

Catalytic post-modification of alkene polymers Chemistry and kinetics of dehydrogenation of alkene polymers and oligomers with pincer Ir complexes

Amlan Ray^a, Yury V. Kissin^{a,*}, Keming Zhu^a, Alan S. Goldman^a,
Anna E. Cherian^b, Geoffrey W. Coates^b

^a Department of Chemistry and Chemical Biology, Rutgers-The State University of New Jersey, 610 Taylor Road, Piscataway, NJ 08854, USA

^b Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

Received 22 March 2006; accepted 5 April 2006

Available online 6 June 2006

Abstract

The paper presents details of catalytic dehydrogenation reactions of two high molecular weight, highly branched hydrocarbons, a polymer of 1-hexene and an oligomer of 1-butene, and describes kinetic analysis of these reactions. The dehydrogenation reactions were catalyzed with two pincer Ir complexes, [4-methoxy-2,6-C₆H₃(CH₂P-*tert*-Bu₂)₂]IrH₂ and [4-methoxy-2,6-C₆H₂(CH₂P-*iso*-Pr₂)₂]IrH₂, and were carried out at 150 °C in *p*-xylene solutions with norbornene as a hydrogen acceptor. The structure of all dehydrogenation reaction products and the Ir species was determined by ¹H and ³¹P NMR. Mechanistically, these reactions are similar to dehydrogenation reactions of low molecular weight alkanes. Kinetic analysis of the reactions yielded the values of effective rate constants for all major reaction steps in the catalytic cycle. The results show that catalytic dehydrogenation of branched polymers in the presence of an alkene hydrogen acceptor is feasible at increased temperatures and represents a viable route to post-synthetic modification of branched polyolefins.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Kinetics of dehydrogenation; Polyolefins; Dehydrogenation; Oligomers; Dehydrogenation; Pincer Ir complexes

1. Introduction

Catalytic dehydrogenation of polyolefins is an important subclass of alkane dehydrogenation reactions. This reaction represents a route to the synthesis of polyolefins with controlled functionalities. Incorporation of specific types of functionality, as well as control of the location of the functionalized groups and their amount, provides the means for the development of new classes of polyolefins with tailored mechanical, physical, and chemical properties [1,2].

There are three main strategies for producing functionalized polyolefins:

1. Direct incorporation of functionalized alkenes into polyolefin chains in the course of polymerization reactions [1–3].

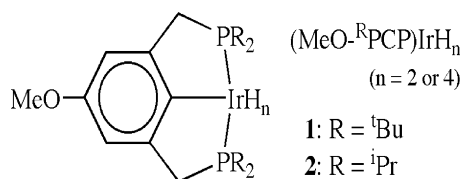
2. Introduction of catalyst-tolerant functionalities, such as hindered alkenes, unprotected and silyl-protected alcohols, etc., into polyolefin chains followed by their post-polymerization modification [1–3].

3. Functionalization of polyolefins via radical [1,2] or metal-mediated methods, for example, borylation of poly(1-butene), polyethylene and polypropylene [4], and oxy-functionalization of polypropylene [5].

One of the options within the third strategy is introduction of unsaturation into polyolefin chains via the catalytic dehydrogenation reaction. This option is based on significant progress that was made in the past two decades in the area of soluble transition-metal catalysts for the dehydrogenation of alkanes [6–8]. Pincer-ligated iridium complexes are particularly promising in this context [9,10]. Selective dehydrogenation of alkanes and alkyl groups in functionalized organic compounds (amines, ketones, etc.) is an important reaction with a wide range of potential applications [11]. Presently, the most effective cata-

* Corresponding author. Tel.: +1 732 445 5882.

E-mail address: ykissin@rutchem.rutgers.edu (Y.V. Kissin).



Scheme 1. Pincer Ir complexes.

lysts for these reactions are pincer-ligated Ir complexes [10,12]. The introduction of C=C bonds into aliphatic polymer chains can offer a starting point for a number of directions for polymer post-modification, including further functionalization and cross-linking with standard techniques to give materials with enhanced mechanical properties.

Two types of the catalytic dehydrogenation reactions of alkanes are practiced: (a) an acceptorless dehydrogenation reaction, a high-temperature reaction resulting in evolution of dihydrogen, and (b) a transfer dehydrogenation reaction in the presence of a sacrificial alkene acceptor. The latter reaction, in effect, represents hydrogen transfer from an alkane to an alkene. Here we present some details of dehydrogenation reactions of two high molecular weight, highly branched hydrocarbons, a polymer and an oligomer, using norbornene (NBE) as a hydrogen acceptor, and present the kinetic study of these reactions. Two polymeric substrates were chosen for demonstration of viability of the approach, poly(1-hexene) (PH) and oligomer of 1-butene (OB). The dehydrogenation reactions were catalyzed with two Ir complexes of the general formula $(\text{MeO-RPCP})\text{IrH}_2$ (see Scheme 1): [4-methoxy-2,6- $\text{C}_6\text{H}_3(\text{CH}_2\text{P-}i\text{-tert-Bu})_2$] IrH_2 (**1**) and [4-methoxy-2,6- $\text{C}_6\text{H}_2(\text{CH}_2\text{P-}i\text{-Pr})_2$] IrH_2 (**2**).

2. Experimental

Metallocene complexes $n\text{-BuCp}_2\text{ZrCl}_2$ and $(\text{Me}_4\text{Cp})\text{Si}(\text{Me})_2\text{N}^t\text{BuTiCl}_2$ were supplied by Boulder Chemical Company. Methylalumoxane (MAO) samples (toluene solutions) were supplied by Albemarle Corp. and Akzo Nobel Co. MAO concentration was ~20 wt.%, free AlMe_3 30 mol.% of the total [Al].

