Long Chain Branched Isotactic Polypropylene

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Received January 11, 2002; Revised Manuscript Received March 7, 2002

ABSTRACT: Long chain branched isotactic polypropylene (LCB-PP) was synthesized using metallocene catalyst (*rac*-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride activated by methylaluminoxane). The branching was in situ generated in a diluted polymerization condition using hexane or toluene as diluent. The polymers have a significant population of branched molecules as evidenced by multiangle laser light scattering analysis. More importantly, such a branching structure in isotactic polypropylene has been, for the first time, identified by ^{13}C NMR spectroscopy. The ^{13}C NMR resonance assignments of the branching structure are based on the model polymer characterization, stereo environment analysis, and chemical shift calculation. The unique stereo environment of the branching structure provides insight into the mechanism of LCB formation in such isotactic polypropylenes. The branching levels determined by ^{13}C NMR are directionally consistent with that estimated from laser light scattering analysis.

Introduction

Isotactic polypropylene is one of the leading and fast growing thermoplastic polymers in the world due to its high melting point, high tensile strength, stiffness, and chemical resistance.[1] However, commercial polypropylenes usually have relatively low melt strength which limits their use in applications such as thermoforming, foaming, and blow molding.[2] Since long chain branching (LCB) is generally known to enhance the melt properties of a polymer,[3,4] several approaches have been developed to make branched polypropylenes. Some include post-reactor treatments such as electron beam irradiation,[5] peroxide curing,[6] and grafting;[7] others use in-reactor copolymerization.[8] The branches in irradiated or peroxide treated polymers are generated through radical-induced random chain scission followed by recombination. Thus, the products are complex, and the processes may be difficult to control. Grafting of polymer chains onto linear macromolocules would lead to comblike branched polymers, but the chemistry to prepare polyolefin graft copolymers is very limited.[9]

Development of metallocene technology provides unprecedented flexibility in polymer design.[10] Many structural features, including LCB, can now be introduced into polymers. For example, long chain branches are formed in linear low-density polyethylene (LLDPE) through incorporation of the in situ generated, vinyl-terminated polyethylene macromonomer.[11] Such polymers display good processability despite having narrow molecular weight distribution.[12] There has been extensive studies on the structures of long chain branched polyethylene, including ^{13}C NMR characterization.[13] The long chain branching through macromonomer incorporation in polypropylene is much less documented. Shiono et al. reported the copolymerization of oligomeric, atactic polypropylene macromonomers with ethylene or propylene to give branched polymers.[14,15] However, definitive structural analysis of such polymers is limited due to the atactic nature of the macromonomers (the branches). In addition, the molecular weights of the branches are far below the entanglement molecular weight (M_e) for PP, which has been reported to be 7000 g/mol.[16]

Recently, we reported the synthesis of isotactic polypropylene macromonomers having predominantly vinyl-terminated chain ends and in size ranges above the M_e.[17] These macromonomers were further incorporated into isotactic polypropylene backbones to make long chain branched polymers.[18] Since metallocene catalysts, such as dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride, are capable of generating and incorporating vinyl-terminated polypropylene macromonomers, it is conceivable that, under appropriate reaction conditions, long chain branching could be generated in situ during polymerization. In this work, we report such in situ generated, long chain branched isotactic polypropylene[19] and the characterization of the branch structure.

Experimental Section

Materials. Polymerization grade ethylene, propylene, and solvents were supplied through pipelines directly from the ExxonMobil chemical plant and further purified by passing through activated basic alumina and molecular sieves. All reagents were obtained commercially and used as received.

Catalyst Preparation. All catalyst preparations were performed in an inert atmosphere with <1.5 ppm of H_2O content. Metallocene catalyst precursor dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride was activated with methylalumoxane (MAO, 10 wt % in toluene, from Albemarle Inc.). The catalyst was added to a stainless steel tube by pipet and transferred to the reactor.

