RAPID COMMUNICATION

Origin of the Formation of the 4-Butenyl End Group in Zirconocene-Catalyzed Propylene Polymerization

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INTRODUCTION

The production of polyolefin materials increased from 25 million tons in 1980 to 100 million tons in 2003.[1] Polypropylene accounts for nearly one-third of the total polyolefin consumption worldwide.[2] Polypropylene obtained with metallocene catalysts accounted for less than 0.5% of this market in 2000. Nevertheless, projections forecast growth for the demand for metallocene-based polypropylene, which is expected to reach 20% of the total global propylene consumption by 2010.[3] Given these promising trends, olefin polymerization with metallocene catalysts has attracted much academic and industrial research interest. Understanding the catalyst systems and reaction conditions has led to the development of new, versatile processes and the next generation of polypropylene products.[1]

The study of polymerization mechanisms is a required step in the design of commercial processes; therefore, many studies have been focused on the elucidation of the elementary reaction steps in the polymerization of olefins employing homogeneous and heterogeneous catalyst systems.[4–11] The analysis of polymer chain ends provides key structural information for the determination of the chain-transfer mechanisms in olefin polymerization.[12] In particular, ^{1}H NMR investigation of unsaturated chain ends has been successfully used to determine chain-transfer mechanisms in *ansa*-zirconocene-catalyzed polymerizations of propylene.[13,14] Four unsaturated end groups that form during propylene polymerization have been identified: vinylidene, allyl, 2-butenyl, and 4-butenyl.[13,15] Vinylidene end groups are produced via β-hydride transfer to the metal and/or to the monomer after a primary insertion.[16] Allyl end groups are formed via β-methyl transfer.[17,18] 2-Butenyl end groups are produced via β-hydride transfer after a secondary insertion of propylene.[19] The mechanism of the formation of the 4-butenyl end group remains unclear. The triplet observed at $\delta = 5.20$ ppm in ^{1}H NMR has been assigned to the 4-butenyl end group.[13,15] The 4-butenyl end group is always observed when the 2-butenyl end group is present in the olefinic region of the ^{1}H NMR spectrum.[12,13]

It has been proposed that 4-butenyl is formed by isomerization of the 2-butenyl end group.[14] Experimental evidence has shown that such isomerization is not produced by heat or an acidic treatment during the workup or analysis of the polymer. Carvill et al.[13] did not observe a change in the number of 2-butenyl unsaturations in polypropylene prepared at 60 °C after the heating of the polymer for 48 h at 103 °C. Resconi and coworkers[12,15] proved that the *cis*-2-butenyl end group was stable in the presence of *p*-toluenesulfonic acid in a $C_2D_2Cl_4$ solution at 130 °C for 30 min. These results suggest that the formation of the 4-butenyl end group

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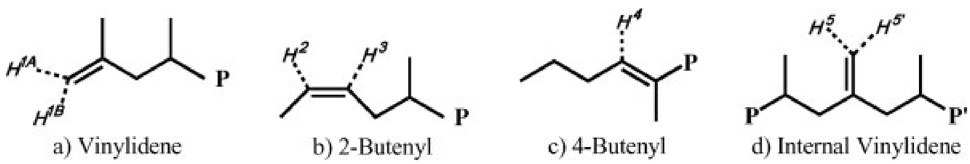

Figure 1. Proton numbering of unsaturated groups detected by ^{1}H NMR.

may be produced by isomerization of the 2-butenyl end group during polymerization. We postulate that the production of the 4-butenyl end group by isomerization might be catalyzed by a zirconocene hydride complex formed during the β-hydride elimination reaction. β-Hydride transfer to metal is one of the main chain-transfer events in most of the studied *ansa*-zirconocene catalysts,[14,15] and it produces a metal hydride initiating species. Interestingly, no trace of the isomer 3-butenyl end group has ever been detected in previous studies on metallocene-catalyzed polypropylene.

