-pot with Cabosil and CuBr/dMBpy. Theoretical M_n curve (—). Shaded symbol = left axis; open symbol = right axis. Polymerization conditions: [MMA]/[Cu]/[BPN] = 100/1/1 in 25% by v/v MMA in toluene at 90 °C.

is likely better solvated in the polymerization solution because of the linker. Zhu and co-workers showed that there was an optimal linker length at which their immobilized ATRP catalysts could achieve well-behaved polymerizations in a related system [35].

Upon completion of the polymerizations, the solid catalyst particles were removed by centrifugation, and the recovered polymerization solutions were analyzed by copper microanalysis for residual copper content, R_{Cu}. Both homogeneous polymerizations ([MMA]/[I] = 100 and 300) had approximately $R_{\mathrm{Cu}} \sim 2000$ ppm. Polymerizations performed with covalently immobilized catalyst had undetectable amounts of copper in the solution, whereas those performed with physisorbed and one-pot methodologies leached copper, but less than the homogeneous polymerizations. For the physisorbed and one-pot polymerization with [MMA]/[I] = 100, the residual copper found was less than that at [MMA]/[I] = 300. The higher copper contents were attributed to poorer recovery of the catalyst particles from the more viscous higher-molecular-weight polymerization solution.

Fig. 6 shows the kinetic plots, the evolution of M_n with conversion, and PDI vs conversion plots for [MMA]/[BPN] = 300. The homogeneous polymerization reached 82% conversion, with M_n = 26800 and PDI = 1.31. All heterogeneous polymerizations had polydispersities greater than 1.50, and there is evidence of chain termination, as indicated by the curvature in the ln[Mo]/[Mt] versus time plots. In general the conversions were higher than those for [MMA]/[BPN] = 100. The higher monomer concentration in these polymerizations may be a reason why higher conversions were achieved. The increase in PDI relative to the



(a)

(b)

Fig. 6. (a) Kinetic plots and (b) evolution of M_n and PDI vs % conversion of MMA plots for polymerizations with (●, ○) homogeneous CuBr/dMBpy, (■, □) covalent Cabosil-CuBr/SdMBpy, (◆, ◇) physisorbed Cabosil(CuBr/dMBpy), and (▲, △) one-pot with Cabosil and CuBr/dMBpy. Theoretical M_n curve (—). Shaded symbol = left axis; open symbol = right axis. Polymerization conditions: [MMA]/[Cu]/[BPN] = 300/1/1 in 50% by v/v MMA in toluene at 90 °C.

homogeneous polymerization was caused by Cabosil support [41]. Addition of the supported catalyst increases the viscosity of the polymerization solution even before the reaction begins. As the conversion increases, the gelation of the polymerization solution is observed, and this can cause significant mass transport problems, thereby decreasing the frequency of the activation/deactivation steps and increasing the PDI. Current research is under way that is seeking alternative supports and methods to increase the active site density on the support to alleviate this problem.

3.3. Catalyst regeneration and recycling

Three different methodologies of regenerating immobilized ATRP catalysts have been reported. The first two involve the addition of zero valent copper in the form of copper powder or wire, Cu(0). The Cu(0) is stirred with the spent catalyst to reduce the Cu(II) to Cu(I): Cu(II) + Cu(0) → 2Cu(I) [36]. In the last method, Matyjaszewski and coworkers use the soluble Me_6TREN ligand with Cu(0) wire to regenerate the spent PS8-dMBpy/$CuBr_2$ catalyst [32]. Similar to its proposed behavior as a deactivator species in the polymerization, the soluble Me_6TREN transports Cu(0) to the immobilized catalyst to be reduced to Cu(I). However, these regeneration methods add additional copper to immobilized catalysts.[4] In most cases, the reuse of these regenerated catalysts leads to poorer polymerization results com-

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[4] Although copper microanalyses were not performed on these catalysts after the regeneration, it can be assumed with these regeneration techniques involving copper wire or powder, additional copper must be added to the system.

