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Consecutive Two-State Statistical Polymerization Models[†]

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ABSTRACT: In polymerizations of vinyl monomers and olefins it may happen that the propagating polymer species can exist in two states, e.g., as a result of solvent interaction (in ionic polymerization) or multiple catalytic sites (in Ziegler–Natta polymerization). If the switching between the states occurs during propagation, the resulting polymer would be a block copolymer, each block obeying a different propagation statistics. The polymer microstructure would follow a two-state model, an example being the Coleman–Fox statistics. In this work, a different approach is taken to treat this general problem of consecutive two-state models. Included in the treatment (for tacticity) are the two-state Bernoullian/Bernoullian, Bernoullian/enantiomorphic, and enantiomorphic/enantiomorphic models. The theoretical expressions corresponding to NMR tetrad and pentad tacticity analysis are derived. These expressions are then combined with a computerized analytical approach to facilitate their application. Illustrative examples are shown of the use of this methodology to treat tacticity tetrads of poly(methyl methacrylate) and tacticity pentads of polypropylene. The same methodology can be readily used for copolymer sequence analysis.

Introduction

In heterogeneous Ziegler–Natta polymerization, it is well-known[1–3] that the catalyst system contains multiple active sites. The resulting polymer would then be an in situ polymer blend of two or more components, each component being made by an active site. Such polymer exhibits a distribution of composition (multistate compositional heterogeneity[4]) and has NMR data that may not fit a single-state statistical model.

Earlier, Zambelli et al.[5a] and Chujo et al.[5b,c] proposed two-state models to interpret the NMR tacticity data of polypropylene. The polymer is presumed to arise from two active sites: a Bernoullian (B) site, characterized by P_m (the reaction probability for meso placement of monomer), and an enantiomorphic (E) site, characterized by P_l (the reaction probability for monomer enchainment in the levo configuration). A similar model has been used[6,7] to analyze the tacticity data of poly(1-butene). Statistical models involving two Bernoullian states have been used to calculate copolymer sequence distributions from NMR triad data.[7–10] Cheng[7] has developed a general methodology for the treatment of NMR data arising from polymers consisting of multiple states. Polymer systems that have been analyzed include ethylene/propylene,[7,11,13,14] propylene/1-butene,[7] ethylene/1-butene,[12,15] ethylene/1-hexene,[16] and epichlorohydrin/ethylene oxide[17] copolymers (for copolymer sequence distributions) and polypropylene[7,18] and poly(1-butene)[7,11] (for the determination of tacticity).

All the multistate models described thus far are "concurrent" models; i.e., each catalytic site is presumed to produce separate polymer chains. Recently, Chien, et al.[19,20] synthesized nonsymmetric *ansa*-titanocene complexes and employed them to polymerize propylene into thermoplastic elastomeric polypropylene (TPE-PP). The available data suggest that the catalyst "switches" from a stereoselective site with one type of propagating statistics to a nonstereoselective site with a different type of propagating statistics while chain growth proceeds. For convenience, the overall statistical models describing such situations would be called "consecutive" models.

Previously, Coleman and Fox[21] developed a two-state B/B model which is applicable to both consecutive and concurrent situations. Frisch et al.[22] derived the two-state B/B expressions for tacticity tetrads and pentads. In our recent investigation of homogeneous olefin polymerization using group 4B catalysts,[19,20] we found it useful to generalize the consecutive two-state models.[23] In this work we used a different approach and systematically derived the theoretical expressions for tacticity tetrads and pentads for the consecutive two-state E/E, B/B, and E/B models. These models can be generally used for the analysis of NMR tetrad and pentad tacticity data where propagating site exchange is suspected.

Pentad Tacticity

Approach. In their classic work on the B/B model, Coleman and Fox[21] used a kinetic approach. We have chosen, instead, a structural approach. For simplicity, we consider an ensemble of infinite polymer chains, made up of polymer blocks A + B. The propagation mechanism within block A is different from that of block B (Figure 1). We assume on the average that there are α monomer residues in block A and β residues in block B. In the middle of each block, the enchainment of each monomer follows the propagation probability of the prevailing mechanism (e.g., P_A for block A and P_B for block B).