Synthesis of LCB-PP. The polymerization was conducted in a 2 L semicontinuous reactor—an autoclave reactor equipped with a HPLC pump that introduces the propylene feed into the reactor (2.5−5 mL/min). Typically, the reactor was charged with 1 L of hexane or toluene, The catalyst (5−10 mg of dimethylsiliylbis(2-methyl-4-phenylindinyl)zirconium dichloride activated with 2 mL of MAO (10 wt % in toluene)) was injected with solvent at the desired temperature. Polymerization reactions commenced with the continuous pumping of propylene. A steady state was achieved in less than 10 min, as measured by the leveling of reactor pressure. After 60 min, the propylene feed was stopped, and the reactor was cooled to 25 °C and vented. The polymer was collected by filtration. (In the cases of toluene being used as solvent, methanol (500 mL) was added before the filtration.) The collected polymer was then washed with hexane and dried in a vacuum oven at 60 °C for 12 h.

10.1021/ma020050j CCC: $22.00

Table 1. Polymerization Parameters and General Characterization of Long Chain Branched Polypropylene Samples

							GPC		^{1}H NMR		DSC	
polymer sample	temp (°C)	solvent	propylene rate (cm^3/min)	polymn time (min)	yield (g)	propylene conv (%)	M_w	M_w/M_n	vinyls / 1000C	% vinyl	T_m (°C)	T_c (°C)
LCB-PP 1	50	hexane	3	60	39	41.7	242 796	2.25	0.08	39.4	153.0	107.8
LCB-PP 2	50	hexane	3	90	82	58.4	294 431	2.07	0.04	33.3	154.9	107.6
LCB-PP 3	55	hexane	3	60	48	51.3	191 352	2.29	0.13	39.4	151.8	112.2
LCB-PP 4	60	hexane	3	60	52	55.6	120 995	2.35	0.11	55.0	148.8	106.6
LCB-PP 5	60	hexane	3	60	58	61.9	99 331	2.34	0.13	54.2	145.8	104.5
LCB-PP 6	60	toluene	3	60	61	65.2	125 006	2.45	0.20	66.7	151.8	105.5

Characterization. Molecular weight characteristics were determined using a Waters 150C high-temperature gel permeation chromatograph (GPC) operating at 135 °C. The NMR spectra of the polymers were recorded on a 500 MHz Varian Unity instrument at 120 °C using tetrachloroethene as solvent. Melting and crystallization temperatures of the polymers were measured on a TA Instrument DSC-912 using a heating and cooling rate of 10 °C/min. The melting temperatures reported were obtained from the second melt.

The light scattering experiments were conducted using an instrument combining multiangle laser light scattering with a Waters 150C gel permeation chromatograph (GPC-MALLS, made by Wyatt Technology, Inc.). This instrument allows the measurement of polymer molecular weight and radius of gyration. The MALLS detector contains a 30 mW argon ion laser and an array of photodiodes. The photodetectors were calibrated with NBS1482, a polyethylene standard with a stated molecular weight of 13 600 g/mol and polydispersity of ~1.2. A radius of gyration, R_g, value of 5 nm was assumed for this polymer.

Results and Discussion

I. Synthesis of LCB-PP. It has been reported that long chain branches in polypropylene can be generated through incorporation of vinyl-terminated macromonomers.[11,18] Therefore, the branching level would largely depend on the amount of macromonomer in the reaction and the rate of macromonomer insertion relative to the rate of propylene insertion. Accordingly, the metallocene catalyst capable of producing vinyl chain end and the reaction conditions favoring macromonomer incorporation were used in our experiments to enhance the in situ generation of long chain branching. To kinetically maximize the relative rate of macromonomer insertion, propylene feed was slowly introduced into the reactor using a small scale (HPLC) pump. Polymerization was carried out in a low but steady propylene concentration, which allows the accumulation of reactive macromonomers and therefore the possibility of their incorporation.

A summary of several LCB-PP samples is provided in Table 1. Polymerization was conducted at temperatures from 50 to 60 °C using MAO-activated dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride as catalyst. In general, the molecular weight of the polymer decreases with increasing polymerization temperature, but the molecular weight distribution remains relatively narrow, ranging from 2.05 to 2.45. The melting point also decreases slightly with increase of polymerization temperature, indicating an increase of regio defects. Interestingly, in the ^{1}H NMR analysis, these samples show relatively high vinyl end group population (39−67% of the total olefinic end groups).[17] It would be difficult to assess the real-time vinyl end group population in the polymerization process as it is being consumed to form LCB. However, it would not be lower than the vinyl end group population in the final product. The high vinyl end group population is believed necessary for macromonomer incorporation and branches formation.

