Polymer 135 (2018) 25–29

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Phase-selectively soluble, polymer-supported salen catalyst prepared using atom transfer radical polymerization (ATRP)

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ARTICLE INFO

Article history:
Received 10 October 2017
Received in revised form
28 November 2017
Accepted 1 December 2017
Available online 5 December 2017

Keywords:
ATRP
Salen
Green chemistry

ABSTRACT

This communication describes the use of atom transfer radical polymerization (ATRP) to prepare a new phase-selectively soluble, polymer-supported Cr^{III} salen catalyst. This catalyst was used to facilitate the asymmetric ring opening of cyclohexene oxide and could be recovered and reused up to 5 times using liquid/liquid separation techniques.

1. Introduction

Ever since the groundbreaking work of Merrifield [1] and Letsinger [2], the chemical community has recognized the broad synthetic utility of polymers and oligomers. Other than serving as handles for peptide synthesis, such materials have been used to thermally regulate chemical reactions [3,4], impart high levels stereoselectivity [5], serve as phase partitions [6], and even act as reaction media themselves [7,8]. However, one of their most widely reported uses is as supports for reagents, ligands, and catalysts [9,10]. In this regard, both insoluble and soluble polymers have been used as heterogeneous and homogeneous catalytic systems, respectively.

Although insoluble supports offer the advantage of easy catalyst recovery, they can often have reduced activity/selectivity when compared to their soluble counterparts. For this reason, much work has gone into the development of soluble polymer supports that can be recovered and reused under either solid/liquid [9–13] or liquid/liquid [9,10,13–16] strategies. The latter of which is arguably superior considering that the former (either in the form of solvent precipitations or thermomorphic systems) often requires excessive amounts of solvent or high temperatures diminishing its "greenness".

Several liquid/liquid separation strategies have been developed and most rely on the use of a nonpolar, phase-selective polymer supports that can be separated as a solution opposite of the product. Both polyacrylamide [17,18] and polystyrene [9,19–21] derived supports have been extensively studied. Most of these examples relied on conventional free radical polymerizations for their preparation. This, however, does not allow for much control over polymer molecular weight or end group identity. On the other hand, controlled radical polymerization [22] (CRP) techniques, as the name suggests, can offer high levels of control. Although CRP techniques (such as reversible addition-fragmentation chain-transfer (RAFT)) have been used to prepare polymer-supported catalysts, these have mostly been focused on polymeric "nanoreactors" [23]. To our knowledge, there exists only one report utilizing a CRP technique (in this case, RAFT) to prepare nonpolar, phase-selective catalyst supports [20].

Another CRP technique, atom transfer radical polymerization (ATRP), has also been used to prepare polymer-supported catalysts [24–26]. However, most of these examples describe the preparation of insoluble polymer supports; reports of the use of ATRP to synthesize soluble, polymer-supported catalysts are sparse [27]. This is somewhat surprising, considering functional α-bromo esters (common ATRP initiators) can be prepared using syntheses no more sophisticated than what is encountered in sophomore organic chemistry courses. This pre-polymerization functionalization can allow for the incorporation of almost any functionality to the polymer α-terminus (Scheme 1) [28–31]. However, this method

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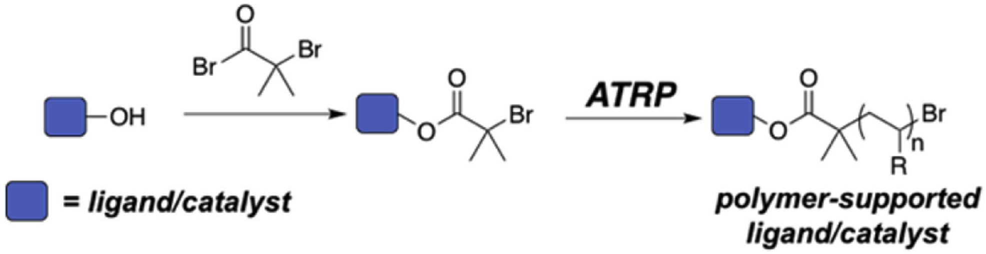
https://doi.org/10.1016/j.polymer.2017.12.001
0032-3861/© 2017 Published by Elsevier Ltd.



Scheme 1. General route toward ATRP-based polymer-supported catalysts.

has only rarely been used for the preparation of soluble polymer-supported ligands/catalysts [32].

Of all catalysts (supported or not) described in the literature, salen ligands and their metal complexes have been among the most widely used and can be used to catalyze a plethora of organic transformations, with high levels of selectivity [33]. It is this property that has placed salens in a class of "privileged ligands" [34]. Furthermore, a variety of salen ligands can be easily prepared using standard organic transformations. Because of this, we have become interested in preparing a new class of polymer-supported salen through the use of functionalized ATRP initiators.

