^{13}C NMR Determination of Monomer Sequence Distribution in Ethylene–Propylene Copolymers Prepared with δ-$TiCl_3$–$Al(C_2H_5)_2Cl$

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ABSTRACT: The accuracy of ^{13}C nuclear magnetic resonance (^{13}C NMR) measurements has been examined by using ^{14}C-labeled ethylene–propylene (EP) copolymers. The monomer compositions calculated from the methylene and methine resonances are in agreement with those determined by radioassay within a relative error of 4%. These results indicate that the NOEs are uniform, at least for such carbons, and, therefore, the monomer sequence distributions obtained are sufficiently reliable. Monomer reactivity ratios, r_1 (ethylene) and r_2 (propylene), have been calculated from the dyad distribution and the monomer feed composition. The observed triad distribution, compared with that calculated by a first-order Markovian scheme using r_1 and r_2, shows the peculiarity that ethylene tends to copolymerize either in alternation or in runs.

A number of studies on monomer sequence distribution in EP copolymers have been carried out by means of ^{13}C NMR spectroscopy,[1-7] infrared (IR) spectroscopy,[8,9] and X-ray diffraction.[10] These investigations and the monomer reactivity ratios obtained from copolymerization data indicate that the copolymers prepared with heterogeneous titanium catalysts have a wide copolymer composition distribution. However, despite these studies, the details of the copolymerization mechanism in the presence of heterogeneous catalysts have not been sufficiently elucidated. ^{13}C NMR spectroscopy is obviously an especially powerful method for this field. Most of the studies carried out so far are, however, concerned with EP rubbers (EPR and EPDM). Ray, Johnson, and Knox[6] reported that monomer composition in EP copolymers prepared with a $TiCl_3$-based catalyst system can be calculated from the resonances of the methylene region. Furthermore, they determined complete dyad and triad distributions based on the assumption that NOEs are uniform for all the carbons.

In the present paper, we first examine the accuracy of the ^{13}C NMR measurement using ^{14}C-labeled EP copolymers. Then we apply ^{13}C spectroscopy to the determination of the dyad and triad distributions in cold EP copolymers. On the basis of the monomer distribution determined, we discuss the peculiarity in copolymerization in the presence of such a catalyst system.

Experimental Section

A. ^{14}C-Labeled EP Copolymer.[11] Two copolymers, samples A and B, containing 16.7 and 53.8 mol % ethylene, respectively, were used for this study. These copolymers were obtained by copolymerizing ^{14}C-labeled ethylene diluted with unlabeled ethylene and propylene in the presence of the catalyst system $TiCl_3$–$Al(C_2H_5)_2Cl$. The ethylene contents were determined by liquid scintillation counting, with a relative error of 1%.

B. EP Copolymers. Samples C–H were prepared in an agitated 1-L autoclave. Heptane dried on molecular sieve 13X was used as the polymerization medium. A mixture of ethylene, propylene, and hydrogen as a chain transfer agent was prepared in advance in a stainless steel container and then bubbled into the polymerization slurry. The amount of monomer in the feed was kept at 10 times that consumed by polymerization to hold the monomer composition constant throughout a run. In all polymerization runs, the monomer composition determined by gas chromatography did not change before and after the polymerization. Polymerization was carried out at 60 ± 1 °C for 2 h under atmospheric pressure in the presence of $TiCl_3$ (supplied by Toho Titanium Co.) and $Al(C_2H_5)_2Cl$ (supplied by Nippon Aluminum Alkyls). The polymerization was terminated by adding isobutyl alcohol. After the catalyst residues were extracted with a mixture of 1 N HCl and methanol (1/1 v/v), the products were dried at 50 °C for 4 h.

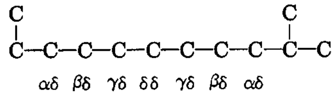
Table I
Area Measurements for Samples A and B

carbon type	% area[a]					
	sample A			sample B		
	1[b]	2	3	1	2	3
Sαα	25.9	26.0	25.4	11.3	12.0	11.8
Sαγ	5.2	5.4	5.8	8.5	8.0	7.9
Sαδ	1.6	1.6	1.4	5.4	5.6	5.5
Sγγ	0.9	0.8	0.8	2.9	2.8	3.6
Sγδ	1.2	1.0	1.1	3.6	4.1	3.8
Sδδ	2.2	2.2	2.1	20.5	20.3	19.6
Sβδ	1.6	1.5	1.3	5.8	5.6	5.7
Sββ	2.7	2.8	3.0	4.4	4.8	4.3
Tββ	22.2	22.1	22.6	7.7	7.5	7.4
Tβδ	5.8	5.7	5.8	7.8	7.7	7.8
Tδδ	1.1	1.3	1.1	3.4	3.0	3.8
Pββ	21.8	21.6	21.6	7.1	7.5	7.3
Pβδ	6.3	6.0	6.5	7.2	7.1	7.1
Pδδ	1.5	1.9	1.5	4.3	4.0	4.3

[a] Areas are normalized to 100%. [b] Measurements were repeated three times.