Transition-metal compounds are known to catalyze the isomerization of unsaturated molecules.[20–22] Transition-metal isomerizations proceed generally via the metal hydride addition/elimination mechanism,[23] which has been reported to be operative in the homogeneous isomerization of olefins by hydrides, such as $HNi[P(OC_2H_5)_3]_4^+$,[24] $H_2Ru_4(CO)_{13}$,[25] $RuClH(CO)(PPh_3)_3$,[26] and $HRh(CO)(PPh_3)_3$.[27] This mechanism is also valid for systems in which inactive metal complexes are converted to hydrides by a reaction with a cocatalyst, such as $[(C_2H_4)_2RhCl]_2/HCl$,[28] $Co_2(CO)_8/H_2$,[29] and $RhCl_3 \cdot nH_2O/BH_3{\cdot}THF$ (where THF is tetrahydrofuran).[30] Wilkinson's catalyst {chlorotris(triphenylphosphine)-rhodium(I) [$RhCl(PPh_3)_3$]} has been reported to catalyze the isomerization of internal alkenes. Pereira[31] reported the isomerization of *cis*-2-methyl-3-hexene in rhodium- and zirconocene-catalyzed hydroboration with pinacol borane. The cycloisomerization of allenynes with $RhCl(PPh_3)_3$ was observed by Shibata et al.[32]

This study was an investigation of the formation of 4-butenyl end groups present in isotactic polypropylene (iPP), which was prepared by the polymerization of propylene with the catalyst system *rac*-$Et(Ind)_2ZrCl_2$/MAO (where MAO is methylaluminoxane).[33] Preformed polypropylene was treated with the intermediate hydride complex $RhCl(PPh_3)_2H_2$, which was derived from $RhCl(PPh_3)_3$, to test for the production of 4-butenyl chain ends by transition-metal hydride isomerization of *cis*-2-butenyl end groups. The isomerization reaction was carried out in toluene at 65 °C to mimic polymerization conditions.

EXPERIMENTAL

Materials

$RhCl(PPh_3)_3$ (99%) was purchased from Strem Chemicals. A 1.0 M triisobutylaluminum (TIBA) solution in toluene was purchased from Sigma–Aldrich. Hydrogen (prepurified-grade) was supplied by Merriam Graves Corp. Toluene (anhydrous, 99.8%), purchased from Sigma–Aldrich, was dried over sodium and distilled under nitrogen. iPP was produced with *rac*-$Et(Ind)_2ZrCl_2$/MAO in toluene at 65 °C and 3.2 atm of propylene partial pressure.[33] The polypropylene had a weight-average molecular weight of 15,000 g/mol and a polydispersity of 2.19.[33]

Reaction with $RhCl(PPh_3)_3$

The catalyst solution was prepared in an inert atmosphere by the addition of 1.2 μmol of $RhCl(PPh_3)_3$ in 10 mL of dry toluene. Prepurified hydrogen was infused into the catalyst solution for 30 min. The absorption of molecular hydrogen with $RhCl(PPh_3)_3$ in solution produced the transient dihydrido species $RhCl(PPh_3)_2H_2$ after oxidative addition.[34] The reactant medium was prepared under an inert atmosphere in a 50-mL, round-bottom flask with a condenser on top. One gram of the polymer (iPP) was dissolved in 30 mL of dry toluene, and 0.5 mL of TIBA was added as a scavenger. The isomerization reaction was initiated by the transfer of the catalyst solution to the reactant medium. Hydrogen was not flushed during the isomerization reaction to avoid hydrogenation of unsaturated end groups. The reaction temperature was regulated at 65 °C with a silicone oil bath. Aliquots were taken after reaction times of 6 and 24 h. The final solution was washed with a mixture of methanol and hydrochloric acid (10:1 v/v) and dried *in vacuo*.

