Iron-Catalyzed Polymerization of Isoprene and Other 1,3-Dienes

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Published Version</td>
<td>doi:10.1002/ange.201205152</td>
</tr>
<tr>
<td>Citable link</td>
<td><a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:10861168">http://nrs.harvard.edu/urn-3:HUL.InstRepos:10861168</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Open Access Policy Articles, as set forth at <a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#OAP">http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#OAP</a></td>
</tr>
</tbody>
</table>
Iron-Catalyzed Polymerization of Isoprene and Other 1,3-Dienes

Jean Raynaud, Jessica Y. Wu, and Tobias Ritter*

Iron is the most abundant transition metal in the Earth’s crust. As such, it is potentially useful for catalysts that can be employed in high-volume processes, like the Haber-Bosch process that functions with iron oxide as pre-catalyst. Maintaining the economic and environmental benefit of iron catalysis, well-defined molecular iron catalysts provide the opportunity to also control selectivity, such as stereoselectivity, during catalysis, if the ligands employed are appropriately selected. Here we report on the iron-catalyzed polymerization of 1,3-dienes to afford elastomers with catalyst content as low as 0.02 mol%. Iminopyridine ligands, as part of the catalyst and made in one step from commercially available chemicals in the case of catalyst 1, can control and invert the stereoselectivity of the polymerization.

Iron complexes are suitable pre-catalysts for the polymerization of olefins, such as ethylene, to afford linear polyethylene of molar masses greater than 10^6 g/mol. Less attention has been dedicated to the iron-catalyzed polymerization of dienes such as isoprene. Polysoprene is a naturally occurring unsaturated hydrocarbon polymer that can be refined from the latex produced by rubber trees such as Hevea Brasiliensis. Polymerization of isoprene can afford several isomers of polysoprene; for example, the double bond in 1,4-polysoprene can both be of cis and trans geometry (Scheme 1). Selective polymerization is important because the identity of the isomer influences the properties of the resulting material. Natural polysoprene can reach cis-1,4 content of >99.9% in the case of Hevea Brasiliensis and trans-1,4 content of >99.9% for Gutta Percha. Natural rubber, which displays high performance mechanical properties, is preferred over synthetic rubber in elastomer applications that require high quality rubber, including aircraft tires and surgical gloves. As a result, more than 10 million tons of natural rubber are harvested annually from Hevea trees: rubber trees only grow in tropical climate, such as in Asia and West Africa, where they supplant food crops and are an environmental burden due to heavy use of arsenic-based pesticides. Synthetic rubber has been introduced to replace natural rubber in less demanding applications and reduce extensive culturing of rubber trees.

Scheme 1. Polymerization of isoprene using precatalysts 1 and 2: complex 1 affords trans-1,4-polysoprene preferentially whereas complex 2 affords cis-1,4-polysoprene preferentially. The 3,4-insertion motif is a minor component in both polymers (7–8% for 1, and 15% for 2). R = iBu for 1 and Et for 2.

Industrial polydienes can be made by alkylithium-based anionic polymerization. Catalysts based on titanium and, more recently, rare earth metals such as neodymium can selectively afford up to 98% of high molar mass cis-1,4- and trans-1,4- polysoprene and polybutadiene. The molecular iron complexes we report here can provide both cis and trans isomers of polysoprene and other 1,3-dienes in greater than 99:1 selectivity, and provide new elastomer materials. Iron catalysis, if appropriately developed, could have a future impact on elastomer production due to low cost and low environmental burden of iron compared to other transition metals.

Our catalyst design was inspired by the iron bisiminopyridine complexes, introduced by Gibson and Brookhart in 1998, that are used for ethylene polymerization, and can also be employed for hydrosilylation reactions as reported by Chirik. The iminopyridine ligands of 1 and 2 we chose for our studies feature the redox-active behavior of the bisiminopyridines, but provide an additional available coordination site to accommodate diene coordination as opposed to alkene coordination. We have previously reported the application of iminopyridine-based iron catalysts for 1,4-addition reactions across 1,3-dienes with control of regio-, chemo-, and stereoselectivity through appropriate substitution of the iminopyridine ligands. Iron-catalyzed polymerizations of isoprene have been reported previously but...
typically do not afford the 1,4-polyisoprene microstructure, and control over selectivity as reported here has, to the best of our knowledge, not been reported.

