

A¹³ CNMR Determination of Monomer Composition in EP Copolymers, EPB and EPDM Terpolymers

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EP 공중합체, EPB 및 EPDM 삼중합체의 단량체조성에 관한 ¹³C-NMR 분석

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Abstract: The monomer compositions in a series of propylene heterophasic copolymer, propylene random copolymer, propylene random terpolymer and ethylene-propylene-ENB terpolymer have been determined from ¹³C NMR spectra. The simplified and highly resolved ¹³C NMR spectra made it possible to assign unambiguously and calculate the monomer composition. A complete sets of NMR chemical shift assignments and the way to measure the quantity of monomer are newly given in diverse polymers. Furthermore complete dyad, triad, tetrad and pentad distributions have been able to be determined. These NMR quantitative analytical results for monomer composition have consistent with those from Infrared spectral data.

요약: 일련의 polypropylene 계통의 공중합체 및 삼중합체 중에서 단량체의 조성에 관한 조성비를 ¹³C-NMR 스펙트럼을 이용하여 정량하였다. 고온에서 얻어진 고분자의 ¹³C-NMR 스펙트럼은 아주 높은 분해능을 보이며, 이는 모든 시그널을 명확하게 지정하는 것을 가능하게 하였으며, 또한 단량체의 조성비를 계산할 수 있도록 하였다. 따라서 단량체의 조성비를 계산하는 방법을 새롭게 제시하였으며, 고분자에서 dyad, triad, tetrad 및 pentad의 조성비도 계산할 수 있다는 것을 보여 주었다. 이러한 단량체 조성에 관한 NMR 분석 결과는 표준 물질을 이용하여 정량한 IR data와 잘 일치한다는 것을 보여 준다.

Key words: Polypropylene, ¹³C-NMR

Introduction

It has been demonstrated that carbon-13 nuclear magnetic resonance (¹³C-NMR) is sensitive to mon-

omer sequence structure in high polymers.^{1, 2} This technique has proven quite useful in the determination of polymer microstructure such as stereoregularity as well as an analytical tool for composi-

tional studies. ^{13}C -NMR spectroscopy is a unique spectroscopic tool in representing copolymer molecular structure because unlike connecting comonomer sequences can be detected independently of like connecting sequences. Quite often, this structural information is not just limited to just dyads but also includes triad, tetrad, and even pentad connecting sequences. Thus, copolymer structure can be determined with considerable detail.^{3, 4} The translation of ^{13}C -NMR data to meaningful quantitative terms, however, is not always readily accomplished. The observed spectral information is also related to factors other than the simple comonomer distribution. Configuration and mode of addition can seriously complicate analysis of ^{13}C copolymer spectra.

The nature of Fourier transform techniques, which are used to acquire the data, requires a relatively detailed knowledge of the relaxation parameters of the particular polymer investigated if the subsequent analysis is to be quantitative and unambiguous. Thus, the choice of pulse delays and possibly, pulse angles is dependent upon the spin-lattice relaxation time(T_1) of the nonequivalent polymer carbons. In order to get a true equilibrium spectrum, a spectrum is acquired only after a time of approximately $4\sim 5 \times T_1(\text{max.})$ has elapsed since the last pulse. Thus integrated peak intensities will not be misleading.⁵

Another problem of concern is the possibility that different carbons in the same molecule may possess different nuclear Overhauser enhancement (NOE).⁶ The concentration of different groups or isomers obtained from the integrated intensities may be seriously affected by such a phenomenon.

This problem can be circumvented by the use of inverse gated decoupling or chemical modification of the sample (addition of paramagnetic reagent). However, both of these techniques lower experimental efficiency in terms of the time required to obtain a spectrum since the NOE is eliminated. Therefore, in order to establish conditions for the quan-

titative analysis of high polymers, the before-mentioned problems have to be recognized. The most serious barrier to the quantitative analysis in the polymers from ^{13}C -NMR spectrum would be the unambiguous assignment of the resonances. However, the chemical shift assignments taken from the several studies are very comprehensive and in good general agreement.

In this report we have attempted to develop a quantitative analytical methodology from the area of each resonances in a ^{13}C -NMR spectrum of copolymers and terpolymers, their result will be compared with Infrared spectral data calibrated by standard reagents⁷

Experimental section

A) Sample preparation

Propylene heterophasic copolymers, propylene random copolymers, propylene random terpolymers and ethylene-propylene-ENB terpolymers were prepared in Yugong complex, Korea as described previously.² Polymer solutions were prepared for the NMR measurements by dissolving the polymers into orthodichlorobenzene and adding sufficient chlorobenzene- d_5 to maintain a lock signal. The final solution concentrations were approximately 10 wt % copolymer.