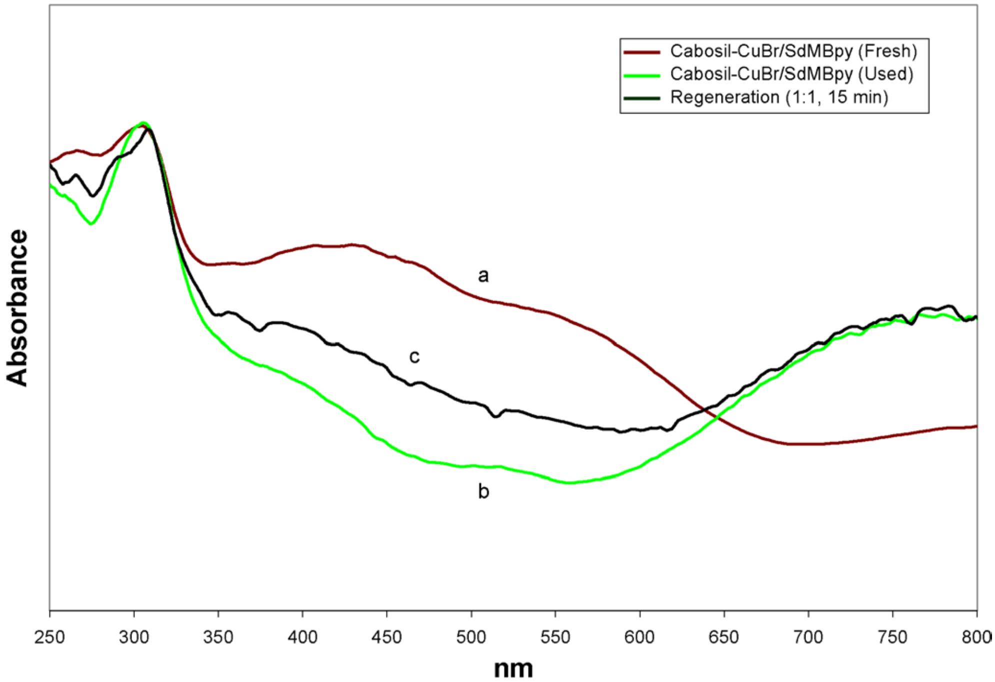

Fig. 7. UV/vis comparison (vs PTFE) of covalent Cabosil-CuBr/SdMBpy (a) fresh, (b) used, and (c) regenerated catalysts. Polymerization conditions: [MMA]/[Cu]/[BPN] = 100/1/1 in 25% by v/v MMA in toluene at 90 °C. Regeneration conditions: [AIBN]/[Cu] = 1 in 4 ml of toluene at 90 °C for 15 min.

pared with the first use (i.e., lower conversions and higher PDIs) [32,36]. In our previous work, we have shown that the covalently tethered Cabosil-CuBr/SdMBpy catalysts can be recycled up to three times by regeneration of the catalysts, without the addition of copper, by a simple treatment with AIBN [41]. Without the catalyst regeneration, the recycle reactions proceeded slowly, with the polymerization reaching 25% conversion after 24 h and 45% after 89 h (compared with first use: conversion = 73% and PDI = 1.31 after 24 h). Upon completion of the polymerization, a higher concentration of immobilized Cu(II) species was hypothesized to exist on the catalyst support because of chain termination and the tendency of the Bpy ligand to stabilize Cu(II) relative to Cu(I) [63]. The existence of Cu(II) species on the catalysts was supported by the bright green color of the catalyst during and after the polymerization caused by chain termination events. Further evidence for the presence of immobilized Cu(II) species comes from the UV–vis spectra of the used Cabosil-CuBr/SdMBpy shown in Fig. 7b. The MLCT band for Cu(I) has a much lower absorbance intensity compared with the fresh catalyst (Fig. 7a), and a distinct Cu(II) band between 600 and 750 nm appears. After catalyst regeneration, the recycled catalysts achieved higher conversions and activity than polymerizations performed with the used nonregenerated catalyst (first use, fresh catalyst: conversion = 78%, M_n = 13000, PDI = 1.29 after 17 h; second use, nonregenerated catalyst: conversion = 45%, M_n = 5700, PDI = 1.24; third use, regenerated catalyst: conversion = 65%, M_n = 7600, PDI = 1.23 after 48 h, [MMA]/[BPN] = 100) [41]. Fig. 8 shows the Cabosil-CuBr/SdMBpy catalyst before (a) and after (b) regeneration. Over a period of 15 min the catalyst mixture turned from green to a dark reddish brown color. UV/vis spectra for the regenerated catalyst (Fig. 7c) show the intensity increase in the Cu(I) band; however, a Cu(II) band still remains. Optimization of the catalyst regeneration is discussed in a subsequent section.

An attempt to regenerate the physisorbed Cabosil(CuBr/dMBpy) catalyst was also undertaken. The regeneration procedure was modified because the recovered catalyst could not be washed with DCM; therefore the catalyst was washed extensively with toluene. During regeneration, the color of the regenerated catalyst did not change significantly compared with the Cabosil-CuBr/SdMBpy catalyst (Figs. 8c and 8d). The UV/vis spectra for the catalyst before and after regeneration show only a slight increase in absorbance intensity of the Cu(I) transition (Fig. 9b and c, respectively). Recycling of the catalyst resulted in a polymerization that reached 12% conversion, M_n = 2400, and PDI = 1.54 after 24 h (compared with first use: conversion = 56 and PDI = 1.39 after 24 h). Thus, reaction rates are depressed and control over the polymerization is poor. The GPC trace shows a small higher-molecular-weight signal (not shown here) that is likely due to desorbed polymer from the first polymerization. This is an important observation, as residual polymer may play a key role in preventing effective catalyst recycling and in determining the amount of leaching of copper species during the reaction. The physisorbed Cabosil(CuBr/dMBpy) catalyst cannot be regenerated or recycled under the conditions described here.

