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A method for determining sequence distributions in ethylene-1-butene copolymers by ^{13}C NMR

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Summary

Sequence distributions of the 1-butene comonomers in ethylene-1-butene copolymers were determined by analyzing the ^{13}C NMR spectra using an optimization calculation technique. The proposed method takes the possible errors in NMR measurements into account. Applying the method to the spectra of some linear low density polyethylenes with 1-butene as the comonomer gave physically reasonable values of triad comonomer distribution. The method was thought to be useful by giving the possible maximum and minimum triad concentrations reflecting the chain structures. We also tried to use the method for determination of larger sequence structures over triad distribution.

Introduction

This work was motivated in the course of determining the comonomer distributions in the linear low density polyethylenes (LLDPE). Distribution of comonomers in LLDPE is one of the most important structural parameters, as it affects crystallization process and hence morphology, solid-state structure, and physical properties. It has been claimed that the recently-developed metallocene catalysts produce LLDPE with more even comonomer distribution when compared with conventional Ziegler-Natta catalysts.

During the last three decades ^{13}C NMR spectroscopy has become one of the most powerful and indispensable structure determination tool in polymer science. For copolymers ^{13}C NMR spectroscopy was used to characterize the structural parameters including concentration, length, and distribution of comonomers (1-7). The method proposed by Randall and coworkers (1-3) has been used to determine the comonomer distributions in ethylene-1-alkene copolymers (4-7). There have been difficulties, however, in using this method when the comonomer content was low. In ethylene-1-butene copolymer the problem is encountered when 1-butene content is below 5 mol% (3,5). Hansen and coworkers (8) proposed a procedure (linear least-square method) to calculate triad concentration. This procedure appears to be more or less a purely mathematical treatment in that the procedure calculates triad concentration without considering chain structure.

We propose an optimization technique determining the comonomer distribution. Optimizations have been used for the analysis of NMR spectra. Cheng employed a

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computerized model fitting approach with the reaction probability model to analyze the spectra of ethylene-1-butene copolymer (9,10). Hay and coworkers have utilized the simplex method to analyze the relative concentrations of short and long chain branches in low density polyethylene (11). We also employ the simplex method as the optimization tool, which, in addition, would take the errors in NMR analysis into account.

Errors are inevitable in quantitative analysis using ^{13}C NMR. This is attributed to various spin-lattice relaxation times and suppression of dipolar coupling to prevent peak from splitting. In addition, although the nuclear overhauser enhancement effect in gate decoupling experiment is small, it could affect effectiveness of quantitative analysis. Therefore, quantitative measurements require either complete relaxation or identical amounts of partial relaxation to obtain reliable results. There are two methods to provide more complete relaxation; lowering the pulse flip angle and lengthening the pulse delay time. The first method has the effect of perturbing the spin populations only very slightly, by which a large fraction of the equilibrium longitudinal magnetization is retained. In the second method a long enough delay time between the pulses may result in complete repolarization of all nuclei. However, these two methods, which are commonly employed for improving effectiveness of quantitative analysis, suffer from a severe loss of sensitivity. In addition, the solvent used frequently gives rise to ^{13}C NMR signals of its own, which can be very strong and problematic. These factors cause imprecise integration of signal considering signal-to-noise ratio. It is obvious that this effect is more severe when the intensity of signal is low. In the case of LLDPE, this happens when concentration of comonomer is low.

Considering these possible errors, the maximum and minimum triad concentrations can be calculated when the extent of relaxation is set identical. It was thought that the accuracy of optimization calculation and thus the reliability of structure determination could be improved by taking these errors into account. In the present study the distributions of comonomers in LLDPEs with 1-butene as the comonomer were characterized using the method to analyze the sequence distribution from ^{13}C NMR spectra. The method was applied to LLDPEs from Ziegler-Natta catalysts and from metallocene catalysts to investigate the difference in comonomer distribution in the two serieses of LLDPE.

Experimental

The characteristics of the polymers examined are shown in Table 1. Weight average molecular weights (M_w) and polydispersity indices (M_w/M_n) were determined with a Waters 150C ALC/GPC instrument at 140 ℃ in 1,2,4-trichlorobenzene. Melt indices (MI) were measured at 190 ℃ with a Kayeness melt indexer at a load of 2.16 kg.

