Carbon-13 Nuclear Magnetic Resonance Determination of Monomer Composition and Sequence Distributions in Ethylene–Propylene Copolymers Prepared with a Stereoregular Catalyst System

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ABSTRACT: The ^{13}C nuclear magnetic resonance (NMR) spectra of ethylene–propylene copolymers prepared by an isotactic catalyst system are less complicated than those of ethylene–propylene rubbers. In the latter polymer, the presence of propylene inversions, as well as atactic methyl placements, causes a large number of peaks which are absent in the polymer prepared by an isotactic catalyst. The simplified spectrum made it possible to calculate monomer composition using only the data from the methylene region of the ^{13}C NMR spectrum. Furthermore complete dyad and triad, as well as partial tetrad and pentad, distributions have been determined for copolymers containing from 15 to 92 mol % propylene. Both the fraction of each monomer in sequences of length one and two as well as the fraction of sequences of each monomer having length one and two have also been calculated.

Carbon-13 NMR spectra have been used to determine monomer composition and sequence distributions in ethylene–propylene copolymers,[2–6] most of which were ethylene–propylene rubbers (EPR). The copolymer system reported upon in this paper differed significantly from those studied previously in two important aspects. First, we found no propylene head-to-head or tail-to-tail inversions. Second, we found that, within the limits of our detectability, the propylene present in the system gave rise to isotactic linkages exclusively. Both factors lead to a simplification of the resonance patterns in several spectral regions. This simplification led to the assignment of certain tetrads and pentads which have not been reported previously. We also describe a method for calculating monomer compositions in the copolymer which relies only on the methylene region of the spectrum. This method has been applied to copolymers ranging from 15 to 92 mol % propylene. Finally, we show how the ^{13}C NMR data can be used to determine some monomer and sequence distributions.

Experimental Section

(A) Materials. The monomers were Phillips polymerization grade ethylene and propylene. The propylene was purified further by passage through a column of 13X molecular sieves. Linde high purity hydrogen was used as the chain transfer agent.

(B) Polymerization Procedure. The copolymers were prepared in a batch process under solvent free conditions in an agitated 2-L autoclave. The desired quantities of both monomers and hydrogen were added to the reactor and brought up to the polymerization temperature. Then polymerization was initiated by the $TiCl_3$-based catalyst, which was washed into the reactor with a small quantity of liquid propylene. Throughout the run the temperature was maintained at ±1 °C by a heat transfer fluid circulated through a jacket on the outside of the reactor. No additional monomer was added during the run because monomer conversion was held to about 2%. Finally, the monomers were vented rapidly to terminate polymerization. Before analysis, the nonextracted polymers were devolatilized at 160 °F for 2 h in a vacuum oven.

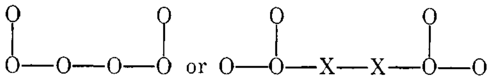
(C) Instrumental Conditions. Random-noise, proton-decoupled ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer, which operates in the Fourier transform mode at 20 MHz. The spectra were the result of from 4K to 20K acquisitions using an acquisition time of 2.73 s and 8192 word memory, which gave a spectral width of 1500 Hz. A pulse width of 16 μs (~80 °C) was used with no delay between acquisitions. Spectra were obtained at 120 to 130 °C. Several peak positions were found to be temperature dependent, and optimum resolution was obtained above 120 °C. Peak areas were measured by a planimeter. Peak positions were referenced to tetramethylsilane (TMS). This was accomplished by adding 5% (v/v) TMS to a sample and accumulating 100 transients. The resultant spectrum had sufficient signal to noise to determine the chemical shift of the $^{t}C_{EPE}$ peak. In all other spectra this value (33.1 ppm) was assigned to the $^{t}C_{EPE}$ peak and other chemical shifts were assigned relative to this value.

Samples were prepared as 10% (w/v) of polymer in tetrachlorothiophene (TCT) and sufficient benzene-d_6 was added to provide a deuterium lock signal. *o*-Dichlorobenzene (ODCB) and 1,2,4-trichlorobenzene (TCB) were also tried as solvents. No significant solvent dependence was observed. However, both ODCB and TCB have protonated aromatic carbons which have relatively short T_1's that, combined with their high concentration, give rise to a dynamic range problem. This limits the effective signal averaging to about 4K transients. Because all the carbons in TCT are bonded to a chlorine, they all have long T_1's and, consequently, are readily saturated by the data acquisition process we used. As a result we were able to increase our effective averaging to at least 20K transients without encountering dynamic range problems.

The nomenclature used to assign peaks to various carbons in the polymer follows that suggested by Carman and Wilkes.[4] A methylene carbon is identified by a pair of Greek letters which indicate 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 indicates that a methylene is at least δ to a tertiary carbon but may be farther removed. The methylene carbon nomenclature is summarized in Figure 1. Tertiary carbons and methyl carbons are denoted by ^{t}C-XXX and CH_3-XXX, respectively. For example, the central tertiary carbon in a run of three propylene units is denoted as ^{t}C-PPP, while the central methyl carbon in a propylene unit bonded to two propylene units on one side and two ethylene units on the other is denoted as CH_3-PPPEE.

