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Ni(II) α-Diimine-Catalyzed α-Olefins Polymerization: Thermoplastic Elastomers of Block Copolymers

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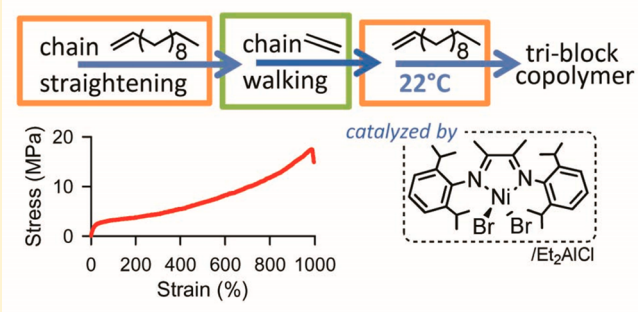
Supporting Information

ABSTRACT: The polymerization of ethylene with late transition metal complexes typically provides highly branched amourphous poly(ethylene)s through a chain-walking mechanism, while the chain-straightening polymerization of α-olefins gives semicrystalline polymers. Herein, we report the polymerization of 1-hexene, 1-octene, and 1-dodecene catalyzed by an α-diimine Ni(II) complex in combination with diethylaluminum chloride. The effect of monomer chain length and monomer concentration on the productivity, polymerization "livingness", selectivity of monomer insertion, and polymer structure/properties is investigated. The polymerization results indicate the possibility of precise microstructure control, depending on the monomer employed and monomer feedstock concentration, which in turn strongly affects the physical polymer properties. Additionally, di- and triblock copolymers were successfully fabricated in an easy, high-yielding route, at room temperature. The synthesis was accomplished through the sequential monomer addition from 1-dodecene and ethylene, without requiring any intermediate separation step. Each block exhibited distinct features from semicrystalline to amorphous, taking advantage of the different mechanism involved in the polymerization of 1-dodecene and ethylene. Investigation on mechanical behavior by uniaxial stretching until failure and step-cycle tensile tests showed that the block copolymers behave as thermoplastic elastomers with different performances depending on the composition, length of the blocks, and crystallinity. We demonstrate that this approach is a route to fabricate thermoplastic elastomers from readily accessible starting materials.



INTRODUCTION

Thermoplastic elastomers (TPEs) are generally low modulus polymers that can be stretched repeatedly, at room temperature, to at least twice their original length without being permanently deformed.[1] In contrast to thermoset elastomers, TPEs do not require curing or vulcanization and can be softened, melted, and repeatedly processed by injection molding, extrusion, and blow molding. TPEs can be classified into two generic classes: block copolymers (styrenics, polyesters, polyurethanes, and polyamides) and thermoplastic/elastomer blends and alloys (thermoplastic polyolefins and thermoplastic vulcanizates, TPVs). In addition, new technologies have emerged: the group IV metallocene-catalyzed olefin plastomers (POPs) and elastomers (POEs).[2]

Currently, research in the field of TPEs has focused on the development of post-metallocenes Pd(II) and Ni(II) α-diimine complexes.[3] The application of such complexes allowed the synthesis of new polymers with a precise control of polymer microstructure. These include in particular branched and hyperbranched polyolefins[4] and olefin block copolymers.[5] Block copolymers with both semicrystalline and amorphous regions, which offer mechanical stability and flexibility, respectively, may have interesting applications as TPEs.[6]

The peculiarity of these catalysts is attributed to the ability of the active growing site to "walk" on the polymer chain during the propagation step (chain-walking) so that the new incoming monomer unit is assembled onto the polymer backbone rather than at the end, giving branched polymers (Scheme 1).[7] By exploiting this mechanism, ethylene[8] and propylene[9] block copolymers with segments from linear (semicrystalline) to highly branched (amorphous) can be fabricated by changing the monomer pressure and/or temperature, two parameters that regulate the competition between chain-walking and chain-propagation. Other combinations are possible, especially when the polymerization involves α-olefins with a high number of carbon atoms.[10−13] A different enchainment becomes competitive for longer α-olefins: a significant fraction of monomer insertions occur in a 2,1 manner. Chain-walking to the terminal carbon (ω-position, where ω is the number of carbon atoms, Scheme 1) followed by a new insertion results in a ω,1-enchainment (chain-straightening). The result of this ω,1-enchainment is the placement of the monomer into the growing polymer chain in a linear manner, resulting in

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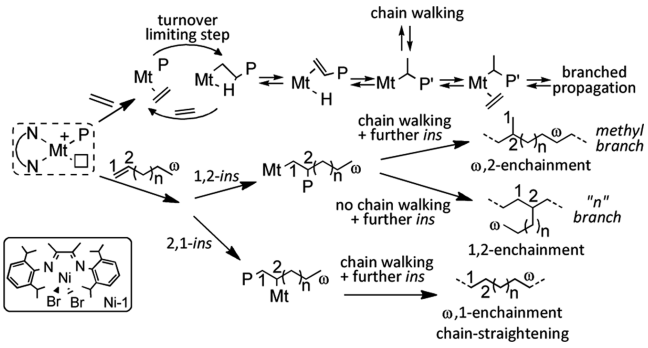
Scheme 1. Mechanism for Ethylene Polymerization and α-Olefin Enchainment (Mt = Ni, Pd; NN = Diimine Ligand) and α-Diimine Ni(II) Complex (Ni-1) Used in This Work



crystalline domains. Block copolymers containing a semicrystalline and an amorphous block can be obtained accordingly through a sequential monomer addition from living polymerization of α-olefins and ethylene, respectively.[14]

The sequential monomer addition approach differs from the techniques used for block copolymers synthesis, wherein the construction of each block is achieved in a one-pot synthesis.[8,9] It is particularly severe when liquid α-olefins are first polymerized, requiring the need for elaborate separation step to strip off the residual monomer due to the poor volatility of α-olefins. To address this issue, Brookhart and Gottfried developed a successful procedure that consists in running the polymerization of 1-octadecene, catalyzed by a Pd−diimine complex, at 0−5 °C in a concentrated solution, which is then diluted. Ethylene is hence loaded at high pressure, taking advantage of the higher binding affinity of ethylene than the α-olefin.[15] However, lowering polymerization temperature is often inconvenient and generally leads to low catalytic productivity and limits the polymer molecular weight.[16] Meanwhile, studies on block copolymerization with Ni−diimine complexes are rare,[6] especially at room temperature or above. Recent literature examples highlight how innovative new ligand−Ni(II) combinations continue to emerge with the goal of expanding the range of properties of α-olefin polymers.[17] For example, Daugulis and Coates recently discovered that aryl-naphthyl-α-diimine Ni(II) complexes polymerized 1-decene in a controlled manner at 22 °C.[18] The complex, in combination with methylalumoxane, is highly selective for ω,1-enchainment to give semicrystalline polymers with high melting temperature ($T_m \geq 100$ °C). However, a better chain growth and monomer insertion selectivity control of these new complexes is paid by more complicated diimine ligand synthesis. In addition, short lifetime and rapid deactivation of the metal centers throughout the course of polymerization usually give low monomer consumption which limits the practical use in precise block copolymerizations.