The ability to remove the reacted polymer after the catalyst recovery during the regeneration procedure is important. The entangled polymer may coat the catalyst particle, thus

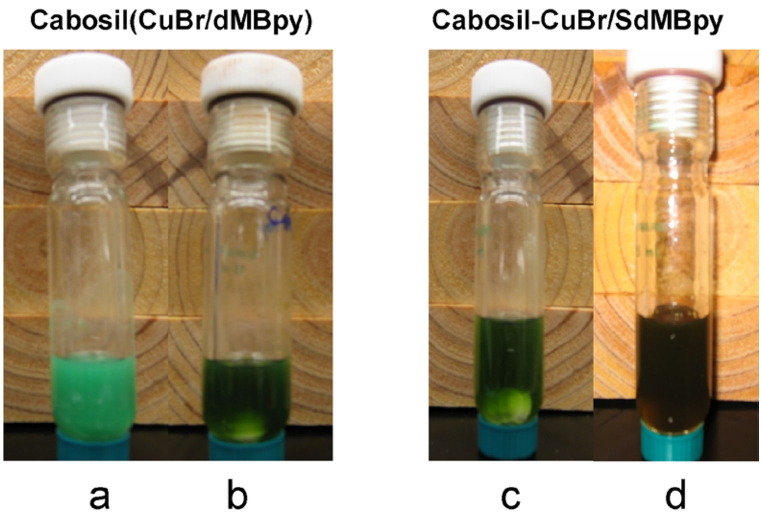

Fig. 8. Digital images of (a) used and (b) “regenerated” physisorbed Cabosil(CuBr/dMBpy) catalyst and (c) used and (d) regenerated covalent Cabosil-CuBr/SdMBpy. Polymerization conditions: [MMA]/[Cu]/[BPN] = 100/1/1 in 25% by v/v MMA in toluene at 90 °C. Regeneration conditions: [AIBN]/[Cu] = 1 in 4 ml of toluene at 90 °C for 15 min.

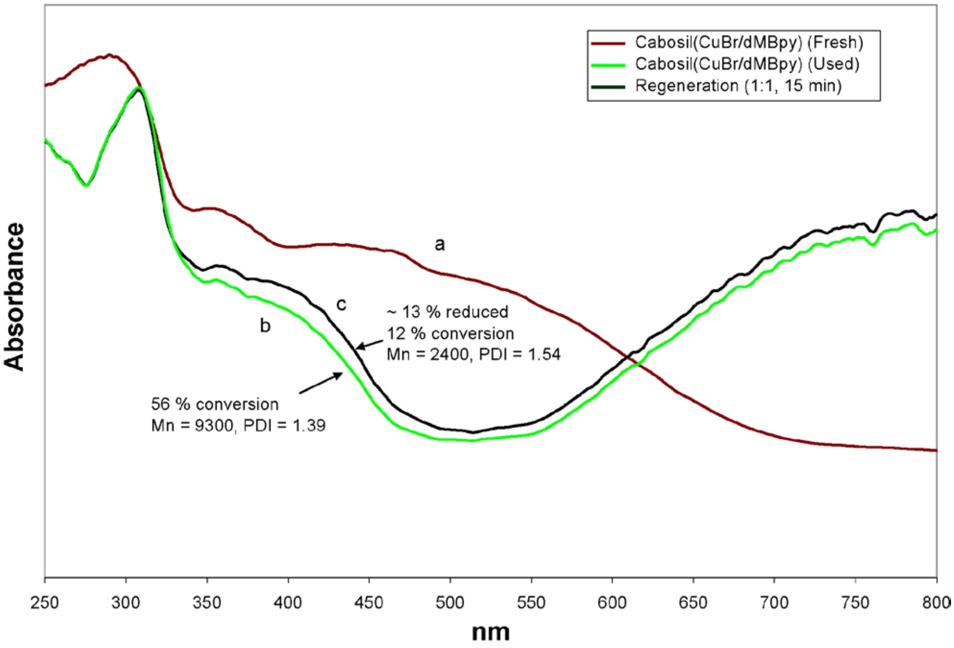

Fig. 9. UV/vis comparison (vs PTFE) of physisorbed Cabosil(CuBr/dMBpy) (a) fresh, (b) used, and (c) regenerated catalysts. Polymerization conditions: [MMA]/[Cu]/[BPN] = 100/1/1 in 25% by v/v MMA in toluene at 90 °C. Regeneration conditions: [AIBN]/[Cu] = 1 in 4 ml of toluene at 90 °C for 15 min.

preventing the AIBN radical’s ability to reduce the immobilized Cu(II) species. The amount of polymer entangled on the catalyst particle after recovery was quantified by thermogravimetric analyses; the results are summarized in Table 2. The organic content of the physisorbed catalyst increased up to 76% and as high as 91%, for [MMA]/[BPN] = 100 and 300, respectively. In the case of the covalently tethered catalyst washed with DCM, the increased organic content was as low as 4% and as high as 30%, for [MMA]/[BPN] = 100 and 300, respectively. Clearly, the effective washing of the used catalyst with DCM was important for polymer recovery and catalyst regeneration.