Results and Discussion

Chemical Shifts. Figure 2 shows the ^{13}C NMR spectra of (a) a typical ethylene–propylene rubber and (b) of an ethylene–propylene copolymer prepared by an isotactic catalyst. The most obvious difference between the two spectra is the absence of peaks at 34.8, 33.4, and 27.7 pm in Figure 2b. The peak at 34.8 is assigned to an $\alpha\beta$ carbon which can occur only in sequences in which the propylene units take head-to-head or tail-to-tail configuration, i.e.,



$$\overset{\overset{\textstyle O}{|}}{O}—O—O—\overset{\overset{\textstyle O}{|}}{O} \quad \text{or} \quad O—\overset{\overset{\textstyle O}{|}}{O}—X—X—\overset{\overset{\textstyle O}{|}}{O}—O$$

where O's represent propylene carbons and X's represent ethylene carbons. The peak at 27.7 ppm is assigned to a $\beta\delta$ carbon, which is a methylene carbon in a sequence having ethylene between two tail-to-tail propylenes or two ethylenes between head-to-head propylenes. The peak at 33.4 ppm is assigned to a methine carbon in the sequences $P\underleftarrow{\bar{P}}E$ and $E\underleftarrow{\bar{P}}E$, where $\underleftarrow{\bar{P}}$ denotes an inverted propylene[5] molecule. The absence of these peaks in Figure 2b leads to the conclusion that there are no propylene inversions in the copolymer prepared

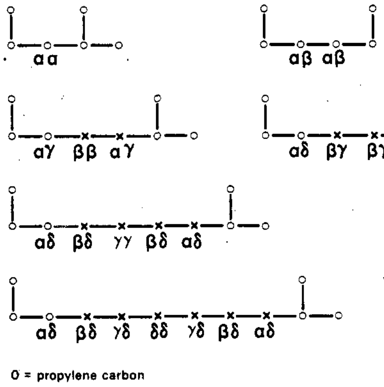


Figure 1. Description of the nomenclature used to designate methylene carbons in ethylene–propylene copolymers.

by the isotactic catalyst system. Also, the spectrum in Figure 2a has peaks at 33.7 and 38.4 ppm, which have been assigned[3,5] to the $\alpha\beta$ and $\alpha\gamma$ resonances in sequences having a racemic configuration. The absence of a peak at 38.4 ppm in Figure 2b indicates that racemic configurations are absent and that only meso configurations are formed by the isotactic catalyst. Further evidence to support this observation is the sharpening of the lines in the $\alpha\alpha$ and CH_3 regions of the spectrum. 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 $\alpha\alpha$ and CH_3 regions of the spectrum in Figure 2a. On the other hand, the chemical environment of the $\alpha\alpha$ and CH_3 carbons in the copolymer prepared by an isotactic catalyst is influenced only by the ethylene–propylene sequence distributions and thus gives rise to the sharp resonances shown for the $\alpha\alpha$ and CH_3 carbons in Figure 2b.

Figure 3 shows the ^{13}C spectra of three isotactic copolymers which vary from 28 to 85 mol % in propylene content. The variation in peak intensity with propylene content was used to assign various peaks to specific tetrad and pentad sequences as discussed below.

Figures 4 thru 7 are partial spectra of samples B (85 mol % P), C (46 mol % P), and D (28 mol % P). Figure 4 shows an expansion of the $\alpha\alpha$ region of these spectra. Because the $\alpha\alpha$ resonance is due to a propylene dyad, the next highest sequence distribution to affect this resonance would be tetrads of which three are expected (PPPE and EPPP tetrads are identical in the NMR). Indeed, three peaks are observed and, from low to high field, were assigned to the PPPP, PPPE, and EPPE tetrads from their relative intensities at different propylene levels.

