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^{13}C NMR Characterization of Short Chain Branches of Nickel Catalyzed Polyethylene

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ABSTRACT: All peaks in the ^{13}C NMR spectrum of a sample of nickel-catalyzed polyethylene can be assigned to linear short chain branches having specific spatial arrangements along the polymer backbone. The chain walking mechanism of branch formation controls the specific spacing and conformational arrangements between these linear short chains. Certain unusual short chain branching sequences, involving two branches separated either by two or four methylene backbone carbons, were observed. Invariably one of the two branches in these structures was found to be methyl. The observed frequency of the second branch, whether it be methyl, ethyl, or a longer short chain branch, correlated roughly to the relative overall abundance of each branch in the bulk polymer sample. The existence of "branches on branches" was not confirmed, based on the peaks present in this spectrum. No clusters of short chain branches, i.e., branches separated by one methylene carbon, were found in this polymer sample.

Introduction

The branching analysis of polyethylene has been a subject of considerable interest in the past two decades due to the importance of branching type and distribution in such materials. The ^{13}C NMR technique is the primary method that is commonly used for such analysis.[1−4] Recently, a new catalyst system based on nickel for branched polyethylene has been reported.[5] Polyethylene produced by this catalyst family in the absence of comonomers contains a variety of in situ formed short chain branches.[5,6] These branches are believed to be formed by a chain walking mechanism (Scheme 1) rather than by generating and incorporating short-chain oligomers. The ^{13}C NMR of low-density polyethylene made with the Ni catalyst contains resonances corresponding to short chain, linear branches. The positions of the ^{13}C NMR chemical shift of carbons that correspond to such branches are well-known and have been discussed in detail.[6] However, we found that, in order to understand several unassigned resonances in the ^{13}C NMR spectrum of the nickel-catalyzed polyethylene spectrum, one needs to determine the specific spacing arrangement between them. The purpose of this article is to correlate these unassigned peaks with specific branching arrangement patterns.

One of the most common approaches used for solving the peak assignments is the theoretical modeling of their position with help of existing computational methods. The ^{13}C NMR chemical shift values of polymers have been the subject of many theoretical studies. Grant and Paul,[7] who developed an empirical procedure for the prediction of the ^{13}C NMR chemical shift of alkanes, developed one of the earliest approaches. Their procedure was later modified to be applicable for polymers at a temperature of 125 °C by Randall.[8] This method is suited for branches longer than methyl. For our analysis, one of the most useful methods was the procedure proposed by Cheng and Bennett.[9,10] This method combines several existing procedures and is based on a large number of model compounds containing methyl branches. Because the nickel-catalyzed polyethylene contains predominantly methyl branches,[5] this method is well suited to this type of polymer.

Experimental Section

A sample of polyethylene was made in a continuous loop pilot plant reactor using a nickel-based catalyst similar in structure to those reported by Brookhart and co-workers.[5] The catalyst contained the diimine ligand bis(2,6-diisopropylphenyl)-2,3-butanediimine (see structure in Scheme 1). The nickel complex was activated with supported MAO (methylaluminoxane) on silica (TA 02794/HL/04, purchased from Witco Corporation) in isobutane at 60 °C. Ethylene was maintained at a concentration of approximately 12 mol % throughout the polymerization. Polyethylene product was removed from this continuous polymerization system at regular intervals and isolated by flashing off isobutane. The NMR sample was

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Scheme 1. Walking Mechanism for Methyl Branch Formation by Nickel Catalyst