Special consideration needs to be taken for the junction points between the A and B blocks. For pentad tacticity analysis, the two monomer residues nearest the junction point would have propagation probabilities that reflect both blocks A and B (Figure 1). Thus, for pentads there are $\alpha - 4$ monomer residues each with propagation probabilities P_A and $\beta - 4$ residues each with propagation

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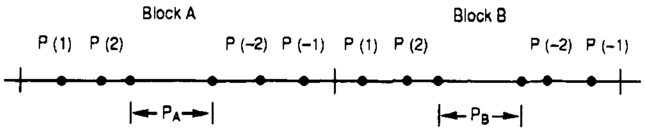

Figure 1. Chain propagation probabilities for tacticity pentads in the consecutive two-state model. Note that in the pentad analysis each monomer unit can "sense" the configuration of two adjacent neighbors on each side. Thus, all the monomers that are two or more units removed from the junction points have the same propagation probabilities (P_A and P_B). P_A, P_B, and junction probabilities {P(i)} correspond to the probabilities that a monomer unit is centered in a particular pentad.

Chart I

block	no. of monomer residues	propagation probability
A	$\alpha - 4$	P_A
B	$\beta - 4$	P_B
A (junction)	1	P(−2)
	1	P(−1)
	1	P(1)
	1	P(2)
B (junction)	1	P(−2)
	1	P(−1)
	1	P(1)
	1	P(2)

probability P_B. Eight monomer residues at the junction points have their own propagation probabilities as indicated in Chart I. Note that all the propagation probabilities in Chart I represent the probabilities that a monomer unit is centered in a particular pentad.

For each two-state model, it is necessary to determine the junction probabilities, P(j), where j = −2 to +2. The overall probability expression for each pentad is the average of the propagation probabilities for the monomer residues in blocks A and B and all eight junction probabilities; i.e.

$$\text{P(pentad)} = \frac{(\alpha - 4)\text{P}_\text{A} + (\beta - 4)\text{P}_\text{B} + \sum \text{P(j)}}{\alpha + \beta} \qquad (1)$$

E/E Model. In the case where both blocks A and B obey the enantiomorphic-site model, P_A and P_B are simply the E-model conditional probabilities. For completeness, the expressions for the pentads are given in Table I. The enantiomorphic-site conditional probabilities for blocks A and B are designated P_{la} and P_{lb}, respectively.

The junction probabilities, P(j), are different for each of the ten pentads. For illustration, only the derivation of the (mmmm) pentad is shown in its entirety. The following nomenclature (previously designed for polypropylene[24]) will be used. The configuration of each vinyl monomer is shown as 1 and $\bar{1}$ (corresponding to levo or dextro configuration, respectively). The monomer residue being considered is centered in the pentad and has an asterisk above it. In addition, the junction point is shown as a dash (—).

For P(−2), two possible structures contribute to the (mmmm) pentad. These structures and the mode of addition are

$$\begin{array}{lccccccccccc}
 & & & * & & & \quad & & & * & & \\
\text{P}(-2)\ \text{structure} & 1 & 1 & 1 & 1\ - & 1 & & \bar{1} & \bar{1} & \bar{1} & \bar{1}\ - & \bar{1} \\
\text{mechanism} & \text{A} & \text{A} & \text{A} & \text{A} & \text{B} & & \text{A} & \text{A} & \text{A} & \text{A} & \text{B} \\
\text{probability} & \multicolumn{5}{c}{P_{la}{}^4 P_{lb}} & & \multicolumn{5}{c}{(1 - P_{la})^4(1 - P_{lb})}
\end{array}$$

The junction probabilities for these structures are as indicated. We have arbitrarily associated 1 (levo configuration) with conditional probabilities P_{la} and P_{lb}; the $\bar{1}$ configuration (dextro) then has $(1 - P_{la})$ and $(1 - P_{lb})$ as conditional probabilities in the blocks A and B, respectively.