Figure 5 shows an expansion of the $\alpha\gamma$ and $\alpha\delta$ regions of the spectrum. Because the $\alpha\gamma$ carbon occurs in a PEP sequence, any additional splitting of the $\alpha\gamma$ peak should be due to the three pentads: PPEPP, PPEPE, and EPEPE. Only two peaks are observed. The low-field peak is assigned to both $\alpha\gamma$ carbons in the sequence EPEPE as well as the $\alpha\gamma$ carbon associated with the underlined propylene in the sequence PPE$\underline{\text{P}}$E. The high-field peak is assigned to both $\alpha\gamma$ carbons in the sequence PPEPP as well as the $\alpha\gamma$ carbon associated with the underlined propylene in the sequence P$\underline{\text{P}}$EPE. The $\alpha\delta$ carbon occurs in sequences of the form $PE(E)_{n\geq1}$. Two peaks are observed for the $\alpha\delta$ carbon. The low-field peak is assigned to the sequence $PPE(E)_{n\geq1}$ and the high-field peak is assigned to the sequence $EPE(E)_{n\geq1}$. Figure 6 shows an expansion of the ${}^{t}C_{PPP}$, $\beta\delta$, and $\beta\beta$ regions of the spectrum. As with the $\alpha\delta$ resonance, the $\beta\delta$ resonance shows two peaks with the low-field peak assigned to the $EPE(E)_{n\geq1}$ sequence and the high-field peak assigned to the $PPE(E)_{n\geq1}$ sequence. Unlike the $\alpha\gamma$ resonance, the $\beta\beta$ resonance is resolved into three peaks which have been assigned to the sequences EPEPE, PPEPE, and PPEPP in order of increasing field. The ${}^{t}C_{PPP}$ shows some pentad splitting but this information is more easily obtained from the methyl region.

The expansion of the methyl region is shown in Figure 7.

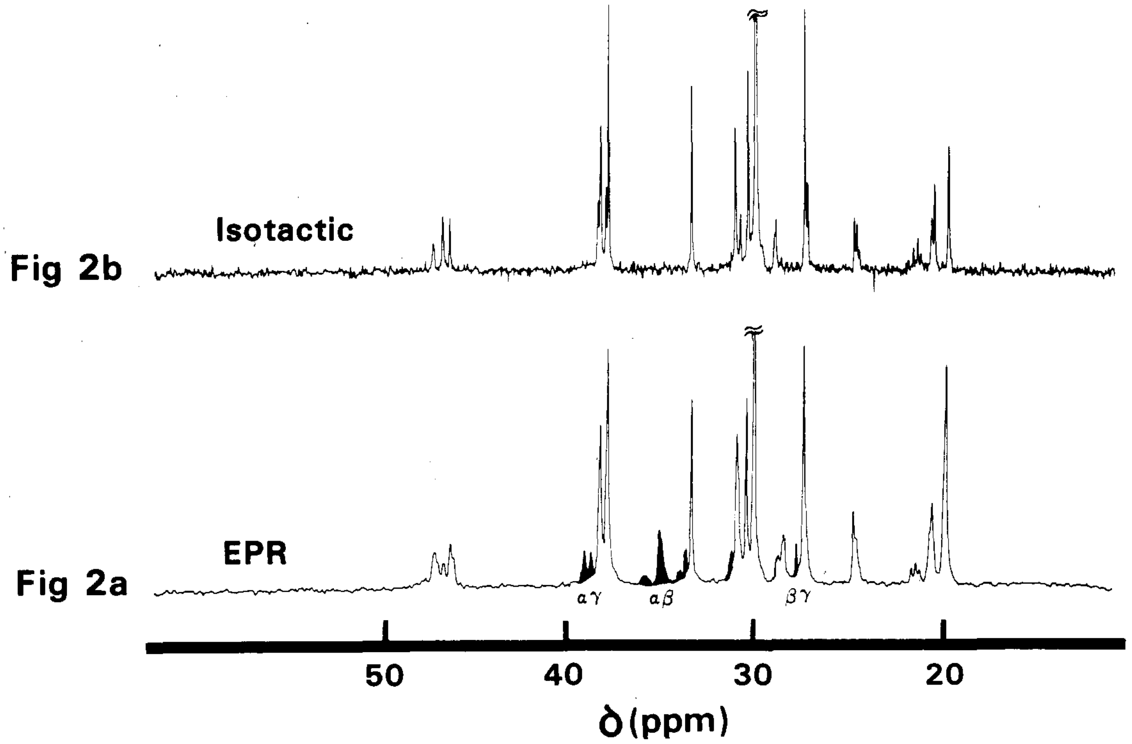


Figure 2. Carbon-13 NMR spectra of typical ethylene–propylene copolymers. (a) A spectrum of an ethylene–propylene rubber (EPR). (b) A spectrum of an ethylene–propylene copolymer prepared by an isotactic catalyst system.