Tackling the goal of preparing block copolymers through moderate polymerization conditions and readily accessible starting materials, a Brookhart-type α-diimine Ni(II) complex (Ni-1, Scheme 1) was employed for 1-hexene, 1-octene, and 1-dodecene polymerization. The effect of monomer size and concentration on productivity, polymerization "livingness", selectivity of monomer insertion, and polymer structure/properties (i.e., total branching, branch type and frequency, intrinsic viscosity, thermal behavior) is discussed. The fabrication of di- and triblock copolymers, consisting of semicrystalline and amorphous blocks, is completed in successive additions of 1-dodecene and ethylene, without requiring any intermediate separation step. The mechanical behavior of block copolymers was investigated by uniaxial stretching until failure and step-cycle tensile tests.

■ EXPERIMENTAL SECTION

Materials. Manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk-line techniques. Toluene (Fluka, >99.5% pure) was refluxed over Na for about 8 h and then distilled and stored over molecular sieves under nitrogen. Diethylaluminum chloride (Et_2AlCl, Fluka) and methylaluminoxane (MAO) (10 wt % solution in toluene, Aldrich) were used as received. The α-diimine Ni(II) complex [2,6-(*i*Pr)$_2$C$_6$H$_3$N=C(CH$_3$)−(CH$_3$)C=N2,6-(*i*Pr)$_2$C$_6$H$_3$)]NiBr$_2$ (Scheme 1) was synthesized according to the procedure previously reported in the literature.[4b] 1-Hexene (Aldrich, 97% pure), 1-octene (Aldrich, 98% pure), and 1-dodecene (Aldrich, 95% pure) were refluxed over CaH_2 for about 4 h, then distilled via trap-to trap, and, finally, stored under dry nitrogen and kept at −30 °C. Ethylene was purified flowing through BTS catalysts, molecular sieves, and $CaCl_2$. Deuterated solvent for NMR measurements ($C_2D_2Cl_4$) (Cambridge Isotope Laboratories, Inc.) was used as received.

Polymerization Experiments. General Procedure. Polymerizations were carried out in a 25 mL round-bottomed Schlenk flask containing a stirring bar. The reactor was first dried by heating at 110 °C and then vacuum was applied for 1 h. Toluene, the monomer, Et_2AlCl, and a toluene solution (2 mg/mL) of nickel complex were transferred into the reactor vessel in that order. Polymerization was quenched with methanol containing a small amount of hydrochloric acid. The precipitated polymers were collected by filtration, repeatedly washed with fresh methanol, and then dried to constant weight.

Block Copolymerizations. General Procedure. The polymerizations were carried out with the same reactor used above. 1-Dodecene, toluene, and Et_2AlCl were combined in the reactor vessel, and the polymerization of the first block was started by adding the toluene solution of the Ni compound. The polymerization solution was stirred for the allotted block time to ensure the almost complete consumption of 1-dodecene monomer. Nitrogen was vented, the reactor was placed under vacuum, and then it was filled with ethylene. The reaction mixture was stirred under constant atmospheric pressure of ethylene for the given block time. Polymerization was quenched as reported above. For triblock copolymer, ethylene was then removed by appliyng vacuum, and the reactor was backfilled with 1-dodecene.

Polymer Characterization. For ^{13}C NMR, about 100 mg of polymer was dissolved in $C_2D_2Cl_4$ in a 10 mm tube. HDMS (hexamethyldisiloxane) was used as internal chemical shift reference. The spectra were recorded on a Bruker NMR AVANCE 400 spectrometer operating at 100.58 MHz (^{13}C) in the PFT mode working at 103 °C. The applied conditions were the following: 10 mm probe, 90° pulse angle; 64K data points; acquisition time 5.56 s; relaxation delay 20 s; 3−4K transient. Proton broad-band decoupling was achieved with a 1D sequence using bi_waltz_16_32 power-gated decoupling. ^{1}H NMR spectroscopy was used to determine overall branching.[17d] The fraction of ω,1-insertions was calculated from the equation reported by Brookhart.[12] ^{13}C NMR spectroscopy was used to examine the types of branches. The quantitative analysis was based on the equations reported by Galland (see Supporting Information for details).[19]

Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer Pyris 1 instrument equipped with a liquid nitrogen device. The scans were carried out from −120 to 200 °C under helium atmosphere using heating and cooling rates of 20 °C/min. The molecular weight-average (M_n), the molecular weight distribution (M_w/M_n), and the intrinsic viscosity ($[\eta]_w$) were obtained by a high-temperature Waters GPCV2000 size exclusion chromatography (SEC) system using two online detectors: a differential viscometer and a refractometer. The experimental conditions consisted of three PL Gel Olexis columns, *o*-DCB as the mobile phase, 0.8 mL/

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Table 1. Polymerization of 1-Hexene (HEX), 1-Octene (OCT), and 1-Dodecene (DD) at Different Monomer Concentrations[a]

entry	monomer type	monomer (mol/L)	yield (g)	conv (%)	TOF[b] (h^{-1})	${}^{th}M_n$[c] (kg/mol)	${}^{exp}M_n$[d] (kg/mol)	M_w/M_n[d]	$[\eta]_w$[e] (dL/g)	branches/1000C[f]	T_m[g] (°C)	ΔH_m[g] (J/g)	T_g[g] (°C)
1	HEX	0.2	0.18	67	59	18.0	31.5	1.18	0.29	88	40	20	−48
2	HEX	0.4	0.35	65	138	34.9	54.9	1.22	0.50	77	38	17	−50
3	HEX	1.0	0.92	68	364	91.8	65.6	1.69	0.61	81	30	16	−52
4	HEX	1.5	1.41	70	558	141.0	102.0	1.66	0.95	92	28	14	−52
5	HEX	2.5	2.38	70	941	237.5	96.5	1.82	0.86	78	23	13	−53
6	OCT	0.2	0.19	54	59	19.7	36.6	1.16	0.34	74	57	36	−42
7	OCT	0.4	0.40	56	118	39.6	74.0	1.20	0.62	68	55	29	−45
8	OCT	1.0	1.10	58	327	110.0	105.6	1.36	0.94	66	49	22	−49
9	OCT	1.5	1.73	65	514	173.0	109.1	1.68	0.95	64	45	19	−51
10	OCT	2.5	2.99	67	888	299.0	175.0	1.73	1.36	65	43	18	−50
11	DD	0.2	0.20	38	40	20.3	35.6	1.18	0.34	48	81	51	−30
12	DD	0.4	0.50	47	98	49.5	66.4	1.20	0.59	43	70	47	−39
13	DD	1.0	1.48	54	293	148.0	158.6	1.35	1.20	39	65	37	−42
14	DD	1.5	2.24	56	443	224.0	197.7	1.42	1.57	38	65	40	−41
15	DD	2.5	4.40	65	871	440.0	250.6	1.68	1.79	37	57	33	−46