Table 1. Characteristics of Polymers Used

Code [a]	Trade name (Supplier)	Mol% of 1-butene	M_w	M_w/M_n	MI
ZN1	RE306 (Yukong)	1.90	89 000	2.77	2.81
ZN3	FU149M (Yukong)	3.16	131 000	3.48	0.98
M3	Exact 3025 (Exxon)	3.49	120 000	2.15	1.12
M6	Exact 4042 (Exxon)	6.89	113 000	1.94	1.13
M12	Exact 4033 (Exxon)	12.62	135 000	1.74	0.69

[a] *ZN and M denote LLDPE from Ziegler-Natta catalyst and metallocene catalyst, respectively.*

^{13}C solution NMR spectra were recorded on a Bruker ARX-300 spectrometer (75.5 MHz for ^{13}C) with the following spectral conditions: pulse angle, 30°; pulse delay, 15 s; acquisition time, 1.31 s; spectral width, 25 kHz. Measurement were carried out at 135 ℃ with gated decoupling. The samples were prepared in *o*-dichlorobenzene/benzene-d_6 (90/10 v/v) with concentrations of 15 wt%. Benzene-d_6 was used as the internal standard. The assignments were made according to Heish and Randall (1). The pulse repetition time of 15 s was thought to be sufficient for quantitative measurement of the carbons in the copolymers, since the spin-lattice relaxation time (T_1) of methyl carbons in isolated ethyl branches - which is supposed to be the longest of the all the carbons - was about 5 s (12). Moreover, when the pulse angle reduces to 30° from 90°, the pulse delay time to ensure appropriate relaxation is known to become approximately $-\ln(\cos 30°)\ T_1$ instead of $5T_1$ (12,13).

Results and Discussion

Determination of Triad Distribution

The spectra of the ethylene/1-butene copolymers are shown in Figure 1, where each spectrum is divided into seven regions which can be integrated. The triads were assigned according to the established procedures (3). It is known that quantitative treatment based on collective assignments is needed to avoid errors due to overlaps and uncertainties produced by unassigned splitting from long range interactions. Intensities in the seven integral regions are expressed as functions of triad concentrations as follows.

$T_{R1} = k\{\mathrm{BBB} + \tfrac{1}{2}(\mathrm{BBE}+\mathrm{EBB}) + \mathrm{EBE}\}$

$T_{R2} = k(\mathrm{EBB}+\mathrm{BBE})$

$T_{R3} = k\{\mathrm{BEB} + \tfrac{1}{2}(\mathrm{BEE}+\mathrm{EEB}) + \mathrm{EBE} + \tfrac{1}{2}(\mathrm{EBB}+\mathrm{BBE}) + \mathrm{BBB}\}$

$T_{R4} = k\{2\mathrm{EEE} + \tfrac{1}{2}(\mathrm{BEE}+\mathrm{EEB})\}$

$T_{R5} = k\{(\mathrm{BEE}+\mathrm{EEB}) + \mathrm{EBE} + (\mathrm{EBB}+\mathrm{BBE}) + \mathrm{BBB}\}$

$T_{R6} = k(\mathrm{BEB})$

$T_{R7} = k\{\mathrm{EBE} + (\mathrm{EBB}+\mathrm{BBE}) + \mathrm{BBB}\}$

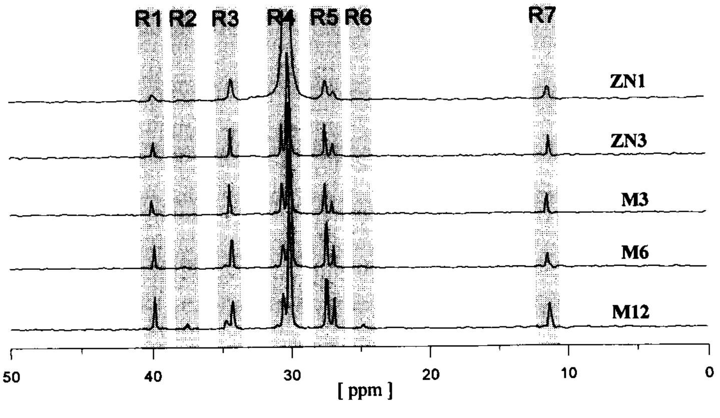


Figure 1. ^{13}C NMR spectra of LLDPEs and the integral regions.

