Determination of the Composition of Common Linear Low Density Polyethylene Copolymers by ^{13}C-NMR Spectroscopy

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SYNOPSIS

A comprehensive ^{13}C-NMR method for the analysis of composition in the most common commercial polyethylene copolymers has been established. The method covers ethene copolymers with propene, butene-1, hexene-1, octene-1, and 4-methyl pentene-1 in the composition range of 1–10 mol %. The chemical shift assignments and T_1 values of the resonances of the copolymers are presented. Results of precision studies and interlaboratory analyses showed that the molar composition could be determined with a relative precision at 2σ of about 6%. This method is being proposed to ASTM as Method X70-8605-2.

INTRODUCTION

The quantitative analysis of branching in polyethylene (PE) has been a subject of much investigation due to the commercial importance of this material.[1-8] The primary analysis tools for the determination of the level and type of branching have been infrared (IR) and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The IR method utilizes the absorbance of the methyl group at about 1380 cm^{-1} for the determination. This method suffers from limitations, namely, that the absorbance must be corrected due to interferences of the methylenes and other bands. The absorbance frequency and absorptivity of the methyl groups are also somewhat dependent upon the type of branch and upon crystallinity.[9] This presents a problem for the quantitative analysis of branching in ethylene copolymers of two or more comonomers. However, the IR method has some distinct advantages over the ^{13}C-NMR method which include precision and analysis time. Therefore, there is a need to provide well-defined and accepted standards for this analysis such that the IR method might be routinely practiced.

The NMR method lists as advantages the fact that it is an absolute method, not requiring standards, and specificity, since the location of the resonance identifies it as being from a given type of branch. In fact, branches shorter than six carbons in length can be unambiguously assigned from their ^{13}C-NMR spectrum. Branches longer than five carbons in length cannot be differentiated from long chain branches.[5] Therefore, the advantages of the NMR technique, accuracy and specificity, can be utilized to define standard materials which can then be used to standardize the IR method.

This document describes a ^{13}C-NMR method for the analysis of ethene copolymers with propene, butene-1, hexene-1, 4-methyl pentene-1, and octene. The method described in this report is valid for products containing 1–10 mol % of the second alkene-1 excluding products containing an extraordinary amount of blocky alkene-1. If needed, corresponding methods for terpolymers can be developed.

QUANTITATIVE NMR SPECTROSCOPY

^{13}C-NMR spectroscopy is an absolute method, not requiring standardization if the appropriate parameters are defined.[1,3] The two parameters which must be determined for quantitative analysis by ^{13}C-NMR
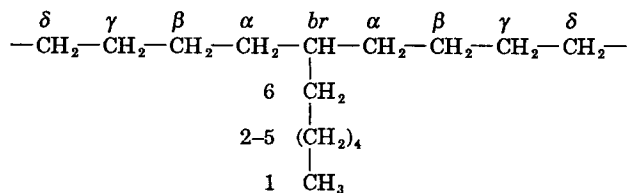
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spectroscopy are the spin lattice relaxation time T_1 and the nuclear Overhauser enhancement (NOE) factor of the carbons used for quantitative analysis. It has been shown for many PE systems that the NOE factor is nearly full and constant for all carbons of the copolymer.[1]

Delay times between pulses in the pulse-FT NMR method must be five times the longest T_1 value for 99% relaxation. Unless five T_1 values are allowed between pulses, saturation will occur and the area of the resonance will be attenuated. The methyl carbons in PE generally have the longest T_1 values, some of which are as long as 8–10 s. Therefore, to be quantitative, a 50 s delay time between pulses would be necessary. Since several thousand scans must be accumulated in order to achieve adequate signal to noise, this delay time is not reasonable. An alternate approach for this analysis would be to ignore the methyls and other carbon resonances which have very long relaxation times. The T_1 values for the majority of the carbons in the samples are less than 2.0 s and, therefore, a delay time of only 10 s would be necessary. Since there are several other carbons in the structure to use for quantitative purposes, the methyls and some branch carbons can be neglected without interfering with the quantitative

aspects. This has the advantage of shortening the delay time between pulses from 50 to 10 s with equivalent accuracy.

