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Branching Regulation in Olefin Polymerization via Lewis Acid Triggered Isomerization of Monomers

Hatice E. Basbug Alhan,[a] Glen R. Jones,*[a] Eva Harth,*[a]

Abstract: We present a new strategy to regulate branching in chain-walking olefin polymerization by triggering a rapid isomerization of 1-alkene monomers into internal olefins by adding a Lewis acid. Polymerization of internal alkenes proceeds *via* chain-walking to give polymers with much higher branching than 1-alkene analogues. The utility of this approach is exemplified by synthesis of well-defined block copolymers with distinct branching characteristics per block by addition of Lewis acid midway through a reaction. We propose a novel mechanism whereby Lewis acid undergoes a counterion swap with the complex which favors isomerization as well as forming adducts with ancillary ligands, freeing coordination sites for internal alkene coordination polymerization.

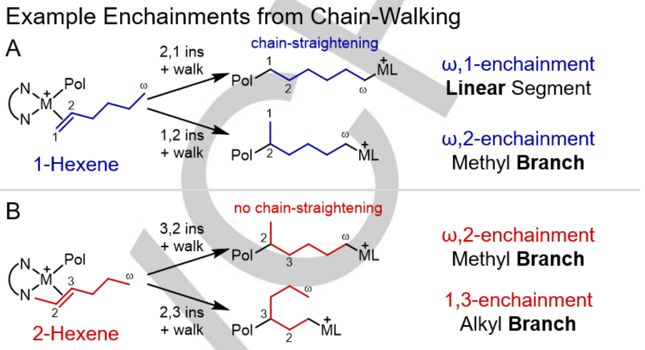
Introduction

Polyolefins are the most important class of polymers in terms of volume of material produced and ubiquity in everyday life. Comprised of alkenes with the general formula C_nH_{2n}, the wide-ranging properties from different polyolefins arise from parameters such as molecular weight, tacticity, and branching.

High branching, such as that found in low-density polyethylene (LDPE), prevents chains from closely packing making the material amorphous with high flexibility and low tensile strength. Low branching allows polymer chains to closely pack into a crystalline form, thus achieving a rigid, inflexible material such as high-density polyethylene (HDPE). Block copolymers which contain segments with both low and high branching are highly valued due to thermoplastic elastomeric behavior[1] and their ability to compatibilize immiscible polymer blends for recycling applications.[2] These materials have typically been prepared by living coordination-insertion polymerization with sequential addition of different monomers, or variation of temperature and pressure.[3] Other techniques[4] developed to vary branching include chain-shuttling polymerization,[5] light mediated approaches with iridium cocatalysts,[6] and redox active catalysts.[7]

In 1995 Brookhart and coworkers first reported the use of palladium and nickel diimine catalysts for the polymerization of olefins.[8] These catalysts are known to be able to incorporate small amounts of polar functionality into a polymer chain[9] and operate with a so-called chain-walking mechanism whereby a series of β-hydride eliminations and insertions can allow the metal to effectively ‘walk’ along the chain.[10]

The nature of chain-walking enables the synthesis polyethylene with branches as well as poly(1-alkenes) with high linearity. Tuning electronics of the catalyst through ligand design has been shown to alter the amount of chain-walking to give polymers with different branching.[11] Differences in branching can also arise from the position of the double bond in the monomer. Scheme 1A shows examples of enchainments from chain-walking; 1,2 vs. 2,1 insertion of a 1-alkene followed by chain-walking can result in either a branched or linear unit. In comparison, chain walking of internal olefins e.g. 2-alkenes are unable to form highly linear sequences due to the internal position of the double bond (scheme 1B). Chain-walking polymerization of these monomers therefore results in highly branched polymers.



Scheme 1: Example enchainments from chain-walking of A) 1-hexene, and B) 2-hexene.

Chain-walking of internal alkenes is of interest because it allows for highly branched polymers. However, polymerization of these monomers is more challenging than 1-alkenes, which has been suggested to be due to steric and electronic barriers to insertion in the Cossee-Arlman mechanism.[12] Early work by Brookhart showed that palladium catalysts polymerized *trans*-2-hexene at a very slow rate, reporting only 0.8% yield of polymer in a typical reaction time frame (scheme 2).[13] Low rates were also observed for cyclopentene with a similar palladium complex, with reactions taking 6 days.[14] Nickel catalysis has been shown to be more successful at polymerizing internal alkenes due to their higher activity, although initial work from Brookhart indicated a strong preference for *trans* isomer; no polymerization of *cis*-2-butene was reported.[15] In 2017 Shiono and coworkers reported successful homopolymerization of a range of 2-alkenes from a nickel diimine catalyst.[12, 16] Nickel catalysts have shown further potential in the polymerization of internal olefins,[17] although block copolymers with 1-alkenes have never been reported. Another downside is the higher cost of internal alkenes compared to 1-alkene counterparts.