Table 2
Thermogravimetric analysis of immobilized catalysts[a]

Catalyst	X	$g_{\text{organics}}/g_{\text{SiO}}$[b]	% Increased organics
Cabosil-CuBr/SdMBpy	0	0.26	–
Cabosil-CuBr/SdMBpy	100	0.28	4.8
Cabosil-CuBr/SdMBpy	300	0.34	30.4
Cabosil(CuBr/SdMBpy)	0	0.25	–
Cabosil(CuBr/SdMBpy)	100	0.44	76.4
Cabosil(CuBr/SdMBpy)	300	0.48	91.9

[a] Polymerization conditions: [MMA]/[Cu]/[BPN] = X/1/1 in Y% MMA in toluene at 90°C for 24 h ($X = 100$, $Y = 25$; $X = 300$, $Y = 50$).

[b] Calculated based on organics loss from 200–500 °C by TGA.

Table 3
Results of experiments on optimization of catalyst regeneration[a]

Condition[b]	% Reduced[c]	Conversion[d] (1 h)	Conversion (final)	$M_{n,\text{Th}}$	$M_{n,\text{Ex}}$	PDI
First use	–	40	73	7300	10000	1.31
0.5:1 15 min	13	10	33	3300	4800	1.28
1:1 15 min	33	18	44	4400	6200	1.24
1:1 30 min	52	19	48	4800	7300	1.27
1:1 60 min	61	20	52	5200	7700	1.36
1:1 90 min	42	17	46	4600	6900	1.32
2:1 15 min	54	21	56	5600	7500	1.40
2:1 30 min	38	18	44	4400	6800	1.35

[a] Polymerization condition: [MMA]/[Cu]/[BPN] = 100/1/1 in 25% MMA in toluene at 90 °C for 24 h.
[b] Regeneration conditions were AIBN:Cu molar ratio for X minutes.
[c] % Cu(II) reduced to Cu(I) estimated by gravimetric analysis of UV/vis plots.
[d] Conversion determined by GC.

Another potential reason why catalyst regeneration was ineffective for the physisorbed case could be that the immobilized CuBr/dMBpy is too tightly bound to the silica surface, as speculated above. If this is true, a covalent tether may be important for regeneration because it may allow for the necessary distance from the support through solvation promoted by the long surface tether. To test this hypothesis, a Cu(II) Cabosil($CuBr_2$/dMBpy) catalyst was prepared, and the reduction of Cu(II) to Cu(I) species was performed with AIBN. In this case, there is no polymer associated with the solid that might block access to the surface sites. Regeneration with AIBN did not occur to any significant extent over 60 min because the catalyst mixture only turned a darker shade of green, not the distinct reddish brown color observed with the covalently immobilized catalyst after 10 min. This result indicates that the CuBr/dMBpy complex may be interacting with the surface in a way that prevents effective regeneration of the catalyst, and that a tethered complex and good solvation of the immobilized $CuBr_2$/dSMBpy complexes are the key items that are necessary for catalyst regeneration.

3.4. Optimization of catalyst regeneration

The standard conditions previously reported for AIBN regeneration were an equivalent ratio of AIBN reducing agent to immobilized copper (1:1 AIBN/Cu) in toluene at 90 °C for 15 min [41]. Here, a series of regeneration conditions were investigated to determine the optimal reducing agent concentration and time for regeneration. The AIBN concentration was varied from 0.5 to 2.0 equivalents to probe the effect of radical concentration (one AIBN molecule creates two radicals). Ultimately, the regeneration appears to be a dynamic process, as it was observed that as the regeneration time increases, the reaction solution changes from green to a dark reddish brown color and then back to bright green again. Therefore, the regeneration time was varied and the increase/decrease in the Cu(I) transition intensity relative to the fresh and used Cabosil-CuBr/SdMBpy catalyst was monitored by UV/vis measurements of the recovered, washed, and dried regenerated solid catalyst samples. Table 3 summarizes the results for catalyst regeneration experiments. The fraction of Cu(II) reduced was roughly estimated by analyses of the UV/vis plots relative to the area in the spectra associated with Cu(I) and Cu(II) species.[5] In a comparison of the conditions in which the AIBN concentration was varied and the regeneration time was kept constant at 15 min, the highest increase in Cu(I) concentration occurred when 2 equivalents of AIBN was used (∼ 54% reduced). Fig. 10 shows the UV/vis spectra for each regenerated catalyst when the AIBN concentration was varied. The polymerization rates correlated with the estimated percentage reduced values determined by UV/vis, as the highest conversion observed in polymerizations with the regenerated catalysts after 1 and 24 h was also for 2 equivalents of AIBN. Next the AIBN concentration was held constant and the regeneration time was varied from 15 to 90 min (1:1 AIBN/Cu). Fig. 11 shows the UV/vis spectra for each regenerated catalyst when the regeneration time was varied. The absorbance intensity of the Cu(I) transition was highest at 60 min and decreased to a lower intensity after 90 min (∼ 61 and ∼ 42% reduced, respectively). The highest conversion in polymerizations with regenerated catalysts was achieved after 24 h with the catalyst regenerated under the following conditions: [AIBN]/[Cu] = 2 for 15 min. Complete reduction of the immobilized Cu(II) back to Cu(I) was never achieved, as there always was a remaining Cu(II) transition above 600 nm. This is not altogether a problem, however, as the initial presence of Cu(II) has been shown to help better control the polymerization at ear-