Table 1. Stereoselective isoprene polymerization

<table>
<thead>
<tr>
<th>conditions</th>
<th>[Fe][Al][PhC]=M /[Fe][Al][PhC]=M</th>
<th>polymer Mw / D</th>
<th>selectivity 1,4 : 3,4, trans : cis</th>
<th>yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 / Al/Bu3, 2h, 23°C</td>
<td>1:3:1:1000</td>
<td>125,000 / 2.0</td>
<td>12:1 &gt;99:1</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>1 / Al/Bu3, 5h, 23°C</td>
<td>1:3:1:5000</td>
<td>650,000 / 3.9</td>
<td>12:1 &gt;99:1</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>2 / AlEt3, 1h, 23°C</td>
<td>1:3:1:1000</td>
<td>150,000 / 1.9</td>
<td>2:1:1:99</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>2 / AlEt3, 4h, −78°C</td>
<td>1:3:1:5000</td>
<td>140,000 / 1.7</td>
<td>6:1:1:99</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>2 / AlEt3, 4h, −78°C</td>
<td>1:3:1:5000</td>
<td>800,000 / 3.5</td>
<td>5:1 1:99</td>
<td>&gt;99%</td>
</tr>
</tbody>
</table>


Combination of iminopyridine-FeCl2 pre-catalyst (1 or 2), alkylating reagent (trialkylaluminum), de-alkylating reagent (trityl BArF), and isoprene in an aprotic solvent, provides polyisoprene with molar masses of >105 g/mol, and with high selectivity for either cis-1,4 or trans-1,4 polyisoprene (Table 1, for kinetic profiles of polymerization, see Supporting Information). Less than 5% conversion was observed in the absence of any of the reaction components. The imine moiety of the iminopyridine ligand controls the stereo- and regioselectivity of monomer insertion on the active iron complex: The octyl-substituted complex 1 yielded polymer with trans-1,4 polyisoprene content in up to 93% at 23°C (Table 1). The supermesityl-substituted complex 2 afforded polymer with cis-1,4 polyisoprene content up to 85% at −78°C. While the catalysts derived from both 1 and 2 can control the double bond geometry with > 99:1 selectivity, the selectivity for control of 1,4- versus 3,4-addition ranges from 2:1 to 12:1. However, the 3,4-addition motif results in the incorporation of pendant terminal olefin side chains into the polymer, which can be useful to modify the properties of the polymer (vide infra).

Treatment of iminopyridine ferrous chloride complexes 1 and 2 with trisobutylaluminum or triethylaluminum as alkylating reagent, presumably to replace the chloride ligands, and trityl BArF20 (PhC=BC6F5Bu), to abstract one of the alkyl groups, forms the active iron catalyst. Both 1 and 2 are soluble in toluene and readily dispersed in heptane and methylcyclohexane, which allows for a fast activation process. Addition of trialkylaluminum to 1 or 2 in apolar solvents resulted in an immediate color change from bright orange (1) and deep green (2) to brown-black. Subsequent addition of a solution (toluene) or of a dispersion (alkanes) of trityl BArF20 resulted in the formation of the active species, a putative cationic Fe(II) complex, to initiate polymerization. The iron-catalyzed polymerizations proceed in alkanes with boiling points that allow for both safe use on large scale and distillation from the polymer after polymerization. The molar masses of the resulting polymer of >105 g/mol and its controlled dispersity (D = 2−4) is appropriate for required tensile strength and elasticity.

Polymers obtained from complexes 1 and 2 contain 7−8% and 15% of the 3,4-insertion motif, respectively; the 1,2-microstructure was not observed. The side-chain olefins resulting from 3,4-insertion can increase toughness of synthetic rubber upon selective crosslinking, which can be beneficial, for example to prevent abrasion of car tires. Subsequent addition of a solution (toluene) or of a dispersion (alkanes) of trityl BArF20 resulted in the formation of the active species, a putative cationic Fe(II) complex, to initiate polymerization. The iron-catalyzed polymerizations proceed in alkanes with boiling points that allow for both safe use on large scale and distillation from the polymer after polymerization.

Ferrous chloride complexes 1 and 2 are also suitable precatalysts for the stereoselective polymerization of other 1,3 dienes, such as myrcene and farnesene (Scheme 2). Catalysts 1 and 2 afford similar cis/trans and 1,4 : 3,4 ratios for other 1,3 dienes as they do for isoprene (Table 2). Both myrcene and farnesene are available as mixtures of isomers (α and β isomers), but polymerization with 1 and 2 is chemoselective, and enables the isomer-selective polymerization of the β isomers. For example, commercially available farnesene consists of a mixture of different farnesene isomers (see 1H NMR spectrum in Figure 1a) but polymerization selectively afforded poly-β-farnesene (see Figure 1b). The other isomers could be conveniently removed as monomers after polymerization. The materials obtained from iron catalyzed polymerization provide access to new elastomers, bearing pendant olefins, from readily available materials.
Scheme 2. Selective polymerizations of β-myrcene and β-farnesene using iminopyridine Fe(II)Cl₃ precatalysts. a) 0.05 mol% 1 or 2, 1.5 mol% AlR₂ (alkylating + drying agent), 0.05 mol% [Ph₃C⁺][B(C₆F₅)₄]⁻. Because farnesene was used as obtained, a larger portion of trialkylaluminum reagent was needed to serve as drying reagent in addition to its function as alkylation reagent. [b] yields based on the β-farnesene content (both 6-Z and 6-E isomers) of commercially available farnesene (mixture of isomers of α- and β-farnesene).

