Notes

Resolution of Signals from Long-Chain Branching in Polyethylene by ^{13}C NMR at 188.6 MHz

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Introduction

The structure of the simplest of all polymers, polyethylene, can be very simple as in the case of linear high-density polyethylene. It can also be very complicated as in the case of low-density polyethylene, which can contain many different types of branch structures. The physical and mechanical properties, melting point, and crystallinity of polyethylene are highly dependent upon the type and number of branches.

High-resolution ^{13}C NMR has been used extensively to study polyethylene structure. It has been used successfully to assign all the carbon resonances for branches shorter than six carbons long. The ^{13}C resonance assignments of branches in low-density polyethylene (LDPE) have also been reported.[1] These assignments have been made with the aid of modified Grant−Paul chemical shift rules,[2] Lindeman−Adams methods,[3] and the spectra of model copolymers, which confirm the presence of short branches.[4] The NMR spectra published thus far do not permit differentiation of many of the signals from chain branches longer than six carbons.

Here we present the 188.6 MHz ^{13}C NMR spectra (corresponding to a 750 MHz ^{1}H resonance frequency) of a homologous series of copolymers from polymerization of ethylene/1-hexene, ethylene/1-octene, ethylene/1-decene, and ethylene/1-dodecene. These spectra permit the resolution of unique ^{13}C resonances from polyethylene chain branches at least up to 10 carbons long.

Experimental Section

The poly(ethylene-*co*-1-hexene) ($M_n \approx 50\,000$) and poly(ethylene-*co*-1-octene) ($M_n \approx 60\,000$) copolymers used in this study were purchased from Aldrich Chemical Co. The poly(ethylene-*co*-1-decene) and poly(ethylene-*co*-1-dodecene) copolymers used in this study were provided by L. McIntosh and R. Quirk at the University of Akron. About 100 mg of copolymer was dissolved in 0.7 mL of 40% benzene-d_6 in 1,2,4-trichlorobenzene. The sample was heated to 120° C for 10 h in an oil bath, after which a clear solution was obtained.

The ^{13}C NMR spectra were obtained on a Varian Unityplus 750 MHz spectrometer with an $^{1}H-^{19}F/^{31}P-^{15}N$ 5 mm switchable pulsed field gradient probe, at 120 °C, with 8.9 μs (90°) pulses, 27 kHz spectral windows, continuous Waltz-16 decoupling, 2 s acquisition time, and 5 s relaxation delay. The data were zero filled to 512K and Fourier transformed without weighting. Typical half-height line widths were 0.5−1.5 Hz.

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Results and Discussion

A general structure for long-chain branches in polyethylene is shown by **1**. The carbons in this structure are labeled based on the nomenclature defined by Randall;[5] methylene carbons along the backbone of an ethylene-1-olefin copolymer chain are identified by a pair of Greek letters to indicate the distance to branches in either direction. Carbons in the side chain are identified by $i\mathrm{B}_n$ where "*i*" indicates the position in the branch starting with the methyl carbon in position 1, and the subscript "*n*" indicates the length of the branch. The carbons at the end of the main chain are identified as 1s(CH_3), 2s(CH_2), 3s(CH_2), etc.

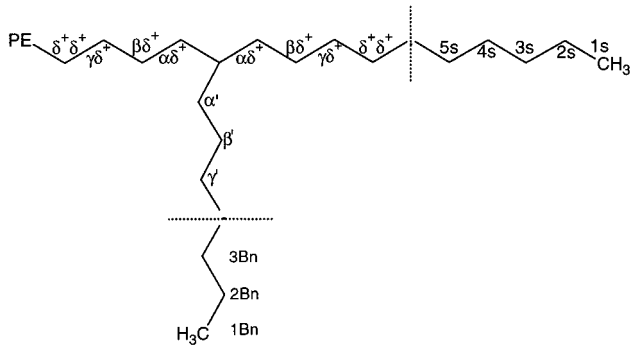

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Figure 1a−d shows sections taken from the 188.6 MHz ^{13}C NMR spectra of poly(ethylene-*co*-1-hexene), poly(ethylene-*co*-1-octene), poly(ethylene-*co*-1-decene), and poly(ethylene-*co*-1-dodecene), respectively. Only the regions of the spectra containing peaks are shown. The assignments of each region are labeled across the top of each spectrum.

