^{13}C-NMR Sequence Determination for Multicomponent Polymer Mixtures*

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Synopsis

A general treatment is developed for the ^{13}C-NMR analysis of polymers which contain several components. Reaction probability models and computer optimization techniques are used to resolve the NMR spectral data into separate components. The use of generalized multistate statistical models is introduced and is found to be very suitable for such systems. The computations are simplified by means of computer programs. The need for, and the relevance of, this approach are illustrated by the tacticity problems in polybutylene and polypropylene where two-state and three-state models are used, and copolymer triad sequence analysis for several olefin and acrylic copolymers where two-state models are needed. Three copolymer examples are given: propylene/butylene, ethylene/propylene, and acrylamide/acrylate.

INTRODUCTION

Many commercially important polymers are actually mixtures of two or more polymer components that differ from one another in composition (for copolymers) or in microstructure (for homopolymers). Such mixtures may be the deliberate result of polymer blending, polymer synthesis (e.g., as a result of sequential additions of comonomers), or the presence of different types of initiators or catalytic sites that produce different polymer chains. The characterization of such systems tends to be somewhat difficult. Fractionation, column separation, and chromatographic techniques are frequently used.[1-5]

The ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectral data of the whole polymer in such systems would include contributions from all its components. A proper treatment of the NMR data is not a trivial task. In this work a systematic examination is made of spectral data of mixtures of homopolymers and mixtures of copolymers. A general approach is described that uses computer methods and reaction probability models to treat such data. Examples are shown that illustrate the use of this methodology.

THEORETICAL CONSIDERATIONS

In studies of copolymerization kinetics and polymer microstructure, the use of reaction probability models can provide a convenient framework whereby the experimental data can be organized and interpreted, and can also give insight on reaction mechanisms.[6,7] These statistical models fall into two categories: those where the chain ends of the propagating polymer chain influence the addition of next monomer units (so-called chain-end control),

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and those where the catalyst/initiator determines the addition (catalytic-site control). The most common chain-end-controlled models are Bernoullian (B) and first- and second-order Markovian (M1 and M2) models.[6,7] The simplest catalytic-site-controlled model is the enantiomorphic site (E) model.[8] Hybrid models incorporating both chain-end and catalytic-site features have also been devised.[9] The relationships between the various models recently have been elucidated.[10]

| | Secondary Chain-end Control | | |
Primary Control Mechanism	None	Terminal	Penultimate
Chain end	B	M1	M2
Catalytic site	E	E-M1 (hybrid)	E-M2 (hybrid)

It may be noted that the models described above apply only to polymers containing one polymer component. In the catalytic-site model, this assumes that the polymer being analyzed arises from one catalytic site only.

For polymers with mixtures of different components, the one-state simple models cannot be used directly. Multistate models are needed. The simplest treatment is to take the linear combinations of different states, viz.,

$$I_t = \Sigma w_i I_i \tag{1}$$

where I_t corresponds to the total theoretical intensity for a given spectral region, and w_i and I_i are the corresponding mole fraction and theoretical intensity for the i-th component in the mixture. As an example, the mathematical expressions for the theoretical intensities in the case of the isotactic triad sequence (mm) for a two-component mixture will be written as:

$$I_{(mm)t} = w_1 I_{(mm),1} + w_2 I_{(mm),2} \tag{2}$$

Components 1 and 2 need not conform to the same statistical model. In fact, different combinations (e.g., B/B, B/E, E/E, and $M1/M1$) are also possible. The use of Eq. (1) is, therefore, completely general.

For convenience, the tacticity triads in various two-state mixed models are given in Table I. In that table standard nomenclature has been used for the reaction probabilities. Extensions to three-state models are straightforward.

