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^{13}C NMR Tetrad Assignments in Ethylene–Propylene Copolymers

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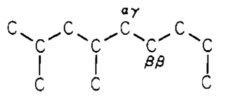
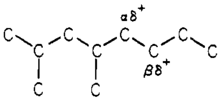
ABSTRACT: Model copolymers were used to finalize ^{13}C NMR chemical shift assignments for the sequences PPEE vs. EPEE and PPEP vs. EPEP. The $\alpha\delta^+$ and $\alpha\gamma$ carbons in PPEE and PPEP sequences gave upfield chemical shifts from their respective EPEE and EPEP counterparts, in contrast to the behavior of the analogous carbons in corresponding sequences in ethylene–1-butene and ethylene–1-hexene copolymers, where downfield shifts were observed. A quantitative procedure is given for determining a reliable and complete triad sequence distribution irrespective of a ^{13}C NMR chemical shift sensitivity to higher order *n*-ad "splitting" or differences in responses to configurational sequencing.

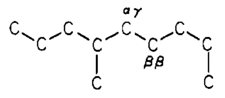
A characterization of sequence distributions in ethylene–propylene copolymers has been the subject of a number of studies utilizing ^{13}C NMR.[1-10] In spite of this effort, there is still not a general agreement among reported ^{13}C NMR chemical shift assignments. In a series of earlier papers, Carman and co-workers[1-4] identified and correctly assigned the basic ethylene–propylene structural features detected by ^{13}C NMR. Complete assignments were not given because their spectra did not display sufficient resolution to permit an identification of some additional and important spectral lines later reported by Ray et al.[5] Of particular interest are the lines corresponding to the PPEP, EPEP, EPEE, and PPEE sequences noted by Ray and co-workers.[5] Resonances unique to these tetrads fall in two regions of the NMR spectrum, 37–39 and 27–28 ppm (from an internal $(CH_3)_4Si$ standard). Smith,[9] in a later study, recognized the possible existence of four resonances identifying these tetrads in the 37–39-ppm region but made assignments completely different from those of both Ray and Carman. The specific methylene carbons leading to an identification of the PPEP, EPEP, PPEE, and EPEE tetrads are depicted below (the nomenclature of Carman[1] is employed, where the locations of the nearest methine carbons are indicated in either direction by appropriate Greek letters):



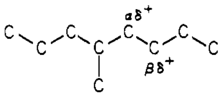
PPEP



PPEE



EPEP



EPEE

Each of the above tetrad sequences contains a centrally situated PE dyad. All four possible permutations of the outer units are shown. The two types of sequences containing $\alpha\gamma$ and $\beta\beta$ carbons differ only by the presence of an initial P unit, as is the case also for the sequences containing the $\alpha\delta^+$ and $\beta\delta^+$ carbons. Note that an initial P unit in the PPEP tetrad has the same structural relationship to an $\alpha\gamma$ carbon as does the last P unit. Carman did not distinguish between the two resulting types of $\alpha\gamma$-, $\alpha\delta^+$-, and $\beta\delta^+$-carbon resonances. Ray et al.[5] noted that four distinct resonances, representing each of these tetrads, could be expected because any substituent effect from a branch present in one direction was also likely to be present in the opposite direction as well. Ray's proposed tetrad assignments for $\alpha\gamma$, $\alpha\delta^+$, and $\beta\delta^+$ are summarized in Table I. The assignments were based on intensity trends vs. composition as observed in a series of copolymers and, from that standpoint, they appear reasonable. There is a question of internal consistency among the $\alpha\gamma$ and $\alpha\delta^+$ assignments because the factors that apparently resulted in an upfield chemical shift for the PPEP vs. EPEP $\alpha\gamma$ carbons caused a downfield shift for the PPEE vs. EPEE $\alpha\delta^+$ carbons. The Grant and Paul parameters predict a downfield shift in both cases.[11] More recently, in analogous studies of ethylene–1-butene copolymers,[12,13] it was established that the corresponding tetrads produced downfield chemical shifts for $\alpha\gamma$ BBEB vs. $\alpha\gamma$ EBEB and $\alpha\delta^+$ BBEE vs. $\alpha\delta^+$ EBEE. In a similar ethylene–1-hexene copolymer study,[14] $\alpha\delta^+$ HHEE was observed to be downfield from $\alpha\delta^+$ EHEE. An upfield shift did occur for $\beta\delta^+$ HHEE vs. $\beta\delta^+$ EHEE, as observed for the corresponding tetrads in the ethylene–propylene and ethylene–1-butene copolymers. It was also noted that $\beta\delta^+$ EHEE had precisely the same chemical shift as $\beta\delta^+$ EBEE. In this latter region, the ethylene–propylene copolymers exhibit analogous behavior because $\beta\delta^+$ PPEE is upfield from $\beta\delta^+$ EPEE. An identification of the chemical shift of $\beta\delta^+$ BBEE was precluded because of overlap,[12] as were the identifications of the $\alpha\gamma$ resonances from the HHEH and EHEH sequences.[14]

