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Removal of Copper-Based Catalyst in Atom Transfer Radical Polymerization Using Ion Exchange Resins

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Introduction

Atom transfer radical polymerization (ATRP) is a method for a controlled/"living" radical polymerization that is catalyzed by transition-metal complexes.[1−3] The main advantage of ATRP over other radical processes lies in the fact that it provides a very efficient method for the synthesis of various polymers with well-defined composition, functionality, and architecture.[4,5] However, a current drawback is the efficient removal and recycling of the catalyst. At the present, removal has been generally achieved by using alumina columns, precipitation of polymer to a nonsolvent, or precipitation of the Cu complex with NaOH or Na_2S. Although these methods are efficient, passing the viscous polymer mixture through a column of alumina is difficult on relatively large-scale reactions (>10 g). Additionally, repeated precipitations require the use of significant amounts of solvent. Also, the ATRP catalyst can be potentially recycled when immobilized on a solid support.[6,7] Herein, we report the removal of an ATRP catalyst by use of an ion exchange resin.

Ion exchange properties of various materials, such as clay minerals and polyelectrolytes, have long been known.[8] When these materials are brought into contact with an ionic solution, an equilibrium is established in which ions from the solid support or exchanger are replaced with ions from the solution; exchange can be cationic or anionic. This equilibrium has been extensively studied because of its importance in separation science,[9−13] particularly in the removal of heavy metals from water. In this paper, we report a study on the removal of ATRP active catalysts, CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (CuBr/PMDETA),[14] $CuBr_2$/PMDETA, CuBr/(2,2′-bipyridine)$_2$ (CuBr/2bpy),[1] and CuBr/tris(2-(dimethylamino)ethyl)amine[15,16] (CuBr/Me_6TREN), using ion exchange resins with acidic counterions.

Results and Discussion

When a solution of cupric or cuprous bromide, complexed by bidentate (bpy), tridentate (PMDETA), or tetradentate (Me_6TREN) nitrogen-based ligands was brought into contact with acidic ion exchange resins, it slowly decolorized and became acidic. After filtration of the resins, addition of CuBr or $CuBr_2$ to the acidic solution did not produce any color, which indicated the absence of the ligand. For Cu(I) complexes, a cationic ion exchange equilibrium (eq 1) is established, in which the cationic Cu(I) complex exchanges with protons that are accessible on the ion exchange resins:

$$\mathrm{R{\sim\!\sim}SO_3H + CuBr/[ligand] \rightleftharpoons R{\sim\!\sim}SO_3Cu[ligand] + H^+ + Br^-} \quad (1)$$

ligand = bpy, PMDETA, Me_6TREN;
R = cross-linked polystyrene

Additionally, for Cu(II) complexes, the amount of Br^- released is dependent on the ligand used.

The position of the equilibrium is dependent on the polarity of the solvent, ionic character of the exchanging complex, pH of the solution, the degree of cross-linking, acidic strength, and size of the ion exchange resins. These factors are very important when considering maximizing removing capacity of the ion exchange resins toward Cu(I) and Cu(II) complexes. In particular, pH of the solution plays a very important role. At pH values lower than 3, protonation of ligand can occur, causing decomposition of the copper complex.

Most commercially available cationic ion exchange resins consist of sulfonated cross-linked polystyrene−divinylbenzene beads. Cations are typically H^+, Na^+, or a mixture of the two, and the anionic counterion is a sulfonyl group. The exchange of ATRP active copper complexes with Na^+ is much slower than with H^+, presumably due to the difference in cation size. Na^+ sites on the ion exchange resins can be converted to H^+ sites by treatment with strong mineral acid such as HNO_3 or HCl. Effective removal of the Cu(I) and Cu(II) ATRP active complexes can be achieved using a large excess of ion exchange resins, i.e., excess of accessible H^+ sites. In that case, the above equilibrium (eq 1) shifts to the right, favoring the complete removal of the copper complex from the solution. Because of the colored nature of the Cu(I) and Cu(II) complexes employed in ATRP, UV−vis spectrometry was used to monitor their concentration in solution.