The terminology for branching is that commonly accepted, using an octene-1 copolymer as example:

$$
\begin{array}{ccccccccc}
\delta & \gamma & \beta & \alpha & br & \alpha & \beta & \gamma & \delta \\
-CH_2- & CH_2- & CH_2- & CH_2- & CH- & CH_2- & CH_2- & CH_2- & CH_2-
\end{array}
$$

$$
\begin{array}{cc}
6 & CH_2 \\
 & | \\
2\text{–}5 & (CH_2)_4 \\
 & | \\
1 & CH_3
\end{array}
$$

This investigation includes the chemical shift assignments (relative to that of the isolated methylene carbons at 30.0 ppm) and a set of experimental conditions for the quantitative analysis of branching in the most common commercial types of linear low density polyethylenes. The method has been submitted to ASTM as Method X70-8605-2.

EXPERIMENTAL

The sample (1.2 g) and 2.8 mL dichlorobenzene (ortho or para) or 1,2,4-trichlorobenzene are trans-
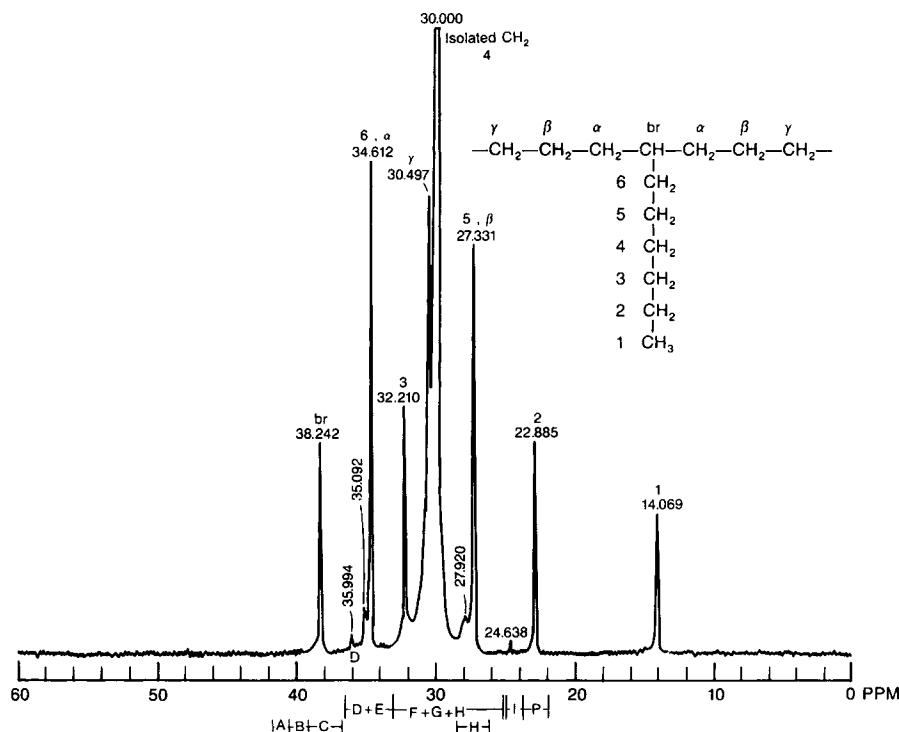

Figure 1   The ^{13}C-NMR spectrum of an E–O copolymer.

