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

Share Your Story

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

Accessibility

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

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

((Dedication----optional))

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.[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 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 polyisoprene can reach *cis*-1,4 content of >99.9% in the case of *Hevea Bransiliensis* and *trans*-1,4 content of >99.9% for *Gutta Percha*.[4,5] 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.[4,5] 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.[4-6] Synthetic rubber has been introduced to replace natural rubber in less demanding applications and reduce extensive culturing of rubber trees.

[*]Dr. J. Raynaud, Dr. J. Y. Wu, and Prof. T. Ritter*
Department of Chemistry and Chemical Biology
Harvard University
12 Oxford Street, Cambridge, MA 02138
Fax: (+) 617 496 4591
E-mail: ritter@chemistry.harvard.edu
Homepage: http://www.chem.harvard.edu/groups/ritter/

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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% for **1**, and 15% 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 up to 98% of high molar mass *cis*-1,4- and *trans*-1,4- polyisoprene and polybutadiene.[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 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,[1,2] and can also be employed for hydrosilylation reactions as reported by Chirik.[15,16] The iminopyridine ligands of **1** and **2** 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.[19-21] 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.[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]

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$_3$ 2h, 23°C	1:3/1:1000	125,000 / 2.0	12:1 >99:1	>99%
1 / Al^{i}Bu$_3$ 5h, 23°C	1:3:1:5000	650,000 / 3.9	12:1 >99:1	>99%
2 / AlEt$_3$ 1h, 23°C	1:3:1:1000	150,000/1.9	2:1;1:>99	>99%
4h, −78°C	1:3:1:1000	140,000/1.7	6:1;1:>99	>99%
2 / AlEt$_3$ 4h, −78°C	1:3:1:5000	800,000 / 3.5	5:1 1:>99	>99%

[a] determined by SEC analysis in THF using an RI detector and a UV detector (λ=212 nm). [b] determined by ^{1}H and ^{13}C NMR spectroscopy. [c] determined gravimetrically. Apolar solvent: toluene, heptane, or methylcyclohexane.

Combination of iminopyridine-FeCl$_2$ 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 >10^5 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 tri*iso*butylaluminum or triethylaluminum as alkylating reagent, presumably to replace the chloride ligands, and trityl BArF$_{20}$ (Ph$_3$C$^+$ B(C$_6$F$_5$)$_4^-$), 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 BArF$_{20}$ 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.[25] The molar masses of the resulting polymer of >10^5 g/mol and its controlled dispersity (D = 2−4) is 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 toughness of synthetic rubber upon selective crosslinking, which can be beneficial, for example to prevent abrasion of car tires,[26,27] and 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 pre-catalysts 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 ^{1}H 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 catalysed-polymerization provide access to new elastomers, bearing pendant olefins, from readily available materials.

conditions	[Fe]:[Al]:[Ph$_3$C$^+$]:[M]	polymer M_w / D	selectivity 1,4 : 3,4 trans / cis	yield
myrcene 1 / Al^{i}Bu$_3$ 12h, 23°C	1:5:1:2000	250,000 / 2.1	12:1 >20:1	91%
myrcene 2 / AlEt$_3$ 12h, 23°C	1:5:1:2000	230,000 / 2.2	4:1 1:>20	87%
farnesene 1 / Al^{i}Bu$_3$ 24h, 23°C	1:30[a]:1:2000	110,000 / 1.5	11:1 >20:1	90%[b]
farnesene 2 / AlEt$_3$ 24h, 23°C	1:30[a]:1:2000	100,000 / 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 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 η^2- or η^4-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.

Scheme 2. Selective polymerizations of β-myrcene and β-farnesene using iminopyridine Fe(II)Cl$_2$ precatalysts. a) 0.05 mol% **1** or **2**, 1.5 mol% AlR$_3$ (alkylating + drying agent), 0.05 mol% [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$. Because farnesene was used as obtained, a larger portion of trialkylaluminum reagent was used to serve as drying reagent in addition to its function as alkylation reagent.

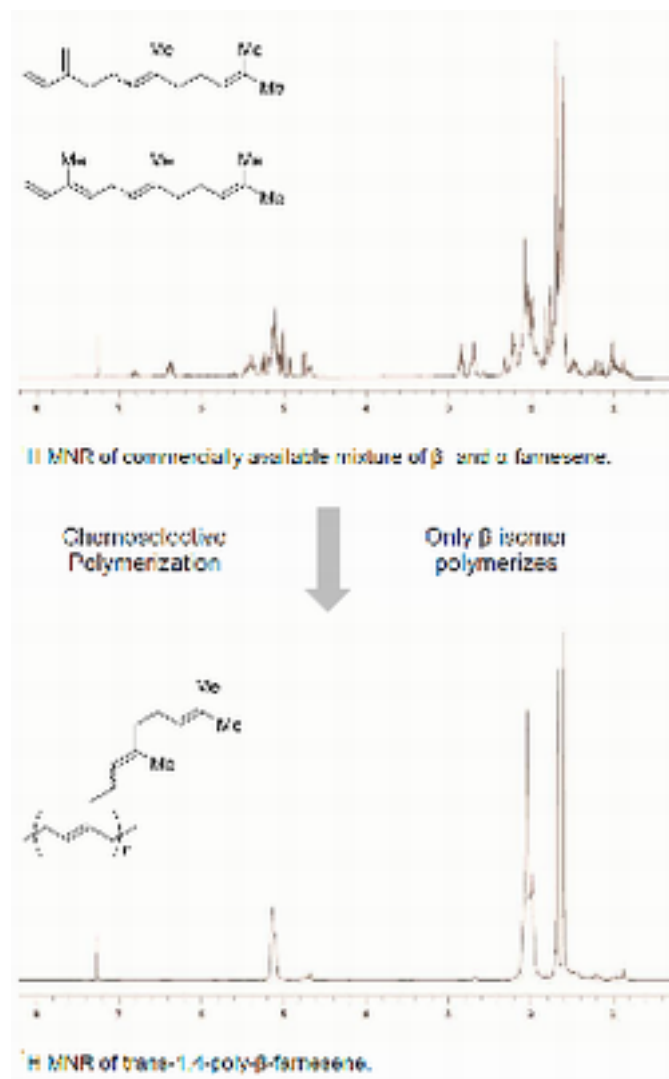**Table 2.** Stereoselective polymerization of myrcene and farnesene