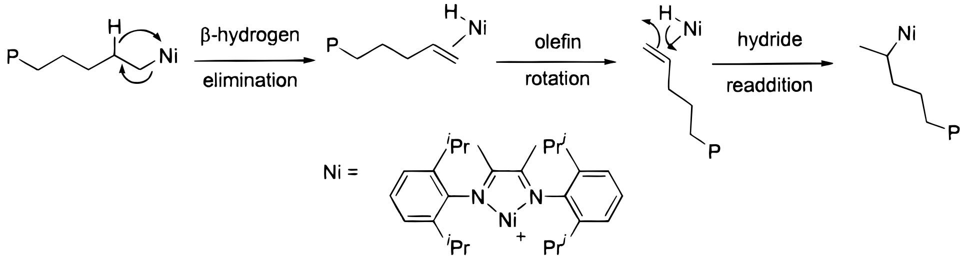


Table 1. Abundance of Short Chain, Linear Branches in Nickel-Catalyzed Polyethylene (expressed as Branches/ 1000 Total Carbons)

branch	abundance/ 1000 C	branch	abundance/ 1000 C
methyl	44	butyl	2
ethyl	3	pentyl	2
propyl	3	hexyl and longer	5

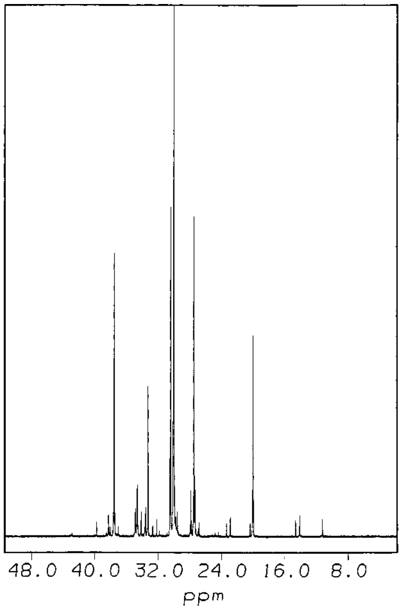


Figure 1. Full ^{13}C NMR spectrum of the nickel-catalyzed polyethylene.

prepared by dissolving a polyethylene sample ($M_n \cong 300\,000$ by GPC) in 1,2,4-trichlorobenzene in a 10 mm tube at 125 °C to form a 15 wt % solution. To ensure good long-term lock stability, deuterated 1,4-dichlorobenzene was used as a lock solvent. The ^{13}C NMR experiment with NOE and a Waltz proton decoupler was carried out on a Varian Inova 500 MHz spectrometer at 125 MHz. The 90° pulse length was 19 μs, the acquisition time was 4 s, and the recycle delay was 11 s. Chemical shift values were referenced against the $\delta+\delta+$ main backbone methylene peak of the polymer, which was set at 30.00 ppm. A DEPT (distortionless enhancement polarization transfer) experiment was performed to distinguish methyls and methines from methylenes.[11]

Polymer Branching Nomenclature

In this paper we use the nomenclature proposed by Carman,[12] in which Greek letters are used to designate the proximity of each of the methine carbons relative to the backbone methylene carbon of interest. Thus, $\alpha\beta$ denotes the methylene group that is one carbon away from the first branch point and two carbons away from the second branch point. A carbon that is located four or more carbons from a branch point is identified as $\delta+$. P, S, and T are used as prefixes to these Greek letters to designate whether the carbon of interest is primary, secondary, or tertiary, respectively.

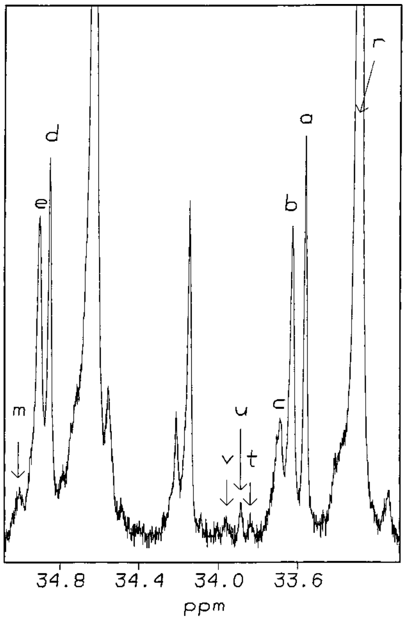


Figure 2. 33−35 ppm region of the ^{13}C NMR spectrum of nickel-catalyzed polyethylene.

