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Analysis of NMR triad distribution in ethylene/1-butene copolymers

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Summary

For Ziegler-Natta polymers where the catalyst system can contain more than one active site, the analysis of NMR triad distribution data needs to be carried out with care. The best result is obtained when the NMR data of fractionated polymers are available. An analysis of the triad sequence distribution from the ethylene/1-butene copolymers indicate that the data are compatible with the occurrence of three discrete catalytic sites.

INTRODUCTION

In the last several years a number of papers[1-10] have appeared on the significance of multiple catalytic sites in the NMR analysis of triad sequence distribution of copolymers. Whereas the presence of multiple catalytic sites in Ziegler-Natta catalysis has been known for a long time,[11-13] a quantitative analysis of the NMR data to resolve the various active sites is not a trivial task. In previous work[9,10], a general methodology was proposed for the analysis of NMR triad data. Computer programs have been written to assist in such analysis. It has shown that the best results are obtained with fractionated polymer samples.

Recently, detailed fractionation and ^{13}C NMR data have become available[14] for ethylene/1-butene copolymer. On the basis of NMR triad sequence distributions, Kuroda et al.[14] deduced that the heterogeneous titanium-based catalyst contains a broad range of catalytic sites that are distributed continuously from sites which are more reactive towards 1-butene to sites which are less reactive towards 1-butene. This finding (of continuous site distribution), if true, would have significant implications in Ziegler-Natta polymerization mechanism. We have therefore used the previously described analytical methodology[9,10] to provide an alternative analysis of Kuroda's data.

RESULTS AND DISCUSSION

Theoretical Considerations. Before one embarks on an analysis of data, a careful look at the model fitting process is desirable. If only one catalytic site exists, then the analysis can be carried out using either the Bernoullian (B) or the first-order Markovian (M1) statistical model.

Model	Unknown Parameters	Number of Unknowns	Number of Independent Variables
B	P_a	1	6
M1	P_{ab}, P_{ba}	2	6

There are six variables that can be measured by NMR; these are the triad sequences: (AAA), (AAB), (BAB), (ABA), (BBA), and (BBB), where A and B are the comonomers, and the subscripts a and b refer to comonomers A and B, respectively. The Bernoullian model has only one adjustable parameter to fit the six independent variables, and the first-order Markovian model has two. In both cases there are enough independent variables (six) to fit the parameters (one or two).

For multisite catalysis, the NMR analysis becomes more tricky. For the Bernoullian model, the following scenario applies:

Model	Unknown Parameters	Number of Unknowns	Number of Indep. Variables
1-site (B)	P_a	1	6
2-site (B/B)	$P_a(1)$, w_1 $P_a(2)$	3	6
3-site (B/B/B)	$P_a(1)$, w_1 $P_a(2)$, w_2 $P_a(3)$	5	6

where w_i is the weight fraction of site i, and $\Sigma w_i=1$. In the scheme above, if one analyzes the triad distribution data for 2-site (B/B) catalysis, then the fitting needs to be done with care. The triad data must have good experimental precision, or else the solution may not be unique. For three-site (B/B/B) catalysis, it is very difficult to fit the triad distribution data with a high degree of confidence.

In view of the difficulty, the approach adopted in two earlier papers[9,10] is to use, wherever possible, the NMR data from polymer fractions. The easiest approach is to take the data from two fractions at once. A total of 12 intensities (two sets of triad distributions) need to be fitted.

Model	Unknown Parameters	Number of Unknowns	Number of Indep. Variables
1-site (B)	P_a	1	12
2-site (B/B)	$P_a(1)$ $P_a(2)$ Frac. 1, w_1 Frac. 2, w_1	4	12
3-site (B/B/B)	$P_a(1)$ $P_a(2)$ $P_a(3)$ Frac. 1, w_1, w_2 Frac. 2, w_1, w_2	7	12

This procedure (using NMR data from pairwise fractions) produces much more reliable results for the 2-site (B/B) case, and acceptable results for the 3-site (B/B/B) model.

Extension of this analysis to treating the triad data of three fraction at once (involving 18 intensities) is straightforward. In practice, however, one needs to be very careful. The problem is that as the number of fitted parameters increases, one needs to exercise good judgement as to what the permissible range of values are for the parameters to assume. A good approach is to scrutinize the results of pairwise fractions and deduce the trend in the reaction probabilities before attempting global fitting.

Methodology. The analytical methodology used is similar to that described in two previous papers[9,10]. Two computer programs have been written:

MIXCO.TRIAD — Two-site (B/B) and (M1/M1) for copolymer triad sequence analysis (for single fraction or for whole polymer).

MIXCO.TRIADX — Two-site (B/B) or three-site (B/B/B) model for copolymer triad sequence analysis (for two polymer fractions).

In both cases the computerized model fitting (analytical) approach[15] was used. For each assignable resonance in the ^{13}C NMR spectrum, the theoretical intensity based on the mixture model is derived. These are expressed as functions of relative proportions (w_i) and reaction probabilities (P_i or P_{ij}). The theoretical and the observed intensities are then compared, and the unknown parameters (w_i and P_i/P_{ij}) are varied until the best fit is obtained.