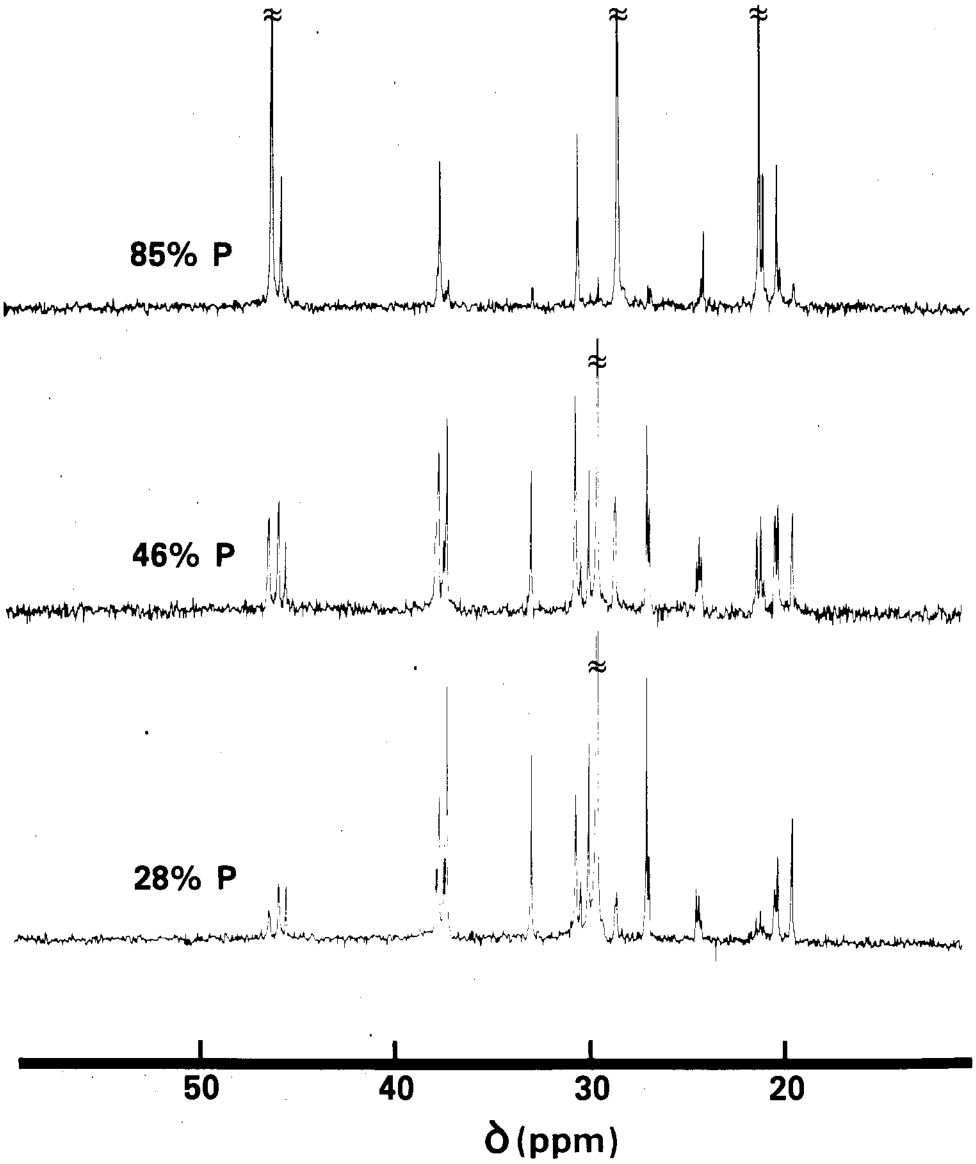


Figure 3. Carbon-13 NMR spectra of ethylene-propylene copolymers containing 28, 46, and 85 mol % propylene.

There are three groups of peaks which have been assigned previously[4,5] to the triads PPP, PPE, and EPE in order of increasing field. The PPP triad is split into three peaks which in order of increasing field can be assigned to the PPPPP, PPPPE, and EPPPE pentads. The EPE centered resonance has no further splitting. The PPE triad can give rise to four pentads: PPPEP, PPPEE, EPPEP, and EPPEE. However, only two pentad peaks are observed. Because the EPE triad shows no splitting into pentads, it is reasonable to assume that once an ethylene has been attached to a propylene, the propylene methyl is no longer affected by what adds to the other side of the ethylene. Consequently, the pentads PPPEP and PPPEE can be expected to give a single peak. The same is true for EPPEP and EPPEE, so that the low field peak of the PPE triad is assigned to PPPE$_{\mathrm{E}}^{\mathrm{P}}$ and the high peak to EPPE$_{\mathrm{E}}^{\mathrm{P}}$ where ~E$_{\mathrm{E}}^{\mathrm{P}}$ refers to ~EP + ~EE.

Quantitative Analysis. The instrumental conditions were chosen to maximize the signal-to-noise ratio of the final spectrum. It is expected that due to the relatively rapid pulse repetition rate that thermodynamic equilibrium is not achieved. As a result, comparison of measured areas between types of carbons is not quantitatively valid. However, the T_1's for the methylene carbons are assumed to be reasonably close so that the area of each methylene peak is a quantitative measure of the number of carbons giving rise to that peak. The method of analysis chosen was to calculate % E, % P, dyad, and, when available, tetrad distributions from the methylene peaks. Triad and pentad distributions were calculated from the methyl region of the spectrum after the measured methyl areas had been normalized to % P calculated from methylene data. In performing these calculations, we assumed that nuclear Overhauser effects were uniform[8] for all the peaks in the spectrum.