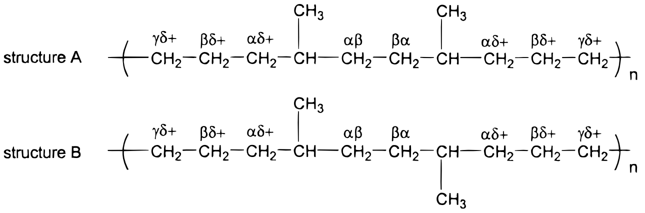


Figure 3. Methyl short chain branches separated by two methylene carbons.

Table 2. Experimental and Theoretical Values of ^{13}C NMR Chemical Shifts for Two Methyl Short Chain Branches Separated by Two Methylene Carbons

structure	carbon	δ(experimental) (ppm)	δ(theoretical) (ppm)
A	$T_{\gamma\delta}+$	33.63	33.62
A	$S_{\alpha\beta}$, $S_{\beta\alpha}$	34.91	34.99
A	$S_{\alpha\delta}+$	37.47	37.36
A	$S_{\beta\delta}+$	27.45	27.43
A	$S_{\gamma\delta}+$	30.40	30.39
A	$P_{\delta\delta}+$	20.09	20.15
B	$T_{\gamma\delta}+$	33.56	33.53
B	$S_{\alpha\beta}$, $S_{\beta\alpha}$	34.85	34.94
B	$S_{\alpha\delta}+$	37.62	37.61
B	$S_{\beta\delta}+$	27.45	27.43
B	$S_{\gamma\delta}+$	30.40	30.39
B	$P_{\delta\delta}+$	20.01	19.96

Results and Discussion

The full spectrum of the nickel-catalyzed polyethylene appears in Figure 1. Most of the peaks in this spectrum

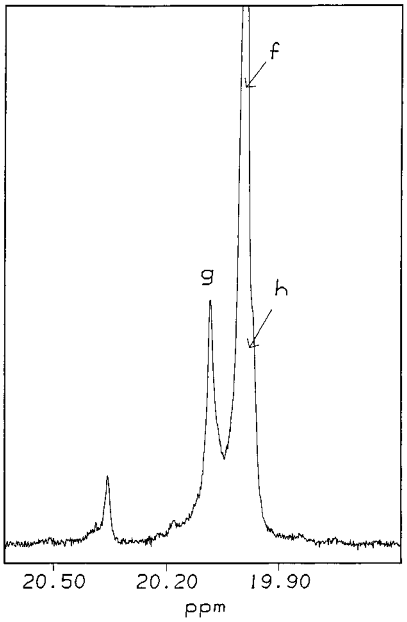


Figure 4. 20 ppm region of the ^{13}C NMR spectrum.

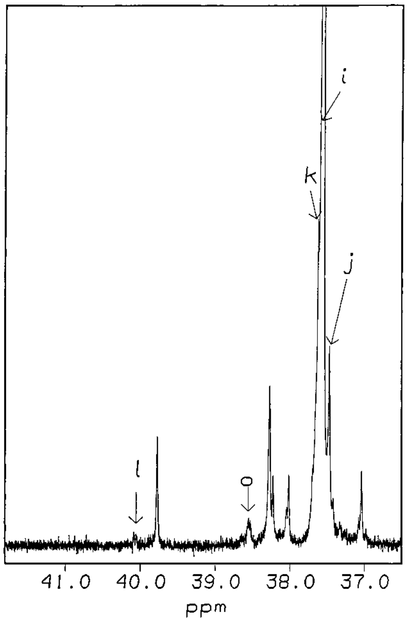


Figure 5. 37−41 ppm region of the ^{13}C NMR spectrum.