C. ^{13}C NMR Measurements. ^{13}C NMR spectra were obtained at 135 °C on a JEOL FX-100 pulsed Fourier transform NMR spectrometer. Samples were prepared as 10% (w/v) solutions of polymer in o-dichlorobenzene. Tetramethylsilane (Me_4Si) was added to the solutions as an internal chemical shift reference. The pulse interval was 10 s, the acquisition time was 4.2 s, the pulse angle was 45°, and the number of transients accumulated was 2000. A pulse interval of 10 s is sufficient to recover to 98.7% of the thermodynamic equilibrium value[12] considering the spin-lattice relaxation time T_1 of the methyl group, which is the slowest relaxing nucleus, with a T_1 of 2.5 s at 135 °C.[13]

D. Peak Assignments and Nomenclature. The nomenclature used to assign peaks to types of carbons follows that suggested by Carman and Wilkes.[3] A methylene carbon is identified as S with two Greek letters indicating its distance in both directions from the nearest tertiary carbons. The letter δ indicates that a methylene is in the δ or further position relative to a tertiary carbon. Similarly, a methine carbon is identified as T with two Greek letters showing the positions of the nearest tertiary carbons. A methyl carbon is given the letter P with two Greek letters that are the same as those for the attached tertiary carbon. An example of the nomenclature for methylene carbon[5] is



$$\overset{\mathrm{C}}{\overset{|}{\mathrm{C}}}-\underset{\alpha\delta}{\mathrm{C}}-\underset{\beta\delta}{\mathrm{C}}-\underset{\gamma\delta}{\mathrm{C}}-\underset{\delta\delta}{\mathrm{C}}-\underset{\gamma\delta}{\mathrm{C}}-\underset{\beta\delta}{\mathrm{C}}-\underset{\alpha\delta}{\mathrm{C}}-\overset{\mathrm{C}}{\overset{|}{\mathrm{C}}}-\mathrm{C}$$

Results and Discussion

Table I summarizes the peak intensities for samples A and B. The measurements, repeated three times, show

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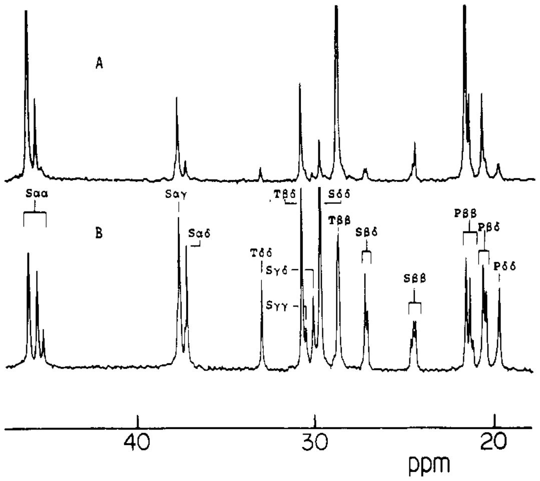

Figure 1. ^{13}C NMR spectra of samples A and B.

Table II
Dyad and Triad Distributions for Samples A and B

dyad or triad	sample A 1	sample A 2	sample A 3	sample B 1	sample B 2	sample B 3
PP	0.74	0.74	0.73	0.29	0.30	0.30
EP	0.20	0.20	0.21	0.35	0.34	0.35
EE	0.06	0.06	0.06	0.36	0.35	0.35
PPP	0.64	0.63	0.64	0.19	0.19	0.19
PPE	0.17	0.16	0.17	0.20	0.20	0.20
EPE	0.03	0.04	0.03	0.09	0.08	0.10
PEP	0.08	0.08	0.09	0.11	0.11	0.10
EEP	0.05	0.05	0.04	0.14	0.14	0.14
EEE	0.04	0.04	0.04	0.28	0.28	0.27

sufficiently good reproducibility. Figure 1 shows the ^{13}C NMR spectra, in which peaks attributable to Sαβ and Sβγ, ascribed to chemical inversion, cannot be found. Therefore it is possible to determine the dyad distribution from the methylene data by the equations

$$\mathrm{PP} = \mathrm{S}\alpha\alpha \tag{1}$$

$$\mathrm{EP} = \mathrm{S}\alpha\gamma + \mathrm{S}\alpha\delta \tag{2}$$

$$\mathrm{EE} = \tfrac{1}{2}(\mathrm{S}\beta\delta + \mathrm{S}\delta\delta) + \tfrac{1}{4}\mathrm{S}\gamma\delta \tag{3}$$