[a]Polymerization conditions: toluene, total volume, 16 mL; Ni-1, 10 μmol; Al/Ni molar ratio, 200; temperature, 22 °C; time, 3 h. [b]Turnover frequency (TOF), calculated by the equation: $mol_{pol} \times mol_{Ni}^{-1} \times h^{-1}$. [c]Theoretical molecular weight (${}^{th}M_n$) calculated from $g_{pol} \times mol^{-1}$. [d]Molecular weight (M_n) and molecular weight distribution (M_w/M_n) from SEC. [e]Weight-average intrinsic viscosity ($[\eta]_w$) data were determined by SEC and measured using the online viscometer. [f]From ^{1}H NMR (see eq 1, Supporting Information). [g]From DSC (second heating) (T_m at peak maximum).

min flow rate, and 145 °C temperature. The calibration of the SEC system was constructed using 18 narrow M_w/M_n polystyrene standards with molar weights ranging from 162 to 5.6 × 10^6 g/mol. For SEC analysis, about 12 mg of polymer was dissolved in 5 mL of *o*-DCB with 0.05% of BHT as antioxidant. The materials for the mechanical characterization were molded in a heated press at 100 °C and 50 bar for 5 min, and then the press plates were cooled at 20 °C/min to room temperature. Films with a thickness of about 100 μm were produced. Tensile dog-bone-shaped specimens (length overall 75 mm, gauge length 25 mm, and width of narrow section 4 mm) were analyzed at 21 °C using a Zwick Roell ProLine Z010 mechanical tester at a constant crosshead rate of 15 mm/min. In the hysteresis experiments performed at various strains, the specimens were cyclically loaded and unloaded in uniaxial tension.

■ RESULTS AND DISCUSSION

While the effect of monomer concentration has been well studied for 1-hexene,[19] 4-methyl-1-pentene,[20] its influence on the polymerization features of higher linear α-olefins has not been investigated in detail. For this purpose, we initially polymerized 1-hexene, 1-octene, and 1-dodecene screening five monomer concentrations from 0.2 to 2.5 mol/L, with the aim to study the effect of monomer size and concentration on productivity, polymerization "livingness", selectivity of monomer insertion, and polymer structure/properties.

We chose a traditional Ni(II) α-dimmine complex (Ni-1, Scheme 1) due to its ease of synthesis and commercially availability and Et_2AlCl because (i) the performance of Ni-1/Et_2AlCl has been previously studied by our group for the (co)polymerization of ethylene, which allows for good comparison,[5a,21] and (ii) the activity is increased by 1.5 when using Et_2AlCl instead of MAO (Table S1, Supporting Information).[22] A summary of polymerization results is shown in Table 1.

Catalyst Ni-1/Et_2AlCl displayed good activity toward the α-olefins polymerization with product obtained in the order of grams. Although TOF (turnover frequencies) is strongly affected by mass transfer limitations, the calculated TOFs increase with monomer concentration. This is especially true in the case of 1-hexene and 1-octene which are consumed significantly faster than 1-dodecene. There is no substantial change in monomer conversion for the polymerization of 1-hexene and 1-octene with the increase of monomer concentration. This is likely due to higher exothermic character at the beginning of the reaction and to the increased viscosity of the reaction mixture. The resultant polymers fast become insoluble in the polymerization medium and precipitate. As a result, M_n of the polymers do not increase linearly with monomer concentration (Figure 1C,D), the data are more disparate than those calculated, and the polymers have M_w/M_n > 1.7.

Increasing the 1-dodecene concentration leads to a continuous increase in the monomer consumption and affords high molecular weight polymers. The M_n of the obtained poly(1-dodecene)s increases 604% from 35.6 to 250.6 kg/mol and linearly with concentration from 0.2 to 1.0 mol/L, close to

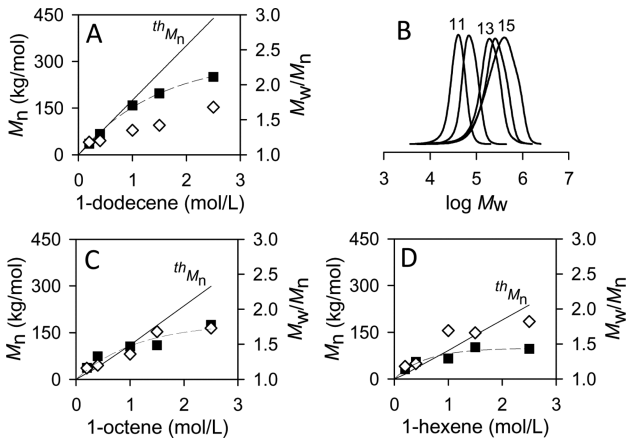

Figure 1. Plot of M_n (■) and M_w/M_n (◇) as a function of 1-dodecene (A), 1-octene (C), and 1-hexene (D) concentration. SEC profile (B) of poly(1-dodecene)s (from entry 11 to entry 15, Table 1). The dashed lines are guides to the eye and illustrate the overall trend.

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the calculated data (Figure 1A). Further increase of the monomer concentration gives polymers with M_n 2 times lower than the theoretical values and $M_w/M_n > 1.4$. The broadening of M_w/M_n and the concomitant presence of a more pronounced tail in the polymer's SEC traces (Figure 1B) suggest the occurrence of chain-breaking reactions and catalyst decomposition, preventing a controlled polymerization with increasing the monomer concentration (≥1.5 mol/L).

The total branching level was calculated by ^{1}H NMR spectroscopy. According to Scheme 1, the exclusive 1,2-enchainment would result in a poly(1-hexene) with 167 branches/1000C, a poly(1-octene) with 125 branches/1000C, and a poly(1-dodecene) with 83 branches/1000C. However, the observed trend is that the branching content of the obtained polymers is lower than the theoretic value, which is a result of nickel migration on polymer chain.[23] Calculation results in Table 1 show that the actual branching content is almost half of that predicted (see also Figure 4), meaning that the ratio between 1,2- and 2,1-insertion is independent of monomer chain length. Besides, the monomer concentration slightly determines the total branching number of the obtained polymer. An observed tendency is that increasing the monomer concentration results in a reducing total branching. For example, it drops from 74 to 65 branches/1000C and from 48 to 37 branches/1000C for poly(1-octene) and poly(1-dodecene), respectively.

Figure 2A shows DSC thermograms of 1-hexene, 1-octene, and 1-dodecene polymers obtained under the same conditions.

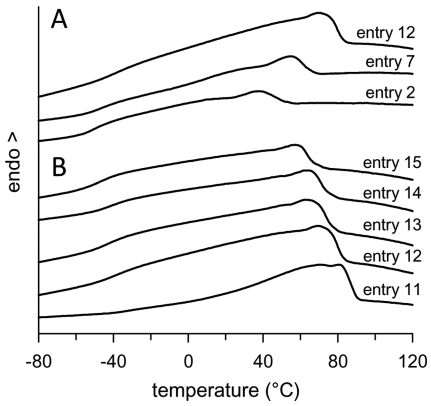

Figure 2. DSC traces of (A) poly(1-hexene) (Table 1, entry 2), poly(1-octene) (Table 1, entry 7), and poly(1-dodecene) (Table 1, entry 12) and (B) polymers obtained at different concentrations of 1-dodecene from 0.2 to 2.5 mol/L (Table 1, entries 11−15).