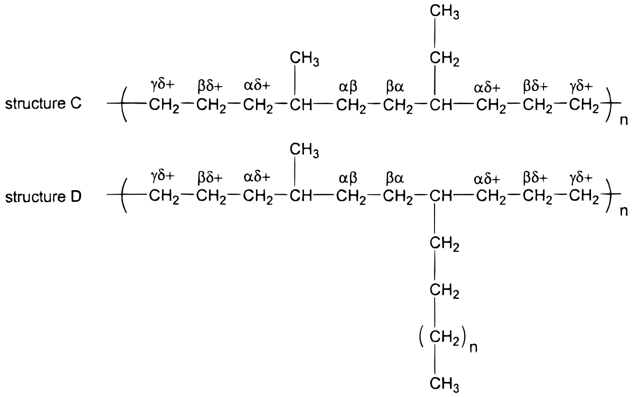


Figure 6. Two branches with different number of carbons separated by two methylene carbons.

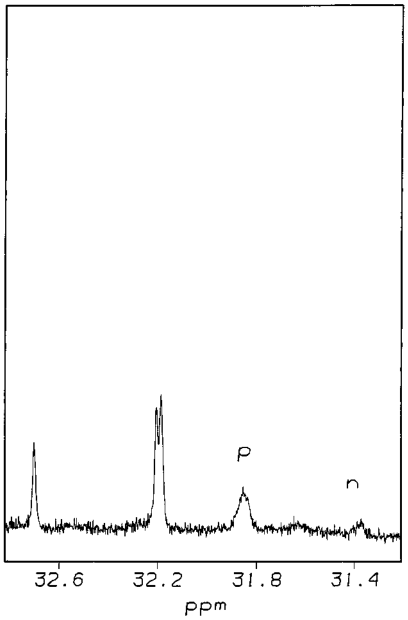
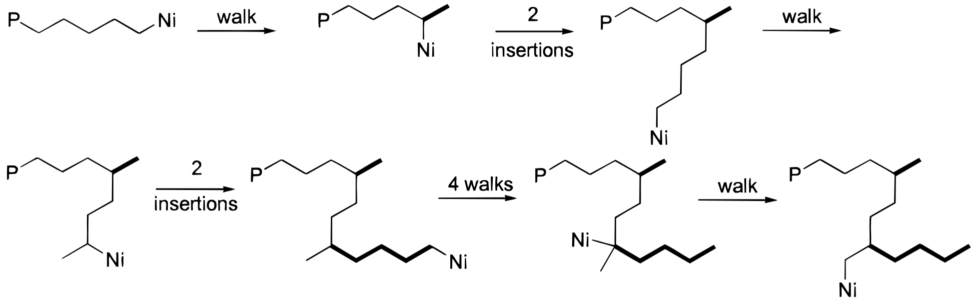


Figure 7. 31−32 ppm region of the ^{13}C NMR spectrum.

have already been assigned to various short chain linear branches.[2,3,6,13] The observed abundance of each of these linear, short chain branches is listed in Table 1. Several peaks in the spectrum remain unaccounted for after these assignments, and their origins are outlined in the remainder of this section.

Two of the unassigned peaks in the ^{13}C NMR spectrum of the nickel-catalyzed polyethylene are two peaks centered at 33.56 ppm (peak a) and 33.63 ppm (peak b), and one broader peak at 33.70 ppm (peak c) (Figure 2). A ^{13}C NMR DEPT (distortionless enhancement polarization transfer) experiment was first performed to determine whether the carbons are primary, secondary, or tertiary.[11] The DEPT experiment showed clearly that they are tertiary (CH) groups. To determine the length of the hydrocarbon chains bound to these methine groups, we utilized the additive rules for ^{13}C NMR shifts proposed by Cheng and Bennett.[9,10] The first model structure tested is one containing two methyl branches separated by two secondary methylene carbons (Figure 3). The results of the calculations of the ^{13}C NMR chemical shift for structures A and B are listed in Table 2. Good agreement exists between observed and calculated values of chemical shifts for all carbons. This model structure can account for not only the existence of 33.56 ppm (peak a) and 33.63 ppm (peak b) peaks but also the existence of 34.91 ppm (peak e) and 34.85 ppm (peak d) peaks that belong to secondary $\alpha\beta$ or $\beta\alpha$ carbons (Figure 2). A peak that corresponds to the methyl carbons would appear in the vicinity of 20 ppm in the spectrum (Figure 4). This region contains two major peaks and one shoulder. The major peak at 19.99 ppm (peak f) can be attributed to isolated methyl carbons. The resonance at 20.09 ppm (peak g) is closest to the predicted value of the $P\delta\delta+$ methyl peak of structure A. The shoulder at 19.96 ppm (peak h) that can be clearly seen in Figure 4 belongs to the methyl $P\delta\delta+$ of structure B. The configurational splitting between those two diastereomeric structures is large enough to play a significant role in the magnitudes of these chemical shifts. To complete the understanding of structures A and B (Figure 3), the resonances of the secondary $S\alpha\delta+$ and $S\beta\delta+$ need to be located. In other regions of the spectrum, the large methylene $S\alpha\delta+$ resonance is centered at 37.56 ppm (peak i, Figure 5). This large resonance shows two splittings at 37.47 ppm