The calculation of % P and % E relies on the structures shown in Figure 1. In these structures every $\alpha\alpha$ carbon counts a propylene fragment which is followed by a propylene. 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 peaks is used to measure propylene. Consequently, the propylene content is given by

$$P = I_{\alpha\alpha} + \tfrac{1}{2}(I_{\alpha\gamma} + I_{\alpha\delta}) \qquad (1)$$

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 due to ethylene. This quantity represents the number of methylenes occurring

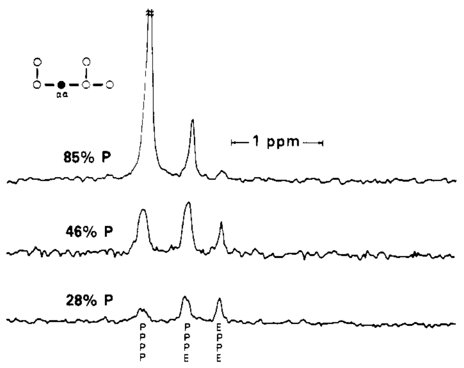


Figure 4. Expansion of the carbon-13 NMR spectra of the $\alpha\alpha$ region of ethylene–propylene copolymers containing 28, 46, and 85 mol, % propylene.

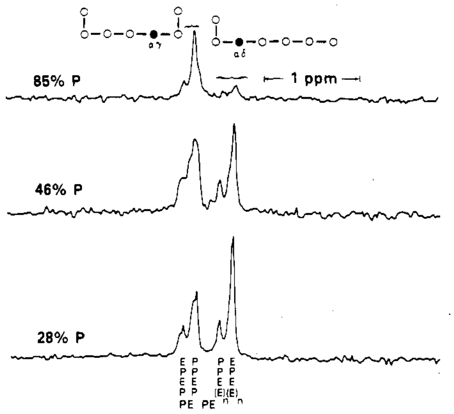


Figure 5. Expansion of the carbon-13 NMR spectra of the $\alpha\gamma$ and $\alpha\delta$ regions of ethylene–propylene copolymers containing 28, 46, and 85 mol % propylene.

in ethylene sequences and division by two gives the number of ethylenes in the copolymer. Thus:

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

The mole fractions of ethylene and propylene in the polymer are then derived from the normalization condition, $E + P = 1$. Several other equations can be derived to estimate E and P. However, we believe that eq 1 and 2, which utilize all the methylene data, will be most consistent over a broad range of monomer compositions.

The dyad distributions are given by the equations

$$\mathrm{PP} = I_{\alpha\alpha} \quad (3)$$

$$\mathrm{PE} = I_{\alpha\gamma} + I_{\alpha\delta} \quad (4)$$

$$\mathrm{EE} = \tfrac{1}{2}(I_{\beta\delta} + I_{\delta\delta}) + \tfrac{1}{4}I_{\gamma\delta} \quad (5)$$

The internal consistency of these calculations can be checked by the Bovey relationships.[7]

$$P = \mathrm{PP} + \tfrac{1}{2}\mathrm{PE} \quad (6)$$

$$E = \mathrm{EE} + \tfrac{1}{2}\mathrm{PE} \quad (7)$$

In all cases the values of P and E calculated from eq 6 and 7 are in good agreement with those values calculated from eq 1 and 2.

The P centered triad distribution is obtained directly from the methyl region of the spectrum after normalization to % P. The E centered triads can be obtained from the methylene data by the following relationships:

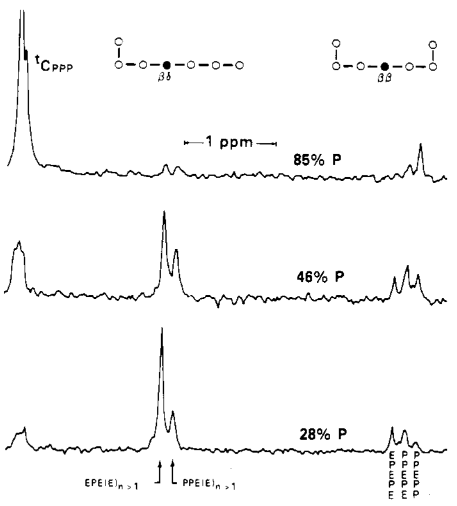


Figure 6. Expansion of the carbon-13 NMR spectra of the ${}^{t}\mathrm{C}_{\mathrm{PPP}}$, $\beta\delta$, and $\beta\beta$ regions of ethylene–propylene copolymers containing 28, 46, and 85 mol % propylene.