Glass transition events at low temperature and broad melting endotherms can be observed. The glass transition temperature (T_g) and the melting peak temperature (T_m) of the obtained polymers increase with the increase of monomer chain length. Generally, T_g ranges from −53 to −39 °C and decreases with increasing the monomer concentration. In the same manner, for example, poly(1-dodecene)s obtained at different monomer concentration show melting endotherms extending to a higher temperature (Figure 2B). Analogously, the melting enthalpy (ΔH_m) decreases with monomer concentration, going from 51 J/g for [1-dodecene] = 0.2 mol/L to 33 J/g for [1-dodecene] = 2.5 mol/L, reflecting the reduced crystallinity. A similar trend of melting behavior as a function of the monomer concentration was observed for 1-hexene and 1-octene polymers (Figures S2 and S3, Supporting Information).

All synthesized polymers were characterized by ^{13}C NMR for quantification of the total content of methyl groups and branching distribution on the basis of previous assignments.[12,18,19] The results are summarized in Table 2.

Table 2. NMR Characterization Results: Total Methyls and Distribution of the Main Branch Levels

			CH_3/1000C[b]					
	entry	ω,1[a] (%)	Me	Et	Pr	Bu	Lg	total CH_3
HEX	1	55	59		3	25	10	97
	2	60	53		2	29	7	91
	3	58	47		1	39	5	92
	4	53	40		1	49	4	94
	5	60	32		1	55	4	92
OCT	6	48	35		2		22	59
	7	52	34		1		26	61
	8	53	27		1		32	60
	9	55	22		1		37	60
	10	54	18		1		41	60
DD	11	56	25		1		15	41
	12	60	23		1		21	45
	13	64	15		1		26	42
	14	65	13				30	43
	15	66	11				37	48

[a]Percentage of ω,1-insertions calculated by eq 2 (see Supporting Information for details). [b]From ^{13}C NMR (see Supporting Information). Blank entries mean that the structures were not detected.

Poly(1-hexene)s show three major branch lengths (i.e., methyl, butyl, and longer than hexyl branches) (Figure S4, Supporting Information) while 1-octene (Figure S5, Supporting Information) and 1-dodecene polymers have almost exclusively methyl and longer branches (Table 2). The ^{13}C NMR spectra of two poly(1-dodecene)s obtained at different monomer concentration are shown in Figure 3. The intense signal at 27.73 ppm of methylene $-CH_2-$ sequences and low intense signals due to methyl and longer branches can be safely identified. No carbons of adjacent methyl branches (13−15 ppm) and ethyl and propyl branch were recorded in the ^{13}C NMR. This is indicative of no occurrence of insertion of 1-

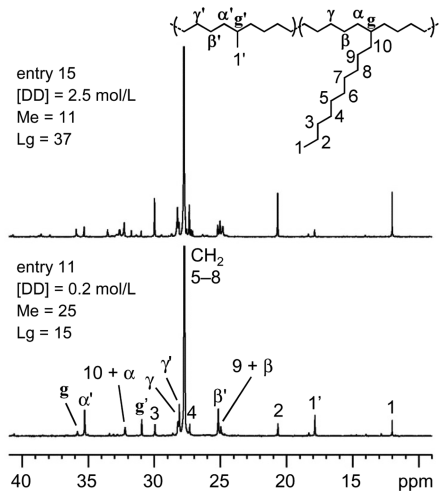

Figure 3. ^{13}C NMR spectra and assignment of poly(1-dodecene)s (entries 11 and 15, Table 1).

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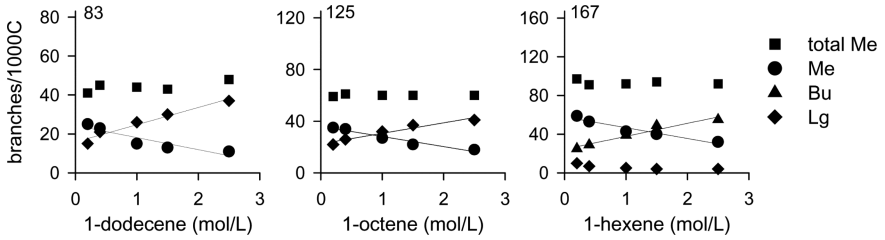

Figure 4. ^{13}C NMR data on total number of branches and the distribution of each branches for polyolefins made at different monomer concentration (the maximum of the *y*-axis is equal to the branching value for the exclusive 1,2-enchainment). The solid lines are guides to the eye and illustrate the overall trend.

dodecene into a secondary Ni−alkyl bond.[23] Therefore, the 2,1-insertion of 1-dodecene always evolves into a 1,12-enchainement to give long methylene sequences (Scheme 1).

The overall trend for all the monomers investigated is that the ω,1-enchainment ranges from 48 to 66%. This suggests that the catalyst does not have a significant selectivity for 2,1- and 1,2-insertion.[24] However, the highest degree of ω,1-enchainment was generally found for the polymerization of 1-dodecene, confirming that the density of branches is primarily controlled by the length of the monomer employed.[6,11] In addition, the ratio of methylene to methyl groups can be tuned by changing the monomer concentration: ω,1-enchainment of 1-dodecene polymers increases from 56% at 0.2 mol/L (48 branches/1000C) to 66% at 2.5 mol/L (37 branches/1000C).

In Figure 4, the total number of methyl groups and the individual branch level is plotted against the monomer concentration. The observed trend suggests that increasing the monomer concentration results in relatively constant total methyls as observed by Guan for the polymerization of ethylene by varying the monomer pressure.[25] Differently, monomer concentration significantly determines the branch-type distribution. The formation of a nonmethyl branch is favored by increasing the length of the monomer and its initial concentration: the amount of methyl branches decreases with the increase of monomer concentration and, conversely, the amount of longer branches increases (Table 2 and Figure 3). The predominance of methyl branches at low monomer concentration means that 1,2-insertion followed by chain-walking (ω,2-enchainment) is much faster than successive 1,2-insertions (1,2-enchainment) (Scheme 1), which is well consistent with previous observation.[18,19]

The amount and the type of branching govern melting temperature and crystallinity.[26] Even though the total methyl groups of the resulting polymers remains unchanged with the variation of monomer concentration, the polymers exhibit marked differences in melting temperature and crystallinity. Since methyl branches can be incorporated into the poly(ethylene) crystal lattice,[27] we attribute this result to the fraction of longer branches as it can be seen clearly in Figure 5A. Figure 5A plots T_m versus the sum of all the branches longer than methyl. For all the polymers there is a direct correlation between the two data and increasing the content of longer side groups the melting temperature decreases. An analogous trend is observed for melting enthalpy.

Another important parameter, strictly related to the polymer topology, is the intrinsic viscosity ($[\eta]_w$).[28] As shown in Figure 5B, $[\eta]_w$ increases in a strictly linear pattern with the increase of M_n (Table 1 and Figure 5B). This suggests that there is no change in the topology of the polymers when comparing materials with similar M_n, even though exists a different content

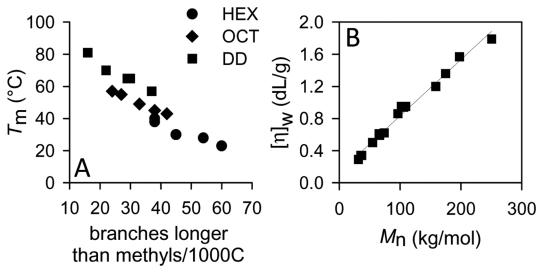

Figure 5. Plot of (A) melting temperature as a function of the total branching longer than methyl and (B) intrinsic viscosity as a function of molecular weight for all the polyolefins under investigation.

of branching and branch-type distribution (entry 6 vs 11, entry 4 vs 8 vs 9, entry 3 vs 12, Tables 1 and 2).