Atactic PH was prepared using as the catalyst components $(\text{Me}_4\text{Cp})\text{Si}(\text{Me})_2\text{N}^t\text{BuTiCl}_2$ and MAO (Akzo Nobel Co., PMAO-IP) which was dried under vacuum to remove residual AlMe_3 . Toluene solutions of the Ti complex (20 μmol) and MAO (40 mmol, [Al]:[Ti] = 2000) were added to a 100- cm^3 glass vial containing 35 cm^3 of 28 vol.% solution of 1-hexene in toluene and kept at 45 °C. The polymerization reaction continued for 30 min, after which the produced poly(1-hexene) was quenched with excess of 3 M HCl and extracted with hexane as a viscous oil (yield ~75%; M_n ~6900, the M_w/M_n ratio ~1.5).

Oligomerization of 1-butene was carried out using $n\text{-BuCp}_2\text{ZrCl}_2$ and MAO as the catalyst components. The reaction was carried out at 80 °C in a 50- cm^3 glass vial under the following conditions: solvent toluene, 20 cm^3 ; MAO 4.6 mmol; the Zr complex 9.2×10^{-3} mmol; [Al]:[Zr] = 500. The reactor was held at a constant 1-butene partial pressure 0.12 MPa; the reaction time was 120 min. The reaction produced 15.5 g of OB. The reaction mixture was treated with excess of isopropanol

to deactivate MAO and was distilled under vacuum into three fractions: the dimer (~5 g, distilled together with toluene); the trimer (~2.2 g); and the mixture of heavier oligomers, ~8 g, a clear, slightly viscous liquid.

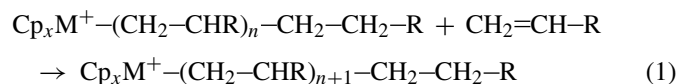
Ir complexes **1** and **2** were used as the dehydrogenation catalysts; they were synthesized as described earlier [13]. Transfer dehydrogenation reactions of PH and OB were carried out in *p*-xylene solutions containing the polymers (~1–2 M of monomer units), 5×10^{-3} M of the Ir complexes, and ~0.2 M of NBE. The reactions were conducted at 150 °C in NMR tubes sealed under argon. The reactions and several model catalyst reactions were monitored by ^1H , ^{13}C and ^{31}P NMR. The spectra were recorded with Varian 300 MHz spectrometer at 25 °C. Trimethylphosphine in deuterated mesitylene and hexamethyldisiloxane were used as external and internal standards, respectively.

Kinetic modeling was carried out using the React program by Alchemy Software.

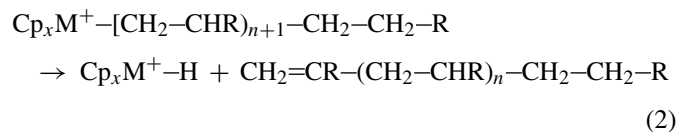
3. Results and discussion

3.1. Substrate species in dehydrogenation reactions of polymers

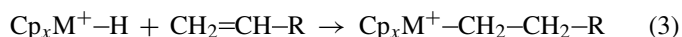
Mechanism of alkene polymerization reactions with Ziegler–Natta catalysts utilizing metallocene complexes is well established [14,15]. The active species in these catalyst systems are metallocenium cations, $\text{Cp}_x\text{M}^+\text{-R}$ ($\text{M} = \text{Zr}$ or Ti , $x = 1$ or 2), formed in reactions between metallocene complexes and MAO. The chain growth reaction in polymerization of an alkane $\text{CH}_2=\text{CH-R}$ is



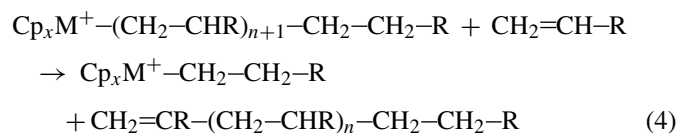
where R is C_2H_5 in the case of 1-butene and $n\text{-C}_4\text{H}_9$ in the case of 1-hexene. Two chain termination reactions are usually considered. One is the $\beta\text{-H}$ elimination reaction in the zirconocenium cation with the formation of the $\text{Cp}_x\text{M}^+\text{-H}$ cationic species:



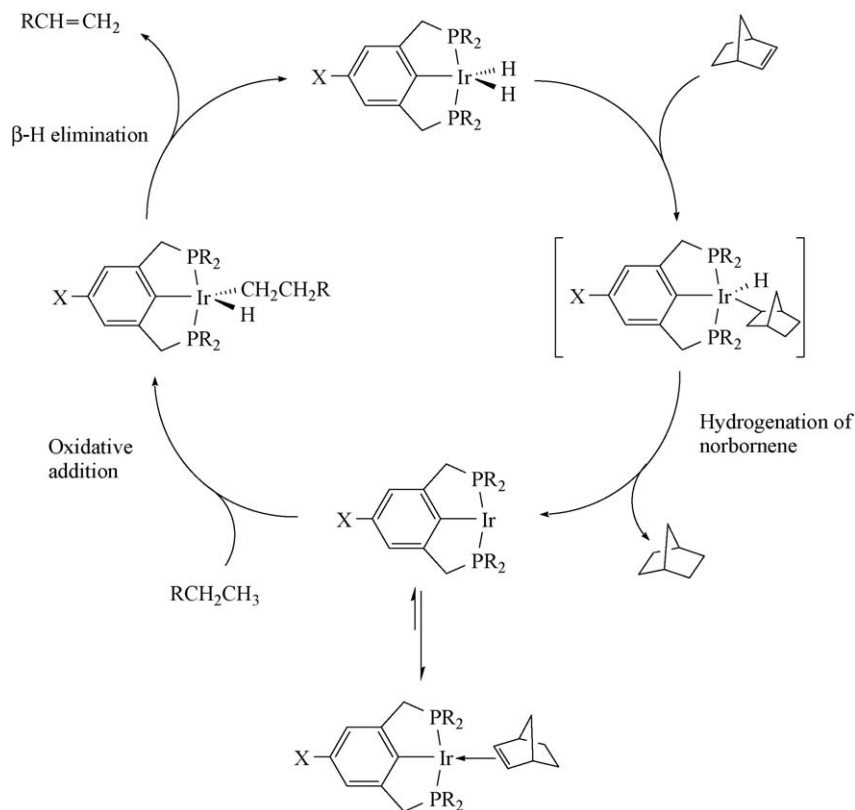
followed by monomer insertion into the M–H bond:



