Polymerization of Allenes by Using an Iron(II) β-Diketiminate Pre-Catalyst to Generate High $M_n$ Polymers

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Abstract: Herein, we report an iron(II)-catalyzed polymerization of arylallenes. This reaction proceeds rapidly at room temperature in the presence of a hydride co-catalyst to generate polymers of weight up to $M_n = 189,000$ Da. We have determined the polymer structure and chain length for a range of monomers through a combination of NMR, differential scanning calorimetry (DSC) and gel permeation chromatography (GPC) analysis. Mechanistically, we postulate that the co-catalyst does not react to form an iron(II) hydride in situ, but instead the chain growth is proceeding via a reactive Fe(III) species. We have also performed kinetic and isotopic experiments to further our understanding. The formation of a highly unusual 1,3-substituted cyclobutane side-product is also investigated.

Introduction

Allenes are emerging as a powerful and unique building block in molecular synthesis, owing to their facile reactivity, range of functionalities and unusual stereochemistry.[1] There are many reported studies that use allenes as coupling partners in annihilation and addition reactions,[2] as building blocks in organic synthesis,[3] and as structural features in molecular materials.[4] In comparison to these, there are relatively few studies into polymerization reactions involving allenes, the first being by Wotiz using Co$_2$(CO)$_8$.[5] These polymers have attracted interest due to their unusual structure, opportunities for further functionalization[6] and development of complex molecular architecture.[7] For example, Li has reported hyperbranched RAFT polymerization using allene-derived monomers.[8]

Owing to its reactivity and ease of handling and synthesis, phenylallene has been used as a key model substrate for these reactions. Radical polymerization of phenylallene leading to low $M_n$ and high $M_D$ polymers were first reported by Anderson[9] and further investigated by Takeshi.[10] Barrett has reported that polymeric products are observed when phenylallene is treated with Grubbs catalyst,[11] while Cui has demonstrated that rare-earth metal catalysts can generate polymers that are considerably longer in chain length and has analyzed the physical properties of the polymers (Scheme 1).[12] Endo and Tomita have also reported examples of living polymerization of phenylallene using a nickel catalyst,[13] as well as multi-component coupling polymerizations.[14] In this study, we report the first polymerization of phenylallene using an iron pre-catalyst and perform mechanistic and analytical studies to further understand how the reaction proceeds and investigate the physical properties of the polymers.

Results and Discussion

We have reported numerous alkene functionalization reactions catalyzed by an iron(II) β-diketiminate complex [Fe],[15] and were interested in applying our previously reported hydroboration chemistry[16] to allene substrates. To our surprise, rather than undergoing an expected hydroboration reaction with phenylallene (1), we instead generate a polymeric...
substance as the primary product; iron β-diketiminate catalysts have previously been shown to competent for some forms of coordination polymerization, for example for polylactide\(^{[15c]}\) and polyethylene synthesis.\(^{[18]}\) Following our serendipitous discovery, we proceeded to optimize the reaction. Phenylallene polymerization proceeds with one equivalent of HBpin relative to substrate (Table 1, Entry 2) and with a co-catalytic amount of HBpin (Table 1, Entry 3). Stoichiometric loading of relative to substrate (Table 1, Entry 2) and with a co-catalytic allene polymerization proceeds with one equivalent of HBpin disubstituted polymer (Figure 1). Supporting Information). Diad structures would be expected to correlate through NOE and 2D NOESY NMR experiments. In both cases, no correlation is observed between the different environments (1.7 : 1.1 ratio) around the main chain, which may be linked to both the lack of reactivity H\(_{2}\)N-BH\(_{3}\) shows in dehydropolymerization chemistry,\(^{[15d]}\) therefore chain termination or side-reactions are minimized, along with the potential role of H\(_{2}\)N-BH\(_{3}\) in pre-catalyst activation (see below). \(^{1}\)H and \(^{13}\)C NMR analysis indicate the terminal (2,3)-substituted polymer (P\(_{1,2,3}\)) is the primary structural product.

Investigating the structure of P\(_{1,2,3}\) in greater detail, the NMR spectra further show that there are three distinct proton environments (1.7:1.1:1 ratio) around the main chain, which we believe relates to the different conformations the polymer can take. NOE NMR spectroscopy indicates that these environments are conformationally distinct from each other (See Supporting Information). Diad structures would be expected to correlate through NOE and 2D NOESY NMR experiments. In both cases, no correlation is observed between the different methylene proton environments, leading us to conclude that each proton is primarily adjacent to protons in the same environment. Although we cannot rule out a random arrangement of diads, based on the data we propose longer blocks of conformers. Using oligomers containing seven repeat units, Density Functional Theory (DFT) calculations (B3LYP-D3/6-31G\(^*\) (SCF = Benzene), 298 K) support the notion that there are three distinct conformers present in the product (one major species and two minor species, which matches observations by NMR spectroscopy), with the ground state species (0.0 kcal mol\(^{-1}\)), followed by a conformer at \(\Delta G = +2.7\) kcal mol\(^{-1}\) and one at \(\Delta G = +6.5\) kcal mol\(^{-1}\) (Figure 1).