In light of polymerization screening results, a monomer concentration of 0.2 mol/L was selected for living polymerization investigation within a longer period of time. The results are summarized in Table 3.

With respect to the polymers microstructure, the basic tendency is that no significant variation of the overall branching density and branch type distribution occurs with the increase of the polymerization time (Table S2, Supporting Information). DSC analysis also supports this claim with the polymers showing a similar melting behavior with a quite constant T_m regardless of the polymerization time, i.e. 39, 56, and 80 °C for 1-hexene, 1-octene, and 1-dodecene polymers, respectively (Figure S6, Supporting Information).

Figure 6A−C shows the plot of M_n against the polymerization time. For 1-hexene and 1-octene polymerization, M_n grows linearly with time in the early stage of polymerization (180 min, Figure 6A,B), but then the slope begins to decrease and also the monomer conversion grows much less. Experimental observation of the reaction reveals that the polymer begins to precipitate from the polymerization mixture. This may be responsible for the embedment of the Ni active center and, therefore, for the decrease in the monomer consumption. Specifically, M_n of poly(1-hexene) increases with time by 64% from 24.3 to 39.8 kg/mol, while for poly(1-octene) the increase is 114%, from 23.0 to 49.2 kg/mol.

Figure 6C illustrates the time dependence of 1-dodecene consumption, M_n, and M_w/M_n. A steady increase of M_n and monomer conversion was found for a much longer reaction time (Figure 6C). The molecular weight increases 243% from 20.7 to 70.9 kg/mol (Figure 6D), keeping a narrow M_w/M_n ($\leq$1.2) and consistent with quasi-living polymerization behavior accompanied by negligible termination and transfer reactions.

The growth of M_n with time and M_w/M_n below 1.2 indicates that 1-dodecene may be tested for the synthesis of block copolymers. Such materials are of interest especially when the

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Table 3. Polymerization of 1-Hexene (HEX), 1-Octene (OCT), and 1-Dodecene (DD) at 0.2 mol/L for Different Reaction Times[a]

	entry	time (min)	yield (g)	conv (%)	TOF[b] (h^{-1})	$^{th}M_n$[c] (kg/mol)	$^{exp}M_n$[d] (kg/mol)	M_w/M_n[d]	$[\eta]_w$[e] (dL/g)	branches/1000C[f]	T_m[g] (°C)
HEX	16	90	0.07	25	54	7.0	24.3	1.18	0.24	nd	40
	1[h]	180	0.18	67	59	15.0	31.5	1.18	0.29	88	40
	17	360	0.22	79	43	21.5	39.4	1.18	0.34	83	36
	18	1080	0.24	89	16	24.3	39.8	1.18	0.34	78	39
OCT	19	45	0.05	15	63	5.3	16.9	1.30	0.21	nd	nd
	20	90	0.10	28	58	9.8	23.0	1.16	0.25	63	nd
	6[h]	180	0.19	54	59	19.7	36.6	1.16	0.34	74	56
	21	360	0.26	72	38	25.7	44.0	1.16	0.39	59	55
	22	540	0.28	78	28	28.8	44.6	1.16	0.36	61	55
	23	1080	0.29	80	14	29.0	49.2	1.16	0.42	61	57
DD	24	45	0.08	15	62	7.8	20.7	1.17	0.22	40	79
	25	90	0.11	21	45	11.4	28.5	1.16	0.29	45	80
	26	135	0.15	29	42	15.3	31.5	1.19	0.31	39	81
	11[h]	180	0.20	38	40	20.3	35.6	1.18	0.34	48	81
	27	540	0.33	61	22	33.0	55.1	1.17	0.43	44	77
	28	1080	0.45	85	15	45.0	70.9	1.20	0.60	42	78

[a]Polymerization conditions: toluene, total volume, 16 mL; Ni-1, 10 μmol; Al/Ni molar ratio, 200; temperature, 22 °C. [b]TOF calculated by the equation: $mol_{pol} \times mol_{Ni}^{-1} \times h^{-1}$. [c]$^{th}M_n$ calculated from $g_{pol} \times mol^{-1}$. [d]From SEC. [e]$[\eta]_w$ from SEC using the online viscometer. [f]From ^1H NMR (see eq 1, Supporting Information). [g]From DSC (second heating) (T_m at peak maximum). [h]First reported in Table 1.

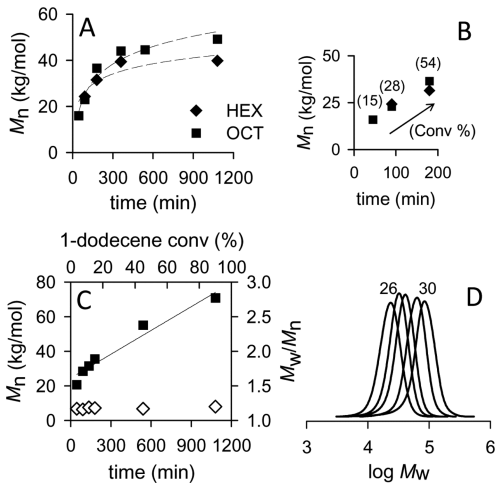

Figure 6. (A) Plot of M_n of 1-hexene and 1-octene polymers as a function of polymerization time. (B) Plot of M_n of 1-hexene and 1-octene polymers as a function of polymerization time up to 180 min. (C) Plot of M_n (■) and M_w/M_n (◇) of 1-dodecene polymers as a function of polymerization time. (D) SEC profile of poly(1-dodecene)s. The solid and dashed lines are guides to the eye and illustrate the overall trend.

segments have different properties.[6,14] While the polymerization of 1-dodecene gives a semicrystalline material with a modest 42 branches/1000C (Table 3, entry 28, T_m = 78 °C), poly(ethylene) obtained under controlled conditions with Ni-1/Et_2AlCl at room temperature is an amorphous branched polymer (Table S3, entry 39, T_g = −60 °C, M_n = 20.2 kg/mol, M_w/M_n = 1.2). Thus, it was of interest to exploit the sequential addition of 1-dodecene and ethylene to fabricate semicrystalline/amourphous block copolymers.

In the following the preparation of diblock (A−B) and triblock (A−B−A) copolymers is reported. Tables 4 and 5 summarize the polymerization results and material characterization data, respectively.

The polymerization of 1-dodecene first block (hereafter named A) was carried out under the screened controlled conditions [i.e., entry 28, [DD] = 0.2 mol/L, temperature = 22 °C, time = 18 h]. Ethylene was then charged to form the amorphous block (hereafter named B) under low and fixed pressure of 1 atm. The second stage polymerization time (t_2) was varied from 2 to 4 min to obtain the amourphous block of different size (entry 29 and 30, respectively). When the ethylene polymerization was carried out for the desired time, ethylene gas was removed, and then 1-dodecene was introduced to form the third block over t_3 (Table 4).