Another possibility is the chain transfer reaction to the monomer:

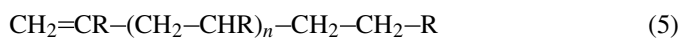


Both reactions result in the formation of an active center carrying a single monomer unit, $\text{Cp}_x\text{M}^+\text{-CH}_2\text{-CH}_2\text{-R}$, and the



Scheme 2. General scheme of transfer dehydrogenation reaction between an alkane $\text{CH}_3\text{—CH}_2\text{—R}$ and a sacrificial alkene, norbornene.

same polymer products:



These products contain three chemically distinct types of monomer units, the starting monomer unit, $-\text{CH}_2-\text{CH}_2-\text{R}$, the internal monomer units $-\text{CH}_2-\text{CHR}-$, and the last monomer unit in the chain, $\text{CH}_2=\text{CR}-$.

3.2. General scheme of transfer dehydrogenation reactions

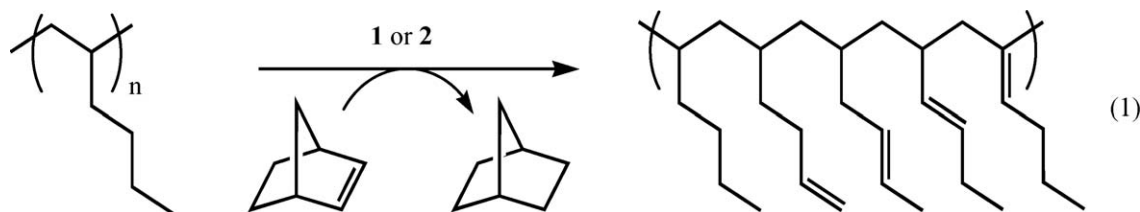
Scheme 2 gives the general reaction sequence in a transfer dehydrogenation reaction between an alkane $\text{R—CH}_2\text{—CH}_3$ and the sacrificial alkene, NBE [16]. Model experiments at room temperature showed that NBE reacts with **1** and **2** independently of the presence of an alkane. Based on the ^{31}P NMR data, the products of these reactions are complexes that have been tentatively identified as $(\text{MeO-}^{\text{R}}\text{PCP})\text{Ir-NBE}$ with $\text{R} = \textit{tert}$ -Bu and \textit{iso} -Pr, respectively (Scheme 2). Their ^{31}P resonances are at δ 62.6 and 53.3 ppm. Another sacrificial alkene used in transfer dehydrogenation of alkanes, 3,3-dimethyl-1-butene, also forms a stable adduct with the Ir species: the vinylene complex $(\text{PCP})\text{Ir}(\text{H})-\text{CH}=\text{CH}-\text{C}(\text{CH}_3)_3$ [16]. Both these species act as precursors of the 14-electron fragments, $(\text{MeO-}^{\text{R}}\text{PCP})\text{Ir}$, containing tri-coordinated Ir(1+) atoms. As was discussed earlier [16], the kinetic analysis of cycloalkane dehydrogenation with a similar p -unsubstituted $(\text{PCP})\text{Ir}$ complex showed that these $(^{\text{R}}\text{PCP})\text{Ir}$ species are the true active centers in alkane dehydrogenation reactions.

3.3. Dehydrogenation of PH: main chemistry of the reactions

Poly(1-hexene) represents the simplest model for the study of polymer dehydrogenation reactions of highly branched polymers. Due to its relatively high molecular weight (the average number of monomer units per polymer molecule, n in Eq. (5), is ~ 80), reactions of the starting and the last monomer units in PH macromolecules can be neglected and the only dehydrogenation reaction to be considered is that involving the n -butyl group, the side-group in the internal monomer units.

Two transfer dehydrogenation reactions of PH were carried out, one with complex **1** and another with complex **2**. The following initial concentrations of reagents were used: the effective concentration of the monomer units, n -butyl groups = 2.0 M, $[\text{NBE}] = 0.22$ M, $[\text{PCPIrH}_2] = 5 \times 10^{-3}$ M. The molecular weight of the polymer did not change under these reaction conditions, demonstrating that chain scission is negligible. GPC measurements of the polymer before and after the dehydrogenation reaction were: M_n 6540 versus 6680, M_w 10250 versus 10680, and M_w/M_n 1.57 versus 1.60.

Judging by ^{31}P NMR spectra, the $(\text{MeO-}^{\text{R}}\text{PCP})\text{Ir-NBE}$ species produced in the reaction of **2** and NBE remains the major NMR-observable species throughout the dehydrogenation reaction of PH as well. As the reaction progresses, additional Ir species are formed, they apparently contain the dehydrogenated polymer bound to the Ir atom, $(\text{MeO-}^{\text{R}}\text{PCP})\text{Ir-alkene}$, with the signals at δ 48.7, 46.8 and 44.7 ppm. These species were iden-



Scheme 3. Products of catalytic dehydrogenation of poly(1-hexene).

tified by comparison with the reaction products of complex **2** and linear octenes. In the case of complex **1**, a number of minor products were also observed during PH dehydrogenation, presumably the analogous (MeO-^RPCP)Ir-alkene complexes (δ 59.2, 57.1 and 55.1 ppm). After prolonged heating, loss of both polymer- and NBE-bound Ir species occurred and a number of minor signals (δ 95.3, 92.8, 81.9 and 81.1 ppm in ³¹P NMR) appeared, in parallel with the loss of catalytic activity.