Furthermore, the triad distribution can be also calculated from both the methine and methylene data by the relationships

$$\mathrm{PPP} = \mathrm{T}\beta\beta \tag{4}$$

$$\mathrm{PPE} = \mathrm{T}\beta\delta \tag{5}$$

$$\mathrm{EPE} = \mathrm{T}\delta\delta \tag{6}$$

$$\mathrm{PEP} = \mathrm{S}\beta\beta = \tfrac{1}{2}\mathrm{S}\alpha\gamma \tag{7}$$

$$\mathrm{EEP} = \mathrm{S}\alpha\delta = \mathrm{S}\beta\delta \tag{8}$$

$$\mathrm{EEE} = \tfrac{1}{2}\mathrm{S}\delta\delta + \tfrac{1}{4}\mathrm{S}\gamma\delta \tag{9}$$

The calculated results for the dyad and triad distributions of samples A and B are summarized in Table II.

The monomer composition can be calculated from both the dyad and triad distributions by the equations

$$\mathrm{P} = \mathrm{PP} + \tfrac{1}{2}\mathrm{PE} \tag{10}$$

$$\mathrm{E} = \mathrm{EE} + \tfrac{1}{2}\mathrm{PE} \tag{11}$$

$$\mathrm{P} = \mathrm{PPP} + \mathrm{PPE} + \mathrm{EPE} \tag{12}$$

$$\mathrm{E} = \mathrm{EEE} + \mathrm{EEP} + \mathrm{PEP} \tag{13}$$

Table III shows that the calculated monomer compositions are in agreement with those determined by radioassay within a maximum relative error of 4%. Therefore, it is concluded that thermodynamic equilibrium has been achieved and the NOEs are uniform, at least for the methylene and methine carbons. We conclude that the data obtained here enable us to discuss quantitatively the monomer sequence distributions.

Table III
Comparison of Ethylene Content (mol %) Determined by Radioassay and ^{13}C NMR Spectroscopy

	E, mol % sample A	E, mol % sample B
radioassay	16.7 ± 0.2	53.8 ± 0.5
dyad	16.1 ± 0.1	52.8 ± 0.7
triad[a]	16.4 ± 0.2	52.9 ± 1.0

[a] The triads are obtained from the tertiary carbon.

Ray and co-workers[6] used methyl peaks for the determination of the P-centered triad distribution. However, as pointed out by Paxson and Randall,[7] the resonances from propylene units in configurational sequences other than isotactic may overlap with corresponding resonances from propylene units associated with the ethylene linkage. Therefore, for quantitative measurement of the P-centered triad distribution we use methine resonances, which are free from configurational chemical shifts.

Next, the monomer sequence distributions of several EP copolymers, obtained by changing the monomer feed composition, were determined by means of ^{13}C NMR spectroscopy under the conditions described above. From the dyad distribution determined, the monomer reactivity ratio product r_1r_2 has been calculated by eq 14 on the

$$r_1r_2 = \mathrm{EE}[\mathrm{PP}/(\mathrm{PE}/2)^2] \tag{14}$$

assumption that the statistical stationary condition is established and the copolymerization is first-order Markovian. Moreover, r_1 and r_2 are given by the following equations as a function of the monomer feed composition and the probability parameters:[14]

$$r_1 = (1 - P_{12})/P_{12}X \tag{15}$$

$$r_2 = (1 - P_{21})X/P_{21} \tag{16}$$

where 1 and 2 represent ethylene and propylene, respectively, X = (feed ethylene)/(feed propylene), and P_{mn} means the probability that the n monomer adds to an m chain end. The probability parameters can be calculated from the dyads as well as the monomer composition in the polymer by the equations

$$P_{11} = \mathrm{EE}/\mathrm{E} = 1 - P_{12} \tag{17}$$

$$P_{22} = \mathrm{PP}/\mathrm{P} = 1 - P_{21} \tag{18}$$

Table IV summarizes the monomer compositions in the polymer, the n-ad distributions, and the monomer reactivity ratios. The r_1 and r_2 values are within the same order of magnitude as the corresponding values reported by Natta, Mazzanti, Valvassori, and Sartori[15,16] for the $\mathrm{TiCl_3{-}Al(C_6H_{13})_3}$ system (r_1 = 15.7, r_2 = 0.11). Their products range from 3.0 to 4.2, i.e., obviously larger than 1. As seen from Table IV, the r_2 value does not change significantly over a wide range of ethylene feed composition, whereas r_1 obviously decreases with increasing ethylene feed composition.