B) Instrumental condition

Carbon-13 NMR spectra were obtained at 50.3 MHz from a Bruker 200 AM spectrometer system equipped with a variable temperature controller. Spectra were collected by using a standard broadband decoupling experiments with interpulse delay, 12 sec. The specific spectrometer conditions for the pulsed NMR measurements are as follows : pulse width, $6.8\mu\text{s}$ (75° flip angle) : spectral width, 12000 Hz : Acquisition time, 1.4 sec : NMR running time, 12~36 hrs / sample. To improve signal to noise ratio, the free induction decays were multiplied by the

3Hz line broadening factor. Chemical shifts for all spectra are referenced to the solvent line, orthodichlorobenzene. Spectra were recorded at 127°C . The free induction decays were stored in a 32K size.⁵

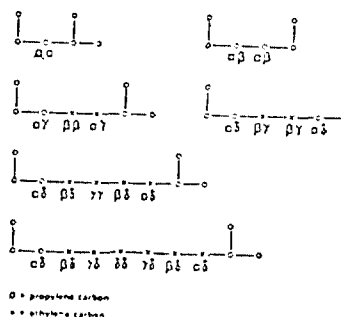
C) Nomenclature

We have used two different nomenclature. At first, the nomenclature used to assign peaks to various carbons in the propylene heterophasic copolymer, propylene random copolymer and propylene random terpolymer follows that suggested by Carman and Wilkes.² A methylene carbon is identified by a pair of Greek letters which indicated its distance in both directions from the nearest tertiary carbon. For example, an $\alpha\gamma$ methylene is one which is α to one tertiary carbon and γ to a second. The letter δ indicated that a methylene is at least δ to a tertiary carbon but may be further removed. Secondly, in ethylene-propylene-ENB terpolymer, we denote each secondary carbon as S with two Greek subscripts indicating its position relative to the nearest tertiary carbons in both directions along the polymer chain. Some of the subscripts are followed by a plus sign, e.g., $S_{\gamma\delta+}$, a combined designation for $S_{\gamma\delta}$, $S_{\gamma\delta+}$, $S_{\gamma\delta}$ and so on, which are not resolved spectroscopically. Similarly, we denote each tertiary carbon as T with two Greek subscripts showing the positions of the nearest tertiary neighbors. Each primary(methyl) carbon is given the letter P, with Greek subscripts which are the same as those for the attached tertiary.⁸

Results and discussion

The instrumental conditions were chosen to maximize the signal to noise ratio of the final spectrum. It is expected that due to the relatively long repetition rate that thermodynamic equilibrium is achieved. Although T_1 's for the diverse carbons are various, pulse repetition rate and 75° pulse were given to be achieved the magnetization equilibrium.

As a result, comparison of measured areas between types of carbons is considered to be quantitatively valid. The method of analysis chosen was to calculate % ethylene, % propylene and % butene-1. In performing these calculations, we assumed that nuclear Overhauser effects were uniform for ethylene, propylene and butylene in the spectrum in terms of neighboring proton numbers. The calculation of % propylene and % ethylene relies on the structure shown in chart I.



In these structures every $\alpha\alpha$ -CH₂, CH and CH₃ counts a 100% propylene fragment. For every propylene followed by an ethylene, either an $\alpha\gamma$ or an $\alpha\delta$ occurs. Because an $\alpha\gamma$ or an $\alpha\delta$ carbon occurs in both an ethylene fragment and a propylene fragment, only half the intensities of these peak is used to measure propylene. Consequently, the propylene content is given by

$$P = I_{\alpha\alpha\text{-CH}_2} + I_{\text{CH}} + I_{\text{CH}_3} + 1/2(I_{\alpha\gamma} + I_{\alpha\delta}) \quad (1)$$

The ethylene content is obtained by summing the intensities of the remaining methylene peaks in the spectrum and adding in the contribution of the $\alpha\gamma$ and $\alpha\delta$ peaks as well as $\beta\beta$, $\beta\delta$, $\gamma\gamma$, $\gamma\delta$ and $\delta\delta$ peaks due to ethylene. Thus, ethylene content is expressed by

$$E = I_{\beta\beta} + I_{\beta\delta} + I_{\gamma\gamma} + I_{\gamma\delta} + I_{\delta\delta} + 1/2(I_{\alpha\gamma} + I_{\alpha\delta}) \quad (2)$$

This quantity represents the number of methylenes occurring in ethylene sequences and division by two

gives the number of ethylenes in the copolymers.

The butylene content is obtained by summing the intensities of the $\alpha\alpha$ -CH₂ of butylene, CH of butylene, 2-CH₂ of butylene and CH₃ of butylene. Consequently, the butylene content is given by

$$B = I_{\alpha\alpha\text{-CH}_2 \text{ of B}} + I_{\text{CH of B}} + I_{2\text{-CH}_2 \text{ of B}} + I_{\text{CH}_3 \text{ of B}} \quad (3)$$

1) Propylene heterophasic copolymers.

A ¹³C-NMR spectrum(B310F) for one of the polypropylene heterophasic copolymers, which is typical of the heterophasic copolymers examined, is shown in Figure 1. Atleast, 13 lines, which are labeled alphabetically from low to highfield are present as compared to 24 lines observed by Ray, Johnson and Knox in a study of related ethylene-propylene copolymers. Less lines are observed in these ¹³C copolymer spectra because of a lower ethylene content which does not allow the propylene-centered tetrads and pentads to be observed. Peaks A, H and J are assigned unambiguously to $\alpha\alpha$ -CH₂, CH and CH₃ of PPP, respectively. Six additional peaks resonated as shoulders of peaks A, H and J seems to be small

amount of tetrads. These signal intensities would not affect overall quantity of propylene and ethylene. Thus, it is not necessary to be considered separately. Peaks B, C, E, F, G and I are assigned to $\alpha\gamma$ -, $\alpha\delta$ -, $\gamma\gamma$ -, $\gamma\delta$ -, $\delta\delta$ -, and $\beta\delta$ -CH₂, respectively. Peak D and K are assigned to CH and CH₃ of EPE sequence, respectively. The peak assignment has been made in terms of the variation in peak intensity with the increase of propylene content. Two other polypropylene heterophasic copolymer with different ethylene quantity were investigated and their spectra were not shown.