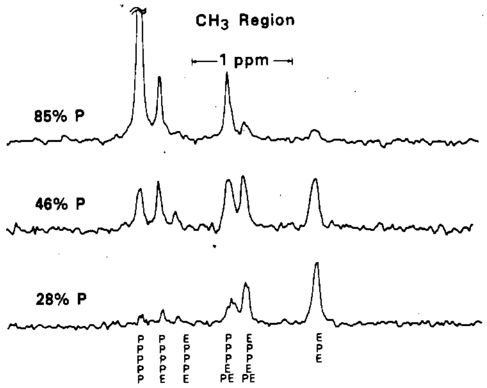


Figure 7. Expansion of the carbon-13 NMR spectra of the methyl region of ethylene–propylene copolymers containing 28, 46, and 85 mol % propylene.

$$\mathrm{PEP} = I_{\beta\beta} = \tfrac{1}{2}I_{\alpha\gamma} \quad (8)$$

$$\mathrm{PEE} = I_{\alpha\delta} = I_{\beta\delta} \quad (9)$$

$$\mathrm{EEE} = \tfrac{1}{2}I_{\delta\delta} + \tfrac{1}{4}I_{\gamma\delta} \quad (10)$$

Partial tetrad and pentad assignments are directly available from individual peaks in the $\alpha\alpha$ and $\mathrm{CH_3}$ regions of the spectrum. Again, these values are normalized.

The chemical shift assignments and area measurements of the various copolymer peaks for samples A thru E, that were determined in this study, are listed in Table I. Equations 1 thru 10 give the monomer content and n-ad distributions for these samples as shown in Table II. The experimental n-ad distributions can be compared with those obtained using Bernoulian and first- and second-order Markovian models to examine the polymerization mechanism. This will be discussed in a future paper. It should be noted, however, that the tetrad and pentad distributions rapidly become unreliable because of the small peak intensities observed as the ethylene or propylene content exceeds 70 mol %.

Information is available from the spectral data concerning the monomer and sequence distributions in the samples. The monomer distribution is defined as the number of moles of a given monomer in a given sequence length divided by the total mole fraction of that monomer in the copolymer. If E_n and P_n are the monomer distributions of ethylene and propylene respectively in sequences n units long, then

Table I
Chemical Shift Assignments and Area Measurements for Samples A, B, C, D, and E

Carbon type	Sequence type	δ^a	% area^b A	B	C	D	E
$\alpha\alpha$	PPPP	46.3	23.75	20.91	4.46	1.27	0.34
	PPPE	45.8	4.53	5.30	4.40	2.06	0.76
	EPPE	45.6	0.49	0.72	1.47	1.32	0.89
$\alpha\gamma$	EPEPE^c	37.9					
	PPEP$_{\mathrm{E}}^{\mathrm{P}c}$	37.8	5.51	7.54	9.86	7.03	3.39
$\alpha\delta$	PPEE$_{n>1}$^{c}	37.5					
	EPEE$_{n>1}$^{c}	37.4	0.61	1.17	7.20	9.09	7.03
^{t}C	EPE	33.1	0.37	0.54	4.13	4.92	3.70
^{t}C	PPE	30.7	5.63	7.13	7.66	5.07	3.24
$\gamma\gamma^d$		30.6	0.00	0.22	1.40	1.69	0.98
$\gamma\delta$		30.1	0.24	0.36	4.06	4.44	5.35
$\delta\delta$		29.8	0.12	0.81	19.19	38.95	58.37
^{t}C	PPP	28.7	25.34	22.07	6.00	2.22	0.76
$\beta\delta$	EPEE$_{n>1}$	25.6	0.0	0.36	5.13	6.29	6.21
	PPEE$_{n>1}$	25.5	0.0	0.45	3.06	2.17	1.10
$\beta\beta$	EPEPE	24.7	0.0	0.27	1.00	1.00	0.70
	PPEPE	24.6	0.61	1.17	2.13	1.16	0.52
	PPEPP	24.4	1.83	2.42	1.47	0.48	0.15
CH_3	PPPPP	21.6	19.09	16.78	2.73	0.58	0.34
	PPPPE	21.4	4.90	3.59	2.53	0.69	0.49
	EPPPE	21.2	0.49	0.54	0.80	0.42	0.24
	PPPE$_{\mathrm{E}}^{\mathrm{P}}$	20.7	4.29	5.48	3.93	2.11	0.82
	EPPE$_{\mathrm{E}}^{\mathrm{P}}$	20.5	0.98	0.99	3.53	2.64	1.28
	EPE	19.8	1.22	1.17	3.86	4.39	3.33

[a] Chemical shifts in ppm downfield from TMS. [b] Areas measured by planimeter and normalized to 100%. [c] The individual areas of these sequence types were not measured separately. [d] Peak which gave a noticeable shift with temperature. Below 120 °C this peak is not resolved from the ^{t}C-PPE peak.