Figure S7 (Supporting Information) shows the SEC traces of block copolymers and poly(1-dodecene). In each run, the peak of block copolymers remains monomodal and shifts continuously to the higher molecular weight region with the increase of ethylene polymerization block time. Specifically, M_n of block copolymers increases with t_2 from 84.4 to 109.7 kg/mol and M_w/M_n is still well controlled ($M_w/M_n \approx 1.2$, Table 4). A slightly broadening in the SEC curve along with an increasingly longer tail of a low M_n fraction is observed with the increase of t_2. This indicates a certain extent of transfer/termination reactions. Therefore, ethylene block with a M_n = 13.5 kg/mol obtained at t_2 = 2 min was used for the fabrication of triblock A−B−A copolymer (entry 31). Like the above diblock copolymers, continuous increase of M_n is also attained during the three-stage polymerization. For the triblock copolymer, M_n is 96.8 kg/mol higher than the corresponding diblock copolymer (entry 29, M_n = 84.4 kg/mol) with maintained narrow M_w/M_n (1.33). This result demonstrates the controlled behavior of this Ni-1/Et_2AlCl-catalyzed three-step sequential monomer addition.

Qualitatively, all the block copolymers are rubbery solids, readily soluble in organic solvents, compared to white poly(1-dodecene) powders and to the darker poly(ethylene) sticky gel.

The overall branching number of block copolymers generally increases with respect to the reference poly(1-dodecene). For example, diblock copolymers have 57 and 65 branches/1000C (entries 29 and 30, respectively) whereas poly(1-dodecene) has

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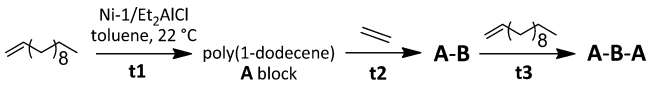
Table 4. Synthesis of Di- and Triblock Copolymers[a] and Molecular and NMR Characterization



		polymerization time (min)						polymer branching					
									CH_3/1000C[d]				
entry	polymer	t_1	t_2	t_3	yield (g)	M_n[b] (kg/mol)	M_w/M_n[b]	branches/1000C[c]	Me	Et	Pr	Bu	Lg
28[e]	A	1080			0.45	70.9	1.20	42	27		1		14
29	A−B	1080	2		0.59	84.4	1.23	57	38	1	1		15
30	A−B	1080	4		0.73	109.7	1.29	65	42	2	2	1	15
31	A−B−A	1080	2	300	0.95	96.8	1.33	54	34	1	1	1	15

[a]Polymerization conditions: toluene; Ni-1, 10 μmol; Al/Ni molar ratio, 200; temperature, 22 °C. [b]From SEC. [c]From ^{1}H NMR (see eq 1, Supporting Information). [d]From ^{13}C NMR. [e]First reported in Table 3.

Table 5. Viscosity and Thermal and Mechanical Properties of Block Copolymers

				tensile data[c]		
entry	$[\eta]_w$[a] (dL/g)	T_m[b] (°C)	ΔH[b] (J/g)	E (MPa)	σ (MPa)	ε (%)
28[d]	0.60	78	52	42.9 ± 3.9	12.4 ± 1.6	664 ± 47
29	0.66	77	37	22.9 ± 1.1	4.1 ± 0.4	657 ± 50
30	0.82	79	29	21.5 ± 1.3	6.1 ± 0.5	968 ± 39
31	0.78	77	36	28.2 ± 4.0	18.3 ± 2.1	994 ± 44

[a]From SEC using the online viscometer. [b]From DSC (second heating) (T_m at peak maximum). [c]E = Young's modulus, σ = ultimate tensile strength, and ε = elongation at break. [d]First reported in Table 3.

42 branches/1000C (entry 28). The most significant difference is the higher amount of methyl groups and the observation of a small fraction of ethyl, propyl, and butyl short branches in the block copolymers. According to the different chain-propagation mechanism involved in the polymerization of 1-dodecene and ethylene (Scheme 1), short branches are generated from the most favored insertion of ethylene into secondary methylene carbons[29] and β-hydrogen transfer to ethylene followed by reinsertion of the formed macromonomer.[30]

The DSC thermogram of block copolymers shows a broad endothermic transition with multiple and somewhat unseparated melting events (Figure S8, Supporting Information). The highest T_m of block copolymers is close to that observed for the reference poly(1-dodecene) (78 °C, Table 5). Differently, diblock copolymers exhibit reduced melting enthalpies which is a result of the reduced crystallinity of block copolymers. Calculation results in Table 5 clearly show that ΔH_m is dependent on ethylene amorphous block length: an increase of the second block length shows a corresponding decrease in ΔH_m (entries 29 and 30). All the block copolymers exhibit a broad glass transition event in the temperature range from −65 to −10 °C, likely due to the presence of two successive and close glass transitions. In fact, the midpoint T_gs of the reference poly(1-dodecene) (entry 28) and the poly(ethylene) prepared under the same polymerization conditions (entry 39 Table S3, Supporting Information) are found to be −31 and −60 °C, respectively.

SEC incorporating viscosity detector measures polymer $[\eta]_w$ that is directly related to the macromolecular chain topology with lower values found with polymer of more branched polymer architecture.[28] The $[\eta]_w$ of block copolymers is strongly reduced with respect to the homopolymers of equal molecular weight, thereby indicating a more compact chain topology for block copolymers.[8,28] For example, $[\eta]_w$ of block copolymer entry 30 (M_n = 109.7 kg/mol, Table 4) is 0.82 dL/g, which drops to 0.95 dL/g for polymer entry 9 (M_n = 109.1 kg/mol, Table 1).

Preliminary investigation on mechanical behavior by uniaxial stretching until failure was carried out for block copolymers and, as a reference point, for the parent poly(1-dodecene). The block copolymers exhibited good features of filmability and the films, with thickness of about 100 μm, were transparent, consistent, and homogeneous. Tensile tests were carried out at 21 °C, and the results are summarized in Table 5.

