A ^{13}C NMR Determination for Monomer Compositions in Ethylene–Propylene Copolymers, Ethylene–Propylene–Butene-1, and Ethylene–Propylene–Diene Terpolymers

Kang-Bong LEE,[†] Jeehye KWEON, Ho-Jin LEE, and Hokoon PARK

*Advanced Analysis Center, Korea Institute of Science and Technology,
P.O. Box 131, Cheongryangri, Seoul 130-650, Korea*

(Received January 19, 1996)

ABSTRACT: The monomer compositions in a series of propylene heterophasic copolymer, propylene random copolymer, propylene random terpolymer and ethylene–propylene–2-ethylidene-5-norborane (ENB) terpolymer have been determined from ^{13}C NMR spectra. The simplified and highly resolved ^{13}C NMR spectra made it possible to assign unambiguously and calculate the monomer compositions. A complete sets of NMR chemical shift assignments and the way to measure the quantity of monomer are newly given in diverse polymers. Furthermore, it is shown that complete dyad, triad, tetrad and pentad distributions can be determined by ^{13}C NMR spectra. These NMR quantitative analytical determinations for monomer compositions are consistent with those from Infrared spectroscopic data.

KEY WORDS ^{13}C Nuclear Magnetic Resonance / Monomer Composition / Ethylene–Propylene Copolymer / Ethylene–Propylene–Butene-1 Terpolymer / Ethylene–Propylene–Diene Terpolymer /

It has been demonstrated that carbon-13 nuclear magnetic resonance (^{13}C NMR) is sensitive to monomer sequence structure in high polymers.^{1–8} This technique has been proven quite useful in the determination of polymer compositional studies.^{9–12} ^{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 comonomer sequences. Quite often, this structural information is not only limited to just dyad but also includes triad, tetrad, and even pentad connecting sequences. Thus, copolymer structure can be determined with considerable details.^{9–12} 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 the analysis of copolymer ^{13}C NMR spectra.

The nature of Fourier transform techniques, which are used to acquire the data, requires a relatively detailed knowledge of the relaxation parameters for the particular polymer investigated if the subsequent analysis is to be quantitative and unambiguous. Thus, the choice of pulse delays and possibly, pulse angles are dependent upon the spin-lattice relaxations (T_1) of the nonequivalent polymer carbons.^{13–15} In order to get a true equilibrium spectrum, a spectrum is acquired only after a time of approximately $4\text{--}5 \times T_1(\text{max.})$ has elapsed since the last pulse. Thus integrated peak intensities will not be misleading.⁶

Another problem of concern is the possibility that different carbons in the same molecule may possess different nuclear Overhauser enhancement (NOE).^{16,17} 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).⁶ 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 quantitative 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 assignments of the resonances. However, the chemical shift assignments taken from the several studies are very comprehensive and in good general agreement.^{2–10}

In this report we have attempted to develop a methodology for quantitative analytical determination of monomer compositions from the area of each resonances in a ^{13}C NMR spectra of copolymers and terpolymers, their results will be compared with those from the Infrared spectral data calibrated by standard reagents.

EXPERIMENTAL

Sample Preparation

Propylene heterophasic copolymers, propylene random copolymers, propylene random terpolymers, and ethylene–propylene–2-ethylidene-5-norborane (ENB) terpolymers were prepared in Yukong Complex, Corporation in Korea as described previously.^{2–8} 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.

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

[†] To whom correspondence should be addressed. Tel. 82-2-958-5957; Fax. 82-2958-5968; e-mail, leekb@kistmail.kist.re.kr.

collected by using a standard broadband decoupling experiments with interpulse delay, 12 s. 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 s; NMR running time, 12–36 hours/sample.

The methylene carbons, in each location, consistently gave T_1 values below 1 s. The methine carbon T_1 's ranged from 0.8 to 1.2 s while the methyl carbon T_1 's were approximately 2 s for the propylene units and 3.5 s for the butene-1 units. Consequently, a pulse spacing of 13.4 s was considered adequate for the ^{13}C NMR quantification in the case of that 75° pulse is given.