Table I
Methylene $\alpha\gamma$, $\alpha\delta^+$, and $\beta\delta^+$ Chemical Shift Assignments for the PPEP, EPEP, EPEE, and PPEE Tetrads As Reported by Ray et al.[5]

carbon	sequence	chem shift, ppm $((CH_3)_4Si)$
$\alpha\gamma$	EPEP	37.9
$\alpha\gamma$	PPEP	37.8
$\alpha\delta^+$	PPEE	37.5
$\alpha\delta^+$	EPEE	37.4
$\beta\delta^+$	EPEE	27.6
$\beta\delta^+$	PPEE	27.5

A comparison of the trends observed in chemical shift behavior for these three ethylene–1-olefin copolymers would suggest that upfield shifts are characteristic for $\beta\delta^+$ carbons in XXEE vs. EXEE sequences. At the same time, the $\alpha\gamma$ and $\alpha\delta^+$ chemical shifts reported by Ray et al. not only appear inconsistent internally but also appear inconsistent with the trends observed in the higher 1-olefin copolymers. Certainly, this chemical shift behavior warrants a closer look.

The chemical shift information reported in Table II for the various EPEE, PPEE, EPEP, and PPEP sequences ($\beta\beta$ pentads are included also for comparison) was obtained for the following series of model copolymers: (A) a hydrogenated polyisoprene, which is the "perfect" alternating ethylene–propylene copolymer; (B) a 1/99 ethylene–propylene copolymer; (C) a 99/1 ethylene–propylene copolymer; and (D) a 4/96 ethylene–propylene copolymer, which contains predominantly blocked ethylene and pro-

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Table II
Observed Chemical Shift Data at 50.3 MHz for a Series of Model Ethylene-1-Olefin Copolymers Containing Unique Tetrad Sequences

carbon sequence	A hydrogenated polyisoprene	B 1/99 E/P copolymer	C 99/1 E/P copolymer	D 4/96 E/P block copolymer	E/B copolymer[12]	E/H copolymer[14]
$\alpha\gamma$ EXEX	37.90			37.96	34.49	obscured
$\alpha\gamma$ XXEX		37.79		37.79	34.81	obscured
$\alpha\delta^+$ EXEE			37.52	37.46	34.01	34.54
$\alpha\delta^+$ XXEE				37.37	34.33	obscured[b]
$\beta\delta^+$ EXEE			27.43	27.38	27.27	27.28
$\beta\delta^+$ XXEE				27.20	obscured	27.09
$\beta\beta$ EXEXE	24.82			[a]	24.54	24.53
$\beta\beta$ XXEXE				24.61	24.39	24.39
$\beta\beta$ XXEXX		24.47		24.47	24.24	24.25

[a] Too low to be detected. [b] The XXEE resonance for E/H copolymers falls necessarily downfield because there are no resonances observed immediately upfield from EXEE (34.54 ppm).

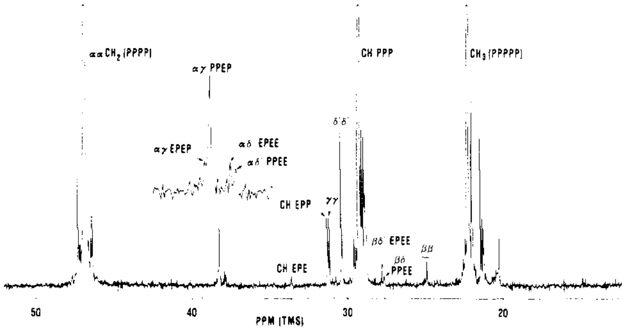

Figure 1. 50.3-MHz ^{13}C NMR spectrum at 125 °C of a 4/96 E/P copolymer containing blocked ethylene and propylene sequences in 1,2,4-trichlorobenzene (10 wt %).