As we discussed earlier [16,17], the primary place of the catalytic attack of the (MeO-^RPCP)Ir species on an alkane molecule is the CH₂-CH₃ bond. In the case of PH, this bond is positioned at the end of each monomer unit. However, the same Ir complexes are effective catalysts of C=C bond migration. The types of the resulting double bonds in PH are shown in Scheme 3.

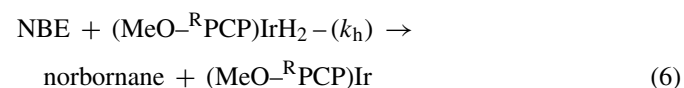
¹H NMR is the most straightforward technique for the study of dehydrogenation reactions of branched polyolefins. The (=C)H signals of four alkene groups were monitored:

1. NBE, the signal at 6.0 ppm;
2. primary dehydrogenation products, polymer-CH₂-CH₂-CH=CH₂, multiplets at 5.1 and 5.8 ppm;
3. isomerized dehydrogenation products, polymer-CH₂-CH=CH-CH₃, the signal at 5.6 ppm;
4. tri-substituted >C=CH-CH₂-CH₂-CH₃ products, the signal at ~5.2 ppm. The last resonance was assigned by comparison with the product of dehydrogenation of 4-propylheptane under the same conditions as in the dehydrogenation reaction of PH.

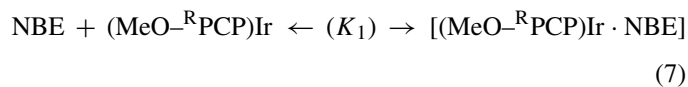
3.4. Dehydrogenation of PH: kinetics

The kinetic scheme of PH dehydrogenation is based on the ³¹P NMR results, as well as on the earlier kinetic analysis of dehydrogenation of cyclooctane with the PCPIrH₂ complex [16]. Dehydrogenation of PH can be represented by the following set of reactions.

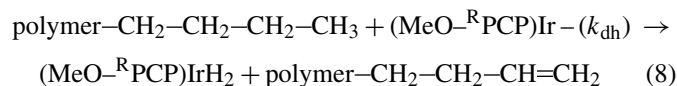
Hydrogenation of NBE and the formation of active species in the dehydrogenation reaction:



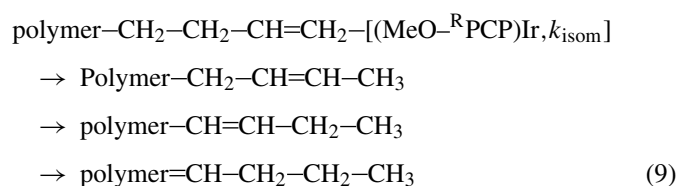
Equilibrium of free and bound active species:



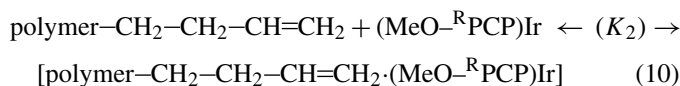
Dehydrogenation reaction of the substrate, the CH₂-CH₃ bond in PH:



Catalytic isomerization of the dehydrogenated substrate:



Binding of active species by the produced double bonds:



The equilibria shown in the reactions in Eqs. (7) and (10) are strongly shifted in favor of the complexes; the (MeO-^RPCP)Ir species are present in the reaction medium in very low concentrations and are not experimentally observed [16].

The overall kinetics of the set of chemical reactions represented by Eqs. (6)–(10) is too complex to be analyzed explicitly. However, it can be modeled with a sufficient degree of precision using a kinetic modeling program. The modeling program React we used takes, as an input, all chemical reactions in the kinetic scheme, initial concentrations of all feeds and the initial (guessed) values of all rate constants. The program calculates concentrations of all reactants versus time. The modeling involves iterative adjustment of the rate constants by comparing the predicted versus the experimentally measured concentrations of different double bonds as a function of time. Earlier applications of the React program demonstrated its usefulness in kinetic analysis of complex multi-stage reactions [18,19].

Several assumptions were used to simplify the kinetic treatment:

1. All rate constants in the equilibrium reactions involving (MeO-^RPCP)Ir (K_1 , K_2) were set as very high values, $>1 \times 10^3$, to exclude these steps from the overall kinetic analysis.
2. In the absence of the data on the concentration of free catalytic species (MeO-^RPCP)Ir, the equilibrium constants K_1 and K_2 could not be independently evaluated. As a result, the values

Table 1
Estimates of the rate constants of transfer dehydrogenation reactions of PH

Reaction	Rate constant	
	2 ^a	1 ^a
Hydrogenation of NBE with (MeO- ^R PCP)IrH ₂	$k_h = \sim 18.6 \text{ M}^{-1} \text{ min}^{-1}$	$k_h = \sim 3.8 \text{ M}^{-1} \text{ min}^{-1}$
Dehydrogenation of <i>n</i> -butyl group in PH	$k_{dh}/K_1 = \sim 0.3 \text{ min}^{-1}$	$k_{dh}/K_1 = 0.15 \text{ min}^{-1}$
Relative strength of (MeO- ^R PCP)Ir complexes with NBE and the dehydrogenated <i>n</i> -butyl group (assumption)	$K_2/K_1 = \sim 5$	$K_2/K_1 = \sim 5$
C=C-bond isomerization in dehydrogenated <i>n</i> -butyl group	$k_{iso} = \sim 0.15 \text{ min}^{-1}$	$k_{iso} = 0.06 \text{ min}^{-1}$
Deactivation of (MeO- ^R PCP)Ir	–	$k_{deact}/K_1 = 0.01 \text{ min}^{-1}$

^a Catalyst.

of the dehydrogenation reaction rate constant, k_{dh} , could not be evaluated as such. Instead, the k_{dh}/K_1 ratios were evaluated as the composite reaction parameters.