It may be noted that some of the mixed statistical models have been previously proposed for specific polymeric systems. For example, the particular combination, E/B, has been proposed earlier by Chujo and Doi[11,12] for the analysis of polypropylene. The combination, B/B, has been proposed by Coleman and Fox,[13] and has been applied to a number of polymers, notably poly(methyl methacrylate).[14-16]

METHODOLOGY

The analytical approach used to handle the ^{13}C-NMR data of polymer mixtures is illustrated in Figure 1. For each assignable resonance in the ^{13}C spectrum, the theoretical intensities based on the separate models of the

TABLE I
Theoretical Expressions[a] for Tacticity Triad Intensities

Mixed Models	(mm)	(mr)	(rr)
B/B	$w_1 P_{m,1}^2 + w_2 P_{m,2}^2$	$2 w_1 P_{m,1} P_{r,1} + 2 w_2 P_{m,2} P_{r,2}$	$w_1 P_{r,1}^2 + w_2 P_{r,2}^2$
M1/M1	$w_1 P_{mm,1} P_{rm,1} + w_2 P_{mm,2} P_{rm,2}$	$2 w_1 P_{mr,1} P_{rm,1} + 2 w_2 P_{mr,2} P_{rm,2}$	$w_1 P_{mr,1} P_{rr,1} + w_2 P_{mr,2} P_{rr,2}$
E/E	$w_1 (P_{l,1}^3 + P_{d,1}^3) + w_2 (P_{l,2}^3 + P_{d,2}^3)$	$2 w_1 (P_{l,1}^2 P_{d,1} + P_{l,1} P_{d,1}^2) + 2 w_2 (P_{l,2}^2 P_{d,2} + P_{l,2} P_{d,2}^2)$	$w_1 (P_{l,1}^2 P_{d,1} + P_{l,1} P_{d,1}^2) + w_2 (P_{l,2}^2 P_{d,2} + P_{l,2} P_{d,2}^2)$
B/M1	$w_1 P_{m,1}^2 + w_2 P_{mm,2} P_{rm,2}$	$2 w_1 P_{m,1} P_{r,1} + 2 w_2 P_{mr,2} P_{rm,2}$	$w_1 P_{r,1}^2 + w_2 P_{mr,2} P_{rr,2}$
B/E	$w_1 P_{m,1}^2 + w_2 (P_{l,2}^3 + P_{d,2}^3)$	$2 w_1 P_{m,1} P_{r1} + 2 w_2 (P_{l,2}^2 P_{d,2} + P_{l,2} P_{d,2}^2)$	$w_1 P_{r,1}^2 + w_2 (P_{l,2}^2 P_{d,2} + P_{l,2} P_{d,2}^2)$
M1/E	$w_1 P_{mm,1} P_{rm,1} + w_2 (P_{l,2}^3 + P_{d,2}^3)$	$2 w_1 P_{mr,1} P_{rm,1} + 2 w_2 (P_{l,2}^2 P_{d,2} + P_{l,2} P_{d,2}^2)$	$w_1 P_{mr,1} P_{rr,1} + w_2 (P_{l,2}^2 P_{d,2} + P_{l,2} P_{d,2}^2)$

[a] P_m, P_r = Bernoullian probabilities of meso and racemic additions; $P_m + P_r = 1$.
P_{ij} = 1st order Markovian probability of the addition of monomer j to a propagating chain ending in i.
P_l, P_d = Enantiomorphic site probabilities of the addition of monomers with l and d configurations; $P_l + P_d = 1$.
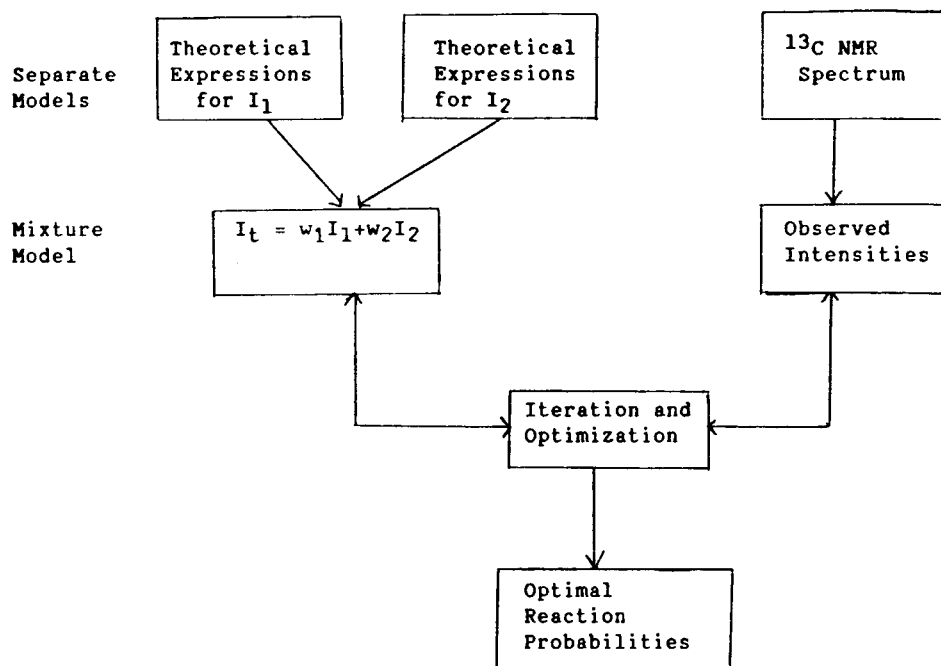
Fig. 1. Logic flow-chart of the ^{13}C-NMR analysis of polymer mixtures; I_t = total theoretical intensity for a given spectral region; w_i, I_i = mole fraction and theoretical intensity for the i-th component in the mixture.