Using the same logic, we can write the structures and the junction probabilities for the other kinds of junctions:

$$\begin{array}{lccccccccccc}
 & & & * & & & \quad & & & * & & \\
\text{P}(-1)\ \text{structure} & 1 & 1 & 1\ - & 1 & 1 & & \bar{1} & \bar{1} & \bar{1}\ - & \bar{1} & \bar{1} \\
\text{mechanism} & \text{A} & \text{A} & \text{A} & \text{B} & \text{B} & & \text{A} & \text{A} & \text{A} & \text{B} & \text{B} \\
\text{probability} & \multicolumn{5}{c}{P_{la}{}^3 P_{lb}{}^2} & & \multicolumn{5}{c}{(1 - P_{la})^3(1 - P_{lb})^2} \\
 & & & * & & & & & & * & & \\
\text{P}(1)\ \text{structure} & 1 & 1\ - & 1 & 1 & 1 & & \bar{1} & \bar{1}\ - & \bar{1} & \bar{1} & \bar{1} \\
\text{mechanism} & \text{A} & \text{A} & \text{B} & \text{B} & \text{B} & & \text{A} & \text{A} & \text{B} & \text{B} & \text{B} \\
\text{probability} & \multicolumn{5}{c}{P_{la}{}^2 P_{lb}{}^3} & & \multicolumn{5}{c}{(1 - P_{la})^2 P_{lb}{}^3} \\
 & & & * & & & & & & * & & \\
\text{P}(2)\ \text{structure} & 1\ - & 1 & 1 & 1 & 1 & & \bar{1}\ - & \bar{1} & \bar{1} & \bar{1} & \bar{1} \\
\text{mechanism} & \text{A} & \text{B} & \text{B} & \text{B} & \text{B} & & \text{A} & \text{B} & \text{B} & \text{B} & \text{B} \\
\text{probability} & \multicolumn{5}{c}{P_{la} P_{lb}{}^4} & & \multicolumn{5}{c}{(1 - P_{la}) P_{lb}{}^4}
\end{array}$$

The overall probability expression for the (mmmm) pentad is then the sum of all the terms

$$\begin{aligned}
(\text{mmmm}) = k\{&(\alpha - 4)[P_{la}{}^5 + (1 - P_{la})^5] + \\
&(\beta - 4)[P_{lb}{}^5 + (1 - P_{lb})^5] + 2P_{la}{}^4 P_{lb} + \\
&2(1 - P_{la})^4(1 - P_{lb}) + 2P_{la}{}^3 P_{lb}{}^2 + 2(1 - P_{la})^3(1 - P_{lb})^2 + \\
&2P_{la}{}^2 P_{lb}{}^3 + 2(1 - P_{la})^2(1 - P_{lb})^3 + 2P_{la} P_{lb}{}^4 + \\
&2(1 - P_{la})(1 - P_{lb})^4\} \qquad (2)
\end{aligned}$$

where $k = (\alpha + \beta)^{-1}$, the normalization constant. The probability expressions for all the pentads are shown in Table I. Note that the pentad (mmmr) is nonsymmetric; we need to calculate the expressions separately for (mmmr) and (rmmm) and then sum up all the expressions. Similar treatment needs to be done on all other nonsymmetric pentads.

B/B Model. For the two-state B/B model, two Bernoullian conditional probabilities are involved: P_{ma} and P_{mb}, corresponding to blocks A and B, respectively. As before, we shall only show the derivation of the probability expression for the (mmmm) pentad. In the Bernoullian model only the relative configuration (meso or racemic) is considered, and we have one structure for each pentad. However, it is necessary to consider the direction of chain propagation. For P(−2), the structures and the junction probabilities are as follows:

$$\begin{array}{lccccccccccccccccccc}
\text{direction} & \multicolumn{9}{c}{\longrightarrow} & \quad & \multicolumn{9}{c}{\longleftarrow} \\
 & & & & & * & & & & & & & & & & * & & & & \\
\text{P}(-2)\ \text{structure} & 1 & & 1 & & 1 & & 1\ - & & 1 & & \bar{1} & & \bar{1} & & \bar{1} & & \bar{1}\ - & & \bar{1} \\
\text{block} & & \text{A} & & \text{A} & & \text{A} & & \text{B} & & & & \text{A} & & \text{A} & & \text{A} & & \text{A} & \\
\text{probability} & \multicolumn{9}{c}{P_{ma}{}^3 P_{mb}} & & \multicolumn{9}{c}{P_{ma}{}^4}
\end{array}$$

Note that the probability term for the enchainment of the rightmost monomer residue is different for the two different directions (P_{ma} vs. P_{mb}). Similar junction probabilities can be derived for the other kinds of junctions. In each of the structures given hereinafter, the asterisk is presumed to reside in the central monomer unit in the pentad (or, in the case of tetrad, between the two central monomer units).