| Entry | Hydride | Conversion [%] | \(M_n\) [kDa] | \(\phi\) | \(P_{1,2,3}\) | DP |
|-------|---------|----------------|---------------|--------|----------|----|
| 1     | None    | 3              | –             | –      | –        | –  |
| 2(a)  | HBpin   | 82             | 53            | 1.12   | 8.1      | 460|
| 3     | HBpin   | 91             | 152           | 1.36   | 5.1      | 1310|
| 4     | H\(_2\)N-BH\(_3\) | 93    | 189           | 1.19   | 7.1      | 1630|
| 5     | Me\(_2\)HN-BH\(_3\) | 89    | 10.5          | 6.25   | 5.1      | 91 |
| 6     | HSi(OEt)\(_3\) | 92     | 62            | 1.18   | 6.1      | 530|
| 7(b)  | H\(_2\)N-BH\(_3\) | 0      | –             | –      | –        | –  |

Conditions: 600 \(\mu\)L \(\text{C}_{6} \text{D}_{6}\), 0.5 mmol 1, 1 mol % \([\text{Fe}], 5\) mol % hydride, 16 h, RT. Conversion determined by \(^{1}\)H NMR spectroscopy. \([a]\) 1 eq. of HBpin relative to allene (0.5 mmol), 7% conversion to hydroborated product observed. \([b]\) No \([\text{Fe}], 60^\circ\) C, 72 h.

As H\(_2\)N-BH\(_3\) gives the highest conversion, \(M_n\) a narrow \(\phi\) and a reasonably high ratio of the two observed isomers (P\(_{1,2,3}\) and P\(_{1,2}\)), further reaction optimization was carried out using this hydride source (Table 2). Whilst there is relatively little difference between stirred and unstirred flasks (Table 2, Entry 2), there is a significant increase in \(M_n\) in more concentrated conditions, albeit at the expense of conversion to polymer (Table 2, Entries 3 and 4). In particular, solvent-free conditions (Table 2, Entry 4) lead to a dramatic reduction in conversion, which we attribute to lack of stabilization of activated pre-catalyst (see below). Raising the temperature has a modest effect on \(M_n\) but increases polydispersity significantly (Table 2, Entry 5). Quenching the reaction with methanol before full monomer conversion enables smaller molecular
weight polymers to be isolated (Table 2, Entry 6). MALDI-ToF analysis shows repeat units of 116 Da and end groups are as determined by \( ^1\)H NMR spectroscopy. (a) Under these conditions, polymer length was greater than 250 kDa and beyond the resolution of the GPC column, data reported in Supporting Information. \( ^1\)H NMR indicates the same polymer structure is forming. (b) 90\% polymer, 6\% dimer, see below for further discussion.

We do not observe any polymerization occurring when using non-aryl allene substrates, such as cyclohexylallene or methoxyallene. Presumably aryl substituents provide the electronic effects necessary to enable reactivity to proceed and has been highlighted by other researchers investigating the reactivity and functionalization of allenes.\(^{[21]}\)

To understand the nature of the polymerization, some mechanistic investigations were performed. Kinetic analysis indicates the reaction is first order with respect to the catalyst, and PMe\(_3\) poisoning experiments indicate the reaction is not nanoparticle mediated. Addition of a radical clock does not significantly alter rate. Application of deuterium-labelled phenylallene (1-d\(_2\), Scheme 2a) in polymerization under standard conditions leads to clean isotopic retention in the product, as indicated by protic signals at 3.46 ppm (methylene protons) that integrate to the quantity of residual protons in 1-d\(_2\), with the protic signal at 6.24 ppm (\(\alpha\) proton) integrating to 1H. If scrambling had occurred we would expect the 6.24 ppm integral to be less than 1H. Furthermore, the \( ^1\)H NMR spectrum, albeit weak, only shows peaks at 3.70-3.45 ppm. Using deuterated hydride sources, such as Me\(_2\)DN-BH\(_3\) or Me\(_2\)HN-BD\(_3\), and quenching the reaction to ensure low M\(_n\) polymer is formed, give no apparent D-incorporation in the polymer (Scheme 2b). We have previously reported that the bridged iron hydride dimer ([FeH]\(_2\)) is an on-cycle species.
some dehydrocoupling reactions. However, ([Fe]H)₂ is a poor catalyst for this transformation (5% conversion, 16 h, RT) in the absence of H₃N·BH₃. Performing the reaction with [Fe] under a hydrogen atmosphere does not lead to reasonable conversion; consequently, we do not believe this particular iron hydride dimer is an active catalyst. We have recently reported evidence for Fe(I) species forming from the reaction of [Fe] with the same hydride sources employed in this reaction. In this previous study, DFT studies supported the reaction proceeding via oxidative addition of C–H bonds to generate Fe(III) intermediates. In light of this, we postulate that the polymerization proceeds in a similar manner (Scheme 3): an initial pre-catalyst activation that involves reduction to an Fe(I) species, I. We anticipate that formation of I proceeds via an η⁶-arene stabilized intermediate, the formation of which is necessary to efficiently access I (supported by the drop-off in conversion in the absence of solvent, Table 2). The η⁶-supported allene then undergoes oxidative addition of a terminal C–H bond (II), consistent with no deuterium incorporation when using Me₂HN·BD₃, followed by a hydride source (III), which generates a propagation intermediate (IV) with subsequent termination/quenching (V). Table 3. Scope and properties of functionalized arylallene polymers.[a]