polymer components are derived. They are weighted by the relative proportions of the components (w_i) and then summed together. The parameters are the reaction probabilities (P_i) and the mole fractions (w_i). An initial set of guess values of $\{P_i\}$ and $\{w_i\}$ is needed. The theoretical intensities are calculated from the theoretical expressions and then compared to the observed intensities. If a discrepancy is found, the parameters (P_i or w_i) are changed. This procedure is repeated iteratively until the best-fit values of P_i and w_i are obtained. The criterion used for the goodness of fit is the root-mean-square deviation (R) between the observed and the calculated intensities. A good fit is obtained when the deviations between the observed and the calculated intensities are approximately equal to the precision of the measurement of the intensities.

A family of computer programs has been written for this procedure called MIXCO. The algorithm used for the iteration and optimization processes is the simplex routine and was adapted from a model-fitting routine, FITCO, reported earlier.[17] Interested readers may write to the author for a listing of MIXCO.

HOMOPOLYMER TACTICITY

The method described above can be used to analyze the NMR tacticity data of polypropylene and polybutylene. Both are commercially important polymers made with Ziegler-Natta catalysts. Such catalysts frequently pro-

TABLE II
Theoretical[a] and Observed Intensities of Methylene Pentads in Polybutylene in the E/B Two-State Model

Line	Shift	Assignment	E/B Expression[b]	Asakura[21]	Doi[22]	Doi[22]
1	27.72	mmmm	$w(1 - 5\beta + 5\beta^2) + (1 - w)P_m^4$	0.56 (0.56)	0.75 (0.75)	0.75 (0.75)
2	27.53	mmmr	$w(2\beta - 6\beta^2) + 2(1 - w)P_m^3(1 - P_m)$	0.08 (0.08)	0.08 (0.07)	0.07 (0.06)
3	27.33	rmmr + mmrr	$w(2\beta - 5\beta^2) + 3(1 - w)P_m^2(1 - P_m)^2$	0.11 (0.11)	0.06 (0.08)	0.07 (0.07)
4	27.14	mmrm + rmrr	$4w_1\beta_1^2 + 2(1 - w)[P_m(1 - P_m)^3 + P_m^3(1 - P_m)]$	0.09 (0.09)	0.04 (0.03)	0.03 (0.03)
5	26.92	rmrm	$2w\beta^2 + 2(1 - w)P_m^2(1 - P_m)^2$	0.03 (0.04)	0.02 (0.01)	0.01 (0.01)
6	26.73	rrrr	$w\beta^2 + (1 - w)(1 - P_m)^4$	0.05 (0.05)	0.02 (0.02)	0.04 (0.04)
7	26.63	mrrr	$2w\beta^2 + 2(1 - w)P_m(1 - P_m)^3$	0.04 (0.06)	0.02 (0.02)	0.02 (0.03)
8	26.49	mrrm	$w(\beta - 3\beta^2) + (1 - w)P_m^2(1 - P_m)^2$	0.04 (0.04)	0.01 (0.03)	0.01 (0.03)
			Two-state, E component: w (fraction) =	0.672	0.887	0.885
			β =	0.0367	0.0321	0.0316
			P_l =	0.962	0.967	0.967
			Two-state, B component: $1 - w$ (fraction) =	0.328	0.113	0.115
			P_m =	0.379	0.373	0.237