We envisioned that a potential way to overcome the limitations and downsides of internal alkene polymerization and to form block copolymers with different branching structures would be to utilize an isomerization reaction in order to transform readily available 1-alkenes into internal alkenes which could then go on to polymerize via a chain walking mechanism to give highly branched polymers. Pioneering work by Otsu and coworkers in the 1960’s and 70’s explored the polymerization of 2-alkenes such

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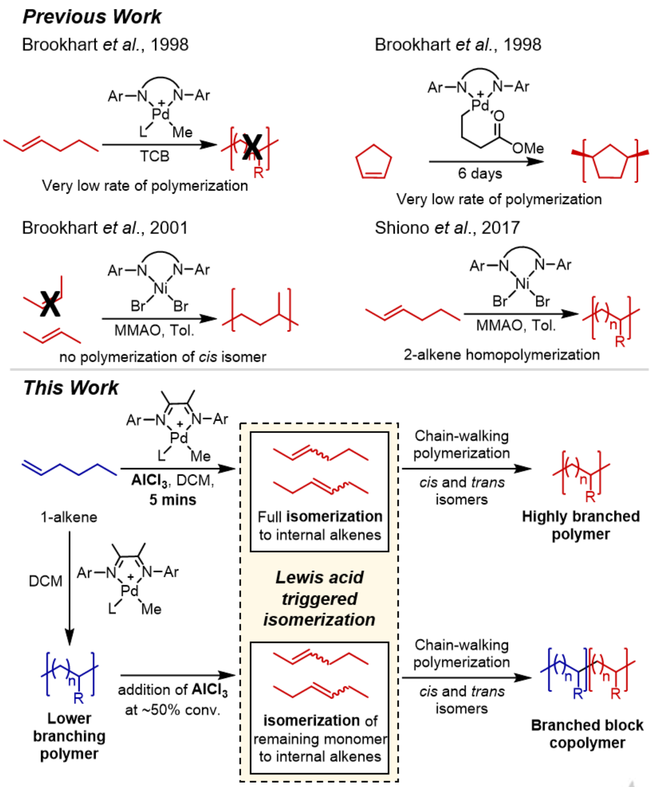
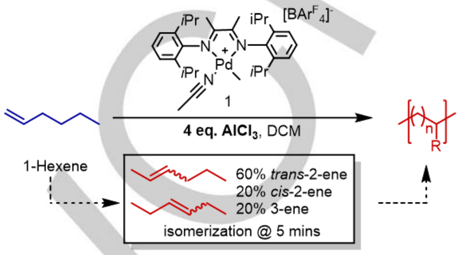


Scheme 2: (Top) Examples of previous work involving the polymerization of internal alkene monomers using cationic palladium and nickel diimine catalysts. (Bottom) The triggered isomerization approach described in this work.

as 2-heptene and 2-octene with Ziegler-Natta catalysts in a process known as monomer-isomerization polymerization.[18] The polymers formed were found to be structurally identical to those of the corresponding 1-alkene. Mechanistically the reaction was found to occur via isomerization of charged 2-alkenes to 1-alkenes which are then consumed in polymerization, driving the isomerization equilibrium to form more 1-alkene. Our approach differs from Otsu's work as we are able to trigger isomerization at a time of our choosing by adding a Lewis acid cocatalyst, our isomerization is very fast compared to polymerization, the MWDs are narrow in our polymerization, and the starting material is the more readily available 1-alkene. More recently, Takeuchi has reported chain-walking catalysts for the polymerization of alkenylcyclohexanes which was dubbed "precise isomerization polymerization".[19] This work is perhaps better described as catalysis with full chain-walking, otherwise known as 'chain-straightening',[20] yielding only ω-1 enchainment.

Herein we describe the use of a Lewis acid cocatalyst with palladium diimine complexes which facilitates an isomerization of 1-alkenes to yield free internal alkene monomers in just 5 minutes. Surprisingly, the polymerization of these isomers occurs to high conversions in just 3 hours to yield polymers with narrow molecular weight distributions (MWDs) and much higher branching than traditional Pd-mediated polymerizations of 1-alkenes. Preliminary mechanistic investigations implicate a counterion switch in the fast isomerization reaction, and the formation of adducts between Lewis acid and ancillary ligands which would otherwise inhibit internal alkene polymerization. Block copolymers of 1-alkenes and internal alkenes can be prepared using triggered isomerization by adding Lewis acid midway through a normal 1-alkene polymerization. This new concept in polyolefin block copolymer synthesis is a one pot process that only requires one starting monomer and an inexpensive additive.