Table I
Pentad Probability Expressions in the Consecutive E/E Model

pentad	P_A	P_B	P(−2)	P(−1)	P(1)	P(2)
(mmmm)	$P_{1a}^5+(1-P_{1a})^5$	$P_{1b}^5+(1-P_{1b})^5$	$P_{1a}^4P_{1b}+(1-P_{1a})^4(1-P_{1b})$	$P_{1a}^3P_{1b}^2+(1-P_{1a})^3(1-P_{1b})^2$	$P_{1a}^2P_{1b}^3+(1-P_{1a})^2(1-P_{1b})^3$	$P_{1a}P_{1b}^4+(1-P_{1a})(1-P_{1b})^4$
(mmmr)	$2P_{1a}^4(1-P_{1a})$ $+2(1-P_{1a})^4P_{1a}$	$2P_{1b}^4(1-P_{1b})$ $+2(1-P_{1b})^4P_{1b}$	$P_{1a}^4(1-P_{1b})+(1-P_{1a})^4P_{1b}$ $+P_{1a}^3(1-P_{1a})P_{1b}+(1-P_{1a})^3P_{1a}(1-P_{1b})$	$P_{1a}^3P_{1b}(1-P_{1b})+(1-P_{1a})^3(1-P_{1b})P_{1b}$ $+P_{1a}^2(1-P_{1a})P_{1b}^2+(1-P_{1a})^2P_{1a}(1-P_{1b})^2$	$P_{1a}^2P_{1b}^2(1-P_{1b})+(1-P_{1a})^2(1-P_{1b})^2P_{1b}$ $+P_{1a}(1-P_{1a})P_{1b}^3+(1-P_{1a})P_{1a}(1-P_{1b})^3$	$P_{1a}P_{1b}^3(1-P_{1b})+(1-P_{1a})(1-P_{1b})^3P_{1b}$ $+(1-P_{1a})P_{1b}^4+P_{1a}(1-P_{1b})^4$
(rmmr)	$P_{1a}^3(1-P_{1a})^2$ $+P_{1a}^2(1-P_{1a})^3$	$P_{1b}^3(1-P_{1b})^2$ $+P_{1b}^2(1-P_{1b})^3$	$(1-P_{1a})P_{1a}^3(1-P_{1b})+P_{1a}(1-P_{1a})^3P_{1b}$	$(1-P_{1a})P_{1a}^2P_{1b}(1-P_{1b})+P_{1a}(1-P_{1a})^2(1-P_{1b})P_{1b}$	$(1-P_{1a})P_{1a}P_{1b}^2(1-P_{1b})+P_{1a}(1-P_{1a})(1-P_{1b})^2P_{1b}$	$(1-P_{1a})P_{1b}^3(1-P_{1b})+P_{1a}(1-P_{1b})^3P_{1b}$
(mmrr)	$2P_{1a}^4(1-P_{1a})$ $+2(1-P_{1a})^4P_{1a}$	$2P_{1b}^4(1-P_{1b})$ $+2(1-P_{1b})^4P_{1b}$	$P_{1a}^3(1-P_{1a})P_{1b}+(1-P_{1a})^3P_{1a}(1-P_{1b})$ $+P_{1a}^3(1-P_{1a})P_{1b}+P_{1a}(1-P_{1a})^3(1-P_{1b})$	$P_{1a}^3P_{1b}(1-P_{1b})+(1-P_{1a})^3(1-P_{1b})P_{1b}$ $+P_{1a}^2(1-P_{1a})P_{1b}^2+P_{1a}(1-P_{1a})^2(1-P_{1b})^2$	$P_{1a}^2P_{1b}^2(1-P_{1b})+(1-P_{1a})^2(1-P_{1b})^2P_{1b}$ $+P_{1a}(1-P_{1a})P_{1b}^3+P_{1a}(1-P_{1a})(1-P_{1b})^3$	$P_{1a}P_{1b}^3(1-P_{1b})+(1-P_{1a})(1-P_{1b})^3P_{1b}$ $+P_{1a}(1-P_{1b})P_{1b}^3+(1-P_{1a})P_{1b}(1-P_{1b})^3$