Figure 1a shows the spectrum of poly(ethylene-*co*-1-hexene). Twelve resonances are observed which are attributed to $1\mathrm{B}_4$ (14.05 ppm), $2\mathrm{B}_4$ (23.37 ppm), $3\mathrm{B}_4$ (β', 29.57 ppm), and $4\mathrm{B}_4$ (α', 34.23 ppm) carbons of butyl branches and $\alpha\delta^+$ (34.63 ppm), $\beta\delta^+$ (27.33 ppm), $\gamma\delta^+$ (30.49 ppm), $\delta^+\delta^+$ (30 ppm), methine (38.24 ppm), and 1s, 2s, and 3s carbons from the main chain. The $\alpha\delta^+$ and $\alpha'(n\mathrm{B}_n)$ carbons are very different and produce two resonances in the 34−35 ppm region with intensity ratio 2:1. For longer chain branches (see the same regions in Figure 1b−d), the $\alpha'(n\mathrm{B}_n)$ carbon is further from the end of the branch and has a shift very similar to the in-chain $\alpha\delta^+$ methylene carbon; however, separate $\alpha\delta^+$ and $\alpha'(n\mathrm{B}_n)$ resonances are still resolved. The $3\mathrm{B}_4$ carbon is $\beta'([n-1]\mathrm{B}_n)$ to the branch point and exhibits a shift very different from the equivalent carbons in longer

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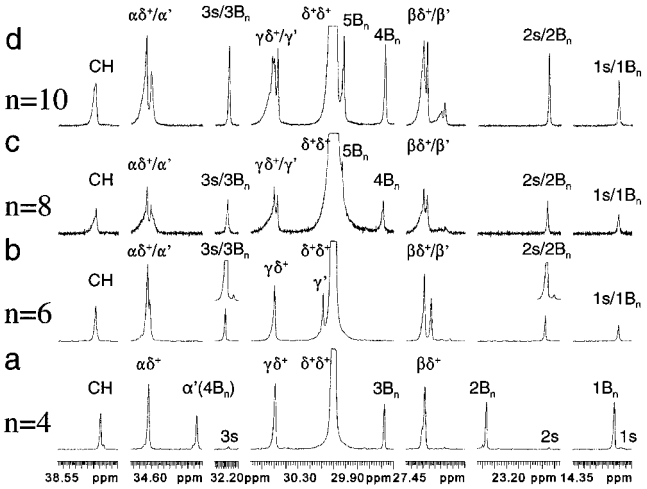

Figure 1. The 188.6 MHz ^{13}C NMR spectra of ethylene–alkene copolymers in 40% benzene-d_6 and 1,2,4-trichlorobenzene: (a) poly(ethylene-*co*-1-hexene), (b) poly(ethylene-*co*-1-octene), (c) poly(ethylene-*co*-1-decene), and (d) poly(ethylene-*co*-1-dodecene). The largest methylene peak was used as a reference (30.0 ppm). (Note the spectrum of poly(ethylene-*co*-1-hexene) also contains three weak signals (ca. 10% of the butyl signal intensities) at 11.16, 26.80, and 39.79 ppm (not shown) from a small number of ethyl branches.)