- The isomerization reaction, Eq. (9), is quite fast and the primary dehydrogenation product of the *n*-butyl group, polymer-CH₂-CH₂-CH=CH₂, is always present in the reaction mixture in a relatively low concentration. Therefore, the kinetic modeling was carried out for a combined yield of all dehydrogenation products, the primary, polymer-CH₂-CH₂-CH=CH₂, and the secondary, polymer-CH₂-CH=CH-CH₃, polymer-CH=CH-CH₂-CH₃ and polymer=CH-CH₂-CH₂-CH₃.

The first attempts at adjusting the kinetic parameters of the reactions in Eqs. (6)–(10) to the experimental data showed that one more step should be added to the reaction scheme in the case of a less vigorous PH reaction catalyzed with complex **1** to account for its kinetic behavior at the late stages of the reaction: irreversible poisoning of the active species (MeO-^RPCP)Ir, a reaction with the rate constant k_{deact} . Such poisoning can be, for example, the result of a slow reaction of (MeO-^RPCP)Ir with minute quantities of nitrogen in the reaction mixture. Addition of the catalyst poisoning reaction has proved to be sufficient for a satisfactory description of the overall reaction scheme in the case of catalysis with complex **1**.

The kinetic data for this reaction are shown in Fig. 1. Even in the case of the less active catalyst **1**, ~7% of all monomer units can be dehydrogenated, i.e., each polymer molecule contains, on average, 5–6 double bonds. This figure also shows the results of kinetic modeling for the dehydrogenation reaction. The dehydrogenation reaction of PH using complex **2** proceeds much faster and the catalyst deactivation reaction can be neglected in the kinetic analysis. The sets of the rate constant estimations for both complexes are given in Table 1.

3.5. Dehydrogenation of OB: main reactions

¹³C NMR analysis of the heavy fraction of OB showed that it contained three distinguishable types of monomer units (see Eq. (5) and Scheme 4):

- The starting monomer unit, the *n*-butyl end-group in the oligomer chain. Its CH₃ signal in the ¹³C NMR spectrum is at 14.65 ppm.

- The internal monomer units; contain ethyl side-groups attached to the oligomer main chain. Their CH₃ signals in the ¹³C NMR spectrum are at 10.80–10.85 ppm.
- The last unit in the oligomer chain; contains the vinylidene double bond (¹³C NMR signals at 110.2 and 150.9 ppm); its CH₃ signal is at 12.75 ppm.

Because the post-treatment of the oligomerization products with an alcohol results in conversion of MAO into a mixture of

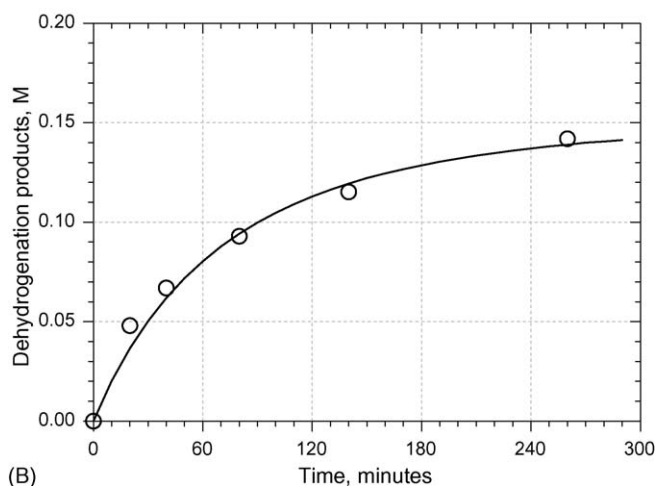
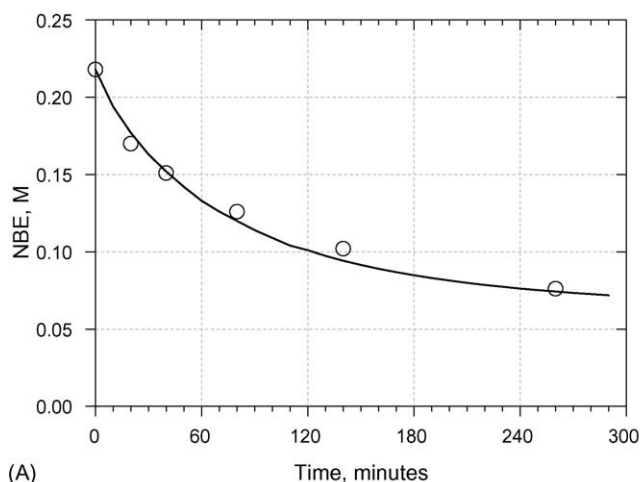
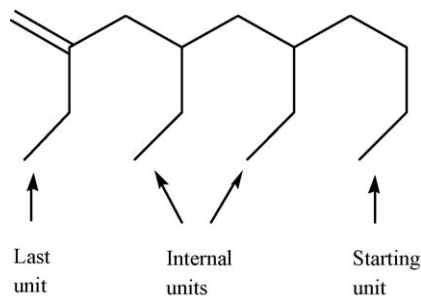
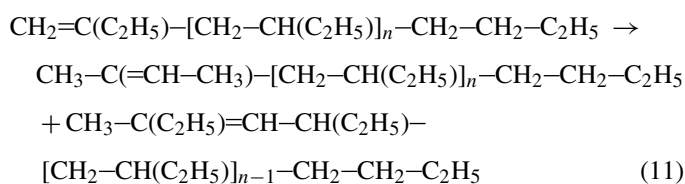


Fig. 1. Kinetics of transfer dehydrogenation of PH with complex **1**. (A) NBE concentration; (B) combined yield of dehydrogenation products (experimental data). Lines: results of kinetic modeling.