Analysis of the Polymer

Unsaturated chain-end groups were analyzed by ^{1}H NMR with a Bruker Avance 400 NMR spectrometer at 100 °C. Tetrachloroethane-d_2 (TCE-d_2) was used as the solvent. The instrument conditions were as follows: a pulse angle of 30°, an acquisition time of 4.0 s, a delay time of 1.0 s, a spectral width of 8278 Hz, and 500 scans.

RESULTS AND DISCUSSION

Four unsaturated groups were detected by ^{1}H NMR analysis of the aliquots (Fig. 1): vinylidene (4.68 H^{1A} singlet and 4.75 H^{1B} singlet), *cis*-2-butenyl (5.39–5.54

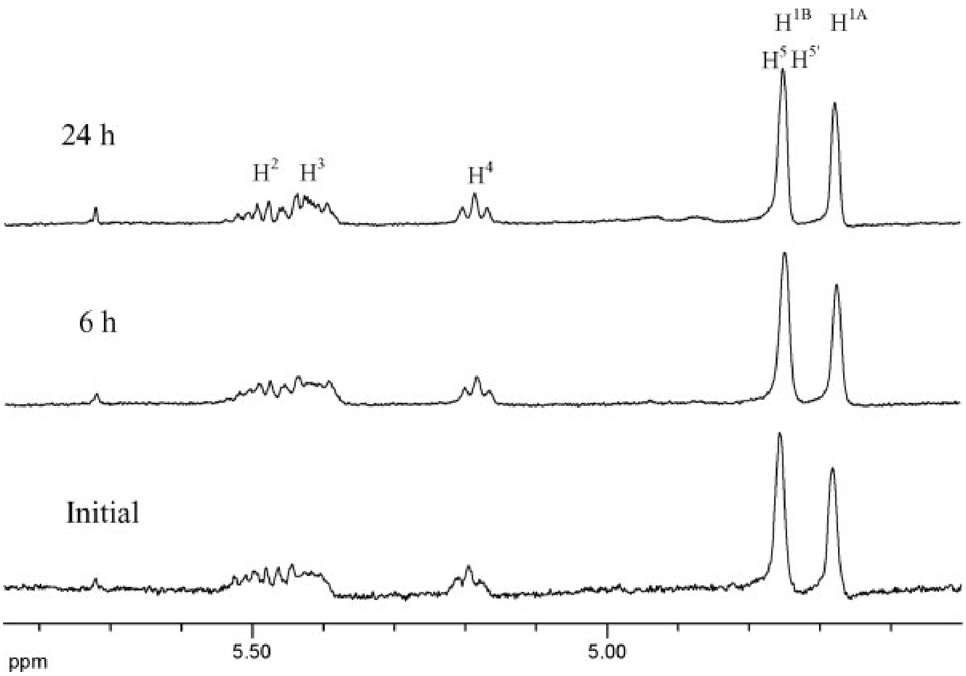

Figure 2. ^1H NMR olefinic region (400 MHz, TCE-d_2, 100 °C, reference C_2HDCl_4 at 5.95 ppm) of iPP during the isomerization reaction.

H^2 and H^3, complex multiplet), 4-butenyl (5.20 H^4 triplet), and internal vinylidene (hidden singlet under the 4.68 H^{1A} singlet). Spectra of the ^1H NMR olefinic region in each sample are shown in Figure 2. The presence of internal vinylidene is detected by the unequal intensity of the two vinylidene peaks. Few authors have observed that the internal vinylidene overlaps the lowest field vinylidene peak when TCE-d_2 is used as the NMR solvent.[12,15,35] The internal vinylidene has been postulated to result from propylene insertion into an allylic-activated zirconocene cation, involving the reversible formation of a zirconocene (allyl) dihydrogen complex.[36]

The evaluation of the intensity of unsaturated groups (Table 1) shows how the percentage of 4-butenyl increases with respect to 2-butenyl in the treatment of the polymer with the hydride complex derived from $RhCl(PPh_3)_3$. The formation of the dihydrido species $RhCl(PPh_3)_2H_2$ is a reversible reaction involving hydrogen gas as a reactant.[34] Hydrogen was not flushed during the reaction to avoid hydrogenation of unsaturated groups, and so the hydride $RhCl(PPh_3)_2H_2$ was expected to be reduced to $RhCl(PPh_3)_3$ during the reaction. This may explain the small change in the 4-butenyl/2-butenyl ratios with the reaction time.

