^{13}C NMR Spectra of Propylene/1-Hexene Copolymers

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Although the first synthesis of propylene/1-hexene copolymers was reported in 1975,[1] no information on their ^{13}C NMR spectra is available in the literature. We carried out a series of propylene/1-hexene copolymerization experiments with the δ-$TiCl_3/Al(C_2H_5)_3$ catalyst system, recorded the ^{13}C NMR spectra of the copolymers and their fractions, and assigned chemical shifts for the spectra.

Experimental Section

Copolymerization reactions of propylene (P) and 1-hexene (H) were carried out in a 0.5-L autoclave, which is routinely used for olefin polymerization experiments.[2] Mixtures of 1-hexene and hexane (1.33 M 1-hexene) were charged into the reactor, followed by 1 mL of the 1.5 M $Al(C_2H_5)_3$ solution in hexane. After the reactor temperature was raised to 80 °C, 0.02–0.07 g of δ-$TiCl_3$ was added and propylene was introduced into the reactor to maintain a constant reaction pressure of 0.5–1.0 MPa. The reactions were continued for 2 h. Polymer products were recovered by precipitation with 2-propanol.

^{13}C NMR spectra of the propylene/1-hexene copolymers and their fractions were recorded with a JEOL GX400 spectrometer at 100.4 MHz for ^{13}C. The samples were prepared as 1,2-dichlorobenzene-d_4/1,2,4-trichlorobenzene solutions; the spectra were acquired at 130 °C. The pulse width was 90° (25 μs) and the pulse decay was 15 s. Continuous ^1H decoupling was used. On the basis of relaxation measurements, we know that these conditions give quantitative results for all but the methyl resonances of olefin polymers.

Peak Assignments for the ^{13}C NMR Spectra of Propylene/1-Hexene Copolymers. We assigned the resonances in the copolymer spectra by calculating chemical shifts for various chemical sequences consisting of propylene and 1-hexene monomer units, using the Grant–Paul and Carman methods.[3,4] The computational results are compared with the experimental data in Table I. In several dubious cases, general considerations on the probabilities of various sequences in these propylene-rich copolymers were used to clarify the assignments. Figure 1 shows expanded regions of two copolymer spectra, together with the peak assignments. One of the copolymers contains only 8 mol % of 1-hexene and, as a result, has very intense peaks of homopropylene sequences in its NMR spectrum. These peaks are not shown in the figure.

Assignment of most peaks was straightforward, especially the CH_3 resonances of propylene and 1-hexene units, the resonances of all propylene-centered triads, and the main-chain CH_2 signals for all PH-centered tetrads. Peaks arising from all propylene-centered sequences have several components due to stereoregularity effects; the largest resonance is always due to isotactic sequences. In one case, the order of peak positions in PHP, HHP, and HHH triads in the copolymers (CH groups in 1-hexene units) is reversed compared to the predictions of the chemical shift calculations (see Table I and Figure 1b). The reported assignment, as well as the β-CH_2 peak assignment in the H-centered triads is based on the differences between the spectra of copolymers with different 1-hexene contents (Figure 1b). Similar problems were encountered by Randall[5] in the peak assignments for propylene/butene copolymers and were explained as being due to chemical shift contributions from carbon atoms five bonds away (neglected in both used computational methods).