To improve signal to noise ratio, the free induction decays were multiplied by the 3 Hz line broadening factor. Chemical shifts for all spectra are referenced to the solvent line, orthodichlorobenzene (128.5 ppm), and its chemical shift was calibrated from that of tetramethylsilane (TMS). Spectra were recorded at 127°C . The free induction decays were stored in a 32 K data size.⁶

Nomenclature

Two different nomenclature have been used. At first, the nomenclature used to assign peaks to various carbons in the polypropylene random copolymer and propylene random terpolymer follows a way suggested by Carman and Wilkers.^{9,12} A methylene carbon is identified by a pair of Greek letters indicating 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 indicate that a methylene is at least 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., γS_δ^+ , a combined designation for γS_δ , γS_ϵ , γS_ζ , 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.⁹

RESULTS AND DISCUSSION

The instrumental conditions were chosen to maximize the signal to noise ratio of the final spectrum. It is expected that thermodynamic equilibrium is achieved due to the relatively long NMR pulse repetition time. Although T_1 's for the carbons are various according to their positions, reasonably slow pulse repetition rate and 75° pulse were given to achieve the magnetization equilibrium. As a result, quantitative determination from measured areas between types of carbons is considered to be valid. The method of analysis chosen is 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 because individual carbons are bound to two protons in average irrespective of kind of monomer. The calculation of % propylene and % ethylene relies on the structure shown below.

○ = propylene carbon, × = ethylene carbon

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

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 $\alpha\delta$ occurs. Because an $\alpha\gamma$ or $\alpha\delta$ carbon occurs in both an ethylene fragment and a propylene fragment, only half of the intensities of these peaks 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 condition 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 numbers 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

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

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. At least, 13 lines labeled alphabetically from lowfield to highfield are present as compared to 24 lines observed by Ray, Johnson, and Knox in a study of related ethylene-propylene copolymers.² Less signals are observed in these ¹³C NMR 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 seem to be from small amounts 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. Peaks 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 copolymers with different ethylene quantities were investigated and their spectra were not shown.

The propylene content is obtained according to eq 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,

$$P = 1/3 [I_{\alpha\alpha\text{-CH}_2} + I_{\text{CH}} + I_{\text{CH}_3} + 1/2(I_{\alpha\gamma} + I_{\alpha\delta})] \times 42.08 \text{ (M.W. of P)}$$

Table I. The chemical shift, signal assignments and peak area for ¹³C NMR spectra of propylene heterophasic copolymer samples (B900F, B310F, B340F) (Chemical shift is referenced to TMS at 127°C.^a)

Label	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	$\beta\delta$ of 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

^a P, propylene; E, ethylene.

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

The ethylene content is obtained by summing the methylene intensities according to eq 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.

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

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

The chemical shifts, assignments and signal areas for the polypropylene heterophasic copolymers are illustrated in Table I.

Propylene Random 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 copolymers examined, is shown in Figure 2. At least, 13 lines labeled alphabetically from lowfield to highfield are present. These series of copolymers allow the propylene-centered tridads and pentads to be observed. Peaks A, E, and G are assigned to $\alpha\alpha\text{-CH}_2$, CH, and CH_3 of PPPP, respectively. Five additional peaks resonated as shoulders of peaks A, H, and J seem to be small amounts 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 $\alpha\alpha\text{-CH}_2$ of EPE, $\alpha\gamma\text{-CH}_2$ of PPE, and $\beta\beta\text{-CH}_2$, respectively. Peaks D, H, I, and J are assigned to CH of PPE and CH_3 of PPPPE, CH_3 of EPPPPE, and CH_3 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 shifts, assignments and signals area are shown in Table II. The quantitative analysis of propylene

and ethylene has been made as described above.

$$P = 1/3 [I_{\alpha\alpha\text{-CH}_2} + I_{\text{CH}} + I_{\text{CH}_3} + 1/2(I_{\alpha\gamma} + I_{\alpha\delta})] \times 42.08 \text{ (M.W. of P)}$$

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

$$E \text{ (wt\%)}_{\text{R141N}} = [E/(P + E)] = 1.8\%$$

Another polypropylene random copolymer with different ethylene quantity was investigated and its spectrum was not shown. The chemical shifts, assignments and signal area measurement for the polypropylene random copolymers are tabulated in Table II.