Table 2. Triad Concentrations in ZN3 Calculated by Different Methods

	Randall's		Hansen's	This work	
Triad	method A	method B		method I	method II
[EEE]	0.851	0.905	0.908	0.909	0.909
[BEE+EEB]	0.057	0.062	0.062	0.064	0.061
[BEB]	0.000	0.000	0.000	0.000	0.001
[EBE]	0.029	0.029	0.014	0.025	0.028
[EBB+BBE]	0.002	0.002	0.003	0.003	0.003
[BBB]	- 0.061	- 0.002	0.014	0.000	0.000

For each equation *T* is the intensity of the integral region, and E and B are ethylene and 1-butene units, respectively. The constant *k* is a normalization constant.

Randall calculated triad concentrations by solving the above equations with the values averaged over the integral regions (3). He obtained two sets of solutions depending on the number of equations included in the calculation. One was the solution using all equations (method A): The other was the method for which the region R7 - of the carbons with longer relaxation times - was omitted from the calculation (method B). We applied both methods to the spectra in Figure 1, and the results for ZN3 are shown in Table 2 in comparison with the other methods. Randall's methods produced peculiar negative BBB concentrations. Similar results were observed by Balbontin and coworkers in the analysis of copolymers with low 1-butene content (5). This anomaly is attributed to the accumulation of errors in the integral regions during calculation procedure. The anomaly became less prominent by omitting region R7, i.e., using method B, although the problem persisted. The problem appeared to be severe when the comonomer content was low as Randall himself mentioned.

Recently Hansen and coworkers proposed a procedure to obtain triad concentration of ethylene-propylene copolymers (8). Triad concentration was determined by solving equations analytically without reducing the number of equations using a linear least-square method. We applied the procedure to the ethylene-1-butene copolymers, and the result for ZN3 is shown in Table 2. It was found that the concentrations of EBE and BBB were the same, which was not physically realistic. This peculiarity sustained in the calculation for all the other copolymers we examined. This method seemed not applicable to ethylene-1-butene copolymers, since the simultaneous equations became linearly dependent mathematically. Since the number of unknown variable was larger than the number of equations, the anomalous value took place.

We propose a method employing an optimization calculation, simplex method, to solve the above equations. In addition, to improve the accuracy of the calculation, possible errors that could be contained in the NMR spectra were considered in the calculation. Simplex method is a mathematical tool that solves a set of linear equations iteratively in a finite number of steps from one vertex to a neighboring one in such a way as to optimize the magnitude of the objective function. In the present calculation the procedure was used in the direction of reducing the magnitude of the sum of the errors. This method is known to be a better optimization tool, since it gives a solution only when the solution exists.

We used two approaches in dealing the possible errors for establishing a set of inequality equations. Since the relaxation mechanisms and relaxation times of the carbons along the chain were not known, the methods were based on an identical extent of relaxation of nuclei. One (method I) assumed that carbon atoms in branches should have not fully relaxed in experimental time. In this case the signal of carbon atoms should be affected by preferential accumulations. This method, therefore, envisaged that the intensities observed might be larger than they were supposed to be. The other (method II) assumed that the intensities of the peaks were measured smaller due to the instrumental limitations in accumulating signals. That is, we would calculate the concentration in the condition that all carbon atoms had been fully relaxed. The linear programming forms of the two methods are as follows.

Method I; MIN ΣX_i
SUBJECT TO $X_i + equation_i = T_i$.

Method II; MIN ΣX_i
SUBJECT TO $-X_i + equation_i = T_i$.