[a] Values calculated by the model are shown in parentheses underneath observed values.
[b] $\beta = P_l(1 - P_l)$ from Ref. 11.

duce more that one catalytic site, and the resulting polymer is a blend of several homopolymers differing only in propagation statistics.[11,12,18,19]

The polybutylene case is first examined. The tacticity of this polymer has been studied only occasionally,[20-22] although the ^{13}C assignments are well known. For the branch methylene carbon, pentad sequences are found; the assignments[20-22] are shown in Table II. For this polymer, the E/B model will be attempted. The expressions for the theoretical intensities in the case of the 8 resolvable methylene resonances for both the E and the B models are also shown in Table II.

Two sets of spectral data of polybutylene have been previously published by Doi et al.,[22] and one set by Asakura et al.[21] From the observed intensities, optimal values of w_1, P_1, w_2, P_m are obtained through the simplex optimization procedure (via program MIXCO). The results are shown in the lower half of Table II. Also given are the fitted intensities. The close agreement between the two sets of results means that the two-state model can be used to describe the polymer structure approximately. Consequently, there should be (at least) two catalytic sites active in the polymer synthesis.

Polypropylene is a popular polymer that has been repeatedly studied for its microstructure. Different statistical models have been used including Bernoullian,[11,23,24] first- and second-order Markovian,[11,23,25] enantiomorphic-site,[11,26] and hybrid EM-1 models.[9] Recent data tend to favor the E/B mixture, called the bicatalytic site model by Inoue et al.,[11] and Doi.[12]

In reviewing the literature data, it appears that improvements on the simple E/B mixture model can be obtained. An alternative E/E mixture model was first attempted in this study, but gave no particular advantage. A more general model and one which gives better fit to many experimental data was eventually found to be the three-state $E/E/B$ mixture model.

TABLE III
Mathematical Expressions for the Theoretical Intensities of the Methyl Pentads
in Polypropylene in the $E_1/E_2/B$ Three-State Mixture Model[a]

No.	Pentad	$f_{1,i}$ (E_1)[b]	$f_{2,i}$ (E_2)[b]	$f_{3,i}$ (B)
1	mmmm	$w_1(1 - 5\beta_1 + 5\beta_1^2)$	$w_2(1 - 5\beta_2 + 5\beta_2^2)$	$w_3 P_m^4$
2	mmmr	$w_1(2\beta_1 - 6\beta_1^2)$	$w_2(2\beta_2 - 6\beta_2^2)$	$2w_3 P_m^3(1 - P_m)$
3	rmmr	$w_1\beta_1^2$	$w_2\beta_2^2$	$w_3 P_m^2(1 - P_m)^2$
4	mmrr	$w_1(2\beta_1 - 6\beta_1^2)$	$w_2(2\beta_2 - 6\beta_2^2)$	$2w_3 P_m^2(1 - P_m)^2$
5	mmrm	$4w_1\beta_1^2$	$4w_2\beta_2^2$	$2w_3 P_m(1 - P_m)^3$
	rmrr			$+ 2w_3 P_m^3(1 - P_m)$
6	rmrm	$2w_1\beta_1^2$	$2w_2\beta_2^2$	$2w_3 P_m^2(1 - P_m)^2$
7	rrrr	$w_1\beta_1^2$	$w_2\beta_2^2$	$w_3(1 - P_m)^4$
8	rrrm	$2w_1\beta_1^2$	$2w_2\beta_2^2$	$2w_3 P_m(1 - P_m)^3$
9	mrrm	$w_1(\beta_1 - 3\beta_1^2)$	$w_2(\beta_2 - 3\beta_2^2)$	$w_3 P_m^2(1 - P_m)^2$

[a] The $E_1/E_1/B$ expressions are obtained by summing the corresponding $f_{j,i}$ terms in columns 3, 4, and 5.
[b] $\beta_i = P_{li}(1 - P_{li})$.