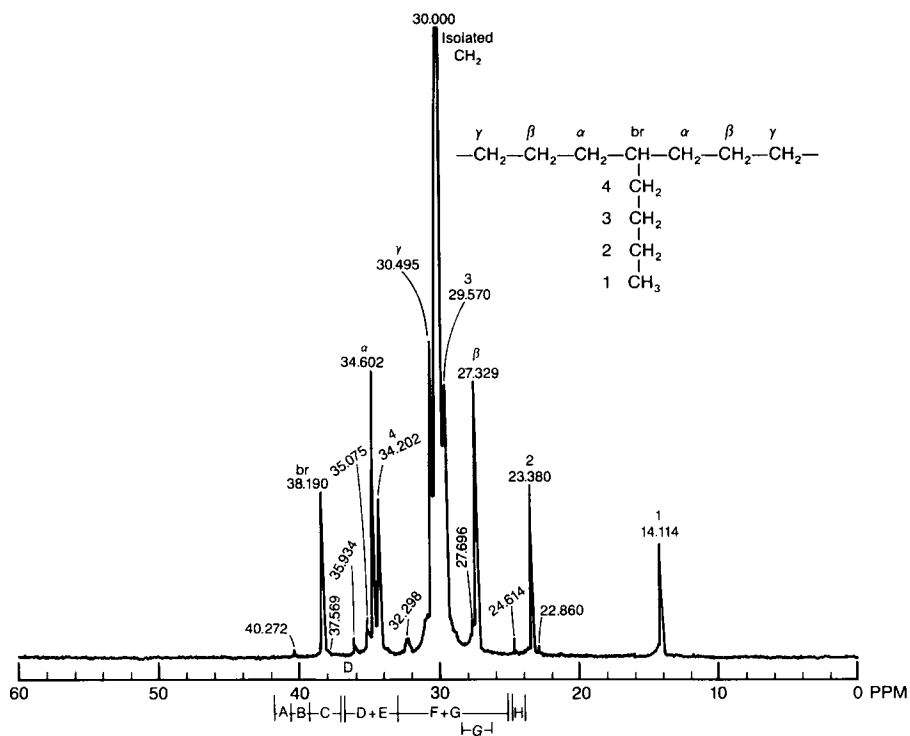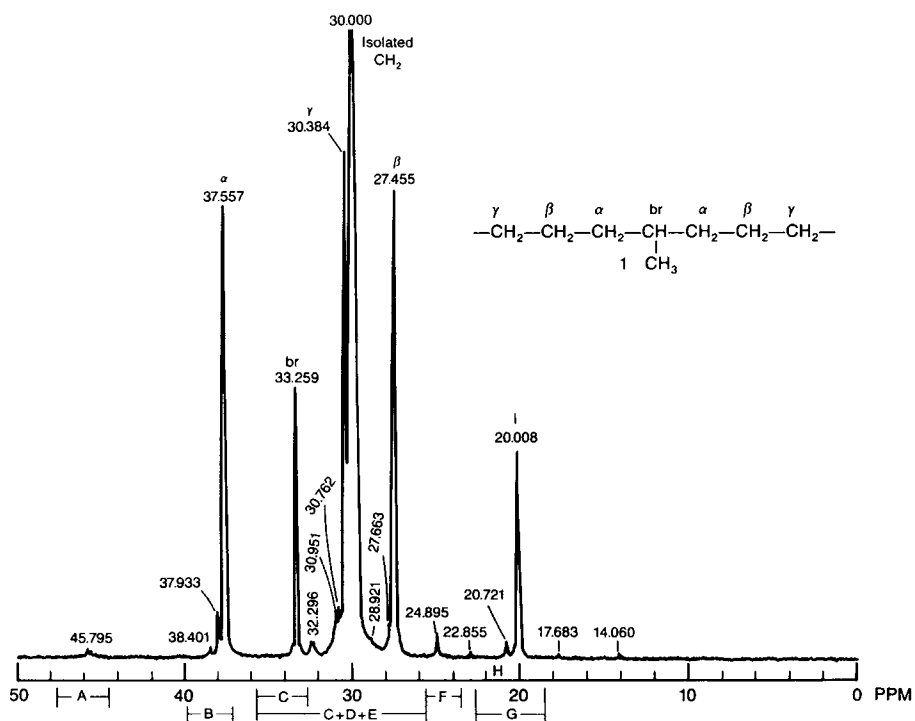**Figure 2**   The ^{13}C-NMR spectrum of an E–H copolymer.

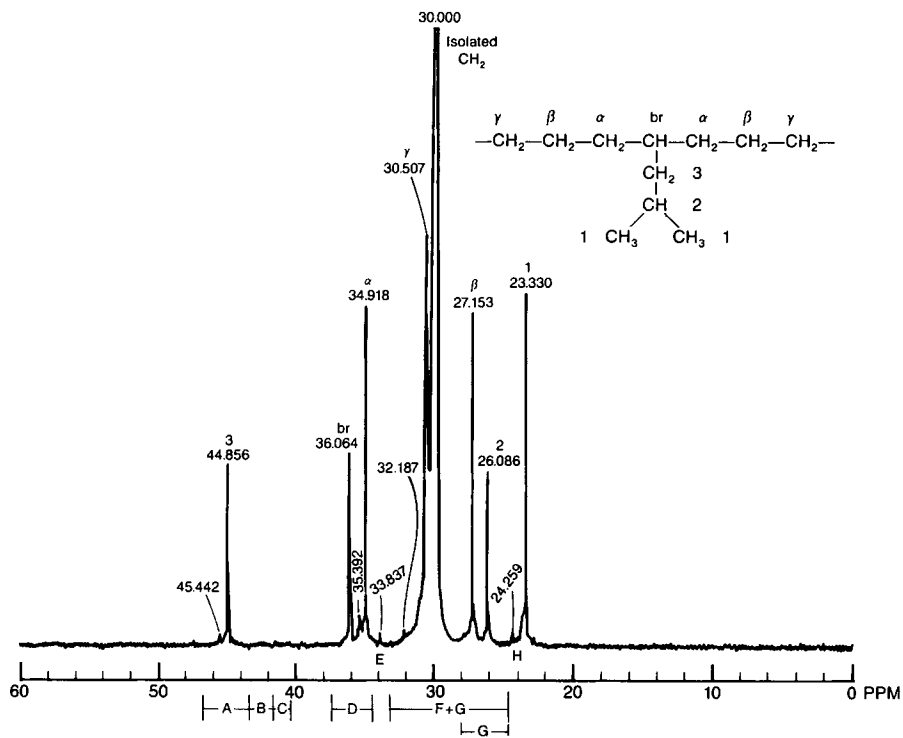**Figure 3**   The ^{13}C-NMR spectrum of an E–P copolymer.

