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^{13}C NMR Analysis of Compositional Heterogeneity in Ethylene-Propylene Copolymers

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ABSTRACT: ^{13}C NMR and temperature rising elution fractionation (TREF) are combined to characterize compositional heterogeneity in an ethylene-propylene copolymer. A methodology is developed involving systematic treatment of data via a computer-assisted analytical approach. The result indicates that the ethylene-propylene copolymer made with a heterogeneous titanium-based catalyst contains three or four separate components, each of which approximately obeys Bernoullian statistics. The Bernoullian probabilities vary from 0.03 to 0.60 and reflect the large differences in ethylene/propylene selectivity of different catalytic sites.

Introduction

Polymers made through heterogeneous Ziegler-Natta catalysts often exhibit compositional heterogeneity. This has been known to arise from multiple catalytic sites.[1-4] Recently, NMR data have been used to evaluate the relative role of multiple sites.[5-12] An analytical methodology has been developed involving a computer-assisted analytical approach to examine the ^{13}C NMR data and to extract information about the proportions and the reaction probabilities of various active sites. This approach has been applied to the tacticity of polypropylene[9] and poly(1-butene)[10] and sequence distributions in ethylene-propylene,[9-11] propylene-1-butene,[9] and ethylene-1-butene[12] copolymers. It was found that the best results are obtained when the NMR data of polymer fractions are available.

In the early 1980s, temperature rising elution fractionation (TREF) was developed[13,14] and was shown to be a powerful technique for the studies of compositional heterogeneity of polyolefins.[15-19] In this work we have combined ^{13}C NMR with TREF to characterize an ethylene-propylene copolymer.

Experimental Section

The ethylene-propylene copolymer was made with heterogeneous δ-TiCl$_3$ catalysts. The details of synthesis have been described previously.[19] Solvent extraction and TREF procedures were also reported before.[19] The ^{13}C NMR data were obtained at 25.2 MHz in *o*-dichlorobenzene at 130 °C. The NMR analysis was carried out with the MIXCO family of computer programs.[9,10] These programs can analyze the triad sequence distribution (and homopolymer tacticity) in the whole polymer or in polymer fractions through reaction probability models. For tacticity, Bernoullian (B), first-order Markovian (M1), and enantiomorphic-site models and their combinations can be fitted. For copolymer sequences, B and M1 models and their combinations can be used. The program MIXCO.TRIAD can be used for analysis of whole polymer triad data. Both two-site (B/B) and two-site (M1/M1) models can be fitted. The program MIXCO.TRIADX can be used for analysis of polymer fractions. Two fractions at a time need to be analyzed. Two-site (B/B) and three-site (B/B/B) models can be fitted. The program MIXCO.TRIAD/X can also be used for analysis of polymer fractions. Two fractions at a time need to be analyzed. Both two-site (B/B) and two-site (M1/M1) models can be fitted.

Table I
^{13}C NMR Data of Whole Polymer and Heptane Fractions[a] (Observed vs Calculated Data on the Basis of the Two-Site B/B Model)

	whole[b]		heptane soluble[c]		heptane insoluble[c]	
	obsd	calc	obsd	calc	obsd	calc
PPP	0.09	0.09	0.10	0.09	0.00	0.00
PPE	0.15	0.15	0.18	0.19	0.00	0.00
EPE	0.11	0.10	0.11	0.09	0.01	0.01
PEP	0.09	0.08	0.10	0.10	0.00	0.00
EEP	0.19	0.20	0.19	0.19	0.02	0.02
EEE	0.38	0.38	0.32	0.33	0.97	0.97

[a] Observed data taken from ref 19 (sample A-4). [b] Analyzed via the program MIXCO.TRIAD for the B/B model: site 1, $P_P(1) = 0.52$, $w_1 = 0.63$; site 2, $P_P(2) = 0.06$, $w_2 = 0.37$. *R* (mean deviation) = 0.007. [c] Both heptane fractions analyzed togther via MIXCO.TRIADX for the B/B model ($R = 0.003$). Heptane soluble: site 1, $P_P(1) = 0.51$, $w_1 = 0.75$; site 2, $P_P(2) = 0.01$, $w_2 = 0.25$. Heptane insoluble: site 1, $P_P(1) = 0.51$, $w_1 = 0.00$; site 2, $P_P(2) = 0.01$, $w_2 = 1.00$.