The propylene content is obtained according to the equation(1), only a third the intensities of these peaks multiplied by 42.08(molecular weight of propylene) is used to measure propylene weight percent. Consequently,

$$\begin{aligned} P &= 1/3 [I_{\alpha\alpha\text{-CH}_2} + I_{\text{CH}} + I_{\text{CH}_3} + 1/2(I_{\alpha\gamma} + I_{\alpha\delta})] \\ &\quad \times 42.08(\text{M.W. of P}) \\ &= 1/3(4363+4428+4035+91+89+1/2 \\ &\quad (128+197) \times 42.08 = 184710.2 \end{aligned}$$

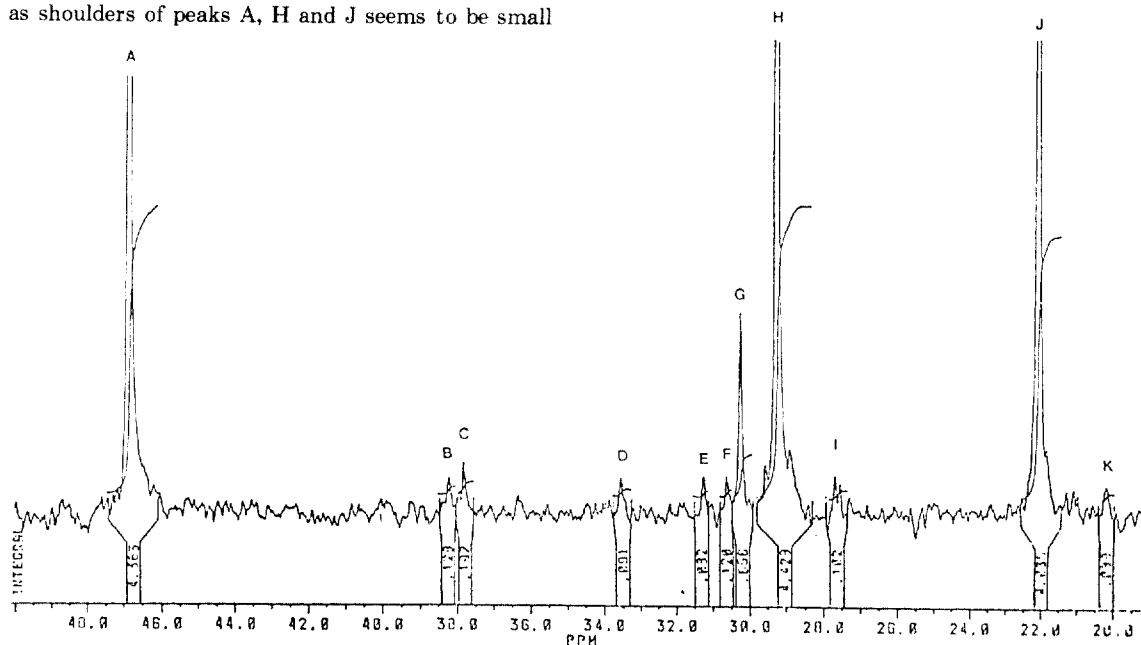


Figure 1. 50.3 MHz ¹³C NMR spectrum of propylene heterophasic copolymer in orthodichlorobenzene at 127°C (B340F).

Table 1. The chemical shift, signal assignments and peak area of ^{13}C NMR spectra for polymer samples (B900F, B310F, B340F)

Lable	Chemical Shift(PPM)	Assignment	Area		
			B900F	B310F	B340F
A	46.8	$\alpha\alpha$ -CH ₂ of PPP	3695	6192	4363
B	38.2	$\alpha\gamma$ -CH ₂	119	79	128
C	37.8	$\alpha\delta$ -CH ₂	102	116	197
D	33.5	CH of EPE	44	140	91
E	31.2	$\gamma\gamma$ -CH ₂	41	111	82
F	30.6	$\gamma\delta$ -CH ₂	47	129	120
G	30.2	$\delta\delta$ -CH ₂	457	946	656
H	29.2	CH of PPP	3799	5994	4428
I	27.7	$\beta\delta$ -CH ₂	40	156	102
J	22.0	CH ₃ of PPP	3559	3273	4035
K	20.2	CH ₃ of EPE	0	121	89

The ethylene content is obtained by summing the methylene intensities according to the equation (2). This quantity represents the number of methylenes occurring in ethylene sequences and division by two and the multiplication by 28.05(molecular weight of ethylene) gives the weight percent of ethylene in the propylene heterophasic copolymer.

$$E = 1/2 [I_{\beta\beta} + I_{\beta\delta} + I_{\gamma\gamma} + I_{\gamma\delta} + I_{\delta\delta} + 1/2(I_{\alpha\gamma} + I_{\alpha\delta})] \times 28.05 (\text{M.W. of E})$$

$$= 1/2 [0 + 102 + 82 + 120 + 656 + 1/2(128 + 197)] \times 28.05 = 15743.1$$

$$E(\text{Wt. \%})_{\text{B340F}} = [E / (P + E)] \times 100 = 7.9\%$$

The chemical shift, assignment and signal area for the polypropylene heterophasic copolymers are illustrated in Table 1.