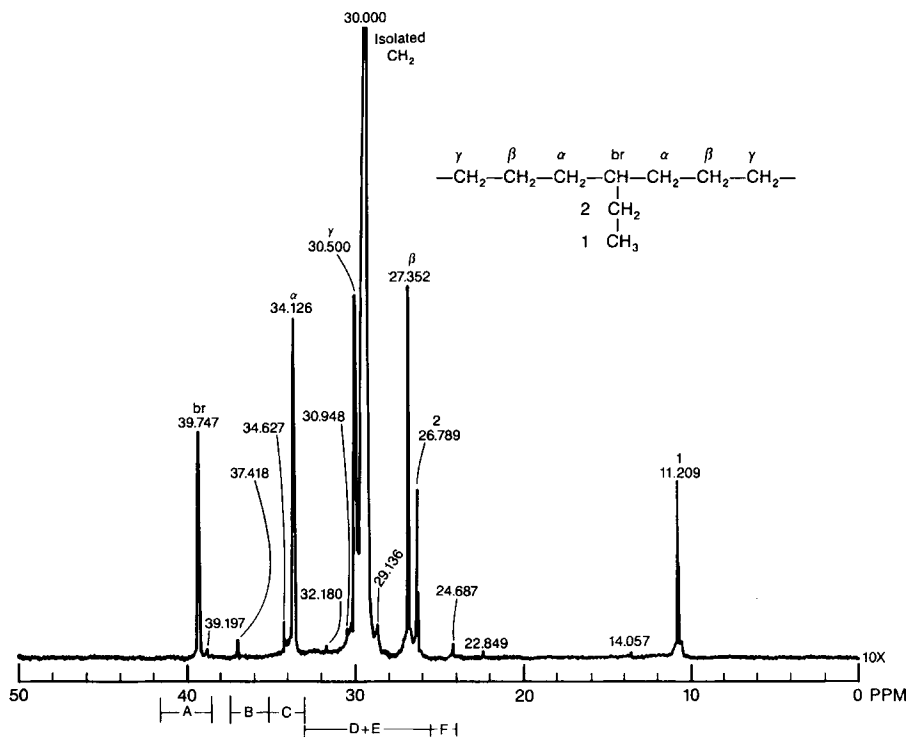**Figure 4**   The ¹³C-NMR spectrum of an E–(4-MP) copolymer.

Figure 5   The ¹³C-NMR spectrum of an E–B copolymer.

ferred into a 10-mm NMR sample tube. Deuterated analogues of these solvents may be substituted for purposes of external locking. The content of the sample tube is homogenized in a well-ventilated oven or heating block at 150°C for 3–4 h. (Preferably Büchi GKR-50 glass tube oven or similar).

Data Acquisition Parameters

1. The sample temperature is 130°C. (The NMR spectrometer temperature readout should be verified.)

2. A digital resolution of at least 0.5 Hz per point should be used. For example, at 50 MHz, a 150 ppm sweep width would require 32K data points to meet this criterion. One zero fill of the data is permitted.

3. The pulse width should be 90° as measured using the resonance of the isolated methylenes at 30.0 ppm.

4. The transmitter frequency should be centered and quadrature detection used. A large enough sweep width should be used such that the solvent resonances are not reflected into the spectrum.

5. The number of scans should be sufficient to reach a signal to noise ratio of 5000 to 1 for the resonance of the isolated methylene carbons at 30.0 ppm. The signal to noise ratio is defined as 2.5 × (signal intensity of the isolated methylene resonance)/(peak to peak noise for the region from 14 to 20 ppm).

6. The pulse repetition rate is 10.0 s.

7. The proton decoupling mode is complete.

8. The apodization is exponential, 2 Hz broadening.

RESULTS

Representative ^{13}C-NMR spectra of the five ethylene copolymers are given in Figures 1–5 with assignments. The integration limits given below not only take into account the isolated branches, but also branches which are separated by one ethylene unit and branches next to each other. These latter two structures occur very infrequently in most commercial products but are significant to the calculations.

