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Iron Catalysis

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

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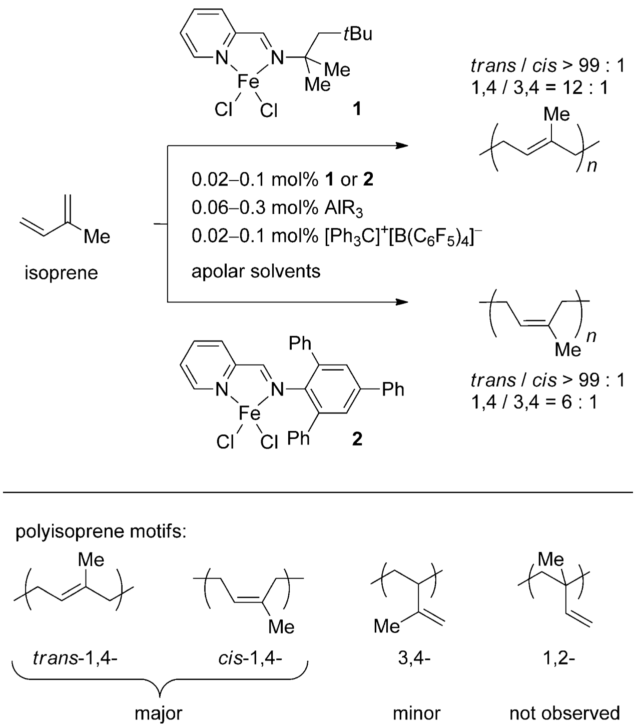
Iron is the most abundant transition metal in the Earth's crust. As such, it is potentially useful for catalysts that can be employed in high-volume processes, like the Haber–Bosch process that functions with iron oxide as the precatalyst. Maintaining the economic and environmental benefit of iron catalysis, 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 precatalysts for the polymerization of olefins such as ethylene to afford linear polyethylene of molar masses greater than 10^6 g mol^{-1}.[1,2] Less attention has been dedicated to the iron-catalyzed polymerization of dienes such as isoprene.[3] Polyisoprene is a naturally occurring unsaturated hydrocarbon polymer that can be refined from the latex produced by rubber trees such as *Hevea brasiliensis*.[4,5] Polymerization of isoprene can afford several isomers of polyisoprene; for example, the double bond in 1,4-polyisoprene can have either *cis* or *trans* geometry (Scheme 1). Selective polymerization is important because the identity of the isomer influences the properties of the resulting material. Natural polyisoprene can reach a *cis*-1,4 content exceeding 99.9% in the case of *Hevea bransiliensis* and a *trans*-1,4 content exceeding 99.9% for *Gutta-percha*.[4,5] Natural rubber, which displays high-performance mechanical properties, is preferred over synthetic rubber in many elastomer applications, including aircraft tires and surgical gloves.[4,5] As a result, more than 10 million tons of natural rubber is harvested annually from *Hevea* trees. Rubber trees grow only in the tropics, such as in Asia and West Africa, where they supplant food crops and are an environmental burden because of the heavy use of arsenic-based pesticides.[4–6] Synthetic rubber has been introduced to replace natural rubber in less demanding applications and to reduce the extensive culturing of rubber trees.



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

Industrial polydienes can be made by alkyllithium-based anionic polymerization.[3,7] Catalysts based on titanium and, more recently, rare-earth metals such as neodymium can selectively afford high-molar-mass *cis*-1,4- and *trans*-1,4-polyisoprene and -polybutadiene in up to 98% yield.[3,4,8–14] The molecular iron complexes we report here can provide both *cis* and *trans* isomers of polyisoprene 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 because of the 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[1,2] and can also be employed for hydrosilylation reactions, as reported by Chirik et al.[15,16] The iminopyridine ligands in **1** and **2** which we chose for our studies feature the redox-active behavior of the bisiminopyridines,[15–18] but provide an additional available coordination site to accommodate diene coordination as opposed to alkene coordination (Scheme 1).[19–21] We previ-

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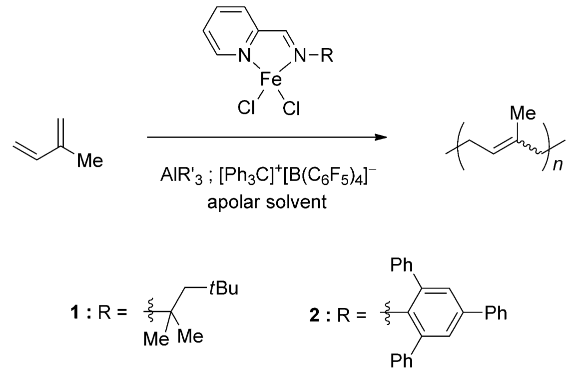
ously reported the application of related iminopyridine-based iron catalysts for 1,4-addition reactions across 1,3-dienes with control of regio-, chemo-, and stereoselectivity through appropriate substitution of the iminopyridine ligands.[19–21] Iron-catalyzed polymerizations of isoprene have been reported 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.[3,22–24]

The combination of the precatalyst **1** or **2**, an alkylating reagent (trialkylaluminum), a dealkylating reagent (Ph_3C^+ $B(C_6F_5)_4^-$, trityl BArF), and isoprene in an aprotic solvent provided polyisoprene with molar masses greater than 10^5 g mol^{-1}, and with high selectivity for either *cis*-1,4 or *trans*-1,4 polyisoprene (Table 1; for kinetic profiles of the polymerization, see the 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 of 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).