Results and Discussion

Kakugo et al.[19] have published ^{13}C NMR data for a whole polymer (designated A-4 in their paper) as well as ^{13}C NMR data for polymer fractions separated by heptane extraction and polymer fractions separated by TREF. The data are reproduced in Tables I and II. The analysis is given in the following sections.

Analysis of Whole Polymer. The triad data for the whole polymer can be readily analyzed by the two-site (B/B) model. The fit is satisfactory (Table I) with a small mean deviation (*R*). On the basis of this analysis, there are at least two catalytic sites, both obeying Bernoullian statistics: $P_P(1) = 0.52$ and $P_P(2) = 0.06$, where $P_P(i)$ is the Bernoullian probability of adding a propylene monomer to a propagating chain for the *i*th fraction.

Analysis of Heptane Fractions. The ^{13}C NMR data for heptane-soluble and heptane-insoluble fractions can be fitted via MIXCO.TRIADX. In this case, the triad data for both fractions are fed into the computer. Both two-site (B/B) and three-site (B/B/B) models are tested. In such data fitting, one needs to be careful to make sure that there are enough independent variables to fit the unknown parameters (see Chart I).

In all cases there are 12 triad intensities (6 from each fraction) and therefore 12 independent variables. The number of unknowns range from 4 to 10. Obviously,

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Table II
TREF Fractions of Ethylene–Propylene Copolymer and ^{13}C NMR Data[a]

					obsd triads					
fract no.	elution temp, °C	wt %	intrinsic visc, dL/g	ethylene content, mol %	PPP	PPE	EPE	PEP	EEP	EEE
F-1	−30	62.6	1.51	51	0.14	0.22	0.13	0.13	0.22	0.16
F-2	0	3.5		62	0.11	0.14	0.13	0.08	0.24	0.30
F-3	10	1.8	0.91	73	0.05	0.10	0.12	0.05	0.24	0.44
F-4	20	2.4		74	0.06	0.08	0.12	0.04	0.23	0.47
F-5	30	3.0	1.69	76	0.06	0.07	0.11	0.05	0.21	0.50
F-6	40	2.9	1.77	76	0.07	0.07	0.11	0.06	0.18	0.52
F-7	50	2.9	1.83	84	0.04	0.04	0.08	0.03	0.15	0.67
F-8	60	3.2	1.88	85	0.04	0.04	0.07	0.02	0.14	0.69
F-9	70	3.2	1.96	88	0.04	0.03	0.05	0.01	0.11	0.75
F-10	80	3.3	1.97	92	0.02	0.02	0.04	0.01	0.08	0.83
F-11	90	5.6	2.30	97	0.01	0.00	0.02	0.01	0.05	0.91
F-12	100	5.7	2.95	99.5	0.00	0.00	0.00	0.00	0.01	0.99
F-13	110	tr								

[a] Data taken from ref 19 (sample A-4).

Chart I

model	unknowns	no. of unknowns	no. of indep var
two-site (B/B)	site 1: $P_P(1)$ site 2: $P_p(2)$ frac 1: w_1 frac 2: w_1	4	12
two-site (M1/M1)	site 1: $P_{PE}(1)$, $P_{EP}(1)$ site 2: $P_{PE}(2)$, $P_{EP}(2)$ frac 1: w_1 frac 2: w_1	6	12
three-site (B/B/B)	site 1: $P_P(1)$ site 2: $P_P(2)$ site 3: $P_P(3)$ frac 1: w_1, w_2 frac 2: w_1, w_2	7	12
three-site (M1/M1/M1)	site 1: $P_{PE}(1)$, $P_{EP}(1)$ site 2: $P_{PE}(2)$, $P_{EP}(2)$ site 3: $P_{PE}(3)$, $P_{EP}(3)$ frac 1: w_1, w_2 frac 2: w_1, w_2	10	12