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TABLE IV
$E/E/B$ Model in Polypropylene: Observed and Calculated (in Parentheses)
Intensities for Soluble and Insoluble Fractions

	Doi[a]	LY97.5[b]	VHY97.5[b]	HY97.5[b]	HY96[b]	HY90[b]
Solubles						
mmmm	39.34	36.71	39.63	48.4	44.22	43.52
	(39.54)	(37.55)	(39.27)	(48.31)	(44.16)	(43.79)
mmmr	9.31	8.66	9.42	9.03	11.19	10.85
	(8.53)	(8.82)	(8.89)	(8.42)	(10.77)	(10.40)
mmmr	3.00	4.10	4.91	3.55	3.58	0
	(1.83)	(2.19)	(2.22)	(1.62)	(1.74)	(1.59)
mmrr	12.81	10.21	10.23	9.26	9.84	13.15
	(9.67)	(10.78)	(10.81)	(9.88)	(11.86)	(11.5)
xmrx	7.40	11.86	11.05	8.51	8.51	9.20
	(10.69)	(11.54)	(11.22)	(8.66)	(8.74)	(8.66)
rmrm	3.70	3.64	2.45	2.58	3.13	3.21
	(3.66)	(4.39)	(4.45)	(3.23)	(3.48)	(3.18)
rrrr	12.71	10.03	9.01	8.14	8.06	9.01
	(13.03)	10.22	(9.04)	(8.02)	(6.92)	(8.54)
rrrm	6.40	8.03	7.03	4.74	5.54	5.51
	(8.17)	(9.11)	(8.69)	(6.89)	(6.35)	(6.57)
mrrm	5.30	6.72	6.23	5.72	5.91	5.51
	(4.83)	(5.39)	(5.40)	(4.94)	(5.93)	(5.75)
Insoluble						
mmmm	82.7	92.98	92.91	92.19	89.34	89.37
	(82.6)	(92.78)	(93.21)	(92.14)	(89.23)	(89.63)
mmmr	6.0	1.54	1.64	1.97	3.97	2.91
	(5.23)	(2.07)	(1.47)	2.45	(3.27)	(2.83)
rmmr	1.2	0.60	0.54	0	0.55	0.20
	(0.37)	(0.11)	(0.17)	(0.11)	(0.15)	(0.16)
mmrr	4.4	1.49	1.64	3.33	3.32	3.12
	(5.26)	(2.17)	(1.64)	(2.52)	(3.37)	(2.96)
xmrx	1.30	0.60	0.82	0.62	0.93	0.90
	(1.57)	(0.56)	(0.89)	(0.53)	(0.76)	(0.92)
rmrm	0.80	1.13	0.22	0	0	0.10
	(0.74)	(0.21)	(0.35)	(0.21)	(0.29)	(0.32)
rrrr	1.10	0.60	0.88	0.69	0.69	2.05
	(0.69)	(0.53)	(0.74)	(0.40)	(0.66)	(0.97)
rrrm	0.90	0.35	0.65	0.25	0.25	0.24
	(0.87)	(0.46)	(0.70)	(0.38)	(0.58)	(0.72)
mrrm	1.50	0.70	0.71	0.94	0.94	1.10
	(2.63)	(1.08)	(0.82)	(1.25)	(1.69)	(1.48)
E/E/B Model						
E_1 component, P_l	0.981	0.989	0.995	0.991	0.984	0.988
E_2 component, P_l	0.806	0.887	0.895	0.909	0.867	0.876
B component, P_m	0.201	0.294	0.311	0.285	0.277	0.244
Sol. frac. w_1'	0.274	0.091	0.085	0.128	0.134	0.104
w_2'	0.432	0.519	0.535	0.580	0.644	0.658
Insol. frac. w_1''	0.863	0.974	0.941	0.925	0.952	0.926
w_2''	0.129	0.005	0.028	0.061	0.026	0.047

[a] Data from Ref. 11.
[b] Data from Ref. 27.