Table II
Monomer Content and *n*-ad Distributions for Samples A through E

	A	B	C	D	E
P	0.917	0.857	0.447	0.282	0.155
E	0.083	0.143	0.553	0.718	0.845
PP	0.83	0.74	0.24	0.10	0.04
PE	0.18	0.24	0.40	0.36	0.22
EE	0.00	0.02	0.35	0.55	0.74
PPP	0.72	0.63	0.16	0.04	0.02
PPE	0.16	0.19	0.19	0.12	0.05
EPE	0.04	0.04	0.10	0.11	0.08
PEP	0.07	0.10	0.11	0.06	0.03
PEE	0.02	0.03	0.17	0.20	0.15
EEE	0.00	0.01	0.23	0.43	0.63
PPPP	0.68	0.57	0.10	0.03	0.02
PPPE	0.13	0.14	0.10	0.04	0.05
EPPE	0.01	0.02	0.03	0.03	0.08
PEEP	0.00	0.01	0.10	0.09	0.03
PEEE	0.02	0.02	0.10	0.15	0.15
EEEE	0.00	0.00	0.18	0.36	0.63
PPPPP	0.55	0.46	0.06	0.01	0.01
PPPPE	0.14	0.10	0.06	0.02	0.01
EPPPE	0.01	0.01	0.02	0.01	0.00
PPPE$_{\mathrm{E}}^{\mathrm{P}}$	0.12	0.15	0.09	0.05	0.02
EPPE$_{\mathrm{E}}^{\mathrm{P}}$	0.03	0.03	0.08	0.06	0.03
PPEPP		/	5	0.07	0.03
0.01	0.00				
PPEPE	0.02	0.03	0.05	0.02	0.01
EPEPE	0.00	0.01	0.02	0.02	0.02

$$E_1 = I_{\beta\beta}/E = \tfrac{1}{2}I_{\alpha\gamma}/E \qquad (11)$$

$$E_2 = 2I_{\gamma\gamma}/E = (I_{\beta\delta} - I_{\gamma\delta})/E \qquad (12)$$

$$P_1 = (I_{\mathrm{CH_3\text{-}PE}})/P \qquad (13)$$

$$P_2 = 2(I_{\alpha\alpha\text{-}\mathrm{EPPE}})P \qquad (14)$$

Table III
Monomer Distribution and Sequence Distribution for Samples A through E

Distribution	A	B	C	D	E
% P	91.7	85.7	44.7	28.2	15.5
% E	8.3	14.3	55.3	71.8	84.5
E_1	0.96	0.72	0.21	0.11	0.04
E_2	0	0.09	0.18	0.12	0.05
SD_{E1}	0.80	0.89	0.54	0.33	0.26
SD_{E2}	0	0.05	0.24	0.25	0.19
P_1	0.04	0.04	0.22	0.40	0.51
P_2	0.03	0.05	0.16	0.21	0.25
SD_{P1}	0.41	0.29	0.49	0.64	0.71
SD_{P2}	0.16	0.16	0.17	0.16	0.17

In eq 12, we use the identity $I_{\gamma\gamma} = \tfrac{1}{2}(I_{\beta\delta} - I_{\gamma\delta})$ which can be derived from examining the structures in Figure 1. The chemical shift of the $\gamma\gamma$ carbon was found to be temperature dependent and was only resolved from the $^t\mathrm{C}_{\mathrm{PPE}}$ peak at temperatures above 120 °C. Also, the $\gamma\gamma$ peak area is generally small and difficult to measure. These factors suggest that the most reliable measurement of $I_{\gamma\gamma}$ is given by $\tfrac{1}{2}(I_{\beta\delta} - I_{\gamma\delta})$.

We can calculate the sequence distribution because each ethylene sequence begins with either an $\alpha\gamma$ or $\alpha\delta$ carbon. When the sequence begins with an $\alpha\gamma$ carbon it must end with an $\alpha\gamma$ carbon, and when a sequence begins with an $\alpha\delta$ carbon it must end with an $\alpha\delta$ carbon so that the number of ethylene sequences is given by $\tfrac{1}{2}(\alpha\gamma + \alpha\delta)$. Because the termination of an ethylene sequence is the beginning of a propylene sequence, the number of propylene sequences equals the number of ethylene sequences at high molecular weight. We define SD_{En} and SD_{Pn} as the sequence distributions of length n for ethylene and propylene respectively so that

$$SD_{E1} = I_{\beta\beta}/\tfrac{1}{2}(I_{\alpha\gamma} + I_{\alpha\delta}) \qquad (15)$$

$$SD_{E2} = I_{\gamma\gamma}/\tfrac{1}{2}(I_{\alpha\gamma} + I_{\alpha\delta}) = (I_{\beta\delta} - I_{\gamma\delta})/(I_{\alpha\gamma} + I_{\alpha\delta}) \qquad (16)$$

$$\mathrm{SD_{P1}} = (I_{\mathrm{CH_3\text{-}EPE}})/\tfrac{1}{2}(I_{\alpha\gamma} + I_{\alpha\delta}) \quad (17)$$

$$\mathrm{SD_{P2}} = (I_{\alpha\alpha\text{-}\mathrm{EPPE}})/\tfrac{1}{2}(I_{\alpha\gamma} + I_{\alpha\delta}) \quad (18)$$

The values of the monomer distribution and sequence distribution are given in Table III. These values combined with the distributional information can be used to deduce the copolymerization mechanism.