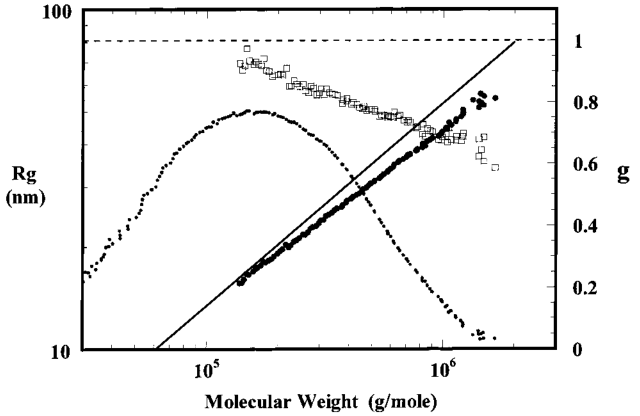


Figure 1. GPC-MALLS analysis of long chain branched polypropylene (LCB-PP 3).

II. Characterization of LCB by GPC-MALLS. The LCB characterization was carried out using multiangle laser light scattering analysis coupled with a gel permeation chromatography instrument (GPC-MALLS) which measures the polymer molecular weight and the radius of gyration $\langle R_g \rangle$ as polymer fractions are eluted from the GPC columns. The absolute molecular weight is determined by light scattering at each retention volume, and the R_g value of the polymer is obtained by fitting the angular dependence of the light scattering signal to a random coil model (both linear and branched molecules).[20] The branching index (g) is defined as $g = R_g{}^2{}_{\text{branched}}/R_g{}^2{}_{\text{linear}}$ (same molecular weight). Since the radius of gyration for a branched molecule is smaller than that of a linear molecule of same molecular weight, a g value smaller than 1 indicates a branched polymer. Figure 1 shows the R_g (solid dots) and the g (open squares) values plotted vs molecular weight for a typical branched polypropylene sample (LCB-PP 3). The deviation of R_g from linear behavior can be readily noticed, even at relatively low molecular weights. The molecular weight distribution (GPC curve) is also plotted, showing that significant amount of molecules are branched. For comparison of branching levels in these LCB-PP samples, we may use the weight-average branching indices ($g_{\langle W \rangle}$) as defined in eq 1. The R_g vs molecular weight (M) for linear polymers is described by power law, and both K and α values are experimentally determined.[20] The $g_{\langle W \rangle}$ values of six LCB-PP samples are listed in Table 2, indicating these polymers are highly branched.[21]

$$g_{\langle W \rangle} = \frac{\sum C_i R g_i{}^2}{\sum C_i (K M_i{}^{\alpha})^2} \qquad (1)$$

III. ^{13}C NMR Analysis of Branching Structure. The long chain branching structures in the LCB-PP samples was investigated in detail using ^{13}C NMR. A typical spectrum (LCB-PP 5) is shown in Figure 2. The