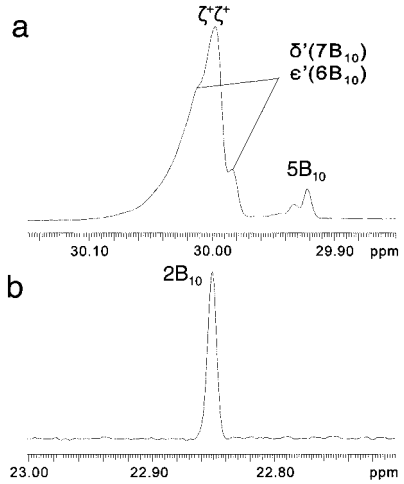

Figure 2. Expansions from the 188.6 MHz ^{13}C NMR spectrum of poly(ethylene-*co*-1-dodecene) in the Figure 1d: (a) $\delta^+\delta^+$ region; (b) $2B_{10}$ region.

branches. These assignments are consistent with those previously reported.[5]

Figure 1b shows the spectrum of poly(ethylene-*co*-1-octene). The ^{13}C NMR spectrum is dominated by the resonance from main-chain $\delta^+\delta^+$ repeat units. The intensities of the unique resonances associated with the branching are several orders of magnitude weaker than the signals from the main-chain repeat units. All the resonances from main-chain $\alpha\delta^+$, $\beta\delta^+$, and $\gamma\delta^+$ carbons and from $1B_6$, $2B_6$, and $3B_6$ are clearly resolved. This spectrum has some interesting features compared to previously reported, lower field ^{13}C spectra. The resonances of the main-chain methylenes $\alpha\delta^+$, $\beta\delta^+$, and $\gamma\delta^+$ from the branch points are resolved from the resonances of side-chain methylenes $\alpha'(nB_n)$, $\beta'([n-1]B_n)$, and $\gamma'([n-2]B_n)$ from the branch points. The differences between these resonance are $\Delta\alpha = 4$ Hz, $\Delta\beta = 11$ Hz, and $\Delta\gamma = 77$ Hz, and they exhibit the expected 2:1 area ratios. It is also observed that two resonances with intensity ratios ca. 20:1 are resolved near 22.9 and 32.2 ppm. The more intense peaks in these regions are attributed to $2B_6$ (22.88 ppm) and $3B_6$ (32.21 ppm) carbons. The weaker signals in these regions can attributed to the 2s (22.85 ppm) and 3s (32.18 ppm) carbons at the end of the main chain. Usami et al.[6] previously reported resolution of these resonances at lower field; however, when the ratios of $2B_6$/2s and $3B_6$/3s signals were much different from 1 (i.e., when the numbers of C_6 branches and saturated chain ends were not comparable), they were unable to resolve separate signals for these carbons. A group of weaker signals are seen to the right of the $\beta\delta^+/\beta'([n-1]B_n)$ resonances; these are attributed to the $\beta\delta^+$ carbons from OOEE or EEOO structures (O = octene, E = ethylene).[5]

Table 1. ^{13}C Chemical Shift Assignments for Polyethylene-Based Polymers (±0.003 ppm)

branch length	C_{10}	C_8	C_6	C_4	C_2
main chain					
$\alpha\delta^+$	34.653	34.646	34.639	34.626	34.145
$\beta\delta^+$	27.355	27.351	27.343	27.334	27.357
$\gamma\delta^+$	30.508	30.505	30.500	30.491	30.491
$\delta^+\delta^+$	30.000	30.000	30.000	30.000	30.000
1s				13.992	
2s			22.846	22.846	
3s			32.182	32.182	
methine	38.293	38.286	38.283	38.243	39.790
side chain					
nB_n (α')	34.612	34.615	34.623	34.226	26.797
$[n-1]B_n$ (β')	27.326	27.325	27.286	29.573	
$[n-2]B_n$ (γ')	30.479	30.478	30.093	23.367	
$1B_n$	14.015	14.018	14.020	14.046	11.158
$2B_n$	22.852	22.864	22.881		
$3B_n$	32.184	32.195	32.213		
$4B_n$	29.574	29.591			
$5B_n$	29.925	29.935			
$6B_n$ or $7B_n$	29.985				
$6B_n$ or $7B_n$	30.016				