Scheme 4. Structure of 1-butene oligomer.

acidic species, some of the vinylidene double bonds in the last monomer units are converted into tri-substituted internal double bonds:



The average polymerization degree n in the heavy fraction of OB was estimated from the signal area of different CH_3 signals in the ^{13}C NMR spectrum: $n \sim 4.7$.

The transfer dehydrogenation reaction of OB was carried at 150°C with complex **2** and with NBE as a hydrogen acceptor. The following initial concentrations of reagents were used: the total concentration of oligomer molecules, equal to the concentration of the starting units (see Eq. (5)), 1.08 M; the concentration of the internal units (ethyl groups) 2.93 M; the concentration of the last units with vinylidene double bonds 0.94 M; the concentration of isomerized last units with internal double bonds 0.14 M; $[\text{NBE}] = 0.30\text{ M}$; $[\mathbf{2}] = 5 \times 10^{-3}\text{ M}$.

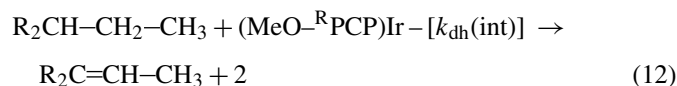
From the chemical and the kinetic standpoints, dehydrogenation of OB represents a more complex case compared to that of PH: reactivities of different CH_2-CH_3 groups in the dehydrogenation reactions of the three dehydrogenation substrates, the starting, the internal and the last monomer units, a priori are expected to be quite different. The dehydrogenation reaction of OB was also followed by ^1H NMR. The $(=\text{C})\text{H}$ signals of the following groups were monitored:

1. NBE, 5.97 ppm;
2. the last units with the vinylidene double bond, a doublet at 4.8–4.9 ppm;
3. the sum of the last units with internal double bonds (Eq. (11)) and the isomerized dehydrogenation products of the internal monomer units, a multiplet centered at 5.28 ppm;
4. dehydrogenation products of the last units, $\text{CH}_2=\text{CH}-\text{C}(=\text{CH}_2)-\text{R}$, multiplets in the 4.9–5.05 ppm and 6.3–6.4 ppm. The resonances attributable to conjugated double bonds were assigned by comparison with 2,4-hexadiene;
5. primary dehydrogenation products of the internal units, $\text{CH}_2=\text{CH}-\text{R}$, a multiplet at ~ 5.7 ppm;
6. primary dehydrogenation products of the starting units, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{R}$, a multiplet at 5.83 ppm;

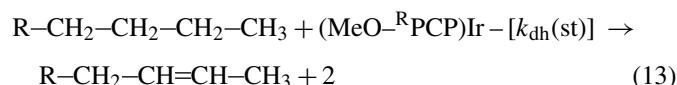
7. secondary (isomerized) dehydrogenation products of the starting units, $\text{R}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$, a signal at 5.45 ppm.

3.6. Dehydrogenation of OB: kinetics

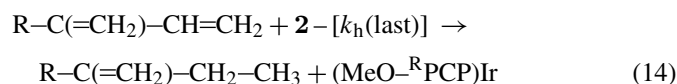
The kinetics of the OB dehydrogenation reaction was also modeled using the React kinetic program. Dehydrogenation reactions of the three types of monomer units were analyzed separately using the same set of reactions as in the case of PH, Eqs. (6)–(10). The respective rate constants are $k_{\text{dh}}(\text{st})$, $k_{\text{dh}}(\text{int})$ and $k_{\text{dh}}(\text{last})$. As before, the active species in the dehydrogenation reactions is assumed to be the tri-coordinated $(\text{MeO}-^{\text{R}}\text{PCP})\text{Ir}$ species, which is present in the reaction medium in a very low concentration and is not experimentally observable. All rate constants in the equilibrium reactions involving $(\text{MeO}-^{\text{R}}\text{PCP})\text{Ir}$ (K_1 and K_2 in the reactions in Eqs. (7) and (10), respectively) were also set as very high values to exclude these steps from the overall kinetic analysis. The primary dehydrogenation product of the internal monomer unit, $\text{R}_2\text{CH}-\text{CH}=\text{CH}_2$, rapidly isomerizes into tri-substituted double bond $\text{R}_2\text{C}=\text{CH}-\text{CH}_3$. This isomerization step was omitted from the kinetic scheme and the overall dehydrogenation reaction for the internal units was described as



Dehydrogenation product of the starting monomer unit, $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$, also rapidly isomerizes into the di-substituted double bond, $\text{R}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$, the same reaction as in Eq. (9). This isomerization step was also omitted and the overall dehydrogenation reaction for the internal units was described as



The first attempts at adjusting the kinetic parameters to the experimental data showed that two more reaction steps should be added to the scheme to account for the kinetic behavior of the dehydrogenation reaction at its final stages. The first of the reactions accounts for the fact that the product of dehydrogenation of the last monomer unit containing the conjugated vinyl bond $-\text{CH}=\text{CH}_2$ can also serve as a hydrogen acceptor, similarly to the double bond in NBE or in 3,3-dimethyl-1-butene [16]:



The second added reaction is irreversible poisoning of the active species (rate constant k_{deact}), the same as in the dehydrogenation reaction of PH. Addition of these reactions to the set of reactions represented by Eqs. (6)–(10) has proved to be sufficient for the satisfactory description of the overall reaction scheme.