Integration Limits

An accurate full scale integral is recorded from 10 to 50 ppm (the isolated methylene resonance is assigned to 30.0 ppm). The spectrum should not contain peaks other than those originating from the copolymer under consideration. Partial integrals are adjusted such that the integral of the second large peak in the spectrum is about 50% of full scale. The

Table I   Integration Limits for Ethylene Copolymers[a]

Copolymer	Area	Region (ppm)
Ethene–propene	A	47.5 to 44.5
	B	39.8 to 36.8
	C	35.5 to 32.5
	C + D + E	35.5 to 25.8
	F	25.8 to 23.8
	G	22.5 to 18.5
	H	Peak at 21.6
Ethene–butene-1	A	41.5 to 38.5
	A'	Peak at 39.4
	B	37.8 to 36.8
	C	36.0 to 33.2
	D + E	33.2 to 25.5
	F	25.2 to 24.0
Ethene–hexene-1	A	41.5 to 40.5
	B	40.5 to 39.5
	C	39.5 to 37.0
	D	Peak at 35.8
	D + E	36.8 to 33.2
	F + G	33.2 to 25.5
	G	28.5 to 26.5
	H	24.9 to 24.1
Ethene–octene-1	A	41.5 to 40.5
	B	40.5 to 39.5
	C	39.5 to 37.0
	D	Peak at 35.8
	D + E	36.8 to 33.2
	F + G + H	33.2 to 25.5
	H	28.5 to 26.5
	I	25.0 to 24.0
	P	24.0 to 22.0
Ethene–4-methylpentene-1	A	46.5 to 43.5
	B	43.0 to 41.8
	C	41.8 to 40.5
	D	37.5 to 34.2
	E	Peak at 33.7
	F + G	33.2 to 25.2
	G	28.0 to 25.2
	H	Peak at 24.1

[a] Isolated methylene carbons at 30.0 ppm.

Table II ^{13}C-NMR Chemical Shift Assignments for Several Ethylene Copolymers

Comonomer	δ (ppm)[a]									
	br	α	β	γ	1	2	3	4	5	6
Propene	33.3	37.6	27.5	30.4	20.0					
Butene-1	39.7	34.1	27.1	30.5	11.2	26.7				
Hexene-1	38.2	34.6	27.3	30.5	14.1	23.4	29.6	34.2		
Octene-1	38.2	34.6	27.3	30.5	14.1	22.9	32.2	30.0	27.3	34.6
4-Methylpentene-1	36.1	34.9	27.2	30.5	23.3	26.1	44.9			

[a] Referenced to the isolated methylene resonance at 30.0 ppm.

Table III Spin-Lattice Relaxation Times of the Predominant Carbons of Various LLDPE's Measured at 50 MHz

Carbon Type	Propene-1	Butene-1	Hexene-1	Octene-1	4-Methylpentene
α	1.38	1.23	0.96	0.79	0.92
β	1.54	1.46	1.21	0.92	1.14
γ	1.56	1.51	1.36	1.22	1.24
δ, $\delta+$	1.64	1.64	1.75	1.60	1.62
CH	2.14	1.91	1.48	1.06	1.33
6				0.79	
5				1.30	
4			1.19	~ 2.0[a]	
3			1.98	4.24	1.09
2		1.56	4.16	6.21	1.66
1	2.96	5.65	7.96	9.57	3.01

[a] Estimated value.

Table IV Relaxation Times and Correction Factor Designations for Different Carbon Types[a]

Monomer		Branch Type	Label
Propene	(P)	Methyl	M1
Butene-1	(B)	Ethyl	E1–E2
Hexene-1	(H)	Butyl	B1–B4
4-Methylpentene-1	(MP)	Isobutyl	IB1–IB3
Octene-1	(O)	Hexyl	H1–H6