pylene sequences. It is unnecessary to report complete chemical shift data, as it would only confirm the remaining assignments already established by both Ray and Carman. Care was taken to maintain uniform experimental conditions during data acquisition: each sample was prepared at 10 wt % in 1,2,4-trichlorobenzene and the temperature controlled at 125 ± 1 °C. A Varian XL-200 spectrometer was used in the analyses, with the following acquisition conditions: frequency, 50.3 MHz; pulse width, 90°; acquisition time, 1 s; pulse delay, 15 s; spectral width, 8000 Hz; data points per spectrum, 16K.

The $\alpha\gamma$ assignments could be unequivocally established. The $\alpha\gamma$ PPEP resonance does occur upfield from $\alpha\gamma$ EPEP resonance as indicated by Ray et al., in sharp contrast to the higher ethylene–1-olefin copolymers. It does appear, however, that Ray's $\alpha\delta^+$ assignments are incorrect, as $\alpha\delta^+$ PPEE also appears upfield from $\alpha\delta^+$ EPEE, in accord with the $\alpha\gamma$ behavior. The $\beta\delta^+$ assignments as proposed by Ray are confirmed and there appears to be a uniformity in behavior among these various ethylene–1-olefin copolymers with respect to the $\beta\delta^+$ carbons. The spectrum of copolymer D is shown in Figure 1 as all six resonances are observed for the sets of $\alpha\gamma$, $\alpha\delta^+$, and $\beta\delta^+$ resonances. The block nature of the copolymer is also indicated by the strong resonances observed for the methyl(PPPPP), methine(PPP), methylene($\alpha\alpha$-PPPP), and $\delta^+\delta^+$(EEE)$_n$ sequences.

In his original study, Carman noted an additional pair of low broad resonances downfield approximately 1 ppm from the lowest field $\alpha\gamma$ EPEP resonance. They are assigned, respectively, from low to high field to $\alpha\gamma$ PPEP and $\alpha\delta^+$ PPEE sequences displaying a yet undetermined configurational sensitivity. Carman's assignments still appear reasonable as these resonances were missing entirely in the ^{13}C NMR spectra of copolymers B–D, which were essentially isotactic. These downfield resonances have been consistently observed in this laboratory in E/P copolymer systems possessing irregular configurational sequences.

Model polymers are invaluable when making chemical shift assignments for sequences higher than triad where next-nearest-neighbor interactions or steric factors come into play. Under such circumstances, trends established among a homologous series of copolymers may not be entirely reliable, as seen for the case of the tetrad assignments in ethylene–propylene copolymers vs. the higher 1-olefin copolymers ethylene–1-butene and ethylene–1-hexene. Once the complete ethylene–1-olefin series has been characterized, specific similarities can be established and exceptions noted. The sensitivity of ^{13}C NMR to sometimes subtle differences in comonomer sequencing leads to complex spectra where assignments cannot always be made unambiguously. Even so, there are certain guiding principles when making assignments: methine and side-chain branch carbons will exhibit chemical shifts sensitive to odd-membered sequences (triad, pentad, etc.); methylene carbons adjacent to a branch will exhibit chemical shifts sensitive to even-membered sequences (dyads, tetrads, etc.). Methylene carbons two removed from a branch will show a sensitivity to odd-membered sequences; for example, the $\beta\beta$ carbons and the $\beta\delta^+$ carbons display a pentad sensitivity. The $\beta\delta^+$ carbons are frequently reported as tetrad sensitive, when, in fact, they are more accurately described as pentad sensitive. In the present analyses, the two $\beta\delta^+$ resonances represent two overlapping pentads in each case, that is

$$\beta\delta^+\ (27.6\ \text{ppm}) \qquad [\text{EPEE}] = [\text{EPEEE}] + [\text{EPEEP}] \tag{1}$$

$$\beta\delta^+\ (27.5\ \text{ppm}) \qquad [\text{PPEE}] = [\text{PPEEE}] + [\text{PPEEP}] \tag{2}$$