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[5] Although our UV/vis spectra are not strictly quantitative, it was possible to estimate the amount of Cu(II) that was reduced back to Cu(I) via analysis of the spectra after normalization of the heights of the high-energy peaks associated with the Bpy ligand. Note: This analysis is semiquantitative and is primarily carried out to establish a trend, not the exact amounts of Cu(I) and Cu(II) on the surface. Quantitative analysis of paramagnetic Cu(II) species on the catalyst via SQUID magnetometry proved troublesome with our low copper loadings. X-ray photoelectron spectroscopy was ruled out as a quantification method, as Cu(II) species on the catalyst surface are reduced in situ to Cu(I) during the measurement [64,65].

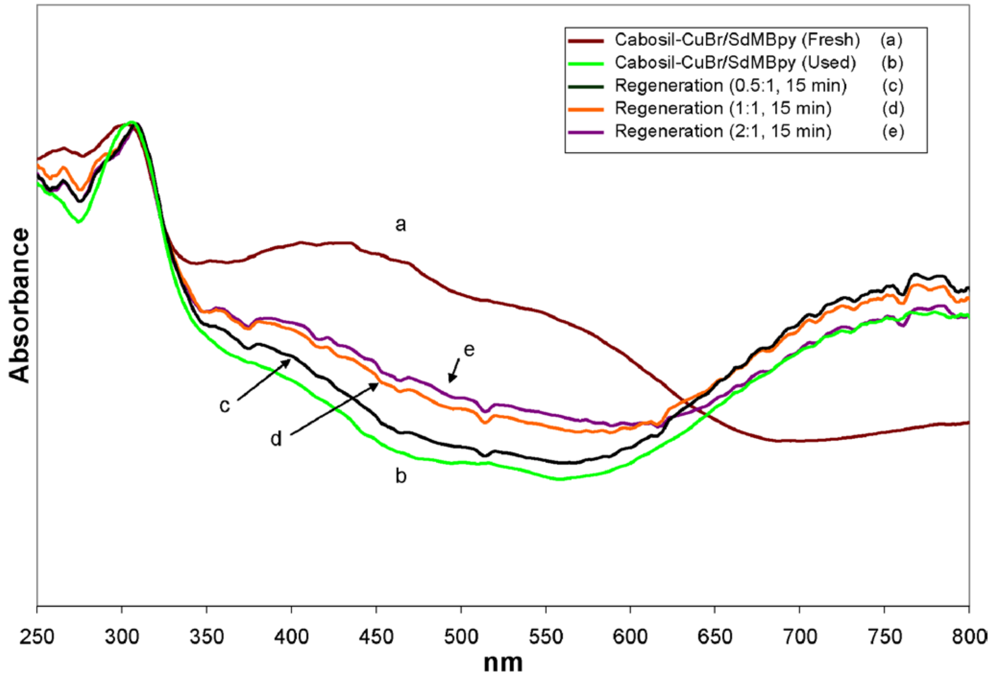

Fig. 10. UV/vis comparison (vs PTFE) of regenerated catalyst of varying treatments of AIBN concentrations. Regeneration conditions: [AIBN]/[Cu] = 0.5, 1, or 2 in 4 ml of toluene at 90 °C for 15 min. Polymerization conditions: [MMA]/[Cu]/[BPN] = 100/1/1 in 25% by v/v MMA in toluene at 90 °C.