The result of calculation for ZN3 is shown in Table 2 in comparison with other methods. The concentration of BBB triad was calculated to be zero, and was not the same to EBE concentration. Since the errors in the integral regions were considered in the calculation, no mathematical problem appeared to take place. Giving more physically reasonable values, the problems encountered in Randall's and Hansen's methods seemed to be taken care of in the proposed method.

We tried to compare our result to that by Cheng (9,10), who estimated the reactivity ratios of ethylene and 1-butene using an optimization technique. However, the calculation of reaction probability from triad concentration appeared to be a different problem. That is, the simultaneous equations for conversion included higher order terms, and the number of unknowns was larger than the number of equations. Therefore we did not compare our methods with Cheng's method, because other mathematical criterion was needed.

The results of calculation for the other copolymers by method I and method II are shown in Tables 3. Method I resulted in lower values for the triad concentrations containing 1-butene units than method II did. This was a mathematically expected consequence, since method I would give underestimated triad concentrations containing the carbons of longer relaxation times.

Table 3. Solutions of Simplex Optimization Calculation of Triad Concentrations

Method	Triad	ZN1	ZN3	M3	M6	M12
Method I	[EEE]	0.948	0.909	0.896	0.805	0.668
	[BEE+EEB]	0.037	0.064	0.070	0.130	0.213
	[BEB]	0.000	0.000	0.000	0.004	0.000
	[EBE]	0.015	0.025	0.035	0.052	0.097
	[EBB+BBE]	0.000	0.003	0.000	0.006	0.022
	[BBB]	0.000	0.000	0.000	0.000	0.000
Method II	[EEE]	0.945	0.909	0.896	0.806	0.662
	[BEE+EEB]	0.034	0.061	0.070	0.126	0.200
	[BEB]	0.003	0.001	0.000	0.004	0.012
	[EBE]	0.019	0.028	0.035	0.056	0.085
	[EBB+BBE]	0.000	0.003	0.000	0.009	0.041
	[BBB]	0.000	0.000	0.000	0.000	0.000

Table 4. Errors in Simplex Optimization of Triad Concentrations for ZN3

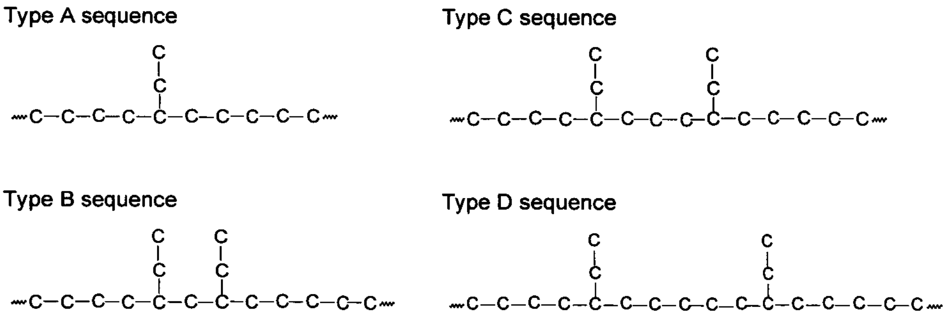
Integral Region	Observed Value	Calculated Value	
		method I	method II
T_{R1}	14.19	14.19	15.76 (1.57)[a]
T_{R2}	1.33	1.33	1.33
T_{R3}	32.44	31.39 (−1.05)[a]	32.44
T_{R4}	1000.00	1000.00	1000.00
T_{R5}	49.25	49.25	49.25
T_{R6}	0.00	0.00	0.27 (0.27)[a]
T_{R7}	16.42	14.85 (−1.57)[a]	16.42

[a] *Difference between observed and calculated values, which corresponds to the value of* X_i *in the equation.*

The errors in the calculation are presented in Table 4. It was observed that the errors in method I were concentrated at the integral regions R3 and R7. The region R7 is of the carbons at the chain ends (1,12) and thus with longer spin-lattice relaxation times. This observation conformed to our assumption in method I, since the carbons of longer relaxation times give rise to larger intensities. It is also observed that the errors in method II were concentrated at the integral regions R1 and R6. This is again consistent with the assumption that the underrated signals be counted for the peaks of low intensities. It is, therefore, considered that the proposed method is useful for calculating the probable maximum and minimum triad concentrations reflecting the real polymer chain structures. It seems to be appropriate to note here that the results by method II should be closer to the actual triad distribution than those by method I, since the experimental condition of this study should have let the carbon atoms sufficiently relax.