Figure 1 shows the effect of the solvent on the removal of CuBr/PMDETA using Dowex MSC-1 macroporous ion exchange resins. From the figure, it is apparent that solvent had little effect on the rate of removal of the Cu(I) complex from either methyl acrylate, methyl acrylate/chlorobenzene mixtures, or ethanol. In fact, using 20.0 mL of 1.2×10^{-2} mol L^{-1} of CuBr/PMDETA (2.420×10^{-4} mol) and 0.815 g of resins, it took approximately 60 min to remove more than 95% of the complex from the solution. Part of the solvent independence on the rate of removal lies in the fact that excess of H^+ sites on the resins were used (4.075×10^{-3} mol, 17 equiv) relative to the amount of CuBr/PMDETA in solution, which shifted the equilibrium (eq 1) to the right. The rate of removal of CuBr/PMDETA became solvent dependent, and increased as solvent polarity increased, when the amount of H^+ relative to the CuBr/PMDETA was reduced below 5 equiv.

In Figure 2 is shown the temperature effect on the removal of CuBr/PMDETA from a 50 vol % methyl acrylate/50 vol % chlorobenzene solution. The rate of removal increased with temperature. At temperatures above 50 °C it took approximately 20 min to remove more than 95% of CuBr/PMDETA from the solution. Similar results were also obtained using methyl acrylate and acetone or THF mixtures.

Figure 3 shows the effect of the solvent on the removal of $CuBr_2$/PMDETA using Dowex MSC-1 ion exchange

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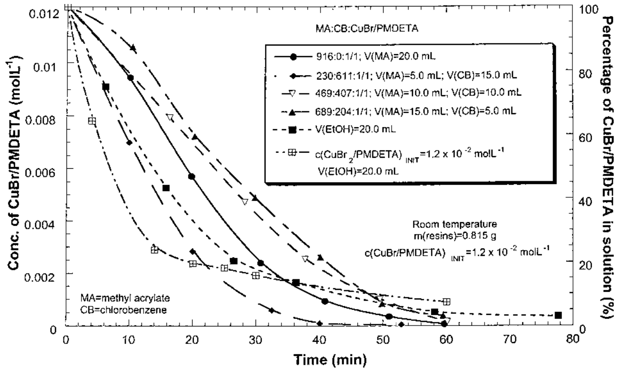

Figure 1. Solvent effect on the removal of CuBr/PMDETA using Dowex MSC-1 ion exchange resins.

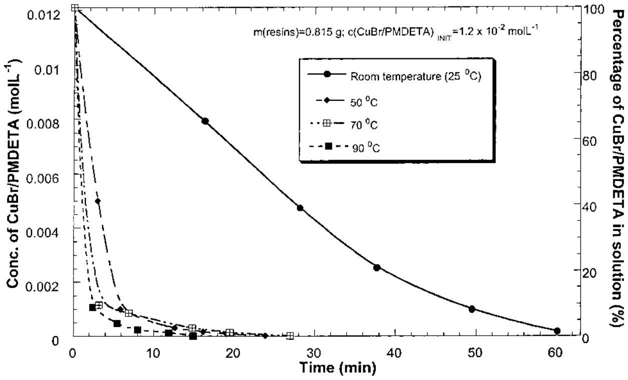

Figure 2. Temperature effect on the removal of CuBr/PMDETA in 50% methyl acrylate/50% chlorobenzene solution using Dowex MSC-1 ion exchange resins.

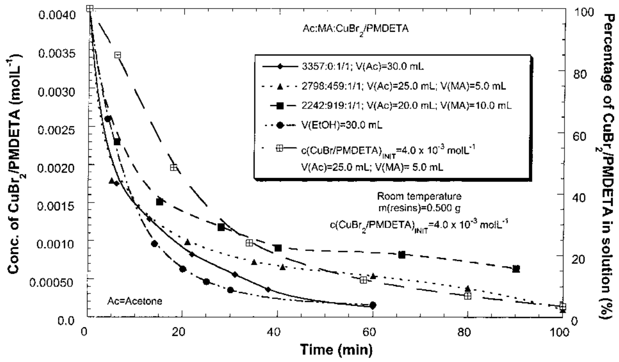

Figure 3. Solvent effect on the removal of CuBr$_2$/PMDETA using Dowex MSC-1 ion exchange resins.