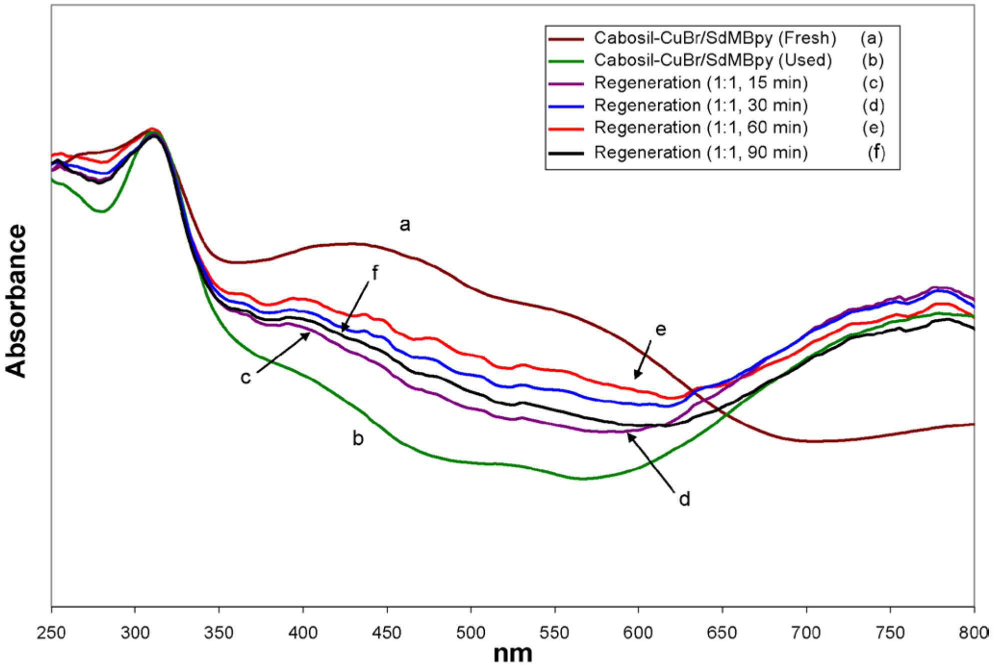

Fig. 11. UV/vis comparison (vs PTFE) of regenerated catalyst of varying treatment times. Regeneration conditions: [AIBN]/[Cu] = 1 in 4 ml of toluene at 90 °C for 15, 30, 60, and 90 min. Polymerization conditions: [MMA]/[Cu]/[BPN] = 100/1/1 in 25% by v/v MMA in toluene at 90 °C.

lier reaction times [40]. Although this UV/vis study is only semiquantitative, its utility is clear, based on an analysis of Fig. 12. The data in Fig. 12 indicate that the fraction of Cu(I) that was reduced to Cu(II) as estimated from the spectra correlates well with the conversion of monomer after 1 h. Thus, this analysis can suggest conditions that would be best for catalyst regeneration if high rates are desired, with the suggested conditions being a 1:1 AIBN/Cu ratio for 60 min.

3.5. *Nature of the catalyst active site*

There has been some speculation on the nature and location of the catalyst active site in the literature because

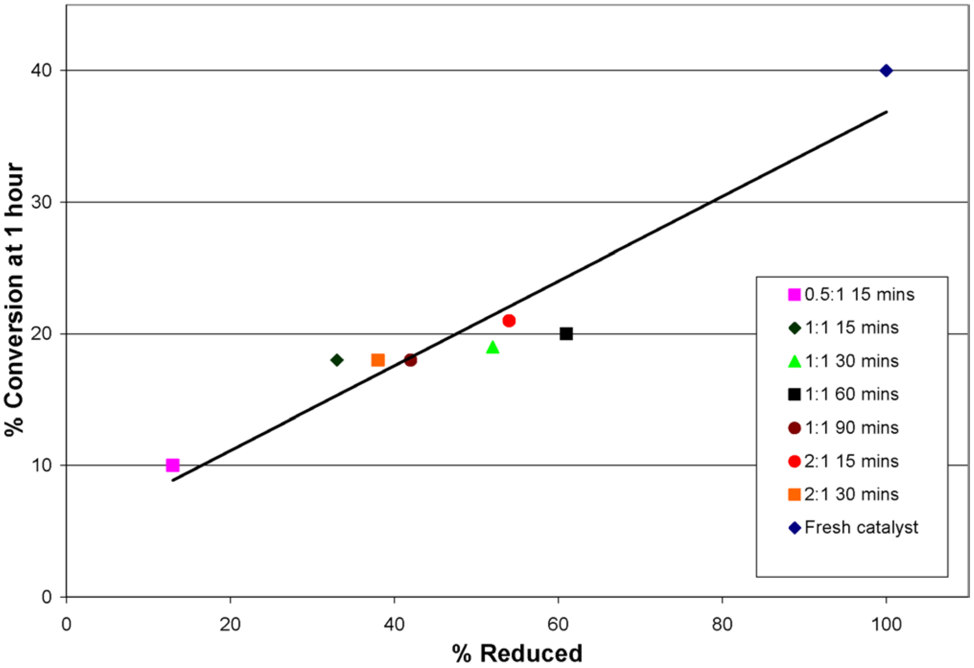

Fig. 12. % Conversion at 1 h vs % reduced plot for regenerated catalysts. Polymerization conditions: [MMA]/[Cu]/[BPN] = 100/1/1 in 25% by v/v MMA in toluene at 90 °C for 24 h.