Results and Discussion



Scheme 3: Polymerization of 1-hexene with palladium catalyst 1 in the presence of $AlCl_3$ showing full isomerization at 5 minutes. Branched polymer structure due to chain-walking is represented by n and R.

Our initial observation of enchanced alkene isomerization in the presence of Lewis acid was noted during a study of reactivity ratios of alkenes and polar monomers in palladium-diimine catalyzed polymerizations. Attempts to alter polar monomer reactivty with Lewis acids showed low rates of polymerization. However, a control reaction in which a Lewis acid, $AlCl_3$, was added to a polymerization of 1-hexene with palladium catalyst, 1, scheme 3, yielded a polymer with a dramatically different structure in ^{1}H NMR (fig. 1A). Poly(hexene) synthesized without Lewis acid was calculated to have 105 branches per 1000 carbon atoms, whereas addition of Lewis acid (4 eq.) yielded a polymer with 152 branches per 1000 carbon atoms.

Regular sampling and kinetic analysis of the polymerization revealed that in the presence of $AlCl_3$ 1-hexene is rapidly isomerized to 2-hexene and 3-hexene within the first five minutes, as evidenced by the disappearance of 1-alkene protons (5.82 ppm and 4.96 ppm, t=0, fig. 2) and the appearance of internal olefin protons (5.42 ppm, t=5, fig. 2). Polymerization of these internal olefins then proceeds with living characteristics including a linear increase in molecular weight with conversion, ESI section 5.3, (85% conversion in 3 hours, M_n = 46.1 kDa (SEC_{THF})) and low dispersity ($Đ$ = 1.10, fig. 1C). Insignificant amounts of oligomeric species are formed in the initial stages of the reaction, which is attributed to cationic polymerization initiated from the Lewis acid. The concentration of these oligomers does not increase after 5 minutes and they are easily removed by precipitation of the final polymer (ESI section 5.3). Optimization of the amount of $AlCl_3$ added to the polymerization (fig. 1C, ESI Section 5.4) shows that ~20% of 1-hexene is isomerized within 5 minutes in the absence of Lewis acid, consistent with previous literature.[13] 1 or 2 eq. with respect to the palladium catalyst yielded ~80% isomerization. Increasing the aluminum chloride to 3 eq. increased the isomerization to >90%. 4 eq. yielded a monomer composition of 80 mol% 2-hexene and 20 mol% 3-hexene with less than 0.5% remaining 1-hexene. The 2-hexene formed in the isomerization is ~75% *trans* (ESI Section 5.4) and the ratio between *cis* and *trans* species remains constant throughout polymerization.

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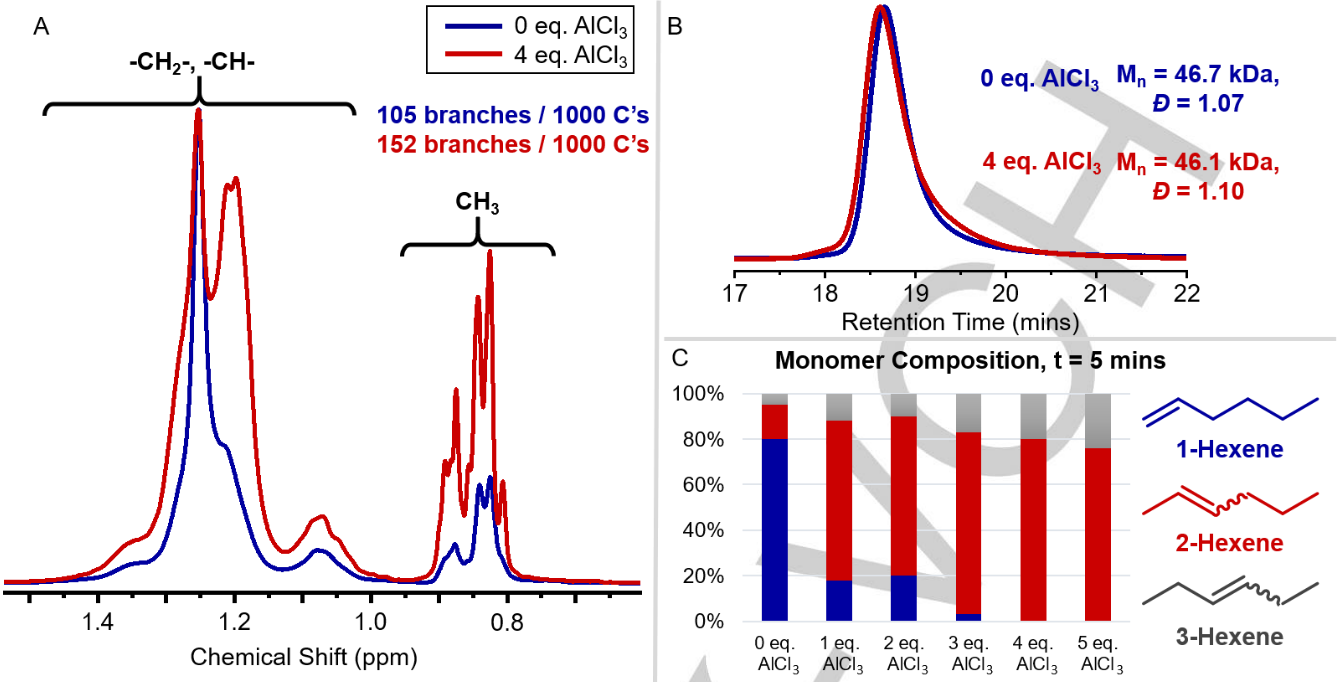