Table 2. Stereoselective polymerization of myrcene and farnesene

<table>
<thead>
<tr>
<th>Conditions</th>
<th>[Fe]:[Al]:[Ph₃C⁺]:[M]</th>
<th>Polymer Mₚ / D</th>
<th>Selectivity</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>myrcene</td>
<td>1 / AlBu₃</td>
<td>1:5:1:2000</td>
<td>250,000 / 2.1</td>
<td>12:1 &gt;20:1 91%</td>
</tr>
<tr>
<td>12h, 23°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>farnesene</td>
<td>2 / AlEt₃</td>
<td>1:5:1:2000</td>
<td>230,000 / 2.2</td>
<td>4:1 1: &gt;20 87%</td>
</tr>
<tr>
<td>12h, 23°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>myrcene</td>
<td>1 / AlBu₃</td>
<td>1:30:1:2000</td>
<td>110,000 / 1.5</td>
<td>11:1 &gt;20:1 90%</td>
</tr>
<tr>
<td>24h, 23°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] Because farnesene was used as obtained, a larger portion of trialkylaluminum reagent was needed to serve as drying reagent in addition to its function as alkylation reagent. [b] yields based on the β-farnesene content (both 6-Z and 6-E isomers) of commercially available farnesene (mixture of isomers of α- and β-farnesene).

The change in stereoselectivity from > 99:1 to < 1:99 for trans- versus cis-polydiene formation is solely based on the imine substituent of the otherwise identical catalysts and not yet well understood. The complete lack of identified intermediates in the catalytic cycle has complicated analysis regarding the source of selectivity, and the selectivity-determining step is currently unknown. Diene coordination (s-cis or s-trans), migratory insertion into an η²- or η⁴-coordinated diene, and σ−π−σ rearrangements of the Fe-allyl complexes may all be relevant for selectivity. We discovered empirically that alkyl-substituted imines favor trans-1,4 insertion, whereas aryl-substituted imines favor cis-1,4 insertion, which could suggest that higher electron density at the iron center increases the trans-1,4 selectivity. Although we have shown that well-defined iron catalysts can be used to control selectivity of 1,3-diene addition reactions, currently, the field is not yet advanced enough to make any rational predictions as to the source of that selectivity.
We have shown that iminopyridine-supported iron catalysts can polymerize 1,3-dienes stereoselectively. Depending on the ligand, either trans-1,4- or cis-1,4-polymers can be obtained. Polysoprenes of high molar masses and controlled polydispersities can be obtained in >99% yield from isoprene. The 3,4-insertion content (7–15%) may allow for post-synthesis functionalization and tuning of mechanical properties. Chemoselective polymerization of other 1,3-dienes such as β-myrcene and β-farnesene gives access to other elastomers. Continuation of this work could include the rationalization of the selectivity induced by the iron catalysts, measurements of the properties of the new elastomers that are now available, and evaluation of the new iron-catalyzed polymerization process toward its suitability for rubber production.

**Experimental Section**

**Example: trans-1,4-Polysoprene**

To a 500 mL round-bottom flask was added complex 1 (9.6 mg, 28 µmol, 1.0 equiv) and 10 mL of toluene, followed by trisobutylaluminum (16.5 mg, 84 µmol, 3.0 equiv) in 5 mL toluene at 23°C. The reaction mixture was stirred for 3 min and trityl tetrakis(pentafluorophenyl)borate (26 mg, 84 µmol, 1.0 equiv) was added as a solution in 5 mL toluene at 23°C. The reaction mixture was stirred for 2 min and 50 mL of Me-cyclohexane was added to bring the total volume to 70 mL, and then isoprene (10.0 g, 14.7 mL, 147 mmol, 5.25 × 10⁻³ mol, 1.0 equiv) and 10 mL of toluene, followed by triisobutylaluminum (16.5 mg, 84 µmol, 1.0 equiv) was added. The reaction mixture was stirred for 5 hours at 23°C. The flask was opened to the atmosphere, and dichloromethane (50 mL) was added. The title compound was isolated by precipitation in cold methanol (700 mL) to yield a colorless gum that was dried in vacuo overnight (yield >99% 10.1 g after drying for 16 h under vacuum): SEC chromatography (eluent: THF, Polystyrene standards): $M_n = 650,000$ g/mol, $D = 3.9$ ; Selectivity 1,4: cis-1,4 > 99:1 (92.5% of trans-1,4-polyisoprene in the bulk)

Received: ((will be filled in by the editorial staff))
Published online on ((will be filled in by the editorial staff))

**Keywords:** Iron · Catalysis · Polymerization · Diene · Isoprene

---

Iron Catalysis

Jean Raynaud, Jessica Y. Wu, and Tobias Ritter*  Page – Page

Iron-Catalyzed Polymerization of Isoprene and Other 1,3-Dienes

Ironing Rubber. The iron-catalyzed polymerization of 1,3-dienes is reported. Iminopyridine-based FeCl₂ catalysts provide stereoselective access to elastomers, such as polyisoprenes, polymyrcenes and polyfarnesenes. The ligand allows for control over double bond geometry of the polymer repeating unit, which can be varied from >99:1 to <1:99.