II) Propylene radom copolymer

As is common in nature(e.g. proteins and polynucleic acids), two or more different monomer units can be incorporated randomly, resulting in a random copolymer. Thus, ethylene monomer unit is incorporated at random structures in propylene in this case. A ^{13}C -NMR spectrum(R141N) for one of the polypropylene random copolymer, which is typical of the random copolymers examined, is shown in Figure 2. At least, 13 lines, which are labeled alphabetically from low to highfield are present. These series of copolymers allow the propylene-centered triads and pentads to be observed. Peaks A, E and G are assigned to $\alpha\alpha$ -CH₂, CH and CH₃ of PPPP, respectively. Five additional peaks resonated as shoulders of peaks A, H and J seems to be small amount of tetrads. These signal intensities would not affect overall quantity of propylene and ethylene. Thus, it is not necessary to be considered separately. Peaks B, C and F are assigned to $\alpha\alpha$ -CH₂

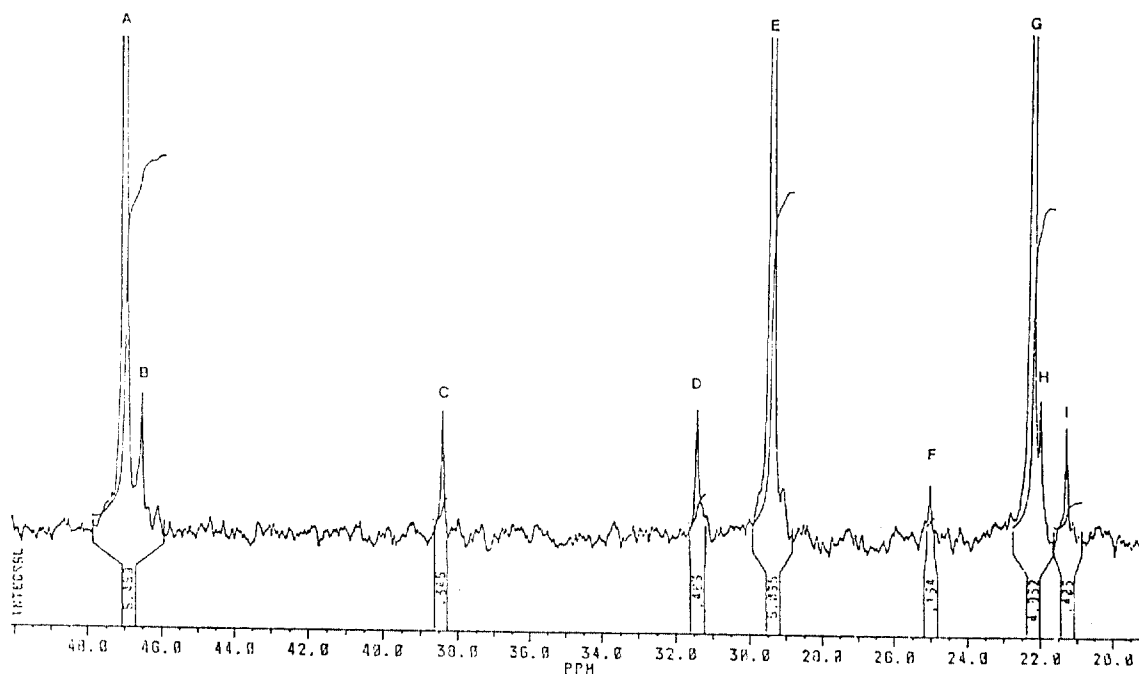


Figure 2. 50.3 MHz ^{13}C NMR spectrum of propylene random copolymer in orthodichlorobenzene at 127°C (R141N).

Table 2. The chemical shift, signal assignments and peak area of ^{13}C NMR spectra for polymer samples (R141N and R930Y)

Lable	Chemical Shift (PPM)	Assignment	Area	
			R141N	R930Y
A	47.0	$\alpha\alpha$ -CH ₂ of PPP	5459	5312
B	46.5	$\alpha\alpha$ -CH ₂ of EPE		
C	38.4	$\alpha\gamma$ -CH ₂ of PPE	345	230
D	31.4	CH of PPE	463	233
E	29.4	CH of PPP	5035	5173
F	25.0	$\beta\beta$ -CH ₂	134	29
G	22.2	CH ₃ of PPPPP	4832	4747
H	22.0	CH ₃ of PPPPE		
I	21.2	CH ₃ of EPPPE	403	206
J	20.5	CH ₃ of EPE	0	54

of EPE, $\alpha\gamma$ -CH₂ of PPE and $\beta\beta$ -CH₂, respectively. Peaks D, H, I and J are assigned to CH of PPE, CH₃ of PPPPE, CH₃ of EPPPPE and CH₃ of EPE, respectively. The peak assignment has been made in terms of the variation in peak intensity with the increase of propylene content as described previously. The chemical shift, assignment and signal area are illustrated in Table 2. The quantitative analysis of propylene and ethylene has been made as described above.