Figure 1: (A) ^{1}H NMR of purified polymers. Blue Trace: poly(hexene). Red trace: poly(hexene) synthesized in the presence of $AlCl_3$. Branches per 1000C = $(CH_3/3)/[(CH+CH_2+CH_3)/2]*1000$. (B) SEC traces for polyhexene synthesized with 0 eq. $AlCl_3$ (blue) and 4 eq. (red). (C) monomer composition at t = 5 minutes for 1-hexene polymerization with increasing amounts of $AlCl_3$ (eq. relative to palladium).

Table 1: Branch distributions for polymerizations ^{a}Denotes monomer that was added to the reaction. ^{b}Mol. eq. relative to Pd cat. ^{c}Branches per 1000 C = $(CH_3/3)/[(CH+CH_2+CH_3)/2]*1000$ by ^{1}H NMR. ^{d}All Branching numbers are given per 1000 carbon atoms and rounded to the nearest whole number. Individual branching numbers were calculated by setting integral of a quantitative ^{13}C NMR to 1000 and then further integrating the CH_3 peak from each contributing branch. ^{e}Determined by differential scanning calorimetry (DSC). ^{f}T_g could not be measured due to broad T_m.

Entry	Monomer^a	$AlCl_3$^{b}	B (^{1}H)^{c,d}	B(^{13}C)^d	Branches / 1000 C					T_g (°C)^e	T_m (°C)^e
					Me^d	Et^d	Pr^d	Bu^d	≥Pe^d		
1	1-Hexene	0	105	99	67	8	7	8	9	-49.4	-9.1
2	1-Hexene	4	152	149	66	36	25	17	5	-70.8	-
3	2-Hexene	4	156	145	70	32	24	15	4	-69.8	-
4	1-Octene	0	84	80	44	9	5	4	18	-41.2	17.7
5	1-Octene	4	116	107	31	21	15	12	28	-71.6	-
6	1-Decene	0	67	53	33	3	>1	>1	17	-^{f}	28.6
7	1-Decene	4	96	86	19	13	9	9	36	-72.0	-

Quantitative ^{13}C NMR branching analysis of the precipitated poly(hexene) samples (table 1, entries 1 & 2) shows good agreement between the branches/1000 carbons as calculated by ^{1}H and ^{13}C NMR. Polymer synthesized in the absence of $AlCl_3$ (table 1, entry 1) shows many methyl branches (67/1000) with much smaller amounts of longer branches. The isomerization of 1-hexene to 2/3-hexene in the presence of $AlCl_3$ significantly increases the amount of longer branches in the polymer (table 1, entry 2) while the methyl branch composition is like regular 1-hexene polymerization, resulting in an overall increase in the number of branches. We envision that the difference in branching between entries 1 & 2 in table one are due to the different enchainments that are possible from 2/3-alkene coordination insertion and chain-walking versus 1-alkene. As described in the introduction, 1-alkene can undergo 2,1-insertion followed by full chain walking to yield linear segments, whereas internal alkenes cannot form linear segments. Similar reactivity (3,2-insertion and chain-walking) results in a methyl branch for 2-hexene. The presence of butyl and pentyl branches in these polyhexene samples is attributed to the palladium chain-walking 'back' along the polymer chain. The physical differences between polyhexenes prepared by regular polymerization and Lewis acid triggered isomerization polymerization are highlighted by the different thermal properties. Regular 1-hexene polymer has a significant degree of linearity, hence chains can pack closely and form crystalline domains, giving a T_m. In contrast, the triggered isomerization to internal alkenes results in a polymerization where a high degree of linearity is impossible. The polymer doesn't exhibit a T_m and the T_g is much lower than regular 1-hexene polymerization, indicating a highly amorphous material.

