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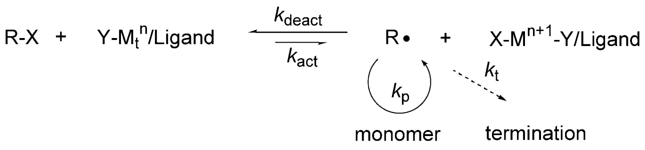
alysts that operate by a coordination-insertion mechanism. Indeed, with catalysts of this type, the final reaction quench, whereby the polymer chains are cleaved from the catalyst, can become quite problematic.

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 $\mathrm{RuCl_2(PPH_3)_3}$ 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 ($\mathrm{M_t}^{n}$–Y/ligand), forming an organic radical ($\mathrm{P}_n^{\bullet}$) and a higher oxidation state transition-metal complex (X–$\mathrm{M_t}^{n+1}$–Y/ligand), shown in Scheme 1. The equilibrium between the $\mathrm{M_t}^{n}$–Y/ligand and X–$\mathrm{M_t}^{n+1}$–Y/ligand species is strongly shifted toward $\mathrm{M_t}^{n}$–Y/ligand complex ($k_{\mathrm{deact}} \gg k_{\mathrm{act}}$); 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.