Scheme 2. Walking Mechanism To Form Methyl and Butyl Branches Separated by Two Methylenes (structure D, *n* = 1)



(peak j) and 37.62 ppm (peak k). These two splittings belong to secondary carbons Sα+ and are significantly affected by the configuration. The other secondary carbon, Sβ+, is too distant to be affected by differences in configuration. Therefore, it overlaps with the 37.56 ppm Sαδ+ resonance.

The origin of the third resonance at 33.70 ppm is more difficult to explain. We found it impossible to explain by utilizing any combination of solely methyl branches. However, it is possible that the structure contains an ethyl short chain branch (Figure 6, structure C) separated by two methylene carbons. The observed position of tertiary carbon $T_{CH(CH_3)}$ is 33.70 ppm and calculated at 33.75 ppm (Figure 2). The second tertiary carbon originating the longer branch $T_{CH(CH_2CH_3)}$ is predicted to be at 40.82 ppm. The nearest resonance is at 40.07 ppm (peak l, Figure 5). The peak of the secondary αβ carbon is predicted to be at 34.83 ppm; the peak appears experimentally at 35.00 ppm (peak m, Figure 2). The peak of the βα carbon is observed at 31.38 ppm (peak n, Figure 7) and calculated to be at 31.46 ppm. The discrepancy between the predicted and calculated values is very significant for this peak. However, the calculation was made using the Grant and Paul parameters,[8] which are apparently less accurate than those developed exclusively for methyl short chain branches.

The intensity of the 33.70 ppm peak is larger than was expected, assuming the above structure, so it can be explained only in part. Additional structures with overlapping ^{13}C NMR resonances have to be involved. If the second branch is longer than ethyl (Figure 6, structure D), the tertiary carbon $T_{CH(CH_3)}$ resonance position will not be affected by the increased length of the second branch because the branch end carbon atoms are too far away to affect the chemical shift. Therefore, all long branches would contribute to a single methine peak for the neighboring branch. Examination of the chemical shifts of the second tertiary carbon and both backbone secondary methylenes might be helpful. We predicted the peak's position in the case of the second branch ($T_{CH(CH_2CH_2CH_2CH_3)}$) to be that of a butyl branch, at 38.31 ppm. The nearest peak by chemical shift is at 38.55 ppm (peak o, Figure 5). Also, the αβ carbon is predicted to be at 32.01 ppm and is observed at 31.86 ppm (peak p, Figure 7). The second tertiary βα is predicted at 34.89 ppm and is not observed as a separate resonance because of the overlap with other resonances present in this region of the spectrum (Figure 2). One could argue that the chemical shift values determined by this calculation might not be highly accurate, although the pattern of several peaks that is predicted matches well with the observed pattern. Therefore, we are convinced that such structures exist. These structures also comply with the general rules of the walking mechanism (Scheme 2).[5] It is also worthy to point out that the second branch may be longer than butyl. However, NMR methods could not be used to determine its exact identity. It is worthwhile to mention that we did not find a peak pattern that would correspond to a methyl and propyl branch separated by two methylenes. Such a branching arrangement is allowed by the walking mechanism, but may be formed in such low quantities as to be unobservable by NMR. Odd carbon branches are formed at lower levels than are even carbon branches due to two mechanisms operating to yield the latter but only one mechanism to generate the former.[6]