An attempt was made to synthesize poly(2-hexene) starting from the internal olefin monomer (*trans*-2-hexene) to compare branching and corroborate the ^{1}H NMR evidence in fig. 2 that the polymerization system essentially allows us to obtain poly(2-hexene) structure from 1-hexene monomer; however, only very low conversion (<1%) was observed in a 3 hour reaction time, in agreement with previously reported polymerization from similar palladium diimine catalysts.[13] Repeating this reaction with 4 eq.

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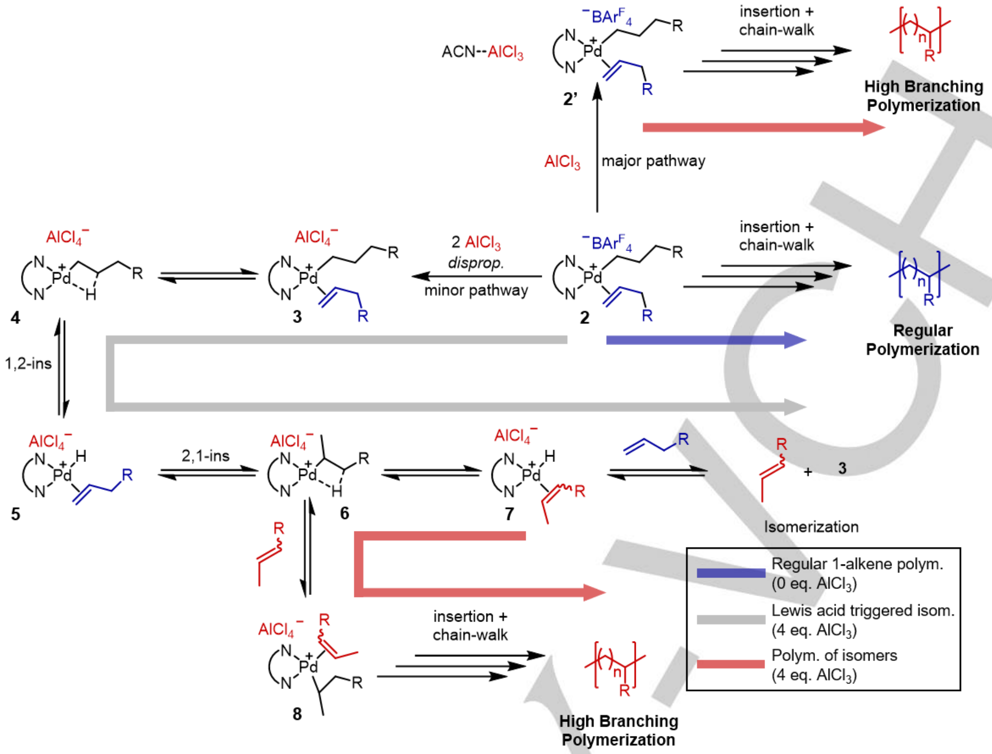

Scheme 4: Proposed mechanism is triggered isomerization polymerization showing: regular polymerization of 1-alkene from $[BAr^{F}_{4}]^{-}$ complex 2 (blue pathway); counterion swap in presence of $AlCl_3$ promoting β-hydride elimation and reinsertion causing isomerization (gray pathway); chain-walking polymerization of internal alkene (red pathway) from $[BAr^{F}_{4}]^{-}$ complex or $[AlCl_4]^{-}$ complex when ancillary ligand (ACN) is adducted with $AlCl_3$.

of $AlCl_3$ allowed a much more rapid polymerization to occur (ESI Section 5.5), thus demonstrating the ability of the catalyst system to directly polymerize internal olefins. This is further exemplified by polymerization of 4-octene (ESI Section 5.5). Polymerization of *cis*-2-hexene by catalyst 1 and $AlCl_3$ was found to occur via isomerization to the *trans* isomer. This is in stark contrast to other diimine catalyst systems which have shown little polymerization of *cis* isomers.[15] The versatility of isomerization-polymerization with respect to regiochemistry and the position of the double bond offers future potential in the polymerization of unconventional alkenes from natural sources and industrial byproducts. Poly(2-hexene) shows very similar branching to poly(hexene) synthesized with $AlCl_3$ (table 1, entry 3), indicating that isomerization followed by polymerization occurs with 1- alkenes; this is further supported by the very similar glass transition temperatures of the two materials. Key benefits of our triggered isomerization and polymerization approach over direct polymerization of 2-hexene (with $AlCl_3$) include a faster rate (85% vs. 46% monomer conversion for a 3 hour reaction time), improved control ($Đ$ = 1.10 vs 1.17), and the higher availability and lower cost of 1- alkene monomers. 1-Octene exhibited the same isomerization behavior (ESI Section 5.6) when polymerized with palladium-diimine catalyst, 1, and $AlCl_3$, yielding polymeric structures with a much higher degree of branching (116 branches per 1000 carbons versus 84 branches, table 1 entries 4 and 5), consistent with polymerization of the corresponding internal olefins. Similar results were obtained with 1-decene (67 vs. 96 branches, table 1 entries 6 and 7, ESI section 5.7). ^{13}C NMR analysis reveals that poly(octene) and poly(decene) synthesized in the presence of $AlCl_3$ also contain larger amounts of longer branches. The higher degree of linearity in regular 1-octene and 1-decene polymerizations is due to the lower theoretical branching maximums for higher 1-alkenes (1 carbon per monomer forming a branching point). This gives a greater difference in physical properties between regular polymerization and the highly amorphous polymers formed in triggered isomerization-polymerization.