Fig. 2 gives some data on catalytic dehydrogenation of OB. After 60 min, $\sim 4\%$ of the starting monomer units and $\sim 7\%$ of the last units were dehydrogenated in the reaction with complex **2**. Fig. 2 also shows the modeling results, and the estimates of

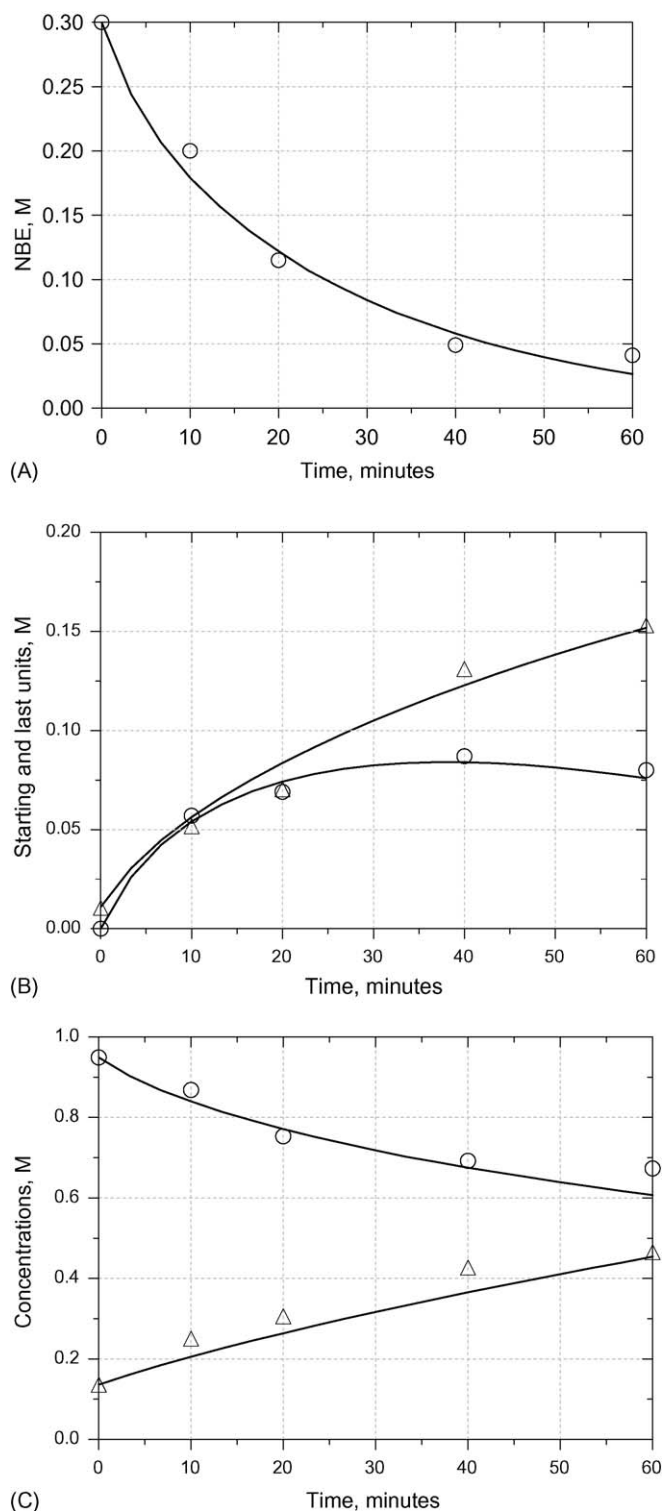


Fig. 2. Kinetics of transfer dehydrogenation of OB with complex 2. (A) NBE concentration; (B) \circ , dehydrogenation products from the starting units and Δ , dehydrogenation products from the last units; (C) \circ , vinylidene bonds in the last units and Δ , combined products from isomerization of the last units and dehydrogenation/isomerization of the internal units. Lines: results of kinetic modeling.

the rate constants are given in Table 2. As before, the values of all dehydrogenation reaction rate constants, k_{dh} , could not be evaluated as such; instead, the k_{dh}/K_1 ratios were evaluated as the composite reaction parameters.

Table 2

Estimates of the rate constants of transfer dehydrogenation reactions of OB with complex 2

Reaction	Rate constant
Hydrogenation of NBE with $(\text{MeO-}^R\text{PCP})\text{IrH}_2$	$k_h \approx 18 \text{ M}^{-1} \text{ min}^{-1}$
Dehydrogenation of the starting monomer unit	$k_{dh}(\text{st})/K_1 = 4.4 \text{ min}^{-1}$
Dehydrogenation of the internal monomer unit	$k_{dh}(\text{int})/K_1 = 0.33 \text{ min}^{-1}$
Dehydrogenation of the last monomer unit	$k_{dh}(\text{last})/K_1 \approx 2.5 \text{ min}^{-1}$
Hydrogenation of the dehydrogenated starting monomer unit	$k_h(\text{st}) \approx 0.012 \text{ min}^{-1}$
Relative strength of $(\text{MeO-}^R\text{PCP})\text{Ir}$ complexes with NBE and the dehydrogenated starting unit (assumption)	$K_2/K_1 \approx 30$
C=C-bond isomerization in the starting monomer unit	$k_{iso} \approx 6 \times 10^{-3} \text{ min}^{-1}$
Deactivation of $(\text{MeO-}^R\text{PCP})\text{Ir}$	$k_{deac}/K_1 \approx 0.03 \text{ min}^{-1}$

4. Conclusions

These data show that transfer dehydrogenation of highly branched polymers, such as PH and OB, catalyzed by pincer PCPIrH_2 complexes in the presence of an alkene hydrogen acceptor is feasible at increased temperatures and represents a viable route to post-synthetic modification of branched polyolefins.

Mechanistically, these reactions are similar to the previously reported transfer dehydrogenation reactions of low molecular weight alkanes [16]. Kinetic modeling of two similar dehydrogenation reactions, those of PH and OB, which were carried out at the same temperature and with the same hydrogen acceptor, NBE, using Ir complexes 1 and 2 showed that the set of reactions previously established for dehydrogenation of cyclooctane at a much lower temperature, 55 °C (see Scheme 2) [16], is also adequate for the description of dehydrogenation reactions involving branched polymer and oligomer molecules. The only additional reaction introduced in the present reaction scheme is a slow catalyst deactivation reaction. This reaction is negligible in alkane dehydrogenation reactions at 55 °C but manifests itself under our experimental conditions. The effective rate constant of the deactivation reaction, k_{deac}/K_1 , assuming that the deactivation involves the tri-coordinated $(\text{MeO-}^R\text{PCP})\text{Ir}$ species, is in the range of $1.0 \times 10^{-2} \text{ min}^{-1}$ to $3.0 \times 10^{-2} \text{ min}^{-1}$.