(mmrm)	$2P_{1a}^3(1-P_{1a})^2$ $+2(1-P_{1a})^3P_{1a}^2$	$2P_{1b}^3(1-P_{1b})^2$ $+2(1-P_{1b})^3P_{1b}^2$	$P_{1a}^3(1-P_{1a})(1-P_{1b})+(1-P_{1a})^3P_{1a}P_{1b}$ $+P_{1a}^2(1-P_{1a})^2P_{1b}+P_{1a}^2(1-P_{1a})^2(1-P_{1b})$	$P_{1a}^3(1-P_{1b})^2+(1-P_{1a})^3P_{1b}^2$ $+P_{1a}(1-P_{1a})^2P_{1b}^2+P_{1a}^2(1-P_{1a})(1-P_{1b})^2$	$P_{1a}^2P_{1b}(1-P_{1b})^2+(1-P_{1a})^2(1-P_{1b})P_{1b}^2$ $+(1-P_{1a})^2P_{1b}^3+P_{1a}^2(1-P_{1b})^3$	$P_{1a}P_{1b}^2(1-P_{1b})^2+(1-P_{1a})(1-P_{1b})^2P_{1b}^2$ $+(1-P_{1a})(1-P_{1b})P_{1b}^3+P_{1a}P_{1b}(1-P_{1b})^3$
(rmrr)	$2P_{1a}^2(1-P_{1a})^3$ $+2P_{1a}^3(1-P_{1a})^2$	$2P_{1b}^2(1-P_{1b})^3$ $+2P_{1b}^3(1-P_{1b})^2$	$P_{1a}^2(1-P_{1a})^2(1-P_{1b})+P_{1a}^2(1-P_{1a})^2P_{1b}$ $+P_{1a}^3(1-P_{1a})(1-P_{1b})+P_{1a}(1-P_{1a})^3P_{1b}$	$P_{1a}(1-P_{1a})^2P_{1b}(1-P_{1b})+P_{1a}^2(1-P_{1a})P_{1b}(1-P_{1b})$ $+P_{1a}^2(1-P_{1a})P_{1b}(1-P_{1b})+P_{1a}(1-P_{1a})^2P_{1b}(1-P_{1b})$	$P_{1a}(1-P_{1a})P_{1b}(1-P_{1b})^2+P_{1a}(1-P_{1a})(1-P_{1b})P_{1b}^2$ $+P_{1a}(1-P_{1a})P_{1b}^2(1-P_{1b})+P_{1a}(1-P_{1a})P_{1b}(1-P_{1b})^2$	$P_{1a}P_{1b}(1-P_{1b})^3+(1-P_{1a})(1-P_{1b})P_{1b}^3$ $+P_{1a}P_{1b}^2(1-P_{1b})^2+(1-P_{1a})P_{1b}^2(1-P_{1b})^2$
(rmrm)	$2P_{1a}^3(1-P_{1a})^2$ $+2(1-P_{1a})^3P_{1a}^2$	$2P_{1b}^3(1-P_{1b})^2$ $+2(1-P_{1b})^3P_{1b}^2$	$P_{1a}^2(1-P_{1a})^2P_{1b}+P_{1a}^2(1-P_{1a})^2(1-P_{1b})$ $+P_{1a}^2(1-P_{1a})^2(1-P_{1b})+P_{1a}^2(1-P_{1a})^2P_{1b}$	$P_{1a}(1-P_{1a})^2P_{1b}^2+P_{1a}^2(1-P_{1a})(1-P_{1b})^2$ $+P_{1a}(1-P_{1a})^2P_{1b}(1-P_{1b})+P_{1a}^2(1-P_{1a})P_{1b}(1-P_{1b})$	$P_{1a}(1-P_{1a})(1-P_{1b})P_{1b}^2+P_{1a}(1-P_{1a})(1-P_{1b})^2P_{1b}$ $+(1-P_{1a})^2P_{1b}^2(1-P_{1b})+P_{1a}^2(1-P_{1b})^2P_{1b}$	$P_{1a}P_{1b}^2(1-P_{1b})^2+(1-P_{1a})P_{1b}^2(1-P_{1b})^2$ $+(1-P_{1a})P_{1b}^2(1-P_{1b})^2+P_{1a}P_{1b}^2(1-P_{1b})^2$
(rrrr)	$P_{1a}^3(1-P_{1a})^2$ $+P_{1a}^2(1-P_{1a})^3$	$P_{1b}^3(1-P_{1b})^2$ $+P_{1b}^2(1-P_{1b})^3$	$P_{1a}^2(1-P_{1a})^2P_{1b}+P_{1a}^2(1-P_{1a})^2(1-P_{1b})$	$P_{1a}^2(1-P_{1a})P_{1b}(1-P_{1b})+P_{1a}(1-P_{1a})^2P_{1b}(1-P_{1b})$	$P_{1a}(1-P_{1a})P_{1b}^2(1-P_{1b})+P_{1a}(1-P_{1a})P_{1b}(1-P_{1b})^2$	$P_{1a}P_{1b}^2(1-P_{1b})^2+(1-P_{1a})P_{1b}^2(1-P_{1b})^2$
(mrrr)	$2P_{1a}^3(1-P_{1a})^2$ $+2P_{1a}^2(1-P_{1a})^3$	$2P_{1b}^3(1-P_{1b})^2$ $+2P_{1b}^2(1-P_{1b})^3$	$P_{1a}^3(1-P_{1a})(1-P_{1b})+P_{1a}(1-P_{1a})^3P_{1b}$ $+P_{1a}^2(1-P_{1a})^2(1-P_{1b})+P_{1a}^2(1-P_{1a})^2P_{1b}$	$P_{1a}^2(1-P_{1a})P_{1b}(1-P_{1b})+P_{1a}(1-P_{1a})^2P_{1b}(1-P_{1b})$ $+P_{1a}^2(1-P_{1a})(1-P_{1b})^2+P_{1a}(1-P_{1a})^2P_{1b}^2$	$P_{1a}^2P_{1b}(1-P_{1b})^2+(1-P_{1a})^2P_{1b}^2(1-P_{1b})$ $+P_{1a}(1-P_{1a})P_{1b}(1-P_{1b})^2+P_{1a}(1-P_{1a})P_{1b}^2(1-P_{1b})$	$P_{1a}P_{1b}^2(1-P_{1b})^2+(1-P_{1a})P_{1b}^2(1-P_{1b})^2$ $+P_{1a}P_{1b}(1-P_{1b})^3+(1-P_{1a})(1-P_{1b})P_{1b}^3$
(mrrm)	$P_{1a}^4(1-P_{1a})$ $+P_{1a}(1-P_{1a})^4$	$P_{1b}^4(1-P_{1b})$ $+P_{1b}(1-P_{1b})^4$	$P_{1a}^3(1-P_{1a})P_{1b}+P_{1a}(1-P_{1a})^3(1-P_{1b})$	$P_{1a}^2(1-P_{1a})P_{1b}^2+P_{1a}(1-P_{1a})^2(1-P_{1b})^2$	$P_{1a}^2P_{1b}^2(1-P_{1b})+(1-P_{1a})^2P_{1b}(1-P_{1b})^2$	$P_{1a}P_{1b}^3(1-P_{1b})+(1-P_{1a})P_{1b}(1-P_{1b})^3$