Another interesting resonance is centered in the vicinity of the $\beta\delta$+ region at 27.85 ppm (peak q, Figure 8). ^{13}C NMR DEPT experiments assured us that this resonance is due to the presence of secondary methylene carbons. The best agreement between the predicted peak positions and the experimental value was achieved when assuming the presence of two methyl short chain branches separated by four methylene carbons as shown in Figure 9. The calculated position of the ^{13}C NMR chemical shift of carbon $\beta\gamma$ is 27.81 ppm, and the

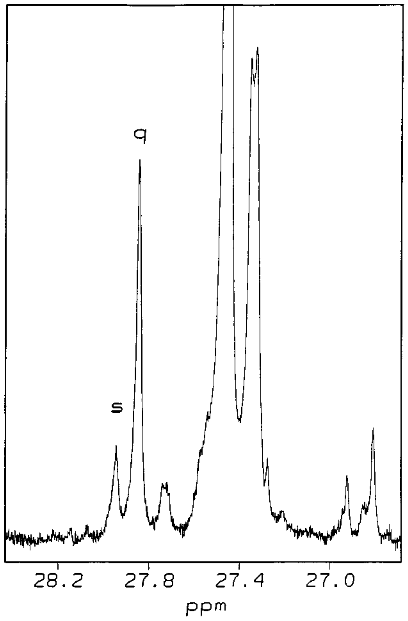
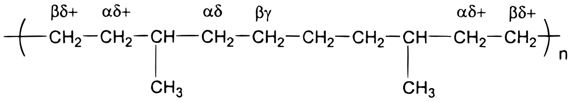


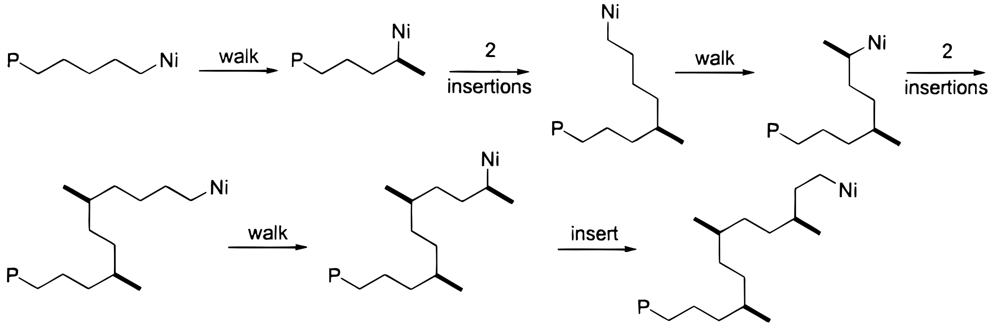
Figure 8. 27−28 ppm region of the ^{13}C NMR spectrum.

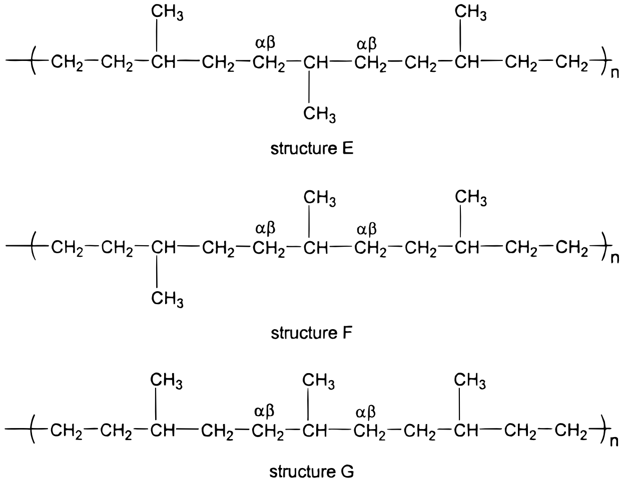


$$\left(\overset{\beta\delta+}{CH_2}-\overset{\alpha\delta+}{CH_2}-\underset{CH_3}{CH}-\overset{\alpha\delta}{CH_2}-\overset{\beta\gamma}{CH_2}-CH_2-CH_2-\underset{CH_3}{CH}-\overset{\alpha\delta+}{CH_2}-\overset{\beta\delta+}{CH_2}\right)_n$$

Figure 9. Two methyl short chain branches spaced by four methylene carbons.

