

Dehydrogenation of aliphatic polyolefins catalyzed by pincer-ligated iridium complexes

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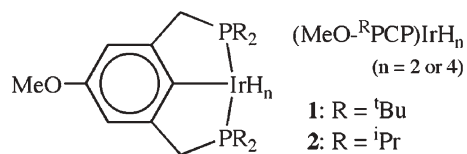
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We report the first example of the catalytic dehydrogenation of aliphatic polyolefins to give partially unsaturated hydrocarbon polymers.

The synthesis of polyolefins with controlled functionality is an important frontier in polymer synthesis. Incorporation of specific types of functionality, with control of location and amount, allows the development of important new classes of polyolefins with tailored mechanical, physical, and chemical properties.^{1,2} The two main strategies for synthesizing functional polyolefins are the direct incorporation of functional olefins, and the post-polymerization modification of catalyst tolerant functionalities (hindered alkenes, silyl-protected alcohols, aromatic groups, *etc.*). A third strategy is the functionalization of saturated polyolefins,³ *via* radical or metal-mediated methods. For example, Hartwig and Hillmyer have reported the borylation of polybutene⁴ and polypropylene⁵ and the oxyfunctionalization of polypropylene.⁶ The introduction of C–C double bonds into aliphatic polymer chains would offer a starting point for a very diverse manifold of such reactivity. Further, a partially unsaturated polyolefin could be cross-linked with standard techniques to give materials with enhanced mechanical properties.⁷

Significant progress has been made in the past two decades toward the development of soluble transition-metal based catalysts for the dehydrogenation of alkanes.^{8–10} Pincer-ligated iridium complexes are particularly promising in this context.¹¹ Herein, we report the use of such catalysts for the dehydrogenation of aliphatic polyolefins.^{12,13}

Poly(α -olefins) were chosen as exemplary substrates based on considerations of solubility and because (^RPCP)Ir-based catalysts had previously been demonstrated to show high reactivity toward the terminal position of *n*-alkyl groups (of *n*-alkanes).¹⁴ The catalysts used were *p*-methoxy-substituted PCP-pincer catalysts, (MeO-^RPCP)IrH_n (Scheme 1), which have recently been shown to be more robust and generally more effective than the parent catalysts.¹⁵

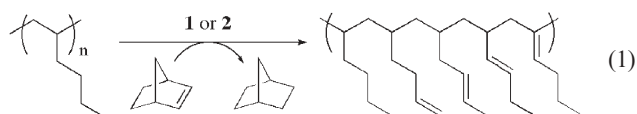


Scheme 1

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Poly(1-hexene) (PH) was synthesized using (Cp(Me)₄Si(Me)₂N^tBu)TiCl₂/methylaluminoxane¹⁶ giving a highly viscous atactic polymer with a number average molecular weight (*M_n*) of 6900 and polydispersity index (PDI) of 1.57. *p*-Xylene solutions were prepared that were ~1 M in poly(1-hexene) repeat units, 5 mM in catalyst, and approximately 0.2 M in norbornene (the sacrificial hydrogen-acceptor; NBE). Reactions were conducted in sealed tubes immersed in an oil bath maintained at 150 °C, and were periodically monitored by NMR.† Trimethylphosphine in deuterated mesitylene, and hexamethyldisiloxane, were used as external and internal standards respectively, for referencing and quantification purposes.

Heating a *p*-xylene solution of (MeO-^tBuPCP)IrH_n (**1**; 5 mM), NBE (0.21 M) and poly(1-hexene) (1.1 M in PH repeat units) at 150 °C for 20 min resulted in the loss of *ca.* 0.04 M NBE. The commensurate appearance of terminal vinyl groups (10 mM) and internal C–C double bonds (30 mM) was indicated by multiplets at 5.1 and 5.8 ppm, and at 5.45 ppm respectively. These assignments were confirmed by comparison with known samples of 1-octene, and *cis*- and *trans*-2-octene, respectively, under the reaction conditions. Presumably the major kinetic product is PH dehydrogenated at the terminal positions of the monomer units, but isomerization is relatively fast under these conditions (eqn. 1).



Accordingly, subsequent heating of the reaction mixture yielded an increased concentration of C–C double bonds with an approximate steady state concentration of terminal double bonds. After 260 min the total concentration of PH double bonds was 0.13 M, of which 7 mM was the terminal double bond; commensurate loss of NBE (62%) was observed. (No further catalysis was observed at longer reaction times indicating catalyst decomposition.†) These results, represent, to our knowledge, the first example of the dehydrogenation of an aliphatic polymer to give any significant yield of unsaturation. The resulting concentration of C–C double bonds, 0.13 M, represents *ca.* 14% of the hexene units (of the PH) in the mixture.