Area	Chemical Shift (ppm)	EEXEE		EEXEXEE		EEXXEE		EEXXXEE		T_1 (s)	Factor
		Type	#	Type	#	Type	#	Type	#		
				Ethene–propene copolymers							
A	~ 45.5					$\alpha\alpha$	1	$\alpha\alpha\gamma$	2	1.38	1.06
B	~ 37.5–37.9	α	2	α, $\alpha\gamma$	4	$\alpha\gamma$	2	$\alpha\gamma$	2	1.38	1.06
C	33.2	CH	1	CH	2					2.14	1.18
D	30.4–31.5	γ	2	γ	2	CHβ, γ	4	CHβ, γ	4	1.56	1.08
	30.0	δ, $\delta*$	3	δ, $\delta*$	3	δ, $\delta*$	3	δ, $\delta*$	3	1.64	1.10
	~ 28							CH$\beta\beta$	1	2.14	1.18
E	27.4	β	2	β	2	β	2	β	2	1.54	1.08
F	24.8			$\beta\beta$	1					1.54	1.08
G	20.0–21.6	M1	1	M1	2	M1	2	M1	3	2.96	1.35
H	21.6										

Table IV (*Continued from the previous page*)

Area	Chemical Shift (ppm)	EEXEE Type	#	EEXEXEE Type	#	EEXXEE Type	#	EEXXXEE Type	#	T_1 (s)	Factor

Ethene–butene-1 copolymers

Area	Chemical Shift (ppm)	EEXEE Type	#	EEXEXEE Type	#	EEXXEE Type	#	EEXXXEE Type	#	T_1 (s)	Factor
A	39.0–39.6	CH	1	CH	2	αα	2			1.91	1.14
	~ 39.4							ααγ	2	1.23	1.04
B	~ 37.2					CHβ	2	CHβ	2	1.91	1.14
C	34–35	α	2	α, αγ	4	αγ	2	CHββ, αγ	3	1.23	1.04
D	30.4	γ	2	γ	2	γ	2	γ	2	1.51	1.08
	30.0	δ, δ*	3	δ, δ*	3	δ, δ*	3	δ, δ*	3	1.64	1.09
E	27.3	β	2	β	2	β	2	β	2	1.46	1.07
	26.7	E2	1	E2	2	E2	2	E2	3	1.56	1.08
F	24.6			ββ	1					1.46	1.07

Ethene–hexene-1 copolymers

Area	Chemical Shift (ppm)	EEXEE Type	#	EEXEXEE Type	#	EEXXEE Type	#	EEXXXEE Type	#	T_1 (s)	Factor
A	~ 40.8							ααγ	2	0.96	1.02
B	~ 40.2					αα	1			0.96	1.02
C	38.1	CH	1	CH	2					1.48	1.07
D	~ 35.8					CHβ	2			1.48	1.07
E	34.5–35.0	α	2	α, αγ	4	B4, αγ	4	B4, αγ	5	0.96	1.02
	34.1	B4	1	B4	2					1.19	1.04
	33.5							CHββ	1	1.48	1.07
F	30.4	γ	2	γ	2	γ	2	γ	2	1.36	1.05
	30.0	δ, δ*	3	δ, δ*	3	δ, δ*	3	δ, δ*	3	1.75	1.11
	29.5	B3	1	B3	2	B3	2	B3	3	1.98	1.15
G	27.3	β	2	β	2	β	2	β	2	1.21	1.04
H	24.5			ββ	1					1.21	1.04

Ethene–octene-1 copolymers

Area	Chemical Shift (ppm)	EEXEE Type	#	EEXEXEE Type	#	EEXXEE Type	#	EEXXXEE Type	#	T_1 (s)	Factor
A	~ 40.8							ααγ	2	0.79	1.01
B	~ 40.1					αα	1			0.79	1.01
C	38.1	CH	1	CH	2					1.06	1.02
D	35.8					CHβ	2	CHβ	2	1.06	1.02
E	34.5–35.2	H6, α	3	H6, α, αγ	6	H6, αγ	4	H6, αγ	5	0.79	1.01
	33.9							CHββ	1	1.06	1.02
F	32.2	H3	1	H3	2	H3	2	H3	3	4.24	1.64
G	30.4	γ	2	γ	2	γ	2	γ	2	1.22	1.04
	30.0	H4	1	H4	1	H4	1	H4	1	~ 2.0**	1.15
	30.0	δ, δ*	3	δ, δ*	3	δ, δ*	3	δ, δ*	3	1.60	1.09
H	27.3	β	2	β	2	β	2	β	2	0.92	1.01
	27.2	H5	1	H5	2	H5	2	H5	3	1.30	1.05
I	24.5			ββ	1					0.98	1.02
P	22.9	H2	1	H2	2	H2	2	H2	2	6.21	2.11