the supported catalyst loses significant activity after recycling and in some cases the ability to mediate a controlled polymerization [17,32,40,41,53–55]. As noted earlier, essentially two potential reasons have been discussed in the literature to explain this loss of activity: (1) accumulation of Cu(II) on the catalyst surface after the polymerization and (2) a loss of immobilized catalyst due to leaching. In Matyjaszewski's polymer-immobilized CuBr/dMBpy system (PS8-dMBpy/CuBr), the catalyst could not effectively mediate a controlled polymerization as an all-heterogeneous system [32,48]. However, when the soluble $CuBr_2$/Me_6TREN deactivator complex was introduced, even in very small amounts (0.3 mol% deactivator to immobilized copper), the polymerization became controlled. Matyjaszewski surmised that the single-component, all-CuBr/dMBpy-immobilized catalyst could not mediate a controlled polymerization because of poor mass transfer around the support that led to a slow deactivation rate for the growing polymer chains. In support of this hypothesis, Brittain showed that a less cross-linked polymer support was better for the solubility of catalyst particle [45]. When Matyjaszewski's immobilized/soluble hybrid catalyst system was used, the effective shuttling of the halogen from the polymer-immobilized **Br**-CuBr/dMBpy (Cu(II)) complex to the growing polymer chain radical ($\mathbf{P}_n^{\bullet}$) was accomplished (deactivating the polymer chain, $\mathbf{P}_n$**–Br**).[6] The importance of the soluble deactivator suggests that polymerization control occurs both in the liquid phase and on the catalyst surface (polymerization is not entirely heterogeneous). After catalyst regeneration with Cu(0), the catalyst activity and ability to control the polymerization decreased (conversion decreased, PDI increased: first = 95%, 1.34; second = 90%, 1.41; third = 70%, 1.58) [32]. A reduction of copper and ligand content per gram of catalyst was also reported, but the "loss" was likely due to growth of grafted polymer on the support and entangled polymer around the support adding to the overall weight of the catalyst. Accumulation of Cu(II) is a more likely cause for the loss in activity. From our results on catalyst regeneration and UV/vis characterization, it is possible that with most regeneration procedures, only some of the Cu(II) species are reduced back to Cu(I). Therefore, the presence of Cu(II) will decrease the polymerization rate. Thus, with covalently tethered catalyst systems, it appears that residual Cu(II), even after regeneration, is at least partly responsible for reduced polymerization rates of the catalysts upon recycling. Copper loss appears to be less of an issue.

Zhu and co-workers recently reported ongoing work discussing the potential location of the catalytic sites for immobilized ATRP catalyst (in solution as soluble species or on the support), particularly the location of the catalytic site for physisorbed hexamethyltriethyltetraamine (HMTETA)/CuBr on silica [55]. Zhu found that after removal of the solid catalyst by hot filtration, reaction in the solid-free polymerization solution continued from 20 to 90% conversion, and effective control was maintained without the solid catalyst. This indicates that the location of the important catalytic sites (and therefore the location of the polymerization activation and deactivation process) was in the homogeneous liquid phase. Zhu indicates that the physisorbed HMTETA/CuBr on silica acts as a catalyst

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[6] For a complete discussion of mass transport and deactivation processes in ATRP, please refer to work reported by Matyjaszewski and co-workers [31,32] and a review written by Shen [17].

reservoir, partitioning significant quantities of complex into solution, and the homogeneous complex mediates the polymerization. Unfortunately, analysis for copper in the final polymerization solution was not performed to quantify the extent of leaching. Even if a relatively small amount of catalyst leached from the surface in this case, it still may be possible to continue to polymerize effectively. This is due to the nature of the catalyst ligand. Copper complexes based on multidentate amine ligands, like HMTETA, are known to possess high transfer rates and good control, even at lower catalyst concentrations [18–20]. The fact that the polymerization continued in Zhu's case is therefore not surprising. Hence, generalizations about the location of the catalyst active site in other systems cannot be made based on results for HMTETA/CuBr/Silica physisorbed catalysts.

We recently reported two silica-immobilized ATRP catalyst systems in our laboratory [39–41]. The first, a CuBr/2-pyridylmethanimine (CuBr/PMI) complex, became immobilized on various silica supports. We found the catalyst allowed for high conversions and moderate control (PDI ∼ 1.50) for the first use, and it still maintained very good conversions and even better control (PDI ∼ 1.25) without catalyst regeneration after recycling. The fact that the catalyst did not need to be regenerated for further recycling suggests that a higher concentration of immobilized Cu(I) was maintained after the polymerization. Klumperman et al. showed that PMI ligands have a tendency to stabilize the Cu(I) oxidation state and Bpy derivatives stabilize Cu(II) oxidation states [63]. This explains the observation that CuBr/Bpy-immobilized catalysts must be regenerated and CuBr/PMI catalysts do not need to be for effective recycling. In the CuBr/PMI case, even though we found that ligand and/or copper leached from the catalyst support during each catalyst use (in each of the six recycles), sufficient activity was maintained to reach high conversions and produce polymers with narrow polydispersities. Since substantial leaching was evident for the CuBr/PMI system, in this work we performed a leaching test to determine whether soluble species could be responsible for all of the activation and deactivation steps in the ATRP cycle. An air-free swivel frit was used to filter the catalyst particle from the hot polymerization solution under a rigorously dioxygen-free argon atmosphere [57]. After the catalyst was removed, the monomer conversion increased only slightly from 8 to 16%, indicating that the solid represents an important component of the catalyst system. The resulting final polymer had a very broad molecular weight distribution (> 2) that was considerably higher than that observed when the solid catalyst was left in the polymerization solution (as low as 1.20) [40]. The low conversions and increased PDI suggest that the immobilized PMI catalyst is necessary to maintain activity and control of the polymerization.