As was recently reported,¹⁵ (MeO-ⁱPrPCP)IrH_n (**2**) is a more active catalyst for transfer-dehydrogenation of *n*-alkanes than the bis(*t*-butyl)phosphino analogue **1**. Accordingly, in a *p*-xylene solution of **2** (5 mM), NBE (0.22 M) and PH (1.1 M in PH repeat units), transfer-dehydrogenation proceeded to *ca.* 50% completion after 20 min at 150 °C. Concentrations of vinyl groups and internal

double bonds produced were 0.039 M and 0.056 M respectively, accompanied by the loss of 0.10 M NBE. After 50 min all NBE was consumed and the concentration of PH double bonds corresponded to 18% of hexene units. Isomerization, relative to dehydrogenation, is even more rapid with **2** than with **1**; no terminal vinyl groups were observed in the ^1H NMR spectrum after 50 min. Further, the use of complex **2**, unlike **1**, led to the formation of trisubstituted and conjugated double bonds (Fig. 1). \ddagger

Importantly, the molecular weight of the PH is unchanged under the reaction conditions, demonstrating that chain scission is negligible. Gel-permeation chromatography (GPC) measurements of the material before and after dehydrogenation reveal no significant difference in M_n (6540 vs. 6680), M_w (10250 vs. 10680), and PDI (1.57 vs. 1.60). Measurements on the dehydrogenated sample were made using both RI and UV detectors, although the saturated polymer is UV-silent; we note in this context the possibility of applications of dehydrogenation in polymer analysis as well as the synthesis of new materials.

In accord with the selectivity for terminal positions previously established for the dehydrogenation of *n*-alkanes,¹⁴ polyethylene (PE) was found to be a much less reactive substrate than PH. Nevertheless, PE could be dehydrogenated in moderate yields using catalyst **2**. \S Heating a solution of **2** (5 mM), NBE (0.21 M) and PE (3.2 M repeat units) for 230 min at 150 °C resulted in formation of 0.05 M PE double bonds and commensurate loss of NBE (no further catalysis at longer times). This corresponds to dehydrogenation of 1.6% of the PE C–C linkages. Using a higher concentration of catalyst **2** (15 mM), the degree of dehydrogenation achieved was 4.4% (0.14 M double bonds) after 230 min. As in the case of PH, no indication of chain scission was noted; molecular weight distributions as determined by GPC before and after dehydrogenation were as follows (0, 2, 8 h reaction time): M_n (606, 696, 599), M_w (3000, 3121, 2974), PDI (4.95, 4.48, 4.96).

In summary, we report a simple homogeneous catalytic method for the incorporation of double bonds into saturated polyolefins. The catalyst appears to be selective for branches vs. backbone (with kinetic selectivity for the terminal position). The molecular weights and molecular weight distributions of the polymer samples are unaffected by the reaction. The degree of unsaturation achieved (up to 18% per repeat unit in the case of PH, 4.4% for PE, without extensive effort at optimization) allows the controlled modification of saturated polyolefins by introducing alkene

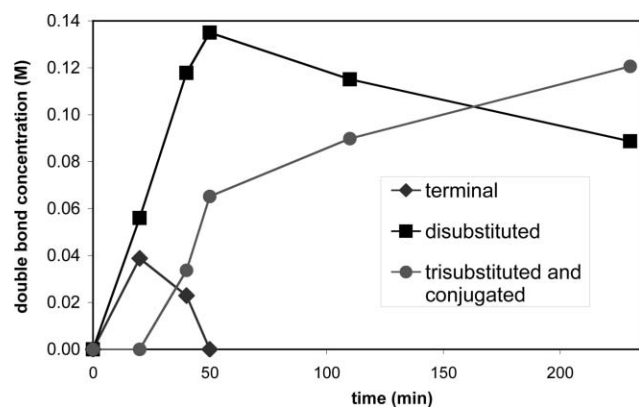


Fig. 1 Type and quantity of alkene groups introduced during PH dehydrogenation by catalyst **2** as a function of time.

functionality for further reactions. We are continuing to explore the development and application of dehydrogenation catalysts for the synthesis of polyolefins with controlled functionality.

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\dagger At room temperature, the reactions of **1** and **2** with NBE (in either the presence or absence of polymer, and in both alkane and arene solvents) give complexes that have been tentatively identified as “(MeO-^RPCP)Ir(NBE)” (R = *t*-Bu and *i*-Pr) (^{31}P NMR resonances at δ 62.6 and δ 53.3 respectively). These species have been found to act as precursors of the corresponding 14-electron fragments, “(MeO-^RPCP)Ir”. In the reaction of **2** and PH/NBE this remains a major species in solution throughout the course of the reaction. In addition, species are formed to which dehydrogenated polymer is apparently bound, “(MeO-^RPCP)Ir(olefin)” (δ 48.7, 46.8 and 44.7), identified by comparison with the reaction of **2** with linear octenes. Similar behavior is observed in the case of **2** and PE/NBE; however in this case one major, catalytically inactive product ultimately forms with a peak at δ 67.8. In the case of **1** and either PH or PE, a number of minor products are also observed, presumably the analogous “(MeO-^RPCP)Ir(olefin)” complexes (δ 59.2, 57.1 and 55.1). Loss of both polymer- and norbornene-bound species is observed upon further heating, with the appearance of a number of minor peaks (δ 95.3, 92.8, 81.9 and 81.1) which correlates with the eventual loss of catalytic activity.

\ddagger The trisubstituted olefinic group resonance was assigned by comparison with the product of dehydrogenation of 4-propylheptane (vinyl proton at δ 5.19) under the same conditions as the PH dehydrogenation. Resonances attributable to conjugated double bonds were assigned by comparison with 2,4-hexadiene.

\S Linear low-density PE (M_w = 4000, PDI = 2.35) was purchased from Aldrich and used without further purification. Low MW material was used to achieve good solubility and viscosity.

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