Ethene–4-methylpentene-1 copolymers

Area	Chemical Shift (ppm)	EEXEE Type	#	EEXEXEE Type	#	EEXXEE Type	#	EEXXXEE Type	#	T_1 (s)	Factor
A	44.7	IB3	1	IB3	2	IB3	2	IB3	3	1.09	1.03
B	42.2							ααγ	2	0.92	1.01
C	41.2					αα	1			0.92	1.01
D	35.9	CH	1	CH	2					1.33	1.05
E	35.8–35.2	α	2	α, αγ	4	αγ	2	αγ	2	0.92	1.01
	33.6					CHβ	2	CHβ	2	1.33	1.05
F	31.0							CHββ	1	1.33	1.05
G	30.4	γ	2	γ	2	γ	2	γ	2	1.24	1.04
	30.0	δ, δ*	3	δ, δ*	3	δ, δ*	3	δ, δ*	3	1.62	1.09
H	27.1	β	2	β	2	β	2	β	2	1.14	1.03
	26.0	IB2	1	IB2	2	IB	2	IB2	3	1.66	1.10
	24.1			ββ	1					1.14	1.03

ᵃ # Number of carbons; * referenced to isolated methylenes at 30.0 ppm; ** estimated T_1 relaxation.

Table V Equations for Calculating Mol % Composition

Ethene–propene copolymers
  Mol propylene
    $P1 = \alpha$ carbons: $(2A + B)/2$ (note a)
    $P2 = br$ carbons: $2A + C - H$
    $P' = (P1 + P2)/2$
  Mol ethylene
    $E' = (C + D + E + F - A)/2$
  Mol % propylene $= 100\% \times P'/(P' + E')$ (note b)
Ethene–butene-1 copolymers
  Mol butene-1
    $B1 = br$ carbons: $(2A + B)/2$ (note a)
    $B2 = \alpha$ carbons: $(A' + 2C + 2B)/4$
    $B' = $ average moles butene $- 1$:
      $(B1 + B2)/2$
  Mol ethylene
    $E' = (2D + 2E + 2F + -A' - B)/4$
  Mol % butene-1 $= 100\% \times B'/(B' + E')$ (note b)
Ethene–hexene-1 copolymers
  Mol hexene-1
    $H1 = br$ carbons: $(A + 2C + 2D)/2$ (note a)
    $H2 = \alpha$ carbons: $[1.5A + 2B + (D + E)$
      $- D]/3$
    $H' = $ average moles hexene $- 1$:
      $(H1 + H2)/2$

Mol ethylene
  $E' = \{[(F + G) - 3A - 3B - G - H]/2\} + Q$
    $+ Q$
  Mol % hexene-1 $= 100\% \times H'/(H' + E')$ (note b)
Ethene–octene-1 copolymers
  Mol octene-1
    $O1 = br$ carbons: $(A + 2C + 2D)/2$ (note a)
    $O2 = \alpha$ carbons: $[1.5A + 2B + (D + E)$
      $- D]/3$
    $O' = $ average moles octene-1 $= (O1$
      $+ O2)/2$
  Mol ethylene
    $E' = \{[(F + G + H) - (3A + 3B + H$
      $+ P + I)]/2\} + O$
  Mol % octene-1 $= 100\% \times O'/(O' + E')$ (note c)
Ethene–4-methylpentene-1 copolymers
  Mol 4-methylpentene-1
    $MP1 = \alpha$ carbons $+ br$ carbons:
      $= (2B + C + D + 1.5E)/3$
    $MP2 = $ isobutyl carbon 3: A
    $MP = $ average moles 4-methylpentene-
      $1 = (MP1 + MP2)/2$
  Mol ethylene
    $E' = \{[(F + G) - (2B + 1.5E + G$
      $+ H)]/2\} + 1.5\ MP$
  Mol % 4-methylpentene-1 $= 100\% \times MP/(MP + E')$

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[a] "α-Carbons" and "CH-carbons" mean predominantly peaks originating from α-carbons and CH-carbons, respectively.

[b] As their relaxation times are completely different, end groups are not included in the area measurement. The formal correction for this omission is: End group concentration in mol % $= (4 \times 1400)/M_n$, where $M_n = $ number average molecular weight.

[c] In the case of octene-1 copolymers, the end group concentration in mol % $= (6 \times 1400)/M_n$.