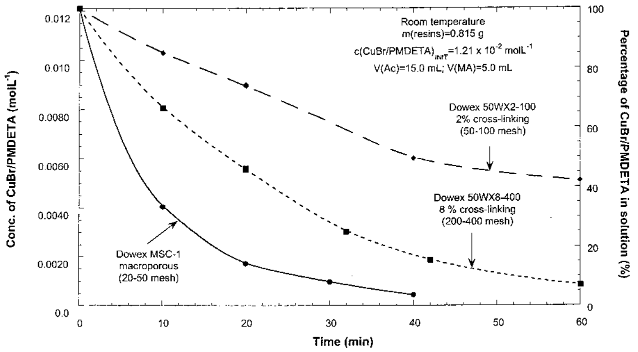

Figure 4. Removal of CuBr/PMDETA using different types of ion exchange resins.

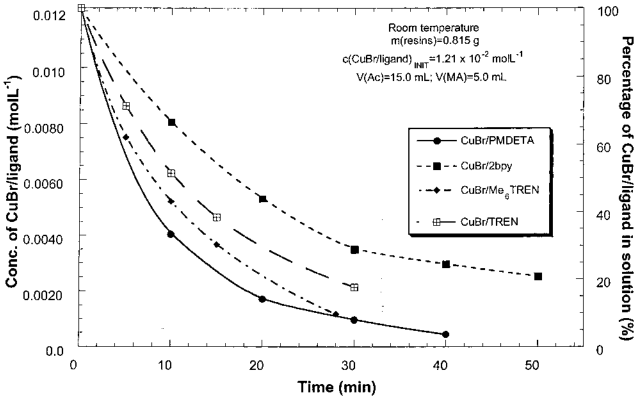

Figure 5. Ligand effect on the removal of CuBr complex using Dowex MSC-1 ion exchange resins.

resins. Studies were performed at much lower concentrations when compared to CuBr/PMDETA due to the limited solubility of the Cu(II) complex. The rate of the removal was dependent on the polarity of the solvent and generally increased as the solvent polarity increased. When comparing Cu(I) and Cu(II) complexes with PMDETA under the same experimental conditions (Figures 1 and 3, boxed +), it can be seen that the rates of removal are comparable.

The effect on the removal of CuBr/PMDETA using different types of ion exchange resins is presented in Figure 4. The exchange was the fastest with macroporous resins and also depended on the degree of cross-linking of polystyrene and bead size. For the same bead size, the rate of removal of CuBr/PMDETA or CuBr$_2$/PMDETA decreased as the degree of cross-linking increased. Presumably, this was due to swelling of the resin network, allowing for the copper salts to gain access to the sulfonated sites in the interior of the beads.

The rate of catalyst removal from an acetone/methyl acrylate mixture was found to be dependent upon the ligands used to complex the catalyst (Figure 5). It was found that the removal was fastest with CuBr/PMDETA and slowest with CuBr/2bpy. The ionic character of these complexes and their structures in solution are not precisely known, and hence no definitive conclusions can be drawn as to why they show different behavior when exchanging with H$^+$ sites on the ion exchange resins. For Cu(II) complexes we also found that the amount of Br$^-$ released to the solution depended on the ligand used. This effect was presumably due to the differences in the overall charge of the Cu(II) center, which depending on the ligand used can be +1 or +2.

Copper complexes can be also removed from the heterogeneous systems such as waterborne emulsions or miniemulsions.[17] The mint color of emulsions due to the Cu(II) species quickly faded to a milk white color in the presence of ion exchange resins without causing any significant coagulation of the polymer latex.

Conclusion

In this paper we have demonstrated an efficient method for the removal of Cu(I) and Cu(II) complexes in ATRP using ion exchange resins with acidic groups. In our laboratories, we have used these resins to remove copper catalysts from bulk (monomer as solvent), polymerization, and organic solutions. It was found that the rate of removal of copper complexes was dependent on the solvent polarity, temperature, type of ion exchange resins used, and ionic character and size of the copper complex. In the limit of using a large excess of H^+ sites on the resins, Cu(I) and Cu(II) complexes can be removed from reaction mixtures relatively fast. It is envisioned that the copper complexes can be recycled by the use of ion exchange resins as well, and this area is currently being explored.

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