Unlike Matyjaszewski's immobilized/soluble hybrid catalyst system, our silica-immobilized CuBr/SdMBpy catalyst could effectively control the polymerization of MMA without the addition of a soluble deactivator, although with lower conversions reported. This catalyst system was better than our reported CuBr/PMI system because the Bpy ligand on the surface was found to be stable, as indicated by the colorless solution of the recovered polymerization liquid, the low PDIs achieved without a catalyst pretreatment, and trace or zero copper leaching. However, since trace amounts of leached copper were found in the polymer [41], one could not rule out the possibility that the leached copper species were critically important in facilitating the deactivation processes in the liquid phase. Matyjaszewski showed the addition of soluble $CuBr_2$/dMBpy as a deactivator was ineffective compared with $CuBr_2/Me_6$TREN; therefore it is unlikely leached $CuBr_2$/Bpy species are critical in the deactivation process for our immobilized catalyst system [32]. Nonetheless, to determine whether leached species are important, a leaching test was performed for Cabosil-CuBr/SdMBpy. The results of the leaching test are summarized in Table 4. The polymerization mixture was charged in the air-free swivel frit [57], and after the catalyst particles were removed the polymerization only continued from 16 to 26% and the PDI increased from 1.60 to 1.91. The reaction rate decreased dramatically and the molecular weight distribution broadened, indicating that the immobilized catalytic species are critical for maintaining activity and achieving good polymerization control. Indeed, copper microanalyses of the recovered polymerization solution showed that no detectable leaching had occurred (< 1 ppm copper).

Finally, the leaching test was also performed on the physisorbed Cabosil(CuBr/dMBpy) catalyst. In this case, the conversion increase was low (17–23%), but the PDI decreased from 1.38 to 1.31. Observations after the polymerization showed leached CuBr/dMBpy accumulated on the flask wall, indicating that substantial leaching occurred. Thus, in this physisorbed system, leached metal species are present in high enough concentration to control the polymerization, although polymerization rates in the presence of only soluble copper were very low.

Thus, control in the tethered Cabosil-CuBr/dMBpy system is derived from reactions associated with immobilized metal complexes. In the tethered CuBr-PMI systems previously reported [40], leached species exist in solution, but these are not present in high enough concentration to mediate a controlled polymerization; thus, tethered active species are also important in this system. In the physisorbed Cabosil(CuBr/dMBpy) system, substantial leached species are

Table 4
Results of leaching experiments[a]

Catalyst	Time (min)	% Conversion	$M_{n,\mathrm{Ex}}$	PDI	R_{Cu}
Cabosil-CuBr/SdMBpy	15	16	3100	1.60	–
Cabosil-CuBr/SdMBpy	1440	26	4200	1.91	< 1
Cabosil(CuBr/dMBpy)	15	17	4900	1.38	–
Cabosil(CuBr/dMBpy)	1440	23	5200	1.31	12

[a] Polymerization conditions: [MMA]/[Cu]/[BPN] = 100/1/1 in 25% MMA in toluene at 90 °C.

observed, and these are capable of mediating a controlled polymerization, although with extremely low rates. These results imply that the physisorbed $CuBr_n$/Bpy species may not play a key role in controlling the reaction because of poor local solvation.

4. Summary

Immobilized Cu(I) complexes represent a rare example of a recoverable and recyclable polymerization catalyst. Here CuBr/dMBpy complexes were immobilized via a covalent tether and via physisorption on nonporous Cab-O-Sil silica supports. The catalysts mediated the controlled polymerization of MMA for low target molecular weights, with PDIs nearly approaching that of the homogeneous catalyst. Both catalysts allowed for recovery of most of the CuBr species, although the physisorbed catalyst leached significant amounts of soluble copper species into solution. In contrast, the tethered system resulted in no detectable leached copper species.

A unique catalyst regeneration method we previously reported was applied to both types of catalyst. Treatment with AIBN effectively reduced some of the copper species from Cu(II) to Cu(I) in the tethered system, with the regeneration process easily monitored by UV/vis spectroscopic analysis of the catalysts. In contrast, the physisorbed catalyst could not be regenerated under the conditions of this study. The fraction of Cu(II) reduced back to Cu(I) as estimated by UV/vis spectroscopy correlated well with the initial polymerization performance of the regenerated systems.

Leaching studies indicate that the soluble copper released from the physisorbed system is capable of mediating a controlled polymerization, even in the absence of the solid catalyst, although reaction rates were low. In contrast, the tethered system did not leach measurable amounts of copper and the silica-supported CuBr species were responsible for mediating a controlled polymerization.

Finally, a one-pot polymerization technique, in which bare silica was added to a homogeneous polymerization, could be used to trap most of the homogeneous CuBr/dMBpy catalyst, allowing recovery of most of the copper species from solution. The one-pot system behaved similarly to the physisorbed catalyst and overall was inferior to the tethered system.

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