The best test of any model is to analyze samples that have been fractionated. Usually, polypropylene is dissolved in hexane or heptane and the (room temperature) soluble and insoluble fractions obtained. These two fractions can then be analyzed at once by the mixture model. The theoretical expressions for methyl pentads corresponding to the three-state $E_1/E_2/B$ model are shown in Table III. The expressions for the E_1/E_2 model can be obtained by deleting the fifth column. Likewise, the E/B model can be derived by deleting the fourth column. The spectral-fitting procedure used was the same as before. For each run, 18 spectral intensities are entered (9 from each fraction). The equations used are:

Fraction 1:

$$I'_{t,i} = w'_1 f_{1,i} + w'_2 f_{2,i} + (1 - w'_1 - w'_2) f_{3,i}$$

Fraction 2:

$$I''_{t,i} = w''_1 f_{1,i} + w''_2 f_{2,i} + (1 - w''_1 - w''_2) f_{3,i}$$

where $i = 1, \ldots, 9$ for the nine pentads, and the theoretical expressions $f_{1,i}$, $f_{2,i}$, and $f_{3,i}$ take on the same values for both fractions 1 and 2. In the fitting procedure, $f_{j,i}$ are held within narrow ranges ($P_{l1} = 0.90 \pm 0.05$, $P_{l2} = 0.80 \pm 0.10$, $P_m = 0.5 \pm 0.2$). The results on polypropylene fractions reported by Martuscelli et al.[27] and by Inoue et al.[11] are summarized in Table IV. In all cases considered, the three-state model provides satisfactory agreement. Thus, at least for these samples, polypropylene can be regarded as arising from three catalytic sites, two isospecific, and one aspecific. Recent data[18, 28-30] do indeed indicate the presence of more than one isospecific site in such catalysts.

TABLE V
Analysis of Propylene (P)-Butylene (B) Copolymer Triads[c] Observed vs. Calculated
Intensities for the B/B Mixed Model

	C_1		C_2		C_3	
	I_{obsd}	I_{calc}	I_{obsd}	I_{calc}	I_{obsd}	I_{calc}
P	91.5	91.16	84.6	79.37	51.4	47.81
B	8.5	8.79	15.4	20.61	48.6	52.17
PPP	76.9	77.20	53.2	53.15	20.4	20.50
PPB	12.7	12.96	23.1	22.53	18.4	19.72
BPB	1.8	1.00	5.9	3.69	8.5	7.59
PBP	5.9	6.48	9.5	11.26	8.8	9.86
PBB	2.2	2.00	6.3	7.38	16.1	15.19
BBB	0.5	0.31	2.1	1.97	27.8	27.12
B/B Model[a]:						
w_1		0.897		0.775		0.655
$P_{p,1}$		0.935		0.858		0.668
w_2		0.103		0.225		0.345
$P_{p,2}$		0.697		0.573		0.098
R^b		0.408		0.959		0.938

[a] $P_{p,i}$ = Bernoullian probability for propylene at state i. For butylene, $P_{b,i} = 1 - P_{p,i}$.
[b] R = Mean deviation between observed and calculated intensities.
[c] Data from Ref. 31.

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The same approach can be used for copolymer mixtures. An example is the propylene-butylene copolymer. The observed compositions and triad distributions of three copolymers reported in the literature[31] are given in Table V. The distributions can be simulated to a two-state B/B mixture. The theoretical expressions for the triad comonomer sequence distribution are shown in Table VI. Computerized fitting follows the same procedure, and the result is summarized in Table V. It appears that the copolymerization obeys the two-state model very well. The copolymers reported in the literature must have been made with a catalytic system containing at least two active catalyst sites.

A similar analysis can be carried out for ethylene-propylene copolymers. The triad distributions for selected copolymers reported in the literature[32-34] are given in Table VII. The same theoretical expressions as in Table V are used in this two-state fitting procedure. The results are given in the lower half of Table VII. For all these copolymers, despite the wide differences in sample origins, the two-state B/B mixture model works very well. Particularly instructive are the last five samples taken from the paper by Abis et al.[34] In that work, they separated the polymer into four fractions. It appears that not only does the two-state B/B mixture model fit the data well, but even the reaction probabilities are approximately the same for all the fractions. This is to be expected if indeed the model is valid.