When the rate constants of different steps in the dehydrogenation reactions of PH and OB are compared, one has to take into consideration that the curve-fitting process without an option of the best-fit calculations gives only approximate modeling of the reaction kinetics, usually not better than ± 20 –25%. Overall, the obtained kinetic results for dehydrogenation of the two highly branched, high molecular weight alkanes are similar. The only significant difference between the dehydrogenation reactions of PH and OB is in the value of the effective dehydrogenation rate constant of the *n*-butyl group with the $(\text{MeO-}^R\text{PCP})\text{Ir}$ species derived from complex 2, k_{dh}/K_1 in Table 1 and $k_{dh}(\text{st})/K_1$ in Table 2. These values differ by a factor of ~ 15 . This difference can be attributed to diffusion retardation of the dehydrogenation reaction of PH which was carried out in a concentrated solution in *p*-xylene, $\sim 140 \text{ g/l}$. The data in Table 2 show also that the values of the dehydrogenation rate constants of two end-groups

in the 1-butene oligomer molecules, the starting unit, the *n*-butyl group, and the last unit, $R(C=CH_2)-CH_2-CH_3$, are comparable and are one order of magnitude higher than the same value for the internal units in OB, the ethyl groups.

Table 1 compares efficiencies of two Ir complexes, **1** and **2**, in the dehydrogenation reaction of PH under the same conditions. The main difference between the two complexes is their reactivity in hydrogenation of the sacrificial alkene NBE (Eq. (6)): the rate constant of this reaction is ~ 5 times higher in the case of complex **2**. On the other hand, the reactivities of the two proposed active species, $(MeO-RPCP)Ir$ (with $R = iso-Pr$ and *tert*-Bu) in the dehydrogenation reaction of the *n*-butyl group in PH (Eq. (8)), as well as their reactivities in the isomerization reactions of the produced vinyl double bonds (Eq. (9)), are very similar.

Acknowledgment

We thank the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, US Department of Energy for support of this research, grant DE-FG02-93ER14353.

References

- [1] (a) G. Moad, Prog. Polym. Sci. 24 (1999) 81;
(b) L.S. Boffa, B.M. Novak, Chem. Rev. 100 (2000) 1479;
(c) N.K. Boen, M.A. Hillmyer, Chem. Soc. Rev. 34 (2005) 267.
- [2] T.C.M. Chung, Functionalization of Polyolefins, Academic Press, San Diego, CA, 2002.
- [3] Y. Kondo, D. Garcia-Cuadrado, J.F. Hartwig, N.K. Boen, N.L. Wagner, M.A. Hillmyer, J. Am. Chem. Soc. 124 (2002) 1164.
- [4] C. Bae, J.F. Hartwig, N.K. Boen Harris, R.O. Long, K.A. Anderson, M.A. Hillmyer, J. Am. Chem. Soc. 127 (2005) 767.
- [5] N.K. Boen, M.A. Hillmyer, Macromolecules 36 (2003) 7027 (references therein).
- [6] M.J. Burk, R.H. Crabtree, J. Am. Chem. Soc. 109 (1987) 8025.
- [7] C.M. Jensen, Chem. Commun. (1999) 2443.
- [8] A.S. Goldman, Dehydrogenation, homogenous, in: I.T. Horvath (Ed.), The Encyclopedia of Catalysis. I, vol. 3, John Wiley & Sons, New York, 2003, p. 25.
- [9] (a) M. Gupta, C. Hagen, R.J. Flesher, W.C. Kaska, C.M. Jensen, Chem. Commun. (1996) 2083;
(b) W. Xu, G.P. Rosini, M. Gupta, C.M. Jensen, W.C. Kaska, K. Krogh-Jespersen, A.S. Goldman, Chem. Commun. (1997) 2273;
(c) I. Göttker-Schnetmann, P. White, M. Brookhart, J. Am. Chem. Soc. 126 (2004) 1804.
- [10] M. Liu, E.B. Pak, B. Singh, C.M. Jensen, A.S. Goldman, J. Am. Chem. Soc. 121 (1999) 4086.
- [11] R.H.J. Crabtree, Chem. Soc. Dalton Trans. 17 (2001) 2437.
- [12] C.M. Jensen, Chem. Commun. (1999) 2443.
- [13] K. Krogh-Jespersen, M. Czerw, K. Zhu, B. Singh, M. Kanzelberger, N. Darji, P.D. Achord, K.B. Renkema, A.S. Goldman, J. Am. Chem. Soc. 124 (2002) 10797.
- [14] B.A. Krentsel, Y.V. Kissin, V.I. Kleiner, L.L. Stotskaya, Polymers and Copolymers of Higher α -Olefins, Hanser, New York, 1997 (Chapter 3).
- [15] E.Y.-X. Chen, T. Marks, J. Chem. Rev. 100 (2000) 1391.
- [16] K.B. Renkema, Y.V. Kissin, A.S. Goldman, J. Am. Chem. Soc. 123 (2003) 7770.
- [17] A. Ray, K. Zhu, Y.V. Kissin, A.E. Cherian, G.W. Coates, A.S. Goldman, Chem. Commun. (2005) 3388.
- [18] J.W. Bozelli, J. Chem. Ed. 77 (2000) 165.
- [19] Y.V. Kissin, Macromol. Theory Simul. 11 (2002) 67.