$$\begin{aligned}
 P &= 1/3 [I_{\alpha\alpha\text{-CH}_2} + I_{\text{CH}} + I_{\text{CH}_3} + 1/2(I_{\gamma\gamma} + I_{\alpha\delta})] \\
 &\quad \times 42.08 (\text{M.W. of P}) \\
 &= 1/3 (5459 + 5035 + 4832 + 463 + 403 + 1/2 \\
 &\quad (345 + 0)) \times 42.08 = 229539.4 \\
 E &= 1/2 [I_{\beta\beta} + I_{\beta\delta} + I_{\gamma\gamma} + I_{\gamma\delta} + I_{\delta\delta} + 1/2(I_{\alpha\gamma} + I_{\alpha\delta})] \times \\
 &\quad 28.05 (\text{M.W. of E}) \\
 &= 1/2 [134 + 0 + 0 + 0 + 0 + 1/2(345 + 0)] \times \\
 &\quad 28.05 = 4298.7 \\
 E(\text{Wt } \%)_{\text{R141N}} &= [E/(P+E)] \times 1.8\%
 \end{aligned}$$

Another polypropylene random copolymer with

different ethylene quantity was investigated and its spectrum was not shown. The chemical shift, assignment and signal area measurement for the polypropylene random copolymers are tabulated in Table 2.

III) Propylene random terpolymer.

In these terpolymer, ethylene and butene-1 are incorporated in polypropylene. A ^{13}C -NMR spectrum (C243/25) for one of the propylene random terpolymer, which is typical of the terpolymers examined, is shown in Figure 3. At least, 14 lines, which are labeled alphabetically from low to highfield are present. These terpolymer allow the propylene-centered triads, tetrads and pentads to be observed. The quantitative analysis of propylene and ethylene has been made as described above. The butylene content is obtained by summing the intensities of the $\alpha\alpha$ -CH₂ of butylene, CH of butylene, 2-CH₂ of butylene and CH₃ of butylene in the spectrum according to the equation (3). The division by four gives the number of butylene in the propyl-

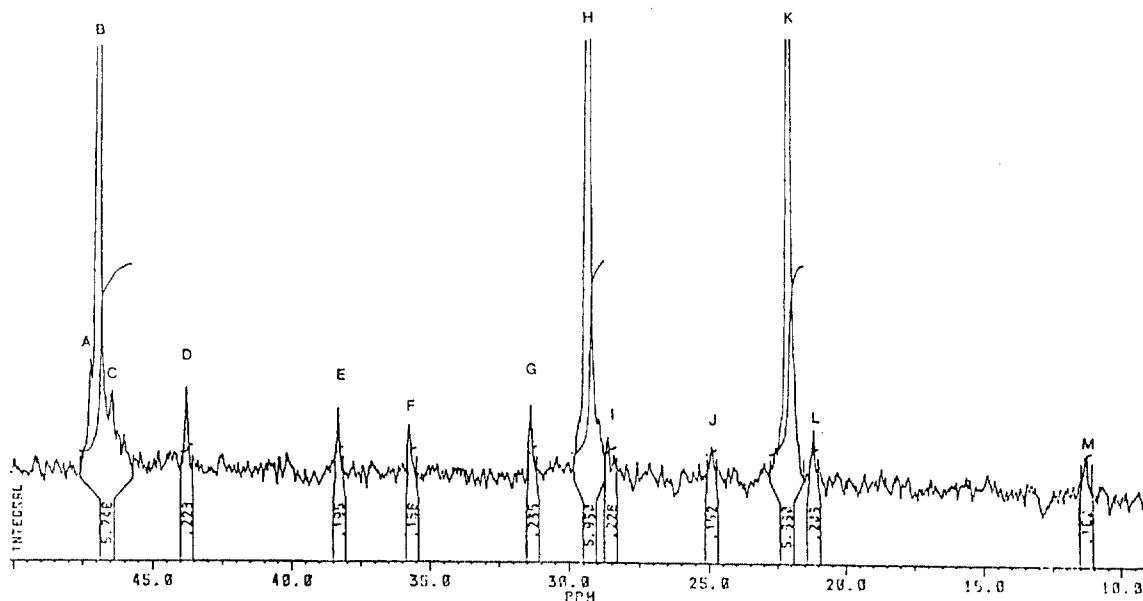


Figure 3. 50.3 MHz ^{13}C NMR spectrum of propylene random terpolymer in orthodichlorobenzene at 127°C (C243/23).

ene random terpolymer. The weight percent calculation for the monomer composition in polypropylene random terpolymer were made as described above.