The engineering stress−strain curves exhibit yielding phenomena to different extents and a steady increase of the stress at small elongations. The stress−strain curve of the triblock copolymer (entry 31) shows strain hardening at the late stage of deformation (Figure 7b). The poly(1-dodecene)

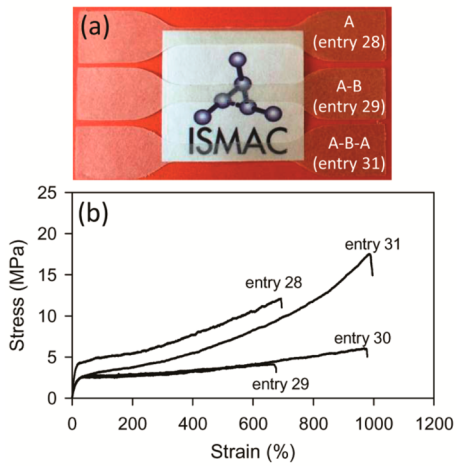


Figure 7. (a) Specimens for mechanical testing. (b) Stress−strain curves of block copolymers and poly(1-dodecene) during monotonic tensile deformation.

sample (entry 28) exhibits a modulus of 43 MPa, a tensile strength of 12 MPa, and an elongation at break of 664%. Compared to entry 28, the A−B diblock copolymers have lower Young's modulus between 21 and 23 MPa and lower ultimate tensile strength in the range from 4 to 6 MPa. As regards the elongation at break, the diblock copolymer entry 29 presents strain fracture similar to that of reference entry 28 whereas the diblock copolymer having the longest amorphous ethylene block shows higher strain. These data are likely ascribed to the reduction in the material's overall crystallinity and to some

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dissipation of energy due to the higher mobility of the free side chains for diblock copolymers. The A−B−A triblock copolymer (entry 31), where the amorphous block is in the middle of the two semicrystalline blocks, exhibits the highest values of tensile strength (18 MPa) and strain at break (ca. 1000%) while the Young's modulus results to be intermediate between those of diblock copolymers and the reference poly(1-dodecene).

The cyclic stress−strain curves of investigated materials were obtained from cyclic loading tests. In the first set of experiments, the samples were cyclically loaded and unloaded 10 times to 300% strain. The poly(1-dodecene) and the block copolymers exhibit a certain amount of unrecovered strain after the first cycle with only a small increase in the unrecovered strain on each subsequent cycle. For example, the cyclic curve of triblock copolymer and poly(1-dodecene) is shown in Figure 8. The main difference between the cyclic deformation behavior

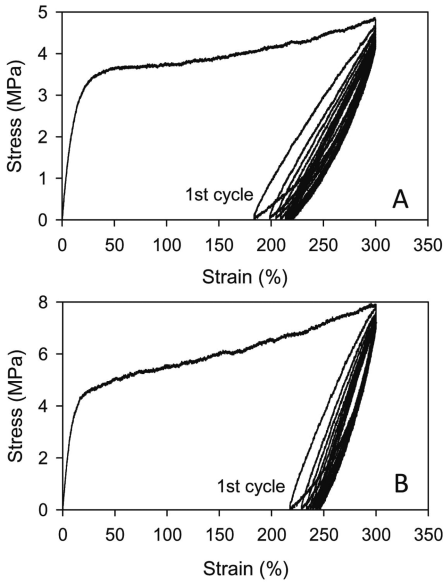

Figure 8. Stress−strain curve of triblock A−B−A copolymer (A) and of poly(1-dodecene) (B) in the hysteresis experiments for a strain of 300%.

of the polymers is in the amount of unrecovered strain after the first cycle. The unrecovered strain from 300% is 220 and 215% for poly(1-dodecene) and diblock copolymer entry 29, respectively, while lower unrecovered strain is obtained for diblock copolymer entry 30 and triblock copolymer, 180 and 175%, respectively (Figure 8 and Figure S10, Supporting Information). For all materials, a permanent structural change takes place during the first cycle, and a material with better elastomeric properties is created.

In the second set of cyclic experiments, the samples were extended step by step up to different strains. As a typical example, the stress−strain curve during cyclic tensile deformation of the diblock copolymer entry 30 is shown in Figure 9A. From the curve the strain recovery (SR) can be calculated as SR = $100(\varepsilon_a - \varepsilon_r)/\varepsilon_a$, where ε_a is the applied strain and ε_r is the strain in the cycle at zero load after the applied strain. The strain recovery is plotted as a function of the applied strain in Figure 9B. For all materials, the strain recovery decreases rapidly at lower applied strains and then levels off at higher applied strains. The diblock copolymer having the longest amorphous ethylene block (entry 30) and the triblock

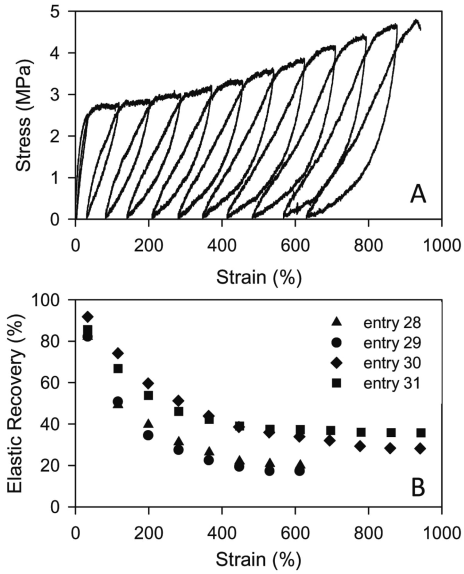

Figure 9. (A) Stress−strain curve of diblock copolymer (entry 30) during step cycle tensile deformation at different strain. (B) Strain recovery as a function of the applied strain.

copolymer (entry 31) present the highest recovery for the whole range of applied strains. Overall, the tensile tests showed that the block copolymers behave as thermoplastic elastomers with properties close to those reported for block and random ethylene−1-octene copolymers.[31]

■ CONCLUSION

In summary, we report the polymerization of 1-dodecene, 1-octene, and 1-hexene catalyzed by an α-diimine Ni(II) complex, in combination with Et_2AlCl, at room temperature. The obtained polymers have fewer branches than expected from successive 1,2-insertions. Quantitative ^{13}C NMR of the polymers suggest that 2,1-insertion followed by chain-walking (ω,1-enchainment) occurs, resulting in linear polymer chain segments. Generally, the fraction of ω,1-enchainment ranges from 48 to 66% with higher values found for 1-dodecene polymers: increases in monomer size lead to a reduction of the branching number and to an increase of the crystalline block length. The monomer concentration dictates the competition between successive 1,2-insertions (1,2-enchainment) and 1,2-insertions followed by chain-walking (ω,2-enchainment), thus strongly influencing the branch-type distribution and polymer physical properties.

The polymerization of 1-dodecene exhibits some living characteristics in a time of hours within which almost all the monomer is converted to polymer. The obtained poly(1-dodecene) is semicrystalline with narrow molecular weight distribution (M_w/M_n = 1.2) and molecular weight of 70.9 kg/mol and shows melting temperature of about 80 °C. Living/controlled polymerization of 1-dodecene provides a viable access to precise synthesis of block copolymers. The fabrication of a triblock copolymer, composed of an amorphous middle block, and diblock copolymers is completed in three and two steps, respectively, through the sequential monomer addition from 1-dodecene and ethylene, without requiring any intermediate separation step. Although chemically identical, each block exhibits distinct features, varying from semicrystalline to amorphous, taking advantage of the different mechanism

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involved in the polymerization of 1-dodecene and ethylene. The tensile tests demonstrate that the block copolymers behave as TPEs, with different performances depending on the composition, length of the blocks, and material's overall crystallinity.

The results make this synthesis attractive for the engineering of functional olefin TPEs produced from readily accessible starting materials. Use of higher α-olefins such as 1-dodecene is particularly challenging since a growth of production of unsatured hydrocarbon commodities is expected.[32]

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and spectra of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Deplace, F.; Scholz, A. K.; Fredrickson, G. H.; Kramer, E. J.; Shin, Y.-W.; Shimizu, F.; Zuo, F.; Rong, L.; Hsiao, B. S.; Coates, G. W. *Macromolecules* **2012**, *45*, 5604−5618. (b) Poon, B. C.; Dias, P.; Ansems, P.; Chum, S. P.; Hiltner, A.; Baer, E. *J. Appl. Polym. Sci.* **2007**, *104*, 489−499.