Fraction 1: $P_{p,1} = 0.65$
Fraction 2: $P_{p,2} = 0.20$

It may be noted that the importance of sample heterogeneity and the relevance of multiple catalytic sites for ethylene-propylene copolymers has been previously indicated by Cozewith and Ver Strate,[35] Abis et al.,[34] and Ross.[36]

The last example is taken from free radical copolymerization of acrylamide and sodium acrylate. Candau et al.[37] carried the copolymerization to high conversion, and since the two comonomers had different reactivities, the sequence distribution of the final product was the sum total of polymer

TABLE VI
Theoretical Expressions for Comonomer Sequence Triads for B/B and $M1/M1$ Mixtures[a]

Triad	B/B Mixture Model	$M1/M1$ Mixture Model
AAA	$w_1 P_{a1}^3 + w_2 P_{a2}^3$	$w_1 P_{aa,1}^2 P_{ba,1} + w_2 P_{aa,2}^2 P_{ba,2}$
AAB	$2 w_1 P_{a1}^2 P_{b1} + 2 w_2 P_{a2}^2 P_{b2}$	$2 w_1 P_{ab,1} P_{aa,1} P_{ba,1} + 2 w_2 P_{ab,2} P_{aa,2} P_{ba,2}$
BAB	$w_1 P_{a1} P_{b1}^2 + w_2 P_{a2} P_{b2}^2$	$w_1 P_{ab,1}^2 P_{ba,1} + w_2 P_{ab,2}^2 P_{ba,2}$
ABA	$w_1 P_{a1}^2 P_{b1} + w_2 P_{a2}^2 P_{b2}$	$w_1 P_{ab,1} P_{ba,1}^2 + w_2 P_{ab,2} P_{ba,2}^2$
BBA	$2 w_1 P_{a1} P_{b1}^2 + 2 w_2 P_{a2} P_{b2}^2$	$2 w_1 P_{ab,1} P_{ba,1} P_{bb,1} + 2 w_2 P_{ab,2} P_{ba,2} P_{bb,2}$
BBB	$w_1 P_{b1}^3 + w_2 P_{b2}^3$	$w_1 P_{ab,1} P_{bb,1}^2 + w_2 P_{ab,2} P_{bb,2}^2$

[a] P_{ai}, P_{bi} = Bernoullian probabilities of A and B respectively; similarly, $P_{aa,i}/P_{ba,i}/P_{ab,i}/P_{bb,i}$ are the conventional 1st order Markovian probabilities for A (a) and B (b).

TABLE VII

^{13}C-NMR results of Ethylene (E)-Propylene (P) Copolymer Triad Sequences: Observed and Calculated (in Parentheses) Intensities for the B/B Mixed Model

	A[a]	B[a]	C[a]	D[a]	E[a]	1[b]	3[b]	5[c]	5a[c]	5b[c]	5c[c]	5d[c]
P	0.917 (0.909)	0.857 (0.845)	0.447 (0.463)	0.282 (0.282)	0.155 (0.150)	0.90 (0.891)	0.79 (0.793)	0.42 (0.44)	0.39 (0.395)	0.35 (0.345)	0.45 (0.449)	0.33 (0.328)
E	0.083 (0.088)	0.143 (0.151)	0.553 (0.534)	0.718 (0.717)	0.845 (0.842)	0.10 (0.112)	0.21 (0.205)	0.58 (0.564)	0.61 (0.603)	0.65 (0.652)	0.55 (0.551)	0.67 (0.671)
PPP	0.72 (0.712)	0.63 (0.629)	0.16 (0.166)	0.04 (0.053)	0.02 (0.014)	0.73 (0.727)	0.54 (0.545)	0.15 (0.151)	0.11 (0.101)	0.11 (0.092)	0.12 (0.120)	0.07 (0.066)
PPE	0.16 (0.158)	0.19 (0.194)	0.19 (0.199)	0.12 (0.125)	0.05 (0.054)	0.15 (0.148)	0.21 (0.212)	0.16 (0.182)	0.16 (0.178)	0.12 (0.138)	0.20 (0.214)	0.14 (0.142)
EPE	0.04 (0.039)	0.04 (0.022)	0.10 (0.098)	0.11 (0.104)	0.08 (0.082)	0.02 (0.016)	0.04 (0.036)	0.11 (0.107)	0.12 (0.116)	0.12 (0.115)	0.13 (0.115)	0.12 (0.120)
PEP	0.07 (0.069)	0.10 (0.097)	0.11 (0.099)	0.06 (0.062)	0.03 (0.026)	0.08 (0.074)	0.11 (0.106)	0.10 (0.091)	0.09 (0.089)	0.07 (0.069)	0.11 (0.107)	0.07 (0.071)
PEE	0.02 (0.019)	0.03 (0.045)	0.17 (0.196)	0.20 (0.208)	0.15 (0.165)	0.02 (0.032)	0.06 (0.073)	0.20 (0.201)	0.23 (0.232)	0.23 (0.23)	0.22 (0.230)	0.24 (0.24)
EEE	0.00 (0.000)	0.01 (.010)	0.23 (0.239)	0.43 (0.447)	0.63 (0.651)	0.01 (0.006)	0.03 (0.026)	0.27 (0.272)	0.28 (0.282)	0.35 (0.353)	0.21 (0.214)	0.36 (0.36)
B/B Model[d]:												
w_1	0.904	0.890	0.594	0.483	0.274	0.814	0.818	0.513	0.535	0.305	0.751	0.421
$P_{p,1}$	0.914	0.881	0.651	0.478	0.370	0.934	0.862	0.661	0.567	0.652	0.540	0.529
w_2	0.096	0.110	0.406	0.517	0.726	0.186	0.182	0.487	0.465	0.695	0.249	0.599
$P_{p,2}$	0.617	0.574	0.192	0.098	0.068	0.683	0.489	0.196	0.198	0.215	0.173	0.183
R	0.0083	0.0067	0.0070	0.0039	0.0038	0.0041	0.0042	0.0071	0.0056	0.0078	0.0069	0.0013