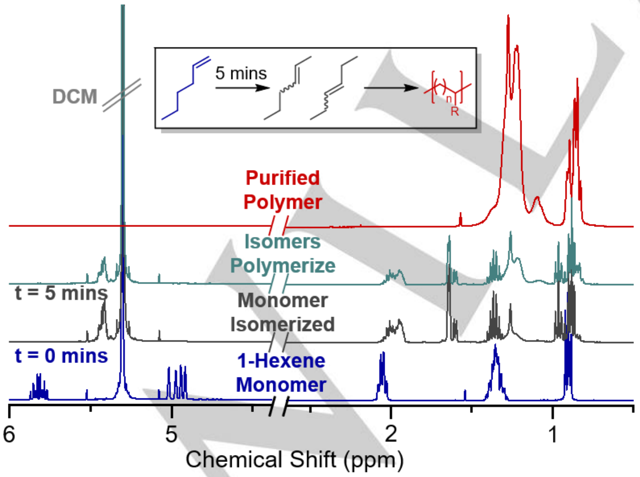

Figure 2. Selected NMR's from the kinetic analysis of 1-hexene polymerization in the presence of 4 eq. $AlCl_3$. t=0 (blue) shows 1-hexene monomer, t=5 (gray) shows shift in 1-hexene alkene protons to 2/3-hexene, t=30 (green) shows appearance of characteristic broad polymer peaks ~1.00-1.35 ppm. Red trace shows purified polymer, isolated after 3 hours.

From a mechanistic standpoint, Pd-diimine catalysts are known to isomerize 1-alkenes to a certain extent, with β-hydrid

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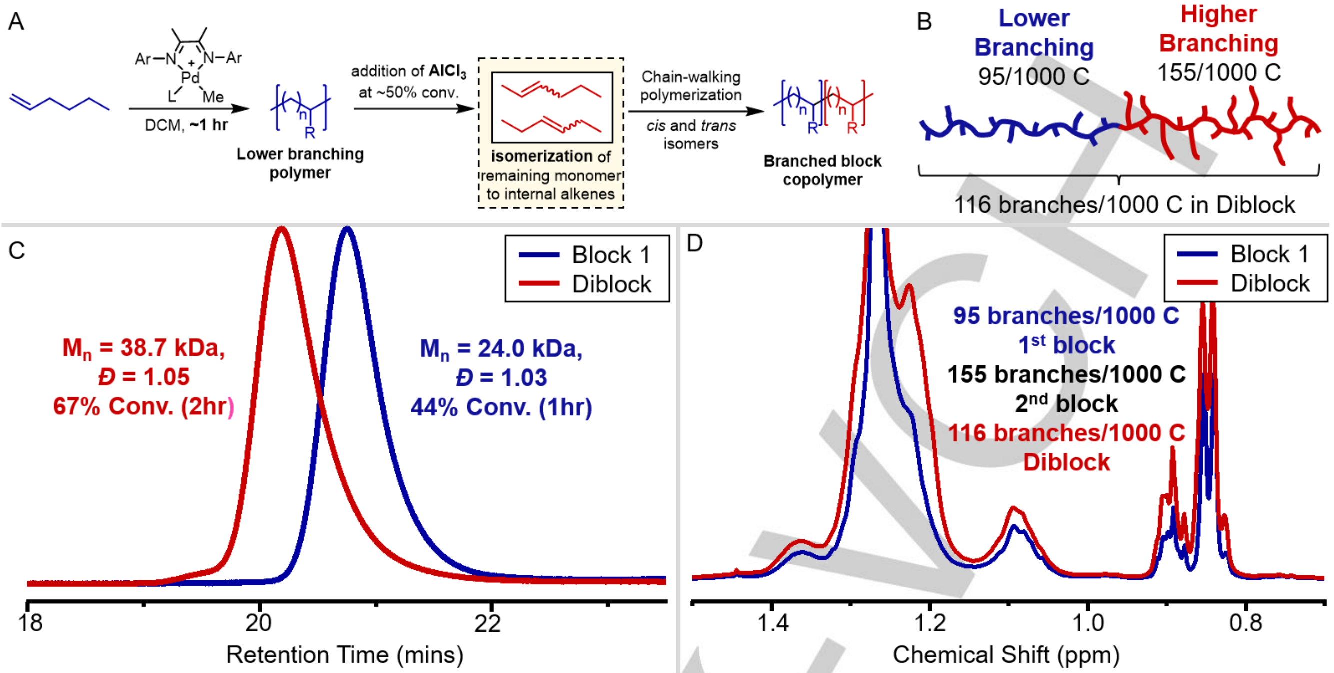