Conclusions

It is possible, using carbon-13 NMR, to determine all n-ad distributions thru triads in ethylene–propylene copolymers using eq 1 thru 10. In the structurally more simple copolymers reported here, we were able to derive partial tetrad and pentad distributions. Since the spectral regions used to obtain this information show considerably less resolution in rubbers it is unlikely that this information can be derived from spectra of these polymers.

Finally, we have shown that it is possible to obtain information concerning both the monomer and sequence distributions. It will be shown in a subsequent paper how this information can be used to examine the mechanism of the polymerization process.

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An NMR Relaxation Study of a Hexafluoroisobutylene/Vinylidene Fluoride Copolymer (HFIB/VF$_2$)

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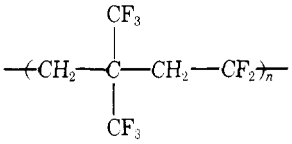
ABSTRACT: Fluorine and proton NMR relaxation data of HFIB/VF$_2$ have revealed an α relaxation associated with the glass transition. This relaxation is characterized by an activation energy of approximately 73 kcal/mol. The transition is observed in both the proton and fluorine data and the proton spin–spin relaxation times can be deconvoluted into crystalline and amorphous components above the glass transition temperature. A local mode relaxation with activation energy of ~9 kcal/mol is observed in the proton data. Reorientation of the CF$_3$ groups is observed in the fluorine data with an activation energy of approximately 5 kcal/mol. What begins as two separate reorientational processes at low temperature probably becomes a complicated reorientational process in the high-temperature limit involving these two processes and the glass transition.

Poly(3,3,3-trifluoro-2-trifluoromethylpropene/1,1-difluoroethylene) (HFIB/VF$_2$) is a copolymer made from a 50/50 molar composition of hexafluoroisobutylene (HFIB) and vinylidene fluoride (VF$_2$).[1,2] The polymer is believed to assume a configuration in which the monomer units add in a head-to-tail fashion giving rise to a copolymer structure of[1]



$$-\!\!\left(\mathrm{CH_2}-\underset{\mathrm{CF_3}}{\overset{\mathrm{CF_3}}{\underset{|}{\overset{|}{\mathrm{C}}}}}-\mathrm{CH_2}-\mathrm{CF_2}\right)_{\!n}\!\!-$$

The copolymer is highly crystalline with a melting point of 600 K.[2] It is reported to have more desirable physical properties at elevated temperatures than other fluoropolymers.[2] For example, HFIB/VF$_2$ has a high modulus and tensile strength retention at high temperatures; its heat distortion temperature is 493 K at 264 psi of stress.[2] It is superior to other fluoropolymers in surface hardness, abrasion, and scratch resistance.[2] Its good resistance to attack by organic and inorganic solvents, low water vapor permeability, and excellent nonsticking and nonwetting properties make it a very attractive material to replace other fluoropolymers in many applications.

A recent dielectric and dynamic mechanical relaxation study of HFIB/VF$_2$ has shown two relaxations in the temperature range 100 to 460 K.[3] The low-temperature relaxation exhibits a maximum in tan δ at 210 K with an activation energy of 9 kcal/mol. The relaxation is ascribed to a local mode motion of low amplitude in the backbone of the polymer. The high-temperature relaxation, which was assigned to the glass transition, has a high activation energy and does not exhibit the characteristic WFL type curve over the frequency range studied. HFIB/VF$_2$ is such a highly crystalline material that preliminary attempts to determine the glass transition by differential scanning calorimetry on quenched low molecular weight materials were unsuccessful.[4]

Nuclear magnetic resonance provides a unique tool for probing molecular motions in polymeric systems. This particular system offers the added advantage of possessing fluorine and hydrogen atoms, both of which have magnetic moments. Protons are found only in the main chain and, as such, a comparison of the relaxation processes for the two magnetic nuclei should throw some light on the nature of the molecular processes taking place.

Experimental Section

The samples of HFIB/VF used in this study were obtained from Dr. S. Chandrasekaran of Allied Chemical Corp. Sample A is a powdered material with a melt flow index of 0.8 g/10 mins for a 5 kg load. Sample B is a film of suspension polymerized material which was compression molded at 350 °C. The melt flow index was 13 g/10 min for a 2.16 kg load. Because HFIB/VF$_2$ is insoluble in all known solvents, molecular weights could not be measured by solution methods. Evacuated samples were obtained by pumping the samples to 10^{-5} mm Hg at 100 °C for 4 h prior to sealing the NMR tube.