$$\begin{aligned}
 P &= 1/3[I_{\alpha\alpha\text{-CH}_2} + I_{\text{CH}} + I_{\text{CH}_3} + 1/2(I_{\gamma\gamma} + I_{\alpha\delta})] \\
 &\quad \times 42.08(\text{M.W. of P}) \\
 &= 1/3(4729 + 5046 + 4882 + 1/2(354) \\
 &\quad + 302 + 415 + 1/2(263)) \times 42.08 = 219973.2 \\
 E &= 1/2[I_{\beta\beta} + I_{\beta\delta} + I_{\gamma\gamma} + I_{\gamma\delta} + I_{\delta\delta} + 1/2(I_{\gamma\gamma} + I_{\alpha\delta})] \times \\
 &\quad 28.05(\text{M.W. of E}) \\
 &= 1/2[143 + 0 + 0 + 0 + 0 + 1/2(263)] \times 28.05 = \\
 &\quad 3849.9
 \end{aligned}$$

$$\begin{aligned}
 B &= [I_{\alpha\alpha\text{-CH}_2 \text{ of B}} + I_{\text{CH of B}} + I_{2\text{CH}_2 \text{ of B}} + I_{\text{CH}_3 \text{ of B}}] \times \\
 &\quad 56.11(\text{M.W. of B}) \\
 &= 1/4[1/2(354) + 157 + 210 + 288 + 66] \times \\
 &\quad 56.11 = 12596.7
 \end{aligned}$$

$$E(\text{Wt } \%)_{\text{C243/25}} = [E / (P + E + B)] \times 100 = 1.6\%$$

$$B(\text{Wt } \%)_{\text{C243/25}} = [B / (P + E + B)] \times 100 = 5.3\%$$

The other polypropylene random terpolymer with different ethylene, butylene quantities were investigated and their spectra were not shown.

The chemical shift assignments and area measurements of various terpolymer samples, that were

Table 3. The chemical shift, signal assignments and peak area of ^{13}C NMR spectra for polymer samples (C243/23, C243/25, C243/37 and C243/34)

	Chemical Shift (PPM)	Assignment	Area			
			C243/23	C243/25	C243/37	C243/34
A	47.2	$\alpha\alpha$ -CH ₂ of PPPB	5746	4729	3541	5271
B	46.9	$\alpha\alpha$ -CH ₂ of PPPP				
C	46.5	$\alpha\alpha$ -CH ₂ of PPPE				
D	43.8	$\alpha\alpha$ -CH ₂ of PPBP+BPBB	228	354	350	242
E	38.3	$\alpha\gamma$ -CH ₂ of PPE	195	263	266	468
F	35.7	CH of B	156	157	199	159
G	31.4	CH of PPE	235	302	304	401
H	29.3	CH of PPP	5930	5046	3783	5292
I	28.7	2-CH ₂ of PBP	226	210	259	181
J	25.0	$\beta\beta$ -CH ₂ of PPE	152	143	154	181
K	22.2	CH ₃ of PPPPP	5830	4882	3719	5200
L	21.2	CH ₃ of PPE	203	415	339	465
M	11.4	CH ₃ PBP	162	288	302	230
N	10.0	CH ₃ of PBB+BBB	—	66	65	—
O	40.7	$\alpha\alpha$ -CH ₂ of BB	—	—	—	62

ed determined in this study are listed in Table 3.

IV) Ethylene propylene methylene linkage

The copolymer system shown in Figure 4 differs significantly from those studied previously. Figure 4 shows the ^{13}C NMR spectra of a typical ethylene-propylene rubber. In the ethylene-propylene rubber, the chemical environment of both the $\alpha\alpha$ carbons and the methyl carbons is influenced by the ethylene-propylene sequence distribution in the vicinity of these carbons as well as the tacticity of the propylene methyl groups. The tacticity effect results in additional peaks in the $\alpha\alpha\text{-CH}_2$ and CH_3 regions of the spectrum in comparison to ethylene-propylene copolymer synthesized by the isotactic catalyst. On the other hand, the chemical environment of the $\alpha\alpha\text{-CH}_2$ and CH_3 carbons in the copolymer prepared by an isotactic catalyst is influenced only by the ethylene-propylene sequence distributions. The nomenclature for this polymer was described above in detail. In this polymer, every αS_α , tertiary carbons and primary carbons counts a 100% propylene frag-

ment. For every propylene followed by an ethylene, either an $\alpha\gamma$ or an $\alpha\delta$ occurs. Because αS_γ , $\alpha\text{S}_{\delta+}$, αS_γ and αS_β carbons occur in both an ethylene fragment and a propylene fragment, only half the intensities of these peak is used to measure propylene.

$$P = 1/3 [\alpha\text{S}_\alpha + 1/2 (\alpha\text{S}_\gamma + \alpha\text{S}_{\delta+} + \alpha\text{S}_\gamma + \alpha\text{S}_\beta) + \gamma\text{T}_{\delta+} + \delta\text{T}_{\delta+} + \beta\text{T}_{\delta+} + \alpha\text{P}_\beta + \beta\text{P}_\beta] \times 42.08 (\text{M.W. of P})$$

$$1/3 [363 + 1/2 (5926 + 395) + 2536 + 223 + 80 + 3187] \times 42.08 = 133947.7$$

$$E = 1/2 [1/2 (\alpha\text{S}_\gamma + \alpha\text{S}_{\delta+} + \alpha\text{S}_\gamma + \alpha\text{S}_\beta) + \gamma\text{S}_\gamma + \gamma\text{S}_{\delta+} + \delta\text{S}_{\delta+} + \beta\text{S}_\gamma + \beta\text{S}_{\delta+} + \beta\text{S}_\beta] \times 28.05 (\text{M.W. of P})$$

$$= 1/2 [1/2 (5926 + 395) + 20420 + 5408 + 357] \times 28.05 = 411570.6$$

$$P(\text{Wt. \%})_{\text{E120}} = [P / (P + E)] \times 100 = 24.6\%$$

The chemical shift assignments and area measurements determined are included in Table 4.