Analysis of Ethylene/1-Butene Copolymers. In their elegant study, Kuroda et al.[14] fractionated the ethylene/1-

Table 1. ^{13}C NMR Comonomer Triad Sequence Distribution in Ethylene/1-Butene Copolymer (from Ref. 14)

	Wt %	(BBB)	(BBE)	(EBE)	(BEB)	(EEB)	(EEE)
F1	18.4	0.047	0.090	0.163	0.075	0.267	0.358
F2	7.0	0.014	0.043	0.141	0.040	0.245	0.517
F3	13.6	0.003	0.020	0.103	0.019	0.188	0.667
F4	32.0	0.000	0.005	0.058	0.004	0.113	0.820
F5	29.0	0.000	0.002	0.030	0.002	0.059	0.907
W	100.0	0.001	0.022	0.080	0.021	0.141	0.735

Table 2. Analysis of Single Fractions by Program MIXCO.TRIAD

Frac	P_i or P_{ij}	w_i	R
F1	Site 1: $P_{be} = 0.712$, $P_{eb} = 0.597$	0.240	0.94
	Site 2: $P_b = 0.222$	0.760	
F2	Site 1: $P_b = 0.224$	0.886	0.91
	Site 2: $P_b = 0.031$	0.114	
F3	Site 1: $P_b = 0.164$	0.752	0.49
	Site 2: $P_b = 0.030$	0.248	
F4	Site 1: $P_b = 0.312$	0.114	0.76
	Site 2: $P_b = 0.038$	0.886	
F5	$P_b = 0.032$		0.03

butene copolymer by successively extracting it with diisopropyl ether at 20°C (Fraction 1), n-hexane at 20°C (Fraction 2), n-hexane at its boiling point (Fraction 3), and cyclohexane at its boiling point (Fraction 4). The residual polymer (cyclohexane insolubles) is designated Fraction 5. The whole (unfractionated) polymer is called W. The ^{13}C NMR triad distribution data reported by Kuroda et al.[14] are summarized in Table 1.

We assume that the Ziegler-Natta catalyst used contains discrete catalytic sites and analyze the ^{13}C NMR triad sequence data (Table 1) by the mixture models (i.e., using the MIXCO.TRIAD program).

We first use the two-site (B/B) model to fit individual fractions. From prior experience[15], a satisfactory fit is obtained when the mean deviation (R) is comparable to the experimental error. For most NMR triad data, this means that R should be between 0.5 and 1.0%. After several iterations, it appears that most of the fractions can be fitted to two Bernoullian sites with $P_b \sim 0.22$ and $P_b \sim 0.03$, respectively. The results (given in Table 2) indicate satisfactory fit for four fractions. Fraction 5 does not need two sites; only one site is sufficient. In contrast, Fraction 1 gives some difficulties. In fact, the only way to decrease the mean deviation is to use a two-site (B/M1) model.

To confirm the findings, we carried out the analysis of pairwise fractions via the program MIXCO.TRIADX. The result (Table 3) indicates that Fractions 2-5 can be adequately fitted to two Bernoullian sites. The fraction pair (1, 2) again gives difficulty. It does appear that Fraction 1 (the diisopropyl ether-soluble fraction) contains a catalytic site that conforms to the first-order Markovian statistics.

Thus, in ethylene/1-butene copolymer data reported by Kuroda et al.[14] it is not necessary to invoke a continuum of catalytic sites. The data can be readily interpreted to infer the presence of three discrete sites:

Site #	Model	Reaction Probabilities	Fraction(s)
1	1st order Markovian	$P_{be} = 0.712$ $P_{eb} = 0.597$	1 - - - -
2	Bernoullian	$P_b = 0.22$	1 2 3 4 -
3	Bernoullian	$P_b = 0.03$	- 2 3 4 5

Table 3. Analysis of Pairwise Fractions by Program MIXCO.TRIADX

Pairwise Fractions (i,j)	(1,2)	(2,3)	(3,4)	(4,5)
3-site (B/B/B)				
site 1, P_b	0.535	-	-	-
site 2, P_b	0.223	-	-	-
site 3, P_b	0.035	-	-	-
2-site (B/B)				
site 1, P_b	-	0.221	0.222	0.221
site 2, P_b	-	0.033	0.033	0.033
Fraction i				
w_1	0.25	0.90	0.55	0.20
w_2	0.75	0.10	0.45	0.80
w_3	0	-	-	-
Fraction j				
w_1	0	0.55	0.20	0
w_2	0.88	0.45	0.80	1.00
w_3	0.11	-	-	-
R	1.13	0.93	0.78	0.37

Table 4. Relative Contributions of the Catalytic Sites to the Copolymerization as Indicated by MIXCO Analysis

		w_i			Wt % * w_i		
Frac	Wt %	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3
1	18.4	0.240	0.760	0	4.42	14.00	0
2	7.0	0	0.886	0.114	0	6.20	0.80
3	13.6	0	0.547	0.453	0	7.44	6.16
4	32.0	0	0.196	0.804	0	6.27	25.73
5	29.0	0	0	1.000	0	0	29.00
Sum	100.0				4.42	33.91	61.69

We can also determine the relative importance of each site through additional computation. In their thorough study, Kuroda et al.[14] have provided the weight per cent of the five fractions they separated. A straightforward calculation (Table 4) indicates that site 3 (with $P_b = 0.03$) produces the most polymer (62%), followed by site 2 (34%). Site 1 (obeying first-order Markovian statistics) only contributes about 4% to the copolymerization.

CONCLUSION

In this work the analytical methodology devised for the NMR analysis of multicomponent polymers[9,10] (MIXCO programs) was shown to be applicable to ethylene/1-butene copolymer sequence distribution. Consistent results were obtained by analyzing the NMR data of pairwise fractions. Information available includes: (1) the minimum number of active sites that fits the data, (2) the reaction probabilities of comonomers at each active site, (3) the contribution of each active site to the amount of copolymers being made. Similar analysis can be made for any copolymers where detailed NMR data for copolymer fractions are available. The approach can also be used to analyze NMR data of polymer samples taken out at various times during a copolymerization.

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