Propylene Random Terpolymer

In these terpolymer, ethylene and butene-1 are incorporated in polypropylene. A ^{13}C NMR spectrum (C24309/25) for one of the propylene random terpolymer, which is typical of the terpolymers examined, is shown in Figure 3. At least, 14 lines labeled alphabetically from lowfield to highfield are present. These terpolymer allow the propylene-centered tirads, terads and pentads to be observed. The quantitative

Table II. The chemical shift, signal assignments and peak area for ^{13}C NMR spectra of propylene random copolymer samples (R141N and R930Y) (Chemical shift is referenced to TMS at 127°C .)

Label	Chemical shift/ppm	Assignment	Area	
			R141N	R930Y
A	47.0	$\alpha\alpha\text{-CH}_2$ of PPP	5459	5312
B	46.5	$\alpha\alpha\text{-CH}_2$ of EPE		
C	38.4	$\alpha\gamma\text{-CH}_2$ of PPE	345	230
D	31.2	CH of PPE	463	233
E	29.4	CH of PPP	5035	5173
F	25.0	$\beta\beta\text{-CH}_2$	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

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

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 eq 3. The division by four gives the number of butylene in the propylene random terpolymer. The weight percent calculation for the monomer composition in polypropylene random terpolymer were made as described above.

$$P = 1/3 [I_{\alpha\alpha\text{-CH}_2} + I_{\text{CH}} + I_{\text{CH}_3} + 1/2(I_{\alpha\gamma} + I_{\alpha\delta})] \times 42.08 \text{ (M.W. of P)}$$

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

$$B = [I_{\alpha\alpha\text{-CH}_2 \text{ of B}} + I_{\text{CH of B}} + I_{2\text{-CH}_2 \text{ of B}} + I_{\text{CH}_3 \text{ of B}}] \times 56.11 \text{ (M.W. of B)}$$

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

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

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 determined in this study are listed in Table III.

Ethylene Propylene Methylene Linkage

The copolymer system shown in Figure 4 differs significantly from those studied previously. Figure 4 shows the ¹³C 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 $\alpha\alpha$ -CH₂ and CH₃ regions of the spectrum in comparison to ethylene-propylene copolymer synthesized by the isotactic

catalyst. On the other hand, the chemical environment of the $\alpha\alpha$ -CH₂ and CH₃ 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 counts a 100% propylene fragment. For every propylene followed by an ethylene, either an $\alpha\gamma$ or an $\alpha\delta$ occurs. Because αS_γ , αS_δ , αS_γ , and αS_β carbons occur in both an ethylene fragment, only half the intensities of these peak is used to measure propylene.

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

Table III. The chemical shift, signal assignments and peak area for ¹³C NMR spectra of propylene random terpolymer samples (C243/23, C243/25, C243/09/37, and C243/34) (Chemical shift is referenced to TMS at 127°C.^a)

Label	Chemical shift/ppm	Assignment	Area			
			C243/23	C243/25	C243/37	C243/34
A	47.2	$\alpha\alpha$ -CH ₂ of PPPB				
B	46.9	$\alpha\alpha$ -CH ₂ of PPPP	5746	4729	3541	5271
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 of 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

^a B, butene-1.

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

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

Table IV. The chemical shift, signal assignments and peak area for ^{13}C NMR spectra of ethylene-propylene rubber and EPDM incorporated with ENB (E120, E512F, E505, and E501A) (Chemical shift is referenced to TMS at 127°C.)

Label	Chemical shift/ppm	Assignment	Area			
			C243/23	C243/25	C243/37	C243/34
A	46.1	αS_α				
B	39.2	αS_γ				
C	38.8	αS_δ^+	363	428	358	1226
D	38.3	αS_γ				
E	38.0	αS_δ^+				
F	35.3	αS_β	395	381	886	1213
G	34.0	γT_δ^+	2536	2264	2888	2809
H	33.7	δT_δ^+				
I	31.4	βT_δ^+	223	555	977	1480
J	31.2	γS_γ				
K	30.8	γS_δ^+	20420	12871	7186	6803
L	30.4	δS_δ^+				
M	28.3	βS_γ	5408	3903	3669	3952
N	27.9	βS_δ^+				
O	25.3	βS_β	357	408	655	872
P	21.1	αP_β	3267	2830	3697	4807
Q	20.3	αP_β				
R	34.4	βT_β	—	103	200	300
S	26.9	βS_δ	—	408	—	—
T	31.7	βT_γ	—	—	180	735

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

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

The chemical shifts, assignments and area measurements determined are included in Table IV.