Determination of Sequence Structure

We applied our method to the determination of the copolymer sequence structures. Actually we opted to expand the applicability of the method over triad, since it is the sequence distribution - rather than triad distribution - that governs the crystallization process, morphology and thus the physical properties of the polyolefin copolymers. The range that could be examined by expanding triad distribution was, however, limited to five carbon atoms between the branching point, as shown in Figure 2.



Type A sequence

Type C sequence

Type B sequence

Type D sequence

Figure 2. Types of sequence structures in the copolymers.

For sequence structure determination, the following constraint equations that contained contributions from the types of sequence.

$$T_{R1} = k(A + B + 2C + 2D)$$
$$T_{R2} = k(2B)$$
$$T_{R3} = k(2A + 2B + 4C + 4D)$$
$$T_{R4}' = k(D)$$
$$T_{R5} = k(3A + 4B + 4C + 6D)$$
$$T_{R6} = k(C)$$
$$T_{R7} = k(A + 2B + 2C + 2D)$$

In the equations T's are the intensities in the integral regions of Figure 1 with one exception. For the region R4 only the signal from the γ carbons between the branching points in type D sequences (often referred to as $\gamma\gamma$ carbons) was counted, since the region R4 contained the signals from main chain carbons and other γ carbons. The peak of $\gamma\gamma$ carbons was the smallest and leftmost peak in the region R4, and the intensity was expressed as T_{R4}' in the equation.

As we did for triad distribution calculation, two methods were utilized. The observed intensities were considered to be either larger (method III) or smaller (method IV) than they are supposed to be. The results of calculation for the copolymers are shown in Table 5, and the errors in the calculation in Table 6. It was found that the major errors in method III occurred at the integral regions R3 and R6, while the error at the region R7 was rather small. This result did not conform to the assumption, and thus the values by method III was not acceptable. The errors in method IV were observed at the integral regions of small intensities, which was consistent to the assumption. It was, therefore, concluded that method IV is more reliable than method III. Better reliability of method IV was confirmed by comparing the values converted into triad concentrations, which gave better agreement to the values by methods I and II. It was thought, in consequence, that our method can be utilized to determine the distribution of larger sequences over triad, especially when method IV was used.

A comparison of the sequence structures of ZN3 and M3 revealed that ZN3 contained a small portion of contiguous 1-butene (type B) sequences while M3 did not have any. This implied that LLDPE prepared by metallocene catalyst had a more even comonomer distribution than the copolymer by conventional Ziegler-Natta catalyst at the same comonomer content.

Table 5. Solutions of Simplex Optimization Calculation of Sequence Distribution

Method	Sequence type	ZN1	ZN3	M3	M6	M12
Method III	A	7.73	13.25	17.35	21.64	30.45
	B	0.00	0.61	0.00	1.48	5.42
	C	0.00	0.00	0.00	0.00	0.21
	D	0.00	0.00	0.00	3.13	8.63
Method IV	A	9.48	14.34	17.40	20.56	19.62
	B	0.00	0.62	0.00	1.46	7.59
	C	0.00	0.00	0.00	2.17	5.77
	D	0.00	0.00	0.00	3.08	8.51

Values are the numbers of sequences per 1000 backbone carbons

Table 6. Errors in Simplex Optimization Calculation of Sequence Distribution for ZN3

Integral Region	Observed Value	Calculated Value	
		method III	method IV
T_A	14.19	14.19	15.49 (1.30)[a]
T_B	1.33	1.33	1.33
T_C	32.44	29.84 (−2.60)[a]	32.44
T_E	49.25	45.42 (−3.83)[a]	49.32 (0.07)[a]
T_F	0.00	0.00	0.00
T_G	16.42	15.58 (−0.84)[a]	16.88 (0.46)[a]

[a] *Difference between observed and calculated values, which corresponds to the value of* X_i *in the equation.*

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