Figure 3: (A) Synthesis of block copolymers of 1-hexene with different branching structures per block via addition of $AlCl_3$ midway through the polymerization. (B) Cartoon structure representing branching in a block copolymer. (C) SEC traces for branched hexene block copolymer. (D) ^1H NMR showing branching in diblock copolymer

elimination from agostic palladium alkyl complexes forming a palladium hydride species which can then undergo 2,1-insertion with 1-alkene followed by reinsertion of the hydride to yield the isomeric 2-alkene.[21] The extent of isomerization seems to be greatly enhanced by addition of $AlCl_3$. Lewis acids have previously been demonstrated to enhance nickel catalyzed olefin isomerization through a Lewis adduct formed with the diimine ligand, altering the electronic environment of the catalyst.[22] However, the diimine ligand employed in this study did not contain any likely binding motifs for Lewis adduct formation. $AlCl_3$ in the absence of Pd catalyst was found to promote an uncontrolled polymerization (possibly cationic) with no evidence of isomerization. We instead postulated that the Lewis acid was forming a new counterion and displacing $[BAr^F{}_4]^-$. An experiment in which 2 eq. of $AlCl_3$ were added to the chloride precursor of 1 and an excess of acetonitrile (ACN) ancillary ligand yielded 1 with an $[AlCl_4]^-$ counterion, which was isolated and characterized by X-ray crystallography (ESI section 5.10). Sen and coworkers have previously investigated $AlCl_3$ as an activator of diimine complexes, proposing that the counterion formed is $[Al_2Cl_7]^-$, however this was not confirmed in a crystal structure.[23] Addition of 1-hexene to this catalyst showed rapid isomerization to internal alkenes in 5 minutes, although no polymerization was observed in a typical 3 hour reaction time. Sen's work only reported polymerization of propylene, which cannot isomerize to give an internal olefin.[23] Our result suggests that an aluminum counterion is responsible for promoting β-hydride elimination and reinsertion to give isomers, possibly due to an electron donating interaction from the less bulky counterion with the palladium center.[24] Low rates of polymerization of internal alkenes is in agreement with Brookhart's work on Pd-catalyzed polymerizations, attributed to low binding rates of internal alkenes. However under our typical polymerization conditions internal alkene polymerization is much faster than previously reported. We hypothesized that the ACN ancillary ligand may be competing for binding sites with the 2-alkene. Repeating the control experiment (chloride precursor, $AlCl_3$, 1-hexene) in the absence of ancillary ligand gave full isomerization in 5 minutes and polymerization to high conversion with high branching in 3 hours. A polymerization of *trans*-2-hexene with a palladium diimine $[BAr^F{}_4]^-$ complex also gave much higher polymerization rates than an analoguous reaction in the presence of ancillary ligand. Proton NMR shows a shift in the protons of acetonitrile with addition of $AlCl_3$, proposed to be formation of a Lewis adduct, preventing competitive binding of ACN to the catalyst. Reactions using other Lewis acids such as $FeCl_3$ and $ZnCl_2$ also cause isomerization of 1-hexene followed by polymerization of internal alkenes, although with varying rates (ESI section 5.10).