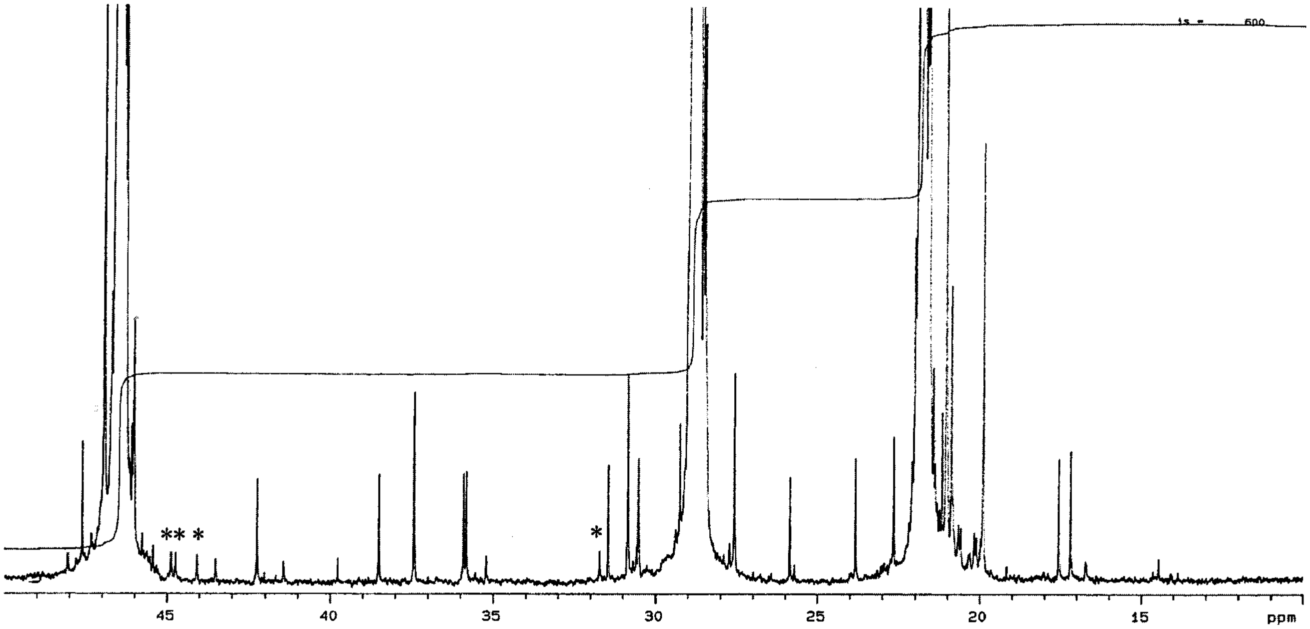


Figure 2. ^{13}C NMR spectrum of long chain branched polypropylene (LCB-PP 5).

Table 2. Weight-Average Branching Indices of Long Chain Branched PP Samples

polymer sample	branch index ($g_{\langle w\rangle}$)	polymer sample	branch index ($g_{\langle w\rangle}$)
LCB-PP 1	0.85	LCB-PP 4	0.67
LCB-PP 2	0.87	LCB-PP 5	0.59
LCB-PP 3	0.78	LCB-PP 6	0.47

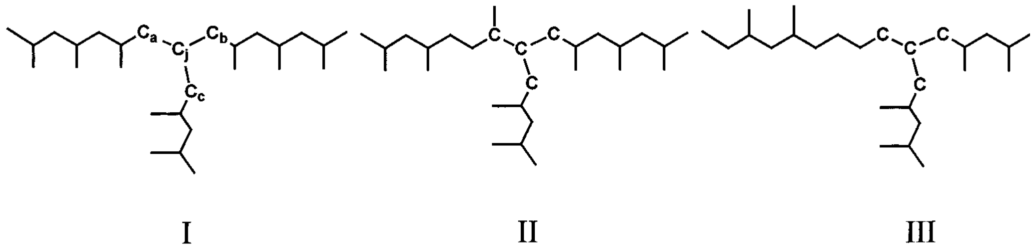
strong resonances of methylene, methine, and methyl carbons of PP are observed at about 46, 28, and 21 ppm. The resonance peaks resulting from regio defects (2,1 erythro and 1,3 misinsertions) and chain ends (isobutyl, *n*-propyl, and vinyl) are properly assigned according to the literature.[22] However, there are four small peaks at 44.88, 44.74, 44.08, and 31.74 ppm in a 1:1:1:1 ratio remain to be assigned (Figure 2, peaks with asterisk). Interestingly, these four peaks are absent in linear isotactic polypropylene polymers.