The results in Table 1 are given as the fractional percentages of the total unsaturated end groups. Because we do not know the total concentration of each end group, the results could indicate that selective hydrogenation of unsaturated end groups at different rates is taking place. However, we rule out this interpretation because the H_2 concentration was low, the catalyst/end-group ratio was high (Rh/end group = 1.8×10^{-2} mol/mol), and a nonpolar solvent was used.

Our experimental results indicate that the isomerization of the 2-butenyl end group to the 4-butenyl end group may occur via an addition/elimination pathway catalyzed by a metal hydride complex. The formation of

Table 1. Percentage of Unsaturated End Groups during the Isomerization Reaction

	Unsaturated Groups (%)				
Reaction Time (h)	Vinylidene	2-Butenyl	4-Butenyl	Internal Vinylidene	4-Butenyl/ 2-Butenyl
0	46.5	26.5	14.4	12.7	0.54
6	45.4	27.6	16.4	10.5	0.59
24	44.3	26.2	18.1	11.4	0.69

a 3-butenyl intermediate [$CH_3—CH_2—CH=CH —CH (CH_3) —P$] is expected. The question that arise is why the 3-butenyl end group has never been detected by ^1H or ^{13}C NMR in the olefinic region of iPP spectra. Predictions of the chemical shift of the 3-butenyl by ACD/CNMR Predictor suggest that if the 3-butenyl end group were present, these resonances would appear in a region of the spectra unobscured by other end groups.[37] For a catalyst system that produced iPP with a high number of regioinsertions and a percentage of *cis*-2-butenyl unsaturations higher than 90%,[19] 4-butenyl was observed in a small percentage, but not a trace of the 3-butenyl end group was detected. Our work does not answer the question why the 4-butenyl would be more stable than the 3-butenyl unsaturation in a thermodynamic equilibrium between isomers.

CONCLUSIONS

Previous attempts to demonstrate the isomerization of *cis*-2-butenyl to the 4-butenyl end group by either thermolysis or acid-catalyzed isomerization were not successful.[12,13,15] We treated iPP having olefinic end groups, obtained with the catalyst system *rac*-$Et(Ind)_2ZrCl_2$/MAO, with the dihydrido complex $RhCl(PPh_3)_2H_2$ derived from $RhCl(PPh_3)_3$ to test for a metal hydride catalyzed isomerization of *cis*-2-butenyl to 4-butenyl end groups under conditions similar to those used during polymerization. With ^1H NMR, the occurrence of the isomerization of *cis*-2-butenyl to 4-butenyl end groups was detected for the first time under the same conditions used for the zirconocene-catalyzed polymerization of iPP. These results suggest that the mechanism of formation of 4-butenyl chain ends may be the isomerization of *cis*-2-butenyl catalyzed by a zirconocene hydride complex formed *in situ* during polymerization.

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37. Advanced Chemistry Development ACD/CNMR Predictor estimates $\delta = 129.2$ ppm and $\delta = 137.0$ ppm as chemical shifts for the unsaturated carbons of 2-methyl-3-hexene, which resembles the 3-butenyl end group. For the unsaturated carbons of cis-5-methyl-2-hexene (cis-2-butenyl), ACD/CNMR Predictor estimates $\delta = 124.37$ ppm and $\delta = 129.64$ ppm, whereas the experimental values for the cis-2-butenyl end group are $\delta = 124.40$ ppm and $\delta = 129.51$ ppm (ref. 13, with respect to tetramethylsilane).