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ATRP catalyst removal and ligand recycling using carbon dioxide switchable materials

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PURPOSE OF THE ABSTRACT

Atom transfer radical polymerization (ATRP) is an important polymerization technique for the synthesis of novel polymeric materials, possessing the ability to give tailored polymer structures with predictable molecular weight, low molar mass dispersity and high chain end functionality. While the significance and value of ATRP as a synthetic tool is widely recognized, the necessity of using transition metal complexes has limited its use thus far on an industrial scale. The material costs of the metal complexes (primarily the ligand cost), toxicity of the compounds involved, and post-polymerization purification costs associated with metal complex removal present serious challenges to the commercial adoption of ATRP. Reducing or removing copper from the final polymer is a primary challenge for ATRP. Copper can be harmful for human health and the environment. When copper collects in soil, it strongly attaches to organic matter and minerals. Copper, like other metals, does not break down in the environment and as a result it can accumulate in living beings when it is present in soils and waters. Given the known effects of copper on health and the environment, the concentration of copper should be reduced after an ATRP reaction, preferably to <~10 ppm. Several approaches for removing catalyst have been developed, often relying on an additional purification step which generates additional waste and increases the cost of polymers prepared by ATRP. An alternative strategy is to reduce the catalyst concentration used in the polymerization, for example ARGET (Activators Regenerated by Electron Transfer) ATRP [1] and e-ATRP (electrochemically mediated ATRP).[2] Other recent work has also focused on reducing copper levels using highly active catalyst,[3] ultrasonication,[4] ion-pair catalysis in miniemulsions[5] and electrolysis with emulsion polymerization.[6] The ligands introduced with the transition metal may also have toxicity concerns. Most are N-containing compounds, for example the widely used Me6TREN (tris[2-(dimethylamino)ethyl]amine, and are also expensive. Thus, not only is the removal of copper of interest, but an efficient route to recycling the ligand would also be desirable. Me6TREN, being a trialkylamine, is also CO2 switchable, which prompted us to consider using CO2 switchable technology to recycle the ligands after an ATRP.
We have designed three approaches to remove copper catalyst and recycle the ligands after atom transfer radical polymerizations, all based on using materials whose properties can be switched using only CO2 and any nonacidic gas (e.g. air, nitrogen, argon) as triggers.[7] The first approach involves use of a CO2-switchable solvent (Cy2NMe, N,N-dicyclohexylmethylamine) as the medium for the ATRP reaction. After adding water to the polymerized reaction mixture and sparging with CO2, the polymer precipitates while the copper salt remains in the solvent. The second approach involves using a conventional ATRP solvent such as toluene to conduct the polymerization. Following polymerization, addition of water and CO2 sparging results in the ligand (Me6TREN) and copper salt transferring into the aqueous phase, while the polymer remains in the organic phase. Finally we demonstrate the effectiveness of the approach in ARGET ATRP using less ligand and copper salt. Residual copper in the polymer was <30 ppb using the switchable solvent and <15 ppb in toluene, while residual nitrogen was <90 ppm using the switchable solvent and <35 ppb in toluene. The feasibility of recovering and re-using the ligand for subsequent polymerizations is also established.

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

ATRP (Atom Transfer Radical Polymerization) | Carbon dioxide switchable | copper removal | ligand recycle

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