Some plausible structures of branching through vinyl-terminated macromonomer insertion in PP are shown in Scheme 1 (stereoisomers are discussed later). As there is no literature evidence that comonomers incorporate preferably after regio errors, structures I would be statistically most significant. In structure I, the three α-carbons are diastereotopic. Considering the C_a and C_b as the α-carbon atoms in the backbone, they become sterically nonequivalent due to the presence of chiral carbon in the branch (analogous to the two methyl carbons in the isopropyl group of 2,4-dimethylhexane).[23] Another way to distinguish the α-carbons is to look at their relative configurations using the conventional *meso* (*m*) and *racemic* (*r*) nomenclature. When looking down from C_c to the branching point and considering C_c as if it was a methyl group, the triads of $C_a{-}C_j{-}C_b$ would be *mm*. However, if one is looking down from C_a or C_b to the branching point, the triads of $C_b{-}C_j{-}C_c$ and $C_a{-}C_j{-}C_c$ would be *rr* and *mr*, respectively. This can be better illustrated in Scheme 2 by rotating one of the α-carbon to C_j bonds. Thus, each α-carbon is in its unique stereo environment. Since the C_a, C_b, and C_c are all connected to C_j-, the stereo configurations of the three triads are interrelated. A change of the stereo configuration of one triads would result in the corresponding changes of the other two. For example, if the triads of $C_a{-}C_j{-}C_b$ become *mr* due to a stereo mistake during macromonomer insertion, then the other two triads ($C_b{-}C_j{-}C_c$ and $C_a{-}C_j{-}C_c$) would change to *rr* and *mm*, respectively. Similarly, if the triads of $C_a{-}C_j{-}C_b$ is *rr*, the triads $C_b{-}C_j{-}C_c$ and $C_a{-}C_j{-}C_c$ would become *mm* and *mr*. In fact, the stereo arrangements or the three triads around branching point would always be *mm*, *mr*, and *rr*. Therefore, it is not necessary to differentiate backbones and branches. The branching structure I would give three, and only three, distinctive ^{13}C NMR resonances as long as both backbones and branches are isotactic.

Rough assignment of the C_a, C_b, and C_c peaks without considering stereo effects may be made from comparison with the corresponding peak positions in propylene/4-methyl-1-pentene copolymer (Table 3). The chemical shift difference between α-carbons in LCB-PP and corresponding carbons in propylene/4-methyl-1-pentene copolymer is an ϵ-substituent effect, which is usually on the order of 0.1 ppm. Therefore, the resonance peaks of the three α-carbons C_a, C_b, and C_c should appear in the neighborhood of 44.27 ppm, where the resonance of the α-carbons in propylene/4-methyl-1-pentene copolymer appears. Considering the fact that the peaks at 44.88, 44.74, and 44.08 ppm are absent in the spectra of polymers with no long chain branches, these three peaks can be reasonably assigned to C_a, C_b, and C_c.

The next step would be to individually assign the three peaks to the three carbons. In Scheme 2a, the stereo environment of C_c is analogous to a methyl group in a triads of *mm*. Similarly, C_b and C_a are in the environment of *mr* and *rr*, respectively (Scheme 2b,c). The chemical shifts of the methyl group in such stereo environments would have an order of *mm* > *mr* > *rr*.[24] Since the C_c, C_b, and C_a are methylene carbons with an attached long chain, and the numbers of the accessible rotational isomeric states near the branching point are probably more limited due to spatial crowdedness, the chemical shift differences among the diastereotopic methylene carbons in LCB-PP (C_c, C_b, and C_a) would likely be smaller than those of the triads methyl splitting in isotactic polypropylene (0.9−1.1 ppm). How-

Scheme 1. Possible Branching Structures through Vinyl-Terminated Macromonomer Incorporation: I, Macromonomer Insertion without Regio Defect; II, Macromonomer Insertion after a 2,1-Mistake; III, Macromonomer Insertion after a 1,3-Mistake



Scheme 2. Stereo Environments around the Branching Point in Branched Isotactic Polypropylene