Scheme 3. Walking Mechanism To Form Three Methyl Branches Each Separated by Two Methylenes (Structures E, F, and G)





$$-\!\!\left(\mathrm{CH_2{-}CH_2{-}\overset{CH_3}{CH}{-}CH_2{-}\overset{\alpha\beta}{CH_2}{-}\underset{CH_3}{CH}{-}\overset{\alpha\beta}{CH_2}{-}CH_2{-}\overset{CH_3}{CH}{-}CH_2{-}CH_2}\right)_n$$

$$-\!\!\left(\mathrm{CH_2{-}CH_2{-}\underset{CH_3}{CH}{-}CH_2{-}\overset{\alpha\beta}{CH_2}{-}\overset{CH_3}{CH}{-}\overset{\alpha\beta}{CH_2}{-}CH_2{-}\overset{CH_3}{CH}{-}CH_2{-}CH_2}\right)_n$$

$$-\!\!\left(\mathrm{CH_2{-}CH_2{-}\overset{CH_3}{CH}{-}CH_2{-}\overset{\alpha\beta}{CH_2}{-}\overset{CH_3}{CH}{-}\overset{\alpha\beta}{CH_2}{-}CH_2{-}\overset{CH_3}{CH}{-}CH_2{-}CH_2}\right)_n$$

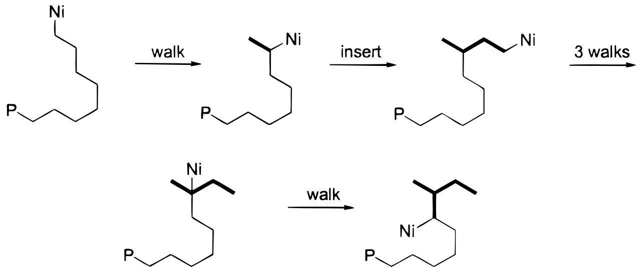
Figure 10. Clustered methyl branches spaced by two methylene carbons.

experimental result gives 27.85 ppm (peak q). The carbon $\alpha\delta$ was predicted at 37.61 ppm, and its position overlaps with overall S$\alpha\delta$+ resonance at 37.56 ppm (peak i, Figure 5). The S$\alpha\delta$+ carbons are predicted to appear at 37.56 ppm and are therefore also indistinguishable from S$\alpha\delta$+ associated with the above-mentioned isolated branching point. The theoretical and experimental results are in excellent agreement, giving us confidence in our assignments. The chemical shifts of tertiary methine carbons are indistinguishable from isolated T$\alpha\delta$+ tertiary carbons at 33.30 ppm (peak r, Figure 2).

A smaller unassigned resonance at 27.95 ppm (peak s, Figure 8) can again be explained due to the presence of a pair of branches in which one of the branches is longer than methyl. According to Grant and Paul's method, modified for polymers,[8] the presence of an additional carbon in one of these branches could shift a $\beta\gamma$ peak about 0.06 ppm downfield of what we are observing. This chemical shift is therefore consistent with a structure containing a methyl and a longer branch separated by four methylene carbons.

One might be anxious to ask the question about presence of more clustered methyl branches that are still spaced by two secondary carbons methyl branches (e.g., if two methyl groups, with any combination of conformations, were spaced two methylenes from a central methyl branch). Representations of such structures are presented in Figure 10. The walking mechanism allows for the formation of such structures (Scheme 3). The prediction of ^{13}C NMR chemical shifts of the internal tertiary carbon of the methyl branch gave the following values for structures E, F, and G: 33.80, 33.89, and 33.98 ppm, respectively. Looking into this region of the spectrum (Figure 2), one notices a very small resonance at 33.89 ppm (peak u) and two neighboring resonances almost at noise level; these latter peaks appear at 33.97 ppm (peak v) and 33.84 ppm (peak t). Their chemical shifts match rather well with the predicted values. However, because this signal is so small, the presence of these branches is speculative.