Table 1: Stereoselective isoprene polymerization.



Conditions	[Fe]/[Al]/ [Ph$_3$C$^+$]/[M]	Polymer M_w/D[a]	Selectivity 1,4/3,4, *trans*/*cis*[b]	Yield [%][c]
1/Al*i*Bu$_3$ 2 h, 23 °C	1:3:1:1000	125 000/2.0	12:1 > 99:1	> 99
1/Al*i*Bu$_3$ 5 h, 23 °C	1:3:1:5000	650 000/3.9	12:1 > 99:1	> 99
2/AlEt$_3$				
1 h, 23 °C 4 h, −78 °C	1:3:1:1000	150 000/1.9	2:1; 1: > 99	> 99
	1:3:1:1000	140 000/1.7	6:1; 1: > 99	> 99
2/AlEt$_3$ 4 h, −78 °C	1:3:1:5000	800 000/3.5	5:1 1: > 99	> 99

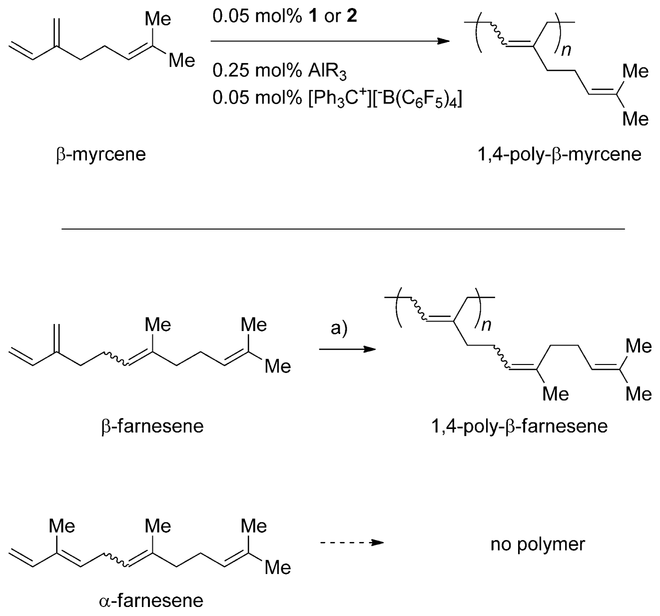
[a] Determined by size-exclusion chromatographic analysis in THF using a refractive index detector and a UV detector ($\lambda = 212$ nm). [b] Determined by ^{1}H and ^{13}C NMR spectroscopy. [c] Determined gravimetrically. Apolar solvent: toluene, heptane, or methylcyclohexane.

Treatment of iminopyridine ferrous chloride complexes **1** or **2** with triisobutylaluminum or triethylaluminum as the alkylating reagent, presumably to replace the chloride ligands, and trityl BArF$_{20}$, 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. The addition of trialkylaluminum to **1** or **2** in an apolar solvent resulted in an immediate color change from bright orange (**1**) and deep green (**2**) to brown-black. Subsequent addition of trityl BArF$_{20}$ as a solution (in toluene) or as a dispersion (in alkanes) 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 a large scale and distillation from the polymer after polymerization.[25] The molar masses of the resulting polymer of more than 10^5 g mol^{-1} and its controlled dispersity ($D = 2$–4) are appropriate for required tensile strength and elasticity.[26]

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 the toughness of synthetic rubber upon selective crosslinking, which can be beneficial, for example to prevent abrasion of car tires.[26,27] The crosslinked material could also find applications in high-performance rubbers with wet-skid resistance and low-rolling resistance tread.[26–28]

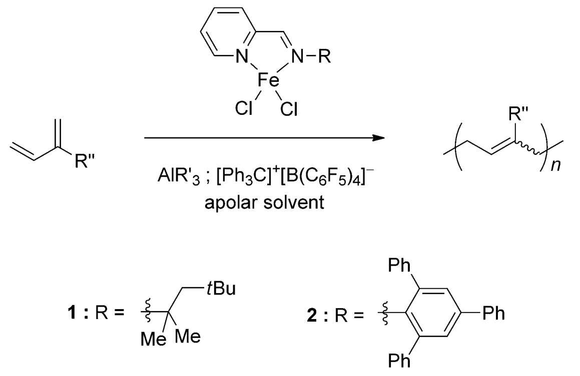
Ferrous chloride complexes **1** and **2** are also suitable precatalysts for the stereoselective polymerization of other 1,3-dienes, such as myrcene and farnesene (Scheme 2). In these reactions catalysts **1** and **2** afford *cis*/*trans* and 1,4/3,4 ratios that are similar to those obtained for the polymerization of isoprene (Table 2). Both myrcene and farnesene are available as mixtures of isomers (α and β isomers), but the polymerization with **1** and **2** is chemoselective and isomer-selective polymerization of the β isomers is possible. For example, commercially available farnesene consists of a mixture of different farnesene isomers (see ^{1}H NMR spectrum in Figure 1 a) but polymerization selectively afforded poly-β-farnesene (see Figure 1 b). 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.