The triad distributions calculated by using the individual r_1 and r_2 are compared in Table V with the observed ones. An apparent discrepancy, beyond experimental error, can be found in the E-centered triads; that is, the observed PEP and EEE triad frequencies are slightly more than

Table IV
Monomer Composition, *n*-ad Sequence Distribution, and r_1 and r_2 Values for Samples C-H

	ethylene feed, mol %					
	5.0 C	8.5 D	10.1 E	21.2 F	38.6 G	50.4 H
P	0.85	0.78	0.75	0.51	0.28	0.25
E	0.15	0.22	0.25	0.49	0.72	0.75
PP	0.76	0.66	0.61	0.33	0.13	0.10
EP	0.19	0.25	0.27	0.37	0.31	0.29
EE	0.05	0.09	0.11	0.31	0.57	0.61
PPP	0.67	0.57	0.50	0.22	0.07	0.04
PPE	0.17	0.18	0.21	0.21	0.13	0.10
EPE	0.02	0.03	0.04	0.08	0.09	0.11
PEP	0.07	0.10	0.10	0.11	0.07	0.05
EEP	0.03	0.06	0.07	0.15	0.16	0.17
EEE	0.04	0.06	0.08	0.23	0.49	0.52
r_1	9.3	7.5	7.0	6.3	6.0	4.2
r_2	0.4	0.5	0.5	0.5	0.5	0.7
r_1r_2	4.2	3.8	3.7	3.0	3.1	2.9

Table V
Observed vs. Calculated Triad Distributions

sample		PPP	PPE	EPE	PEP	EEP	EEE
C	obsd	0.67	0.17	0.02	0.07	0.03	0.04
	calcd	0.68	0.17	0.01	0.06	0.06	0.02
D	obsd	0.57	0.18	0.03	0.10	0.06	0.06
	calcd	0.58	0.20	0.02	0.07	0.10	0.03
E	obsd	0.50	0.21	0.04	0.10	0.07	0.08
	calcd	0.49	0.23	0.03	0.08	0.12	0.05
F	obsd	0.22	0.21	0.08	0.11	0.15	0.23
	calcd	0.22	0.23	0.06	0.07	0.23	0.19
G	obsd	0.07	0.13	0.09	0.07	0.16	0.49
	calcd	0.06	0.14	0.08	0.03	0.24	0.45
H	obsd	0.04	0.10	0.11	0.05	0.17	0.52
	calcd	0.04	0.12	0.09	0.03	0.23	0.50

predicted by a first-order Markovian scheme and the EEP triad is obviously less. In other words, ethylene (strangely) tends to copolymerize either in alternation or in runs. As speculated by several investigators,[17-22] this result may suggest that multiple active sites are present: on one active site ethylene preferentially polymerizes and on another site less ethylene polymerizes.

Acknowledgment. We are grateful to Dr. K. Shirayama, Mr. A. Shiga, and Dr. Y. Fukui for valuable discussions. We also thank Sumitomo Chemical Co. for permission to publish this work.

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Random-Coil Configurations of Poly(vinyl bromide) Chains

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ABSTRACT: Two samples of poly(vinyl bromide) were prepared and purified. Sample A was synthesized by radical polymerization of vinyl bromide at 35 °C, and sample B was obtained by extraction of sample A with dioxane at room temperature. Both samples had an isotactic content (determined by ^{13}C NMR) of 46%. Molecular weight averages were calculated from viscometric measurements in THF solutions and were found to be 52 100 and 27 400 for samples A and B, respectively. Dielectric measurements were performed in solutions of both samples in dioxane and 1-methylnaphthalene at several temperatures, and dipole ratios $D_x = \langle\mu^2\rangle/xm^2$ were found to be 0.53 and 0.45 in dioxane and 1-methylnaphthalene, respectively. No noticeable dependence of D_x with molecular weight was found; the variation of D_x with temperature was too small to allow an accurate determination of its temperature coefficient. A rotational isomeric state model was derived and used to calculate dipole and characteristic ($C_n = \langle r^2\rangle_0/nl^2$) ratios. Theoretical values of both D_∞ and C_∞ are in good agreement with experimental results.

Introduction

The available information on the physical and physicochemical properties of poly(vinyl bromide) (PVB) is meager in comparison with that existing for most vinyl polymers. The reason is that instability of the polymer decreases the precision of the measurements, so that most

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