Scheme 4. Walking Mechanism To Form Branches on Branches

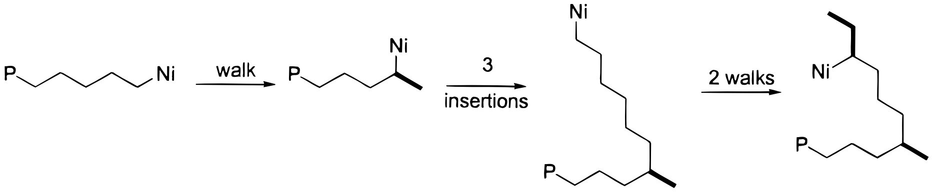


McLain and co-workers suggested the possible creation of hyperbranches during polymerization.[6] This means that a branch from the main chain on the polymer may itself contain one or more branches. Such branches on branches could be formed as depicted in Scheme 4. The nickel center walks back along the chain and then undertakes one or more ethylene insertions. The nickel then migrates back along these inserted ethylenes until it reaches the original branching point. To form a branched branch, the complex must now walk back onto a carbon on the original main chain and then begin ethylene insertions again. The highly choreographed sequence of events necessary to form a branched branch by this mechanism makes their formation highly unlikely. Indeed, we found no evidence of such branched branches in our polymer sample.

^{13}C NMR is able to distinguish between totally isolated branches and those that are within a few methylene backbone groups of each other. The two and four secondary methylene carbons between the tertiary center of branches are clearly detected. Of course, branches can also be spaced by more than four methylene carbons. However, the sensitivity of ^{13}C NMR at the magnetic field of 11.8 T cannot distinguish between tertiary carbons of such structures and isolated branches.

A further structure to consider would be one in which two methyl branches are separated by three methylene spacers. A very small resonance can be detected in the area of 24.2−24.9 ppm that could indicate the existence of such branches. However, the walking mechanism cannot account for the formation of such types of structure (Scheme 5). To form a structure in which the

Scheme 5. Walking Mechanism That Is Able To Form Only One Odd-Carbon Branch When Branches are Separated by Three Methylenes



branches are separated by three methylenes via the proposed walking mechanism, one or more of these branches must contain an even number of carbon atoms (e.g., ethyl, butyl, etc.).

Another interesting feature of the polymer made by the nickel catalyst is the absence of clustering among branches that are separated by one methylene carbon only. Such clustering is common in polyethylene copolymers.[2,3] Again, the walking mechanism does not permit the formation of two methyl branches separated by an odd number of methylene spacers. Because most of the branches formed by the nickel catalyst are methyls,[5] the probability of forming a longer branch with this particular spacing is very low, especially considering the high degree of steric hindrance encountered by the nickel site during such a structure formation.

Conclusion

To account for all of the resonances in the ^{13}C NMR spectrum of nickel-catalyzed polyethylene, it is sufficient to consider the following linear branches: methyl, ethyl, propyl, butyl, pentyl, and hexyl and longer alkyl. However, the unique spatial and configurational arrangements among them need to be taken into account. The nickel catalyst is capable of forming methyl branches that are separated by two or four methylene carbons. In the case of a structure in which two carbons separate the branches, configurational splitting is observed. In some cases the second branch might be ethyl or longer. However, we did not observe propyl branches with this spacing arrangement in the studied polymer, although they are allowed by the walking mechanism. We found no evidence for the formation of branches on branches, a structural variant that was previously suggested in the literature. The nickel catalyst does not make clusters containing two branches separated by one methylene carbon, as is common for other polyethylene copolymers incorporating ethylene and α-olefins. Also, the catalyst does not produce many structures containing two branches spaced by three methylene carbons.

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