The change in stereoselectivity from > 99:1 to < 1:99 for the formation of *trans*- versus *cis*-polydiene 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 η^2- or η^4-coordinated diene, and σ–π–σ rearrangements of the iron–allyl complexes may all be relevant for selectivity. We discovered empirically that alkyl-substituted imines favor



Scheme 2. Selective polymerizations of β-myrcene and β-farnesene using precatalysts **1** or **2**. a) 0.05 mol% **1** or **2**, 1.5 mol% AlR_3 (alkylating + drying agent), 0.05 mol% $[Ph_3C]^+[B(C_6F_5)_4]^-$. Because farnesene was used as obtained, a larger amount of trialkylaluminum reagent was used; it served as a drying agent as well as an alkylation reagent.

Table 2: Stereoselective polymerization of myrcene and farnesene.



Conditions	[Fe]/[Al]/[Ph_3C^+]/[M]	Polymer M_w/D	Selectivity 1,4/3,4 *trans*/*cis*	Yield [%]
myrcene **1**/Al*i*Bu_3 12 h, 23 °C	1:5:1:2000	250000/2.1	12:1 >20:1	91
myrcene **2**/AlEt_3 12 h, 23 °C	1:5:1:2000	230000/2.2	4:1 1:>20	87
farnesene **1**/Al*i*Bu_3 24 h, 23 °C	1:30[a]:1:2000	110000/1.5	11:1 >20:1	90[b]
farnesene **2**/AlEt_3 24 h, 23 °C	1:30[a]:1:2000	100000/1.4	3:1 1:>20	84[b]

[a] Because farnesene was used as obtained, a larger portion of trialkylaluminum reagent was needed to serve as a drying agent 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).

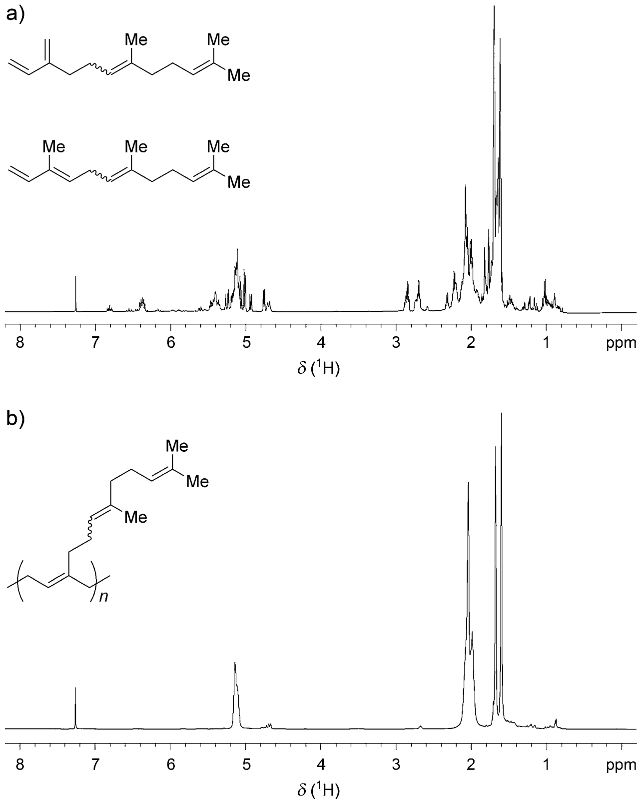


Figure 1. Selective polymerization of β-farnesene. The commercially available mixture can be used (a), only the β isomer is polymerized (b). For details see the Supporting Information.

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. Polyisoprenes of high molar masses and controlled polydispersities can be obtained in greater than 99% yield from isoprene. The 3,4-insertion content (7–15%) may allow for postsynthesis 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

Representative polymerization reaction: *trans*-1,4-Polyisoprene: 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 triisobutylaluminum

(17 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, 28 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 methylcyclohexane 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 equiv) was added. The reaction mixture was stirred for 5 h at 23 °C. The flask was opened to the atmosphere, and dichloromethane (50 mL) was added. The polymer was isolated by precipitation from 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): Size-exclusion chromatography (eluent: THF, polystyrene standards): $M_w = 650\,000\ \mathrm{g\,mol^{-1}}$, $Đ = 3.9$; Selectivity 1,4/3,4 = 12:1 and *trans*-1,4/*cis*-1,4 >99:1 (92.5 % of *trans*-1,4-polyisoprene in the bulk).

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