(2) (a) Chum, P. S.; Swogger, K. W. *Prog. Polym. Sci.* **2008**, *33*, 797−819. (b) Walton, K. L. *Rubber Chem. Technol.* **2004**, *77*, 552−568. (c) Müller, G.; Rieger, B. *Prog. Polym. Sci.* **2002**, *27*, 815−853.

(3) For recent reviews: (a) Wang, S.; Sun, W.-H.; Redshaw, C. *J. Organomet. Chem.* **2014**, *751*, 717−741. (b) Dong, Z.; Ye, Z. *Polym. Chem.* **2012**, *3*, 286−301. (c) Camacho, D. H.; Guan, Z. *Chem. Commun.* **2010**, *46*, 7879−7893. (d) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30−92.

(4) (a) Xiang, P.; Ye, Z.; Morgan, S.; Xia, X.; Liu, W. *Macromolecules* **2009**, *42*, 4946−4949. (b) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415.

(5) (a) Leone, G.; Losio, S.; Piovani, D.; Sommazzi, A.; Ricci, G. *Polym. Chem.* **2012**, *3*, 1987−1990. (b) Rose, J. M.; Deplace, F.; Lynd, N. A.; Wang, Z.; Hotta, A.; Lobkovsky, E. B.; Kramer, E. J.; Coates, G. W. *Macromolecules* **2008**, *41*, 9548−9555. (c) Gates, D. P.; Svejda, S. A.; Onate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320−2334.

(6) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664−11665.

(7) Guan, Z. *Chem.—Eur. J.* **2002**, *8*, 3086−3092.

(8) Xu, Y.; Xiang, P.; Ye, Z.; Wang, W.-J. *Macromolecules* **2010**, *43*, 8026−8038.

(9) Hotta, A.; Cochran, E.; Ruokolainen, J.; Khanna, V.; Fredrickson, G. H.; Kramer, E. J.; Shin, Y. W.; Shimizu, F.; Cherian, A. E.; Hustad, P. D.; Rose, J. M.; Coates, G. W. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15327−15332.

(10) Hu, H.; Gao, H.; Chen, D.; Li, G.; Tan, Y.; Liang, G.; Zhu, F.; Wu, Q. *ACS Catal.* **2015**, *5*, 122−128.

(11) Rose, J.; Cherian, A. E.; Hun Lee, J.; Archer, L. A.; Coates, G. W.; Fetters, L. J. *Macromolecules* **2007**, *40*, 6807−6813.

(12) McCord, E. F.; McLain, S. J.; Nelson, L. T. J.; Ittel, S. D.; Tempel, D.; Killian, C. M.; Johnson, L. K.; Brookhart, M. *Macromolecules* **2007**, *40*, 410−420.

(13) Subramanyam, U.; Sivaram, S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 191−210.

(14) Ye, Z.; Xu, L.; Dong, Z.; Xiang, P. *Chem. Commun.* **2013**, *49*, 6235−6255.

(15) Gottfried, A. C.; Brookhart, M. *Macromolecules* **2003**, *36*, 3085−3100.

(16) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236−2257 and references therein.

(17) (a) Hu, H.; Zhang, L.; Gao, H.; Zhu, F.; Wu, Q. *Chem.—Eur. J.* **2014**, *20*, 3225−3233. (b) Rhinehart, J. L.; Brown, L. A.; Long, B. K. *J. Am. Chem. Soc.* **2013**, *135*, 16316−16319. (c) Liu, F.-S.; Hu, H.-B.; Xu, Y.; Guo, L.-H.; Zai, S.-B.; Song, K.-M.; Gao, H.-Y.; Zhang, L.; Zhu, F.-M.; Wu, Q. *Macromolecules* **2009**, *42*, 7789−7796. (d) Meinhard, D.; Wegner, M.; Kipiani, G.; Hearley, A.; Reuter, P.; Fischer, S.; Marti, O.; Rieger, B. *J. Am. Chem. Soc.* **2007**, *129*, 9182−9191.

(18) Vaidya, T.; Klimovica, K.; LaPointe, A. M.; Keresztes, I.; Lobkovsky, E. B.; Daugulis, O.; Coates, G. W. *J. Am. Chem. Soc.* **2014**, *136*, 7213−7216.

(19) Azoulay, J. D.; Bazan, G. C.; Galland, G. B. *Macromolecules* **2010**, *43*, 2794−2800.

(20) Guo, L.; Gao, H.; Li, L.; Wu, Q. *Macromol. Chem. Phys.* **2011**, *212*, 2029−2035.

(21) Losio, S.; Leone, G.; Bertini, F.; Ricci, G.; Sacchi, M. C.; Boccia, A. C. *Polym. Chem.* **2014**, *5*, 2065−2075.

(22) Peleška, J.; Hoštálek, Z.; Hasalíková, D.; Merna, J. *Polymer* **2011**, *52*, 275−281.

(23) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1203.

(24) The data for ω,1-enchainment with Ni-1/Et_2AlCl were higher than that found with Pd catalysts, ranging from 37 to 53 (see ref 12), thus confirming that polyolefins produced from Pd complexes exhibits highly branched structures. Meanwhile, our results are in disagreement with data by Sivaram et al. (see ref 13). They found that 1,2-insertion was more favorable than 2,1-insertion and that the ω,1-enchainment decreased with the increase of the monomer carbon chain length, ranging from 29 mol % for poly(1-octadecene) to 39 mol % for poly(1-hexene).

(25) Guan, Z. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3680−3692.

(26) Voit, B. I.; Lederer, A. *Chem. Rev.* **2009**, *109*, 5924−5973.

(27) Ruiz de Ballesteros, O.; Auriemma, F.; Guerra, G.; Corradini, P. *Macromolecules* **1996**, *29*, 7141−7148.

(28) Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules* **2000**, *33*, 6945−6952.

(29) Lamberti, M.; Mazzeo, M.; Pappalardo, D.; Pellecchia, C. *Coord. Chem. Rev.* **2009**, *253*, 2082−2097.

(30) Budzelaar, P. H. M. *WIREs Comput. Mol. Sci.* **2012**, *2*, 221−241.

(31) (a) Wang, H. P.; Chum, S. P.; Hiltner, A.; Baer, E. *J. Appl. Polym. Sci.* **2009**, *113*, 3236−3244. (b) Zuo, F.; Burger, C.; Chen, X.; Mao, Y.; Hsiao, B.; Chen, H.; Marchand, G. R.; Lai, S.-Y.; Chiu, D. *Macromolecules* **2010**, *43*, 1922−1929. (c) Hölzer, S.; Menzel, M.; Zia, Q.; Schubert, U. S.; Beiner, M.; Weidisch, R. *Polymer* **2013**, *54*, 5207−5213.

(32) Tullo, A. H. *Chem. Eng. News* **2005**, *83*, 30−33.

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