With the experimental evidence of the counterion effects detailed above, we propose a mechanism of Lewis acid triggered isomerization and internal alkene polymerization in scheme 4. From the known intermediate 2, insertion and chain walking results in a regular 1-hexene polymerization (blue pathway). Addition of $AlCl_3$ is proposed to disproportionate and displace the $[BAr^F{}_4]^-$ counterion to give an $[AlCl_4]^-$ counterion, 3, as evidenced by x-ray crystallography. We envision that only a small fraction of palladium centers would have to undergo this counterion swap (minor pathway), as a control reaction utilizing much lower concentrations of Pd catalyst still showed quantitative isomerization in 5 minutes (ESI section 5.10). β-Hydride elimination from 4 followed by 2,1-insertion and a further β-hydride elimination (5 to 6) gives the complexed internal alkene, 7. This alkene is displaced by much stronger binding 1-alkene to regenerate complex 5 and give free internal alkene. This isomerization pathway (grey) is supported by previous literature examples of diimine mediated isomerzation[21-22] and experimental evidence of enhanced isomerization from $[AlCl_4]^-$ counterioned complexes. Finally, polymerization of the internal alkene (red pathway) occurs when there is no 1-alkene left to compete for the coordination site, occuring via a chain-walking mechanism to give highly branched polymer. The polymerization can either occur from complex 7 or 2‘, as ancillary ligand from the starting complex is most likely in adduct form with the excess aluminum chloride added to the reaction, further promoting the polymerization.

Due to the change in properties associated with higher degrees of branching, the possibility of synthesizing block copolymers using isomerization-polymerization was explored by adding $AlCl_3$ mid-way through a reaction. 1-Hexene was polymerized with Pd-diimine catalyst, 1, and a sample was taken after 1 hour (44% conv., M_n = 24.0 kDa, $Đ$ = 1.03, 95/1000C branches) after which 4 eq. of $AlCl_3$ was added to the reaction. Total isomerization was observed after 5 minutes. Sampling after an hour yielded a polymer with a narrow, monomodal MWD (67% conv., M_n = 32.5 kDa, $Đ$ = 1.05, 116/1000C branches). The narrow MWD and the full shift in the SEC trace indicates the formation of a well-defined block copolymer. Knowing the branching from the total block copolymer and the branching from the first block we were able to calculate the degree of branching in the second block by taking monomer conversion into account (ESI section 5.11). the second block is calculated to have ~155 branches/1000C; this is in perfect agreement with the branching observed in homopolymerizations of 1-hexene and triggered isomerization-polymerizaton (table 1 entries 1-3). The triggered isomerization approach yields poly(1-hexene) as a first block followed by a triggered isomerization of the remaining monomer upon addition of Lewis acid to form a second block of poly(n-hexene) with higher branching (fig. 3). According to our proposed mechanism (scheme 4), addition of Lewis acid midway through the reaction must result in some palladium centers eliminating the first block, in order to be able to isomerize the remaining monomer. The fraction of palladium centers which swap counterions to $[AlCl_4]^-$ is presumed to be small as the clear shift in the SEC trace and low dispersity indicate high fidelity blocks. Triggering isomerization as opposed to performing sequential monomer additions to yield blocks has the advantage of avoiding the typical deviation from first order kinetics seen at high conversions of 1-alkene in typical polymerizations. This new approach to polyolefin block copolymer synthesis is a one pot process in which the composition of the blocks can be tuned by altering the point of addition of the Lewis acid

Conclusion

In conclusion, we have demonstrated a novel approach to branching control in olefin polymerization via triggering an isomerization of 1-alkene to internal alkenes. These isomerized monomers then polymerize with much higher branching. Mechanistically, the reaction is proposed to occur by switching of the counterion with Lewis acid and sequestering of competing ligands as Lewis adducts. The new methodology offers a simple route to vary the branching structure of polyolefins by direct manipulation of the monomer, which can be triggered midway through the reaction to yield block copolymers with distinct branching characteristics per block. Future work will explore the synthesis of block copolymers with drastic differences in crystallinity, polymerization of internal alkenes from natural sources and waste streams, and further probing the effects of the $[AlCl_4]^-$ counterion on of the isomerization-polymerization process.

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Keywords: Isomerization • Olefins • Branching • Block Copolymers • Chain-walking

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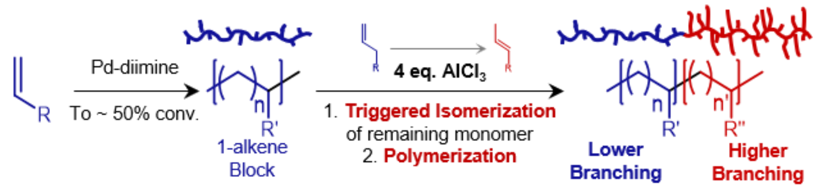

Addition of $AlCl_3$ to a Pd-mediated chain-walking polymerization results in rapid isomerization of 1-alkenes to internal alkenes which polymerize with high branching. Block copolymers can be prepared by adding $AlCl_3$ midway through the reaction.

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Branching Regulation in Olefin Polymerization via Lewis Acid Triggered Isomerization of Monomers