Table III
Analysis of the ^{13}C NMR Data of TREF Fractions

	component 1		component 2		component 3	
frac no.	$P_P(1)$	w_1	$P_P(2)$	w_2	$P_P(3)$	w_3
1	0.60	0.85	0.20	0.15		
2	0.62	0.47	0.20	0.53		
3	0.62	0.18	0.20	0.81		
4	0.69	0.15	0.21	0.75	0.05	0.09
5	0.69	0.12	0.22	0.71	0.05	0.18
6	0.77	0.13	0.22	0.55	0.08	0.32
7	0.77	0.09	0.26	0.41	0.03	0.50
8	0.78	0.05	0.26	0.34	0.03	0.62
9			0.30	0.27	0.03	0.73
10			0.30	0.15	0.03	0.85
11			0.30	0.03	0.03	0.97
12			0.30		0.03	1.00

whereas one has confidence in fitting the 12 triad intensities to the two-site (B/B) model, it would be difficult to fit the 12 intensities to the three-site (M1/M1/M1) model.

In the case of the NMR data of heptane-soluble and -insoluble fractions, the results can be readily fitted to the two-site (B/B) model (see Table I). The data can be fitted to the three-site (B/B/B) model as well, but the mean deviation (0.003) is the same as the two-site model, thereby showing no improvement in the goodness of fit. The two sites have the following P_P values: 0.51 and 0.01. Taking into account the weight percents of heptane solubles (90.4%) and heptane insolubles (9.6%), one can estimate the relative contributions of the two sites in generating the polymer: contribution of site 1 = 67.8%; contribution of site 2 = 32.2%.

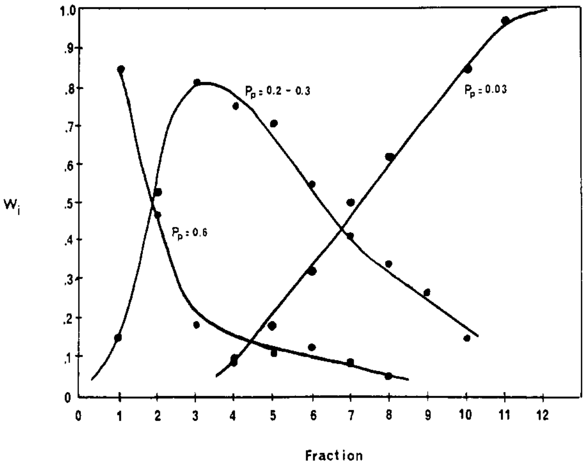

Figure 1. $\{w_i\}$ values for each component in the TREF fractions of ethylene–propylene copolymer.

Table IV
Contribution of Each Active Site to the Overall Polymer Production and the Distribution among the TREF Fractions

	wt % × w_i		
frac no.	$P_P(1)$ = 0.60–0.78	$P_P(2)$ = 0.20–0.30	$P_P(3)$ = 0.03–0.05
1	53.2	9.4	0.0
2	1.6	1.9	0.0
3	0.3	1.5	0.0
4	0.4	1.8	0.2
5	0.4	1.7	0.5
6	0.4	1.6	0.9
7	0.3	1.2	1.5
8	0.2	1.1	2.0
9	0.0	0.9	2.3
10	0.0	0.5	2.8
11	0.0	0.2	5.4
12	0.0	0.0	5.7
sum	56.8	21.8	21.3

Analysis of TREF Fractions. Similar methodology can be used to analyze TREF fractions. The following procedure has been used:

1. The NMR triad data of pairwise contiguous fractions are first fed into the program. Reaction probabilities and relative weight fractions $\{w_i\}$ are obtained.

2. The NMR triad data of every other fraction are fed into the program, two fractions at a time. Reaction probabilities and $\{w_i\}$ are again obtained and compared with the results of step 1.