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

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 >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-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 tri*iso*butylaluminum (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, 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 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 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_w = 650,000 g/mol, D = 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)

[1] Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049-4050.

[2] Britovsek, G. J. P.; Gibson, V. C.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J.; Kimberley, B. S.; Maddox, P. J. *Chem. Comm.* **1998**, 849-850.

[3] Ricci, G.; Sommazzi, A.; Masi, F.; Ricci, M.; Boglia, A.; Leone, G. *Coord. Chem. Rev.* **2010**, *254*, 661-676.

[4] De, S. K.; White, J. R. *Rubber Technologist's Handbook*; Rapra Technology Limited ed.; Rapra Technology Limited: Shawbury, UK, **2001**, pp. 49-51.

[5] Ouardad, S.; Bakleh, M.-E.; Kostjuk, S. V.; Ganachaud, F.; Puskas, J. E.; Deffieux, A.; Peruch, F. *Polym. Int.* **2012**, *61*, 149-156.

[6] Grund, S. C.; Hanusch, K.; Wolf, H. U. "Arsenic and Arsenic Compounds" in *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH, **2000**, section 3, page 228.

[7] Kamienski, C. W. *Industrial & Engineering Chemistry* **1965**, *57*, 38-55.

[8] Osakada, K.; Takeuchi, D. In *Polymer Synthesis*, Springer, Berlin, **2004**, *171*, pp. 137-194.

[9] Zhang, L.; Suzuki, T.; Luo, Y.; Nishiura, M.; Hou, Z. *Angew. Chem.,* **2007**, *119*, 1941-1945, *Angew. Chem., Int. Ed.* **2007**, *46*, 1909-1913.

[10] Gao, W.; Cui, D. *J. Am. Chem. Soc.* **2008**, *130*, 4984-4991.

[11] Zhang, L.; Nishiura, M.; Yuki, M.; Luo, Y.; Hou, Z. *Angew. Chem.,* **2008**, *120*, 2682-2685, *Angew. Chem., Int. Ed.* **2008**, *47*, 2642-2645.

[12] Li, D.; Li, S.; Cui, D.; Zhang, X. *Organometallics* **2010**, *29*, 2186-2193.

[13] Lv, K.; Cui, D. *Organometallics* **2010**, *29*, 2987-2993.

[14] Nishiura, M.; Hou, Z. *Nat. Chem.* **2010**, *2*, 257-268.

[15] Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794-13807.

[16] Tondreau, A. M.; Atienza, C. C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J. *Science* **2012**, *335*, 567-570.

[17] Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901-13912.

[18] Tondreau, A. M.; Milsmann, C.; Patrick, A. D.; Hoyt, H. M.; Lobkovsky, E.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 15046-15059.

[19] Moreau, B.; Wu, J. Y.; Ritter, T. *Org. Lett.* **2009**, *11*, 337-339.

[20] Wu, J. Y.; Moreau, B.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915-12917.

[21] Wu, J. Y.; Stanzl, B. N.; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 13214-13216.

[22] C. Bazzini, A. Giarrusso, L. Porri, *Macromol. Rapid Commun.* **2002**, *23*, 922-927.

[23] G. Ricci, D. Morganti, A. Sommazzi, R. Santi, F. Masi, *J. Mol. Catal. A: Chem.* **2003**, *204–205*, 287-293.

[24] Ricci, G.; Leone, G.; Boglia, A.; Boccia, A. C.; Zetta, L. *Macromolecules* **2009**, *42*, 9263-9267.

[25] Cheremisinoff, N. P. in *Industrial Solvents Handbook*; Marcel Dekker, **2003**, *2nd Ed.*, pages 78-81.

[26] De, S. K.; White, J. R. *Rubber Technologist's Handbook*; Rapra Technology Limited ed.; Rapra Technology Limited: Shawbury, UK, **2001**, pp. 31-36.

[27] De, S. K.; White, J. R. *Rubber Technologist's Handbook*; Rapra Technology Limited ed.; Rapra Technology Limited: Shawbury, UK, **2001**, pp. 36-47 and p. 51.

[28] Wang, B.; Cui, D.; Lv, K. *Macromolecules* **2008**, *41*, 1983-1988.

Entry for the Table of Contents

Ironing Rubber. The iron-catalyzed polymerization of 1,3-dienes is reported. Iminopyridine-based $FeCl_2$ 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.