Figure 1c shows the seven regions from the 188.6 MHz ^{13}C NMR spectrum of poly(ethylene-*co*-1-decene). All the resonances from main-chain $\alpha\delta^+$, $\beta\delta^+$, and $\gamma\delta^+$ carbons and from $1B_8$, $2B_8$, $3B_8$, $4B_8$, and $5B_8$ are clearly resolved. Compared to previously published ^{13}C spectra, the resonances from the 188.6 MHz ^{13}C spectrum provide more detailed structural information. Two sets of peaks are resolved in the α-, β-, and γ-carbon regions of the spectrum; the more intense resonances in these regions are from main-chain carbons $\alpha\delta^+$, $\beta\delta^+$, and $\gamma\delta^+$ to branch points, and the less intense resonances are from side-chain carbons $\alpha'(nB_n)$, $\beta'([n-1]B_n)$, and $\gamma'([n-2]B_n)$ to branch points. The differences between these resonances are $\Delta\alpha = 7$ Hz, $\Delta\beta = 5$ Hz, and $\Delta\gamma = 5$ Hz. Like the poly(ethylene-*co*-1-octene) spectrum, a group of weaker signals are seen to the right of the $\beta\delta^+/\beta'([n-1]B_n)$ resonances; these can be attributed to the $\beta\delta^+$ carbon resonances of DDEE and EEDD structures (D = decene). Additionally, many of the signals have shoulders on the downfield sides of the peaks; these are attributed to the influence of neighboring branches 2, 3, and 4 monomer units away and are not from magnetic field inhomogeneity. (Note that the $1s/1B_8$ and $2s/2B_8$ resonances are sharp and symmetrical.)

Figure 1d shows the seven regions from the 188.6 MHz ^{13}C NMR spectrum of poly(ethylene-*co*-1-dodecene) (decyl branches). All the resonances from main-chain $\alpha\delta^+$, $\beta\delta^+$, and $\gamma\delta^+$ carbons and from $1B_{10}$, $2B_{10}$, $3B_{10}$, $4B_{10}$, $5B_{10}$, $6B_{10}$, and $7B_{10}$ are resolved. Separate signals are also resolved for the $\alpha\delta^+$, $\beta\delta^+$, and $\gamma\delta^+$ carbons in the main chain and the $\alpha'(nB_n)$, $\beta'([n-1]B_n)$, and $\gamma'([n-2]B_n)$ carbons from the side chain. The weaker signals

just upfield of the $\beta\delta^+/\beta'([n-1]B_n)$ resonances can be attributed to the $\beta\delta^+$ carbon resonances from TTEE or EETT structures (T = dodecene).

Figure 2a,b shows the expansions from the $\delta^+\delta^+$ and $2B_{10}$ regions from Figure 1d, plotted with the identical scales (Hz/mm). The sharp symmetrical peak shape of $2B_{10}$ resonance indicates that the spectrum was collected with a very homogeneous magnetic field. If the main peak (30 ppm) is assigned to $\zeta^+\zeta^+$ carbons, then the shoulders can be attributed to $\delta^+\delta^+/\delta'(7B_{10})$ and $\epsilon^+\epsilon^+/\epsilon'(6B_{10})$ resonances. These signals are not likely to arise from TTEE or EETT fragments since similar shoulders are not seen on the $\delta^+\delta^+$ peak of poly(ethylene-*co*-decene) in Figure 1c.

The interpretation of these spectra is supported by 2D-NMR data and spectra of other homologues in the series of polyethylenes, to be reported in a future paper. Chemical shifts are summarized in Table 1. The data presented here indicate the tremendous potential for using ultrahigh field NMR to study structure−property relationships for this most important commercial polymer. The summary of chemical shifts presented here will hopefully be useful for researchers working on the synthesis and characterization of polyethylenes.

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