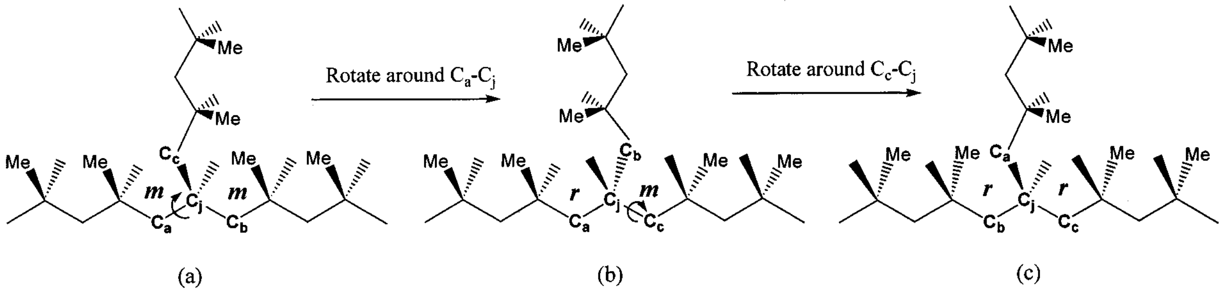


Table 3. ^{13}C NMR Chemical Shifts of α-Carbons and Branching Point in Branched Propylene Polymers

polymer	α-carbons	branching point
LCB-PP	44.08, 44.74, 44.88	31.74
PP/4-MP copolymer[a]	44.27	31.79
iPP-*g*-aPP[14a]	44.24–44.84	31.73
calculated[24]	43.33	29.54

[a] Propylene–4-methyl-1-pentene copolymer was made in hexane using dimethylsiliylbis(2-methyl-4-phenylindinyl)zirconium dichloride activated with MAO. The ^{13}C NMR spectrum was recorded on a 500 MHz Varian Unity instrument at 120 °C using tetrachloroethene as solvent.

ever, the relative order of chemical shifts would probably remain the same as that of methyl groups in the analogous stereo environments. By analogy, the peaks at 44.88, 44.74, and 44.08 may be tentatively assigned to C_c, C_b, and C_a, respectively. It must be noted that the chemical shift differences among the three methylene carbons are very asymmetric, which could be related to the complexity of the stereo environment near the branching point.

The assignment of the resonance at 31.74 ppm to the carbon atom at the branch point (C_j) can be made on the basis of the comparison to the resonance of the corresponding branching carbon of the propylene/4-methyl-1-pentene copolymer (Table 3). The small chemical shift difference between the C_j in LCB-PP and the branching carbon of the propylene/4-methyl-1-pentene copolymer is likely due to the combined effects of the chirality at the β-carbon in the LCB-PP structure and the additional alkyl substituent on the γ-carbon as compared to the propylene/4-methyl-1-pentene copolymer.

To further support these assignments, a ^{13}C NMR DEPT (distortionless enhancement by polarization transfer) experiment was carried out. This experiment differentiates carbons on the basis of the number of