The necessary relationships

$$[\text{EPEE}] = [\text{EEPEE}] + \tfrac{1}{2}[\text{PEPEE}] + \tfrac{1}{2}[\text{EPEEE}] + \tfrac{1}{2}[\text{EPEEP}] \tag{3}$$

$$= 2[\text{EEPEE}] + [\text{PEPEE}] = [\text{EPEEE}] + [\text{EPEEP}] \tag{4}$$

and

$$[\text{PPEE}] = \tfrac{1}{2}[\text{PPEEE}] + \tfrac{1}{2}[\text{PPEEP}] + \tfrac{1}{2}[\text{EPPEE}] + \tfrac{1}{2}[\text{PPPEE}] \tag{5}$$

$$= [\text{PPEEE}] + [\text{PPEEP}] = [\text{EPPEE}] + [\text{PPPEE}] \tag{6}$$

permit the reduction to tetrads EPEE and PPEE. With the basic spectral sensitivities known and with the assistance of the Grant and Paul parameters, one can easily decide within 1–2 ppm where each type of resonance should reside. This approach was precisely what Carman and co-workers did in their original studies; the "basic" $\alpha\gamma$ and $\alpha\delta^+$ resonances were correctly located without distinguishing between $\alpha\gamma$, EPEP and PPEP, and $\alpha\delta^+$, EPEE and PPEE. If each region is then identified along with its basic contributors, whether configurational or sequence sensitive, a quantitative method, which transcends the necessity for assigning very closely spaced lines, can be developed.[12,14] Upon using such an approach, one finds the ^{13}C NMR spectrum of an ethylene–propylene copolymer can be divided into the following spectral regions (in each case, the quantitative description is reduced uniformly to triads through the appropriate necessary relationships[12,14]):

Region A, 45–48 ppm
$\alpha\alpha$-CH$_2$
Contributing n-ads: PPPP, PPPE, and EPPE

$$T_A = k([\mathrm{PPP}] + \tfrac{1}{2}[\mathrm{PPE}]) \tag{7}$$

Region B, 36–39 ppm
$\alpha\gamma$- and $\alpha\delta^+$-CH$_2$
Contribution n-ads: EPEP, PPEP, PPEE, and EPEE

$$T_B = k([\mathrm{PEP}] + \tfrac{1}{2}[\mathrm{EEP}] + [\mathrm{EPE}] + \tfrac{1}{2}[\mathrm{EPP}]) \tag{8}$$

Region C, 33.3 ppm
Methine
Contributing n-ad: EPE

$$T_C = k[\mathrm{EPE}] \tag{9}$$

Region D, 29.5–31.5 ppm
Methine
Contributing n-ad: EPP
$\gamma\gamma$-, $\gamma\delta^+$- and $\delta^+\delta^+$-CH$_2$
Contributing n-ads: PEEP, PEEE, and (EEE)$_n$

$$T_D = k(2[\mathrm{EEE}] + [\mathrm{EPP}] + \tfrac{1}{2}[\mathrm{PEE}]) \tag{10}$$

Region E, 28–29.5 ppm
Methine
Contributing n-ad: PPP

$$T_E = k[\mathrm{PPP}] \tag{11}$$

Region F, 27–28 ppm
$\beta\delta^+$-CH$_2$
Contributing n-ads: EPEE and PPEE

$$T_F = k[\mathrm{PEE}] \tag{12}$$

Region G, 24–25 ppm
$\beta\beta$-CH$_2$
Contributing n-ads: PPEPP, PPEPE, and EPEPE

$$T_G = k[\mathrm{PEP}] \tag{13}$$

Region H, 19–22 ppm
Methyl
Contributing n-ads: PPP, PPE, and EPE

$$T_H = k([\mathrm{EPE}] + [\mathrm{EPP}] + [\ \mathrm{PPP}]) \tag{14}$$

The most appropriate equations, depending upon overlap and proximity to strong resonances, can be selected to determine a complete triad distribution. From this, the comonomer composition, both E and P average sequence lengths, and a "run number" can be determined. Such an approach, while possibly reducing the information available, circumvents the problems of assignments, overlap, and differences in line widths to produce a reliable quantitative result.

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Registry No. E/P copolymer, 9010-79-1; E/H copolymer, 25213-02-9; E/B copolymer, 25087-34-7.

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