V) Ethylene-propylene-ENB terpolymer

In this type of terpolymer, 2-ethylidene-5-norbor-

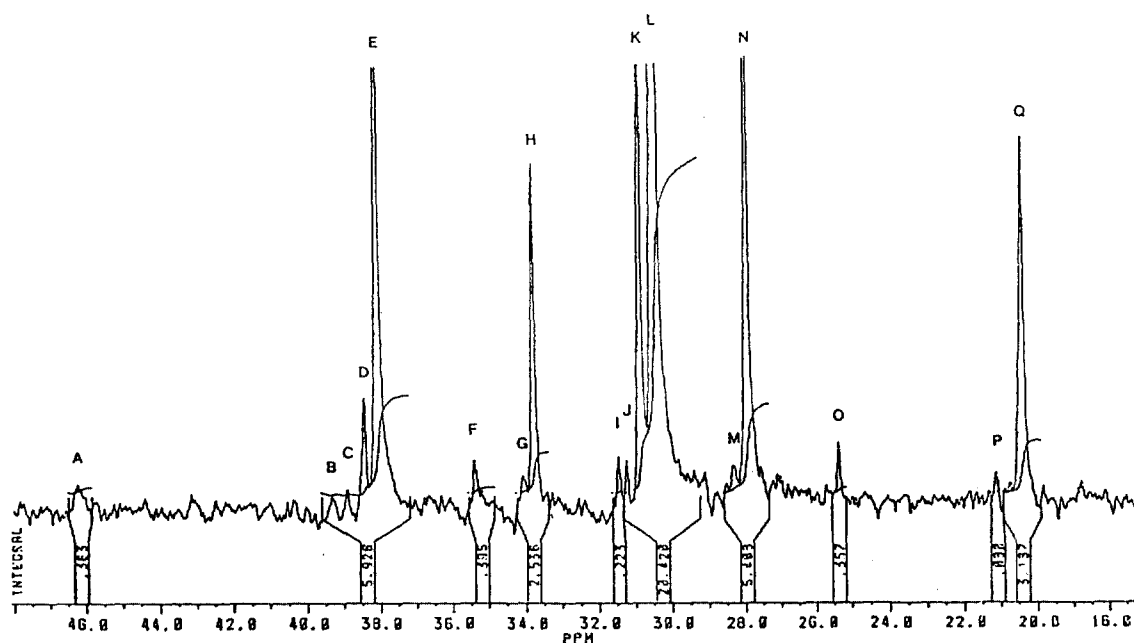


Figure 4. 50.3 MHz ^{13}C NMR spectrum of ethylene-propylene rubber in orthodichlorobenzene at 127°C (E120).

Table 4. The chemical shift, signal assignments and peak area of ¹³C NMR spectra for polymer samples(E120, E512F, E505 and E501A)

	Chemical Shift (PPM)	Assignment	Area			
			E120	E512F	E505	E501A
A	46.1	${}_zS_z$	363	428	358	1226
B	39.2	${}_zS_\gamma$	5926	4639	5193	6534
C	38.8	${}_xS_{\delta+}$				
D	38.3	${}_xS_\gamma$				
E	38.0	${}_zS_{\delta+}$				
F	35.3	${}_oS_\beta$	395	381	886	1213
G	34.0	${}_\gamma T_{\delta-}$	2536	2264	2888	2809
H	33.7	${}_{\delta+} T_{\delta+}$				
I	31.4	${}_\beta T_{\delta+}$	223	555	977	1480
J	31.2	${}_\gamma S_\gamma$	20420	12781	7186	6803
K	30.8	${}_\gamma S_{\delta+}$				
L	30.4	${}_{\delta+} S_{\delta+}$				
M	28.3	${}_\beta S_\gamma$	5408	3903	3669	3952
N	27.9	${}_\beta S_{\delta-}$				
O	25.3	${}_\beta S_\beta$	357	408	655	872
P	21.1	${}_x P_\beta$	3267	2830	3697	4807
Q	20.3	${}_\beta P_\beta$				
R	34.4	${}_\gamma T_\gamma$	—	103	200	300
S	26.9	${}_\beta S_\delta$	—	408	—	—
T	31.7	${}_\beta T_\gamma$	—	—	180	735

ane(ENB) is incorporated in ethylene-propylene copolymer, which give rise to ethylene-propylene-diene terpolymer, known as EPDM rubbers. The small amount(2~9% by weight) of copolymerized diene monomer, which makes these polymers capable of sulfur vulcanization leads to the complicated ¹³C NMR spectrum⁹ as shown in Figure 5.