Ethylene-Propylene-ENB Terpolymer

In this type of terpolymer, 2-ethylidene-5-norborane (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,

Table V. Comparative analytical data list (unit: wt%)

Sample	Comonomer	Uniroyal chemical, U.S.A. ^a (IR)	This study (^{13}C NMR)
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

^a Unpublished results determined by Infrared spectroscopic method.

leads to the complicated ^{13}C NMR spectrum as shown in Figure 5. The ^{13}C 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 was made as described above.

$$P = 1/3 [\alpha S_\alpha + 1/2(\alpha S_\gamma + \alpha S_\delta + \alpha S_\gamma + \alpha S_\beta) + \gamma T_\delta + \delta T_\delta + \beta T_\delta^+ + \alpha P_\beta + \beta P_\beta] \times 42.08 \text{ (M.W. of P)}$$

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

Two additional EPDM rubbers with different ethylene, propylene, and ENB quantities were investigated and their spectrum were not shown. The chemical shifts, assignments and area measurements determined are included in Table IV.

CONCLUSIONS

The ^{13}C NMR determinations for monomer composition in diverse polypropylene polymers are in good

agreement with results obtained from Infrared spectroscopic measurements on the same systems, which were carried out in Uniroyal Chemical, U.S.A. (shown in Table V). Thus, ^{13}C NMR methodology for the determination of monomer compositions in diverse polypropylene polymers would be more reliable and convenient as far as the ^{13}C NMR assignments are unambiguous in terms of the error originated from the uncertainty of standard samples chosen for Infrared spectroscopic determination.^{18,19}

REFERENCES

1. A. E. Tonelli, "NMR Spectroscopy and Polymer Microstructure," VCH, New York, N.Y., 1989.
2. G. J. Ray, P. E. Johnson, and J. R. Knox, *Macromolecules*, **10**, 773 (1977).
3. G. V. D. Velden, *Macromolecules*, **16**, 85 (1983).
4. G. J. Ray, J. Spanswick, J. R. Knox, and C. Serres, *Macromolecules*, **14**, 1323 (1981).
5. M. Kakugo, Y. Natio, K. Mizunuma, and T. Miyatake, *Macromolecules*, **15**, 1150 (1982).
6. D. E. Axelson, L. Mandelkern, and G. C. Levy, *Macromolecules*, **10**, 557 (1977).
7. H. N. Cheng, *Macromolecules*, **17**, 1950 (1984).
8. P. Locatelli, M. C. Sacchi, I. Tritto, and F. Forlini, *Macromolecules*, **23**, 2406 (1990).
9. C. J. Carman, R. A. Harrington, and C. E. Wilkes, *Macromolecules*, **10**, 536 (1977).
10. E. T. Hsieh and J. C. Randall, *Macromolecules*, **15**, 353 (1982).
11. J. C. Randall, *Macromolecules*, **11**, 592 (1978).
12. C. E. Wilkes, C. J. Carman, and R. A. Harrington, *J. Polym. Sci., Symposium*, **43**, 237 (1973).
13. T. Asakura and Y. Doi, *Macromolecules*, **16**, 786 (1983).
14. R. A. Komoroski, J. Maxfield, F. Sakaguchi, and L. Mandelkern, *Macromolecules*, **10**, 550 (1976).
15. T. Asakura and Y. Doi, *Macromolecules*, **13**, 454 (1980).
16. A. E. Derome, "Modern NMR Techniques for Chemistry Research," Pergamon Press Ltd., Oxford, U.K. 1987.
17. D. Neuhaus and M. Williamson, "The Nuclear Overhauser Effect," VCH, New York, N.Y., 1989.
18. F. Ciampelli and A. Valvassori, *J. Polym. Sci., C*, **16**, 377 (1967).
19. G. Bucci and T. Simonazzi, *J. Polym. Sci., C*, **7**, 203 (1964).