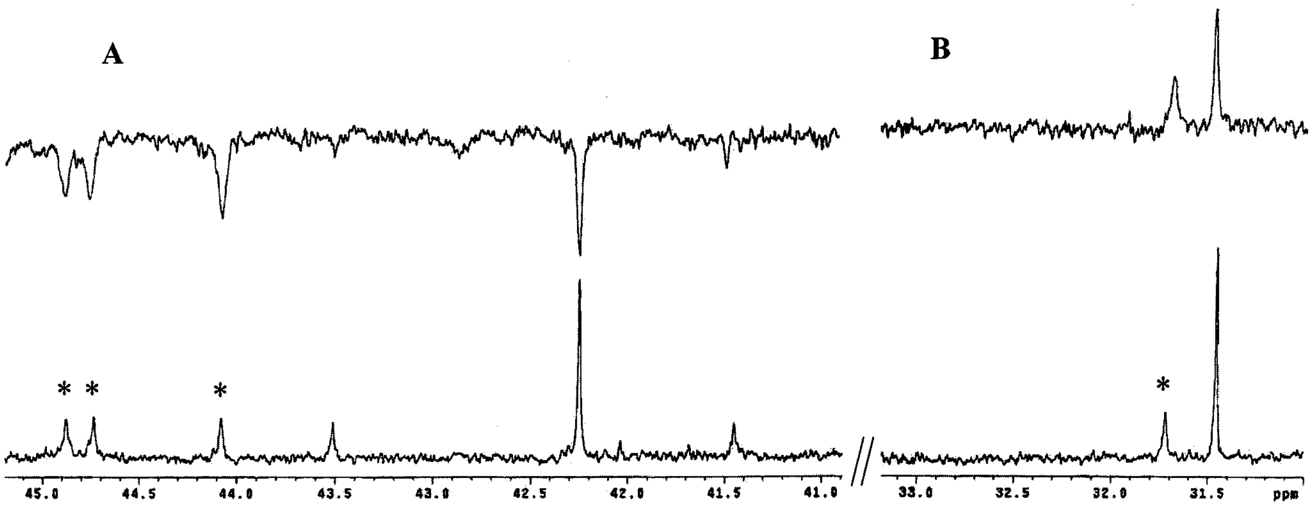


Figure 3. Expanded ^{13}C NMR DEPT spectrum of LCB-PP (top) is compared with a normal ^{13}C NMR spectrum (bottom). Region A: the methylene ($-CH_2-$) signals at 44.88, 44.74, and 44.08 ppm are pointing down in the DEPT spectrum. Region B: the methine (CH) resonance at 31.74 ppm is pointing up in the DEPT spectrum. (Note: the DEPT spectrum was recorded on a different LCB-PP sample made under similar conditions.)

Table 4. Comparison of the Branching Levels Determined by ^{13}C NMR and GPC-MALLS

polymer sample	LCB/1000C by ^{13}C NMR	$g_{\langle w \rangle}$ by GPC-MALLS
LCB-PP 4	0.072	0.67
LCB-PP 5	0.182	0.59
LCB-PP 6	0.296	0.47

attached protons; methylene signals are inverted relative to methine resonances. The expanded DEPT spectrum (Figure 3) indicates that the carbon resonances between 44 and 45 ppm are methylenes and the signal at 31.74 is a methine. Although the DEPT spectrum was recorded on a different LCB-PP sample made under similar conditions, this result clearly indicates that the assignments for the C NMR branching resonances are consistent with the proposed structure.

The peak assignments may also be compared with the ^{13}C NMR resonances for the branched polypropylene with oligomeric atactic branches reported by Shiono[14a] and the calculated (predicted) ^{13}C NMR chemical shifts using the substituent rules.[25] Generally, good agreements are obtained (Table 3).

The branch content, in terms of average LCB/1000C, may be determined by ^{13}C NMR spectral analysis when the resonance peaks associated with branching structure are identified. The numbers of LCB/1000C for some LCB-PP samples are listed and compared with the branching indices determined by GPC-MALLS (Table 4). As the branching level increases with the decrease of branching index (g), the correlation of the branching levels determined by the two methods can be readily observed. These evidences give further support to our ^{13}C NMR assignment and analysis.

The proposed branching structure in LCB-PP may form through the incorporation of in situ generated, vinyl-terminated macromonomer. In metallocene-catalyzed propylene polymerization, the vinyl chain end can be generated through a β-methyl elimination in the chain termination step.[17,26] The initiation by metal methyl complex in such a catalytic cycle would produce predominantly isobutyl as the saturated terminal structure in the initiation end.[17,27] This corroborates with the high population of isobutyl chain end resonances observed in the ^{13}C NMR spectra. The intensity of the isobutyl signals is even higher than the sum of the intensities of *n*-propyl, vinyl, and branching resonances, which suggests that part of the isobutyl group may result from a chain transfer to aluminum.[28] The observation and chain end analysis give credence to the proposed branching structure that is generated through incorporation of vinyl-terminated chain end.

Conclusion

In summary, long chain branched polypropylene was synthesized using metallocene catalyst and characterized by GPC-MALLS analysis and ^{13}C NMR spectroscopy. The branching levels determined by GPC-MALLS and ^{13}C NMR are in a good agreement. The ^{13}C NMR analysis not only gives the average branching level (number of LCB/1000C) but also reveals a unique stereo environment at the branching point, which provides evidence that the branches are formed through the incorporation of in situ generated, vinyl-terminated macromonomers.

Acknowledgment. The authors thank Material Characterization Lab staff for polymer characterization, especially T. Sun for the GPC-MALLS analysis. The permission to publish this work granted by ExxonMobil Chemical Company is also greatly appreciated.

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