| Entry | Major isomer | Conversion [%] | P₂⁻₁⁻P₁⁻₂ | Mₙ [kDa] | D | DP | T_g [°C] |
|-------|--------------|----------------|-------------|----------|---|----|---------|
| 1     | P₂⁻₁⁻Me     | 90             | 8:1         | 229      | 1.63 | 1760 | 86.4    |
| 2     | P₃⁻₁⁻Me     | 96             | 7:1         | 72       | 1.17 | 550  | 63.0    |
| 3     | P₄⁻₁⁻Me     | 91             | 5:1         | 185      | 1.62 | 1420 | 75.4    |
| 4     | P₅⁻₁⁻OMe    | 98             | 11:1        | 174      | 2.05 | 1190 | 81.6    |
| 5     | P₆⁻₁⁻F      | 77             | 13:1        | 53       | 1.12 | 400  | 57.0    |
| 6     | P₇⁻₁⁻Cl     | 74             | 6:1         | 166      | 1.67 | 1110 | 97.1    |

[a] Conditions: 600 μL C₆D₆, 0.5 mmol allene, 1 mol % [Fe], 5 mol % H₃N·BH₃, 16 h, RT. Conversion determined by ¹H NMR spectroscopy. [b] 5 mol % [Fe].

Scheme 3. Postulated catalyst activation step and subsequent polymerization process.
by insertion of monomer into the Fe–C bond (III), which is the key chain propagation process. Given the high degree of polymerization (DP) values across all substrates and conditions, it is likely that only a relative small amount of metal centers are active species. In situ wide sweep NMR spectroscopy confirms that a significant amount of pre-catalyst remains unreacted even after full conversion of the substrate. Preparation of an analogous Fe(I)-η⁴-arene species, \([\text{Fe}(\text{I})]\), leads to similar reactivity without a hydride source present (90% conversion to \(P_1\); 6:1 ratio \(P_{1,1,1}:P_{1,1,2}\), \(M_n = 190\) kDa, \(D = 1.51\)) supporting our hypothesis.

Interestingly, when the polymerization is performed at 80°C, an unusual side-reaction is observed (Scheme 4). 1,3-di(2E)-benzylidene)cyclobutane can also be formed in modest yield in a 2:1 ratio of cis:trans. The product is readily isolable from the polymer residue (See Supporting Information). Attempts to increase the yield of this cyclobutane product using controlled, dilute addition using a syringe pump (e.g. using 1 in 670 μL C₆H₆ added at a rate of 20 μL/min to a flask containing 5 mol% H₂N-BH₃ and 1 mol% [Fe] in 6 mL C₆H₆) failed to give a substantial increase in yield, and polymerization still dominates. Undertaking this [2 + 2] cycloaddition with Me₂DN-BH₃ or Me₂HN-BD₃ does not lead to \(^3\)H incorporation in the product. These cyclobutane structures are unusual, as the thermal dimerization and [2 + 2] cycloadditions of allenes generally produce 1,2-substituted rings as the major product.[25] Furthermore these are challenging synthetic targets: to the best of our knowledge the only previous synthetic route to these molecules was reported by Dixneuf, which used a pinacolborane-allene and Ru pre-catalyst at 100°C to generate the 1,3-disubstituted cyclobutane product as a 1:2 ratio of cis:trans isomers i.e. complementary to our results.[26]

**Conclusion**

In summary, by using an iron(II) pre-catalyst we can polymerize phenylallene and its derivatives to form 2,3-substituted polymers of substantial molecular weight. We have characterized these polymers by using a range of techniques and have postulated a mechanism based on our studies into the nature of the reaction. Work is ongoing to develop our polymerization chemistry with 1 further, as well as investigate its potency in other catalytic allene functionalization reactions.

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**Conflict of Interest**

The authors declare no conflict of interest.

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