Table VI Sample Calculation for the Ethene–Octene-1 Copolymer of Fig. 1[a]

Area	Integral
A	0.0
B	0.2
C	8.1
D	0.6
D + E	26.8
F + G + H	343.6
H	24.8
I	0.6
P	7.9

$$O1 = \frac{A + 2C + 2D}{2} = \frac{0.0 + 16.2 + 1.2}{2} = 8.70$$

$$O2 = \frac{[1.5A + 2B + (D + E) - D]}{3} = \frac{0.0 + 0.4 + 26.8 - 0.6}{3} = 9.27$$

$$O' = \frac{O1 + O2}{2} = 8.98$$

$$E' = \frac{[(F + G + H) - (3A + 3B + H + P + I)}{2} + O'$$

$$E' = \frac{[343.6 - (0.0 + 0.6 + 24.8 + 7.9 + 0.0]}{2} + 8.98 = 164.13$$

$$\text{Mol \% octene-1} = \frac{(100)O'}{O' + E'} = \frac{898.0}{173.11} = 5.19$$

[a] Calculations for 90° pulse angle and 10 s repetition time.

Table VII ^{13}C-NMR Determination of
Comonomer Incorporation Level (mol %)

	EB	E4MP	EH	EO
Freeport	4.86	3.67	4.21[a]	4.92
	4.86	3.79	4.05[a]	4.93
Average	4.86	3.73	4.13	4.93
Terneuzen	5.13	3.77	4.76	5.15
	5.14	3.71	4.56	4.94
	4.95[b]	3.54[b]	4.43[b]	5.04
				5.05
				5.14
				5.00
				5.14
				5.12
				5.16
				5.15
				5.07[b]
				5.07[b]
				5.11[b]
				5.17[b]
Average	5.07	3.67	4.58	5.09[c]
Midland	4.60	3.82	4.43	5.18
	4.90	4.08	4.75	5.20
	4.92			
	4.95			
	4.96			
	4.81			
	4.74			
	4.61			
	5.10			
	4.86			
Average	4.85[d]	3.95	4.59	5.19

[a] Contained approximately 0.8 ethyl branches. This value is not included in the comonomer incorporation.

[b] Operator 2.

[c] The average value for the 14 determinations is 5.09 with a standard deviation of 0.07 (relative precision at 2σ of 2.7%).

[d] The average value for the 10 determinations is 4.85 with a standard deviation of 0.16 (relative precision at 2σ or 6.8%).

integrals must be flat before and after the area to be measured. The integration limits for the various copolymers are assigned in Table I. Table II lists the ^{13}C-NMR chemical shift assignments for *isolated* branches in these copolymers in a simplified form. Table III gives the spin-lattice relaxation times for the isolated branches as measured at 50 MHz. The integration limits are derived from the detailed assignments given in Table IV. The first column of Table IV gives the integration area label with the limits in the next column. The following columns give the type of branch, isolated branches in the third column, branches separated by one methylene in the fourth, etc. The type of carbon of that branching sequence is given below each column

heading and the number of those types of carbons in the sequence. For example, the octene copolymer structure shown in the introduction is an isolated hexyl branch. The third column of the table shows that the branch carbon of an isolated branch resonates at 38.1 ppm and that its integration limit is in area C. The H5 carbon resonates at 27.2 ppm and its T_1 value is given in column 7, 1.30 s.

Calculations

The equations used for the calculation of the branch level of the copolymers take into consideration the isolated branches, as well as those which occur in the proximity of another branch (see Table IV for assignments). These equations are given in Table V for each copolymer analyzed.

A sample calculation for the ethylene–octene-1 copolymer of Figure 1 is given in Table VI.

Spin Lattice Relaxation Measurements and Corrections

The procedure described above utilizes the integrals of carbons which have T_1 values less than 2.0 s. Therefore, a pulse repetition rate of 10 s is adequate for 99% relaxation. However, if shorter pulse repetition rates are utilized or other carbons are used for quantitation, the areas of the resonances need to be corrected for saturation effects. The ^{13}C-NMR T_1 values of the copolymers were determined at 50.3 MHz by the inversion recovery method. These relaxation times and correction factors (reciprocal of the relative intensities) for a 4.0-s pulse repetition time (T_R) are given in Table IV. The correction factor can be calculated using the following relation: relative intensity $= 1 - \exp(-T_R/T_1)$. The integrals obtained by using the shorter repetition time should be multiplied by the correction factor before use in the equations of the Calculations section. Also, these correction factors are only valid for the conditions of temperature, concentration, and magnetic field strength specified above.

Round Robin Analyses and Precision

This analysis method is somewhat time-consuming and tedious, but the precision achieved from its detailed approach is excellent. Several sets of precision studies were performed in which one operator performed the analysis at least 10 times on a given sample and also multiple operators performed the

analysis to investigate operator bias. These precision data are given in Table VII. For one operator, the relative standard deviation at the 95% confidence limit (2σ) was between 2.7 and 7%.

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