The ¹³C resonances assignable to the incorporated diene are designated by “z” and the signals from ethylene and propylene carbons are labeled as described above. The weight percent calculation for the monomer composition in polypropylene random terpolymer were made as described above.

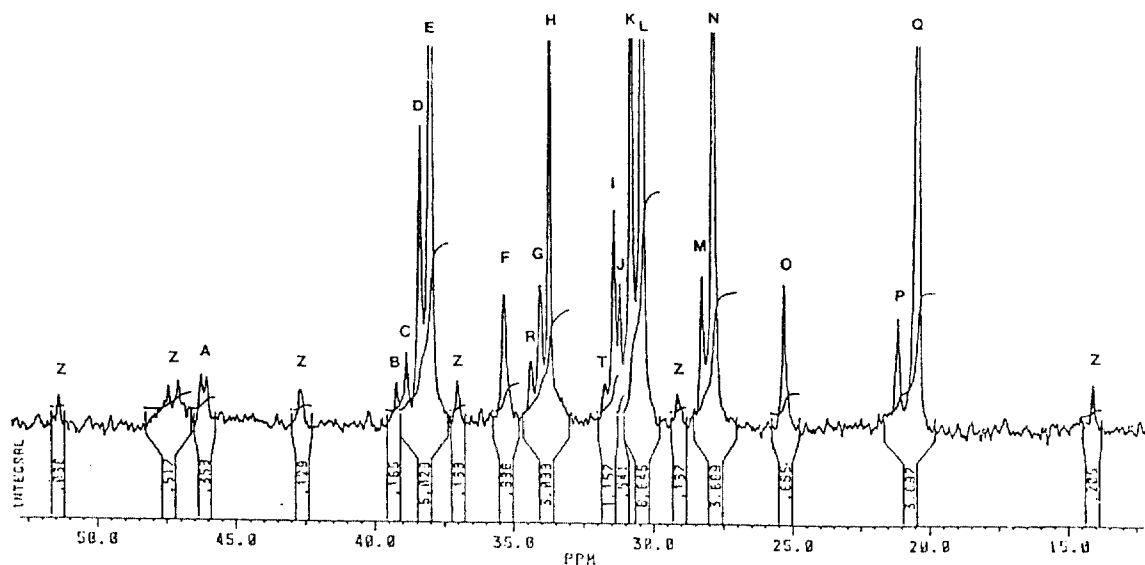


Figure 5. 50.3 MHz ^{13}C NMR spectrum of EPDM incorporated with ENB in orthodichlorobenzene at 127°C (E505).

Table 5. Comparative analytical data list

unit : WT %

Sample	Comonomer	Uniroyal Chemical	This Study
B900F	Ethylene	5.5	5.8
B310F	Ethylene	7.1	7.3
B340F	Ethylene	8.1	7.9
R141N	Ethylene	3.4	1.8
R930Y	Ethylene	2.4	0.9
C243/23	Ethylene, Butene-1	1.7, 3.4	1.3, 3.5
C243/25	Ethylene, Butene-1	2.5, 5.2	1.6, 5.3
C243/37	Ethylene, Butene-1	2.9, 7.5	2.2, 7.5
C243/34	Ethylene, Butene-1	2.8, 4.5	2.3, 4.1
E120	Propylene	24.0	24.6
E512F	Propylene	28.3	30.6
E505	Propylene	44.1	43.8
E501A	Propylene	49.9	49.6

$$P = 1/3 [{}_2S_\alpha + 1/2 ({}_3S_\gamma + {}_3S_\delta + {}_3S_\epsilon + {}_3S_\theta) + {}_7T_{\delta+} + {}_5T_{\delta+} + {}_\mu T_{\delta+} + {}_3P_\beta + {}_\mu P_\beta] \times 42.08 (\text{M.W. of P})$$

$$= 1/3 [358 + 1/2 (165 + 5028 + 886) + 3088 + 1157 + 3697] \times 42.08 = 159055.4$$

$$E = 1/2 [1/2 ({}_3S_\gamma + {}_3S_\delta + {}_3S_\epsilon + {}_3S_\theta) + {}_7S_\gamma + {}_5S_\delta + {}_\mu S_\delta + {}_\mu S_\gamma + {}_\mu S_{\delta+} + {}_\mu S_\theta] \times 28.05 (\text{M.W. of P})$$

$$= 1/2 [1/2 (165 + 5028 + 886) + 541 + 6645 + 3669 + 655] \times 28.05 = 204056.7$$

$$P (\text{Wt. } \%)_{E505} = [P / (P + E)] \times 100 = 43.8\%$$

Two additional EPDM rubbers with different ethylene, propylene and ENB quantities were investigated and their spectrum was not shown.

The chemical shift assignments and area measurements determined are included in Table 4.

Conclusions

Our ^{13}C NMR determination for monomer composition in diverse polypropylene polymers is in good agreement with results obtained from IR measurement on the same systems, which were carried out in Uniroyal Chemical, U.S.A. (shown in Table 5). Thus, ^{13}C NMR methodology in determi-

nation of monomer composition in diverse polypropylene polymers would be more reliable and convenient as far as the chemical shift assignments are unambiguous in terms of uncertainty of standard samples.

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