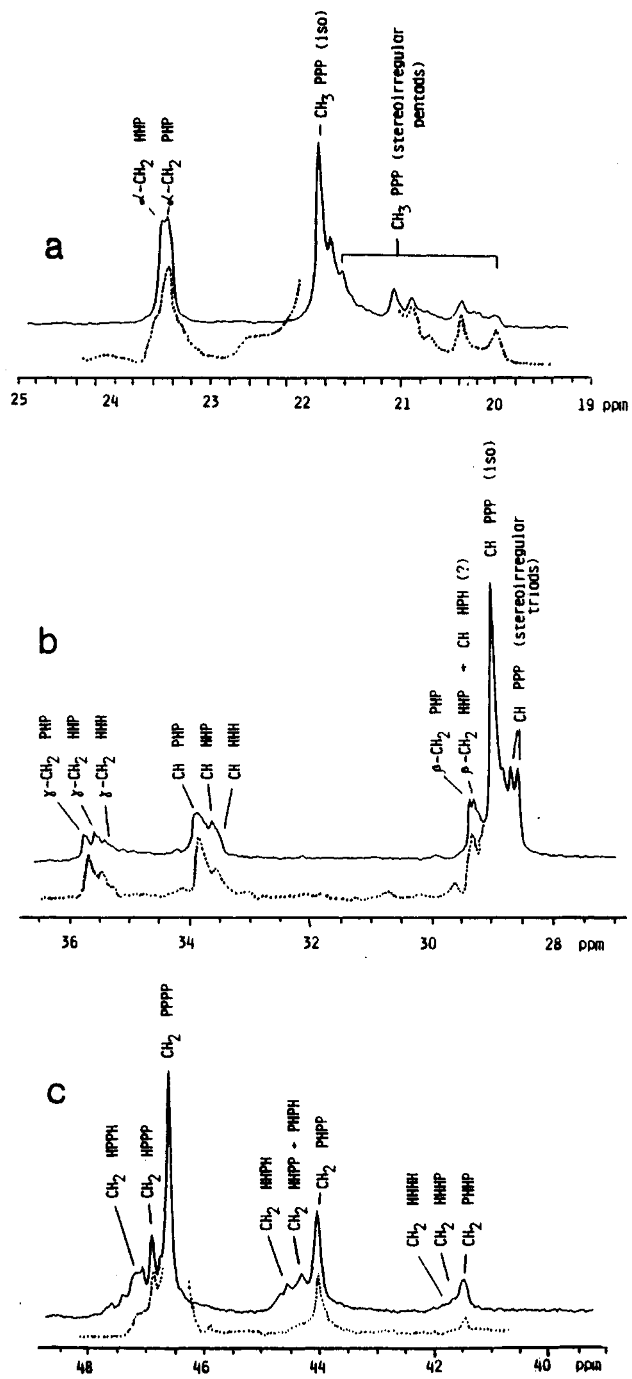

Figure 1. ^{13}C NMR spectra of two propylene/1-hexene copolymers containing 18 mol % 1-hexene (solid line) and 8 mol % 1-hexene (dotted line). (a) The 19–25 ppm range; (b) the 28–36 ppm range; (c) the 40–48 ppm range.

In two other cases peak assignments were complicated by the coincidence of P–H sequence resonances with those due to propylene stereoirregularity: the main-chain CH_2 groups in HPPH and HPPP tetrads vs the PPPP tetrads (Figure 1c), and β-CH_2 groups of 1-hexene units vs the CH groups in propylene sequences (Figure 1b). The peaks arising from the CH_2 groups in HPPH and HPPP tetrads (Figure 1c) could be distinguished from the overlapping peaks of the PPPP CH_2 tetrads by comparing the copolymer spectra with that of polypropylene. The problem of distinguishing the 1-hexene β-CH_2 groups from the propylene CH groups in HPP and HPH triads is more taxing. Although the chemical shift calculations predict clearly distinct chemical shift ranges for these resonances (30.3–30.6 vs 28–29 ppm), in practice all five peaks occupy

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Table I
Peak Assignments in the ^{13}C NMR Spectra of Propylene/1-Hexene Copolymers[a,b]

	CH_3 (propylene units)			CH (propylene units)		
seq	exp	G–P	Carman	exp	G–P	Carman
PPP	21.8	20.83	21.06	29.0	27.45	28.46
HPP		20.94	21.09	29.3 (?)	27.87	28.77
HPH		21.05	21.12		28.29	29.08

	CH_3 (1-hexene units)			CH (1-hexene units)		
seq	exp	G–P	Carman	exp	G–P	Carman
PHP	14.1	14.11	14.01	33.8	31.02	32.87
HHP		14.11	14.01	33.6	31.44	33.18
HHH	(14.1)	14.11	14.01	(33.6)	31.86	33.49