[a] Data from Ref. 32.
[b] Data from Ref. 33.
[c] Data from Ref. 34.
[d] $P_{p,i}$ = Bernoullian probability for propylene addition at state i. For ethylene, $P_{e,i} = 1 - P_{p,i}$.

TABLE VIII
Observed[a] and Calculated Triad Comonomer Sequences of Acrylamide (M)-
Acrylate (A) Copolymer for the $M1/M1$ Model

	AAA	AAM	MAM	AMA	MMA	MMM
Observed	0.030	0.112	0.204	0.093	0.386	0.175
Calculated	0.030	0.112	0.210	0.110	0.314	0.225
$M1/M1$ Model[b]:						
	$w_1 = 0.585$			$w_2 = 0.415$		
	$P_{aa,1} = 0.109$			$P_{aa,2} = 0.433$		
	$P_{ma,1} = 0.411$			$P_{ma,2} = 0.413$		

[a] Data from Ref. 37.
[b] $P_{aa,i}$ and $P_{ma,i}$ are M1 probabilities for acrylate (a) and acrylamide (m).

components obeying incrementally changing statistics, and in general did not conform to a simple reaction probability model. For such systems, the $M1/M1$ mixture model can sometimes be used to approximate the polymer statistics. The theoretical expressions for the triads in the $M1/M1$ model are given in Table VI. The observed and calculated triad values are shown in Table VIII. The agreement, though not perfect, is acceptable. In a heuristic sense, the $M1$ reaction probabilities for state 1 describe the polymers made at the onset of polymerization, whereas the $M1$ reaction probabilities for state 2 simulates the polymerization near the end. The total polymer then can be considered to be a mixture of two statistical copolymers (state 1 + state 2).

CONCLUSION

In the use of NMR for polymer characterization, the common ("analytical") approach consists of the following steps:

Acquisition $\longrightarrow$ Spectral $\longrightarrow$ Spectral $\longrightarrow$ Information
of spectrum   interpretation   analysis

This article addresses the third step: spectral analysis. For multicomponent systems, the use of reaction probability models and computerized optimization technique provides a convenient framework for analysis. The methodology described in this work can: (1) permit differentiation to be made as to whether the given sample comprises one component or a mixture of several components; (2) allow the NMR spectrum of a polymer mixture to be analyzed in an unbiased fashion; (3) give information on mole fractions and probability parameters that can be significant variables in understanding catalyst structures or polymerization mechanisms.

Note Added in Proof. While this paper was in press, one paper [38] appeared that confirmed the importance of two-state model in polybutylene, and two papers [39, 40] on the relevence of two-state model in ethylene-propylene copolymers.

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