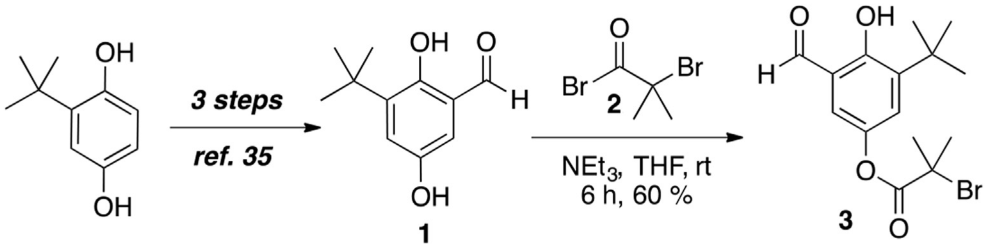
2. Results and discussion

The inspiration for our initial strategy was derived from a previous example [32] in which ATRP was used as a method to directly "grow" polymer chains from pre-functionalized ligands or catalysts. In order to realize this goal, the preparation of a salen ligand, decorated with α-bromo ester groups on either side would need to be prepared. Our synthesis commenced with the preparation of salicylaldehyde-functionalized ATRP initiator **3** from the esterification of **1** (which can be prepared in 3 steps from *tert*-butylhydroquinone [35]) with α-bromoisobutyryl bromide **2** in the presence of triethylamine (Scheme 2). After 6 h, the formation of **3** was confirmed by ^{1}H NMR which revealed a shift of the signals (corresponding to **1**) at 7.11 and 6.85 ppm (Ar-*H*) to 7.25 and 7.24 ppm and the appearance of a singlet at 2.13 ppm (Ar-C(O)CBr(CH_3))$_2$ (Supporting Information, Fig. S1). FT-IR showed a stretch at 1749 cm^{-1}. **3** was purified by column chromatography and isolated in 60% yield.

With the salicylaldehyde derivative **3** in hand, the next step in our plan involved the preparation of a *dimeric* salen-based ATRP initiator. We chose this route as it has been shown that dimeric salen catalysts can show improved reactivity and selectivity over their *mono* salen counterparts [36]. To accomplish this, we first subjected **4** (prepared from literature protocols [36]) to a condensation reaction with mono-HCl salt **5** [37]. Although the intermediate imine was not isolated, its formation was visually confirmed by the appearance of a bright yellow color. Synthesis of dimeric salen **6** could be accomplished by the subsequent addition of **3** and triethylamine (Scheme 3). **6** was isolated after column chromatographic purification in 75%. The formation of dimeric salen **6** was confirmed by the disappearance of signals at 11.75 and 9.87 ppm (Ar-C(O)*H* and Ar-O*H*) and the appearance of signals at 8.27 and 8.23 ppm (-NC*H*-Ar) as well as a shift of the signals associated with the aromatic protons to 6.99, 6.94, 6.83, and 6.78 ppm (Supporting Information, Fig. S2).

Upon isolation of our functionalized ATRP initiator **6**, the next step was to prepare a new polymer-supported salen ligand by "growing" poly(4-*tert*-butylstryrene) chains directly from the salen moiety. Our choice of monomer was deliberate, as poly(4-*tert*-butylstryrene) supports have been studied and their phase selectivity is well documented [19]. This involved subjecting **6** to ATRP in neat 4-*tert*-butylstyrene in the presence of CuBr and 2,2-bipyridine (Bpy) ([M]:[**6**]:[Bpy]:[Cu] = 50:1:1:1) (Scheme 4). ^{1}H NMR unfortunately revealed very little polymer formation (ca. 6% yield). We reasoned that this may due to chelation of the Cu catalyst by the salen species.

To overcome this setback, we devised an alternative synthetic strategy. This plan involved a post-polymerization modification that would allow for the installation the salen moiety by coupling two polymer chains grown from salicylaldehyde **3**. This is a method similar to what has been used for the preparation of polyisobutylene (PIB) and polyethylene (PE)-supports [15]. To accomplish this, we first subjected **3** to ATRP in neat 4-*tert*-butylstyrene in the presence of CuBr and Bpy ([M]:[**3**]:[Bpy]:[Cu] = 20:1:1:1). After 4 h the reaction mixture had become significantly more viscous. This mixture was diluted with methylenechloride and polymer **7** was isolated via solvent precipitation into methanol as a white powder in 65% yield. Confirmation of this was ascertained by ^{1}H NMR (Supporting Information, Fig. S3), which showed the appearance of broad signals in the aromatic region (7.35–6.07 ppm) and significantly broadened peaks at 11.75 and 9.87 ppm (α-end group) as well as the appearance of a broad signal at 4.86–4.40 ppm (ω-end group). End group analysis provided a number-average molecular weight (M_n) of app. 5600 Da. Also, integration of the signals at 11.75 and 9.87 ppm (α-end group) and 4.86–4.40 ppm (ω-end group) provided a ratio of 1:1:1, indicative of a relatively well-controlled polymerization. Furthermore, GPC analysis (Supporting Information, Fig. S7) showed **7** to have M_n of



Scheme 2. Preparation of **3**.