	α-CH_2 (1-hexene units)			β-CH_2 (1-hexene units)		
seq	exp	G–P	Carman	exp	G–P	Carman
PHP	23.4	23.51	23.14	29.4	30.64	30.37
HHP	23.5	23.51	23.14	29.3	30.64	30.37
HHH	(23.5)	23.51	23.14	(29.2)	30.64	30.37

	γ-CH_2 (1-hexene units)		
seq	exp	C–P	Carman
PHP	35.8	35.45	35.93
HHP	35.5	35.56	35.96
HHH	(35.4)	35.67	35.99

	CH_2 (main chain)		
seq	exp	G–P	Carman
PPPP	46.6	44.84	45.67
HPPP	46.9	44.95	45.70
HPPH	47.2	45.06	45.73
PHPP	44.0	42.77	43.64
HHPP	44.3	42.88	43.67
PHPH	44.3	42.88	43.67
HHPH	44.5	42.99	43.70
PHHP	41.4	40.70	41.61
HHHP	41.6 (?)	40.81	41.64
HHHH	(41.4)	40.92	41.67

[a] All peak positions are given as downfield shifts (in ppm) from the peak of TMS. Experimental data in parentheses are taken from the ^{13}C NMR spectrum of poly-1-hexene. P and H are abbreviations for propylene and 1-hexene units in chain sequences. Symbols α, β, and γ describe positions of CH_2 groups in side chains of 1-hexene units with respect to their CH groups. [b] G–P, Grant and Paul[3]; Carman, Carman et al.[4]

a narrow range (29.0–29.4 ppm) immediately downfield from the intense PPP CH peak (Figure 1b). We favor the assignment of the 29.4 and 29.3 ppm peaks to the 1-hexene β-CH_2 carbon atoms. Cheng showed previously[6] that, in propylene/butene copolymers, the experimentally observed downfield shifts for the propylene CH groups in the PPB and BPB triads, compared to the PPP triad peak, are very small, 0.04 and 0.10 ppm respectively. This is much lower than the 0.3–0.4 ppm shifts in our case (Figure 1b). It should be noted that, due to cotacticity effects, the CH peaks and some CH_2-group peaks are broadened.

Estimation of Copolymer Compositions. ^{13}C NMR provides a convenient method for estimating the composition of propylene/1-hexene copolymers. The concentration of CH_2 groups in propylene units of the PP- and PH-centered tetrads was used as the measure of molar propylene content:

$$[P] = [PPPP] + [HPPP] + [HPPH] + 0.5\,([PHPP] + [HHPP] + [PHPH] + [HHPH]) \quad (1)$$

where the [PPPP] + [HPPP] + [HPPH] term is proportional to the area of the main-chain CH_2 groups in the 46.6–48.9 ppm range and the [PHPP] + [HHPP] + [PHPH] + [HPHH] term is proportional to the area of the main-chain CH_2 groups in the 44.0–44.5 ppm range.

The molar content of 1-hexene units was derived from the average of the sums of different signals representing 1-hexene-centered triads:

$$[H] = 0.33\,\big(\underbrace{[HHH] + [HHP] + [PHP]}_{\alpha\text{-}CH_2} + \underbrace{[HHH + [HHP] + [PHP]}_{CH} + \underbrace{[HHH] + [HHP] + [PHP]}_{\gamma\text{-}CH_2}\big) \quad (2)$$

We used three peak areas, α-CH_2 in the 23.4–23.5 ppm range, CH in the 33.6–33.9 ppm range, and γ-CH_2 in the 35.4–35.7 ppm range. In addition, the total monomer content, [P] + [H], is estimated in the following way:

$$[P] + [H] = \underbrace{[PPP] + [PPH] + [HPH]}_{CH} + \underbrace{[HHH] + [PHH] + [PHP]}_{\beta\text{-}CH_2} \quad (3)$$

and is proportional to the peak area in the 28–30 ppm range. As a rule, the independently measured area representing the [H] + [P] content is equal to the sum of the areas proportional to the [H] and the [P] contents within 2–4%. The copolymers and the fractions we prepared contained from 8 to 18 mol % 1-hexene.

References and Notes

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