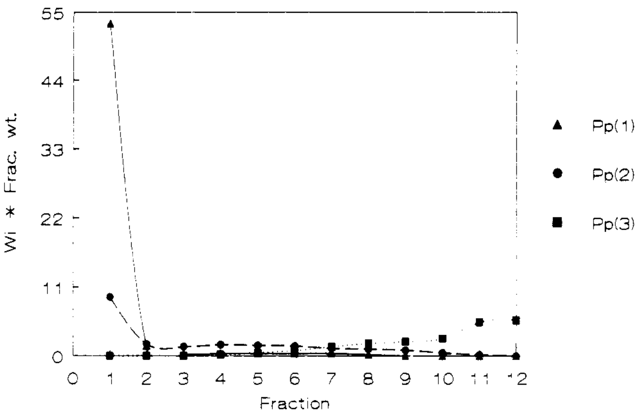

Figure 2. Contribution of each active site to the production of polymer (fraction wt % × w_i) as distributed in the TREF fractions ($P_P(1) = 0.60$; $P_P(2) = 0.2$–0.3; $P_P(3) = 0.03$).

3. The results are compiled and trends in the reaction probabilities and $\{w_i\}$ values are noted. Additional fittings are done to see if the trends hold up and are reasonable.
4. Data fitting was done with both MIXCO.TRIADX (two-site B/B or three-site B/B/B model) and MIXCO.TRIAD/X (two-site M1/M1 model).

It is clear from the data fitting that for fractions 1–3 and 9–12, the data conform to the two-site (B/B) model rather well (Table III). The two-site (M1/M1) model gives no significant improvement over the two-site (B/B) model. For fractions 4 and 8, the data approximately conform to the two-site (B/B) model. Improvements were observed when 10% of a third Bernoullian site was added. Fractions 5–7 clearly call for the three-site models. We chose the three-site (B/B/B) model for convenience, and the goodness to fit is satisfactory in each case.

The results in Table III indicate that there are at least three active sites giving rise to three components in the polymer. A plot of the data (Figure 1) gives the distribution of these components in the 12 fractions. The three components have the following Bernoullian probabilities for propylene addition:

$$P_P(1) = 0.60 \qquad P_P(2) = 0.20\text{–}0.30$$
$$P_P(3) = 0.03\text{–}0.05$$

The second component consists of a reaction probability that progressively increases from 0.20 to 0.30. One can reinterpret the result to say that there are really two components: $P_P(2a) = 0.20$ and $P_P(2b) = 0.30$, with a continuous distribution of those two components (2a and 2b) among the fractions. If one were to take this approach, there should then be four Bernoullian active sites in the copolymerization.

The contribution of each site to the generation of polymers can be readily extracted by multiplying the $\{w_i\}$ values in each component with the weight percent of the TREF fractions (Table II, column 3). The result is shown in Table IV. Thus, active site 1 contributes 57% to polymer production, active site 2 contributes 22%, and active site 3 contributor 21%. The distributions of these contributions among the fractions are shown in Figure 2. As expected, fraction 1 has the largest contribution to the overall amount of polymer.

Some comments can be made as to the results of the analyses of the whole polymer, the heptane-extracted fractions, and the TREF fractions. In general, the more fractions one obtains of the polymer, the more detailed is the information on that polymer. For the ethylene–propylene copolymer at hand, since there are 3–4 components in the copolymer, one needs to have the NMR data of several fractions to unravel the problem. The analysis of the NMR data of the whole polymer alone or of the two heptane fractions involves only limited data in either case and cannot in general give information on the desired three components except under special circumstances. However, the analysis has been helpful: it indicates the multicomponent nature of the copolymer in question and points out the need for a multiple fractionation scheme or TREF. The TREF technique is particularly advantageous because successive fractions follow systematic trends, thereby leading to readily understandable trends (such as those given in Figures 1 and 2). The analysis of the NMR/TREF data therefore produces definitive information on the polymer.

In summary, we showed in this work that the combination of ^{13}C NMR and TREF can provide very detailed information about the polymer. In the case of the ethylene–propylene copolymer made with a heterogeneous catalyst as analyzed above, there are three or four active catalytic sites that produce the polymer. The polymer should be considered an in situ polymer blend of three or four *random* copolymer components. The analytical technique given here can be readily used for the TREF/NMR data of other copolymer systems.

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