Table II
Pentad Probability Expressions in the Consecutive B/B Model

pentad	P_A	P_B	2P(−2)	2P(−1)	2P(1)	2P(2)
(mmmm)	P_{ma}^4	P_{mb}^4	$P_{ma}^3P_{mb}+P_{ma}^4$	$P_{ma}^2P_{mb}^2+P_{ma}^3P_{mb}$	$P_{ma}P_{mb}^3+P_{ma}^2P_{mb}^2$	$P_{mb}^4+P_{ma}P_{mb}^3$
(mmmr)	$2P_{ma}^3(1-P_{ma})$	$2P_{mb}^3(1-P_{mb})$	$P_{ma}^3(1-P_{mb})+P_{ma}^3(1-P_{ma})$ $+P_{ma}^2(1-P_{ma})P_{mb}+P_{ma}^3(1-P_{ma})$	$P_{ma}^2P_{mb}(1-P_{mb})+P_{ma}^3(1-P_{mb})$ $+P_{ma}(1-P_{ma})P_{mb}^2+P_{ma}^2(1-P_{ma})P_{mb}$	$P_{ma}P_{mb}^2(1-P_{mb})+P_{ma}^2P_{mb}(1-P_{mb})$ $+(1-P_{ma})P_{mb}^3+P_{ma}(1-P_{ma})P_{mb}^2$	$P_{mb}^3(1-P_{mb})+P_{ma}P_{mb}^2(1-P_{mb})$ $+P_{mb}^3(1-P_{mb})+P_{mb}^3(1-P_{ma})$
(rmmr)	$P_{ma}^2(1-P_{ma})^2$	$P_{mb}^2(1-P_{mb})^2$	$P_{ma}^2(1-P_{ma})(1-P_{mb})$ $+P_{ma}^2(1-P_{ma})^2$	$P_{ma}(1-P_{ma})P_{mb}(1-P_{mb})$ $+P_{ma}^2(1-P_{ma})(1-P_{mb})$	$(1-P_{ma})P_{mb}^2(1-P_{mb})$ $+P_{ma}(1-P_{ma})P_{mb}(1-P_{mb})$	$P_{mb}^2(1-P_{mb})^2$ $+P_{mb}^2(1-P_{ma})(1-P_{mb})$
(mmrr)	$2P_{ma}^2(1-P_{ma})^2$	$2P_{mb}^2(1-P_{mb})^2$	$P_{ma}^2(1-P_{ma})(1-P_{mb})+P_{ma}^2(1-P_{ma})^2$ $+P_{ma}(1-P_{ma})^2P_{mb}+P_{ma}^2(1-P_{ma})^2$	$P_{ma}^2(1-P_{mb})^2+P_{ma}^2(1-P_{ma})(1-P_{mb})$ $+(1-P_{ma})^2P_{mb}^2+(1-P_{ma})^2P_{ma}P_{mb}$	$P_{ma}P_{mb}(1-P_{mb})^2+P_{ma}^2(1-P_{mb})^2$ $+(1-P_{ma})(1-P_{mb})P_{mb}^2+(1-P_{ma})^2P_{mb}^2$	$P_{mb}^2(1-P_{mb})^2+P_{ma}P_{mb}(1-P_{mb})^2$ $+(1-P_{mb})^2P_{mb}^2+(1-P_{ma})(1-P_{mb})P_{mb}^2$
(mmrm)	$2P_{ma}^3(1-P_{ma})$	$2P_{mb}^3(1-P_{mb})$	$P_{ma}^2(1-P_{ma})P_{mb}+P_{ma}^3(1-P_{ma})$ $+P_{ma}^2(1-P_{ma})P_{mb}+P_{ma}^3(1-P_{ma})$	$P_{ma}^2P_{mb}(1-P_{mb})+P_{ma}^2(1-P_{ma})P_{mb}$ $+P_{ma}(1-P_{ma})P_{mb}^2+P_{ma}^2(1-P_{ma})P_{mb}$	$P_{ma}P_{mb}^2(1-P_{mb})+P_{ma}^2P_{mb}(1-P_{mb})$ $+P_{ma}P_{mb}^2(1-P_{mb})+P_{ma}(1-P_{ma})P_{mb}^2$	$P_{mb}^3(1-P_{mb})+P_{ma}P_{mb}^2(1-P_{mb})$ $+P_{mb}^3(1-P_{mb})+P_{ma}P_{mb}^2(1-P_{mb})$
(rmrr)	$2P_{ma}(1-P_{ma})^3$	$2P_{mb}(1-P_{mb})^3$	$P_{ma}(1-P_{ma})^2(1-P_{mb})+P_{ma}(1-P_{ma})^3$ $+P_{ma}(1-P_{ma})^2(1-P_{mb})+P_{ma}(1-P_{ma})^3$	$P_{ma}(1-P_{ma})(1-P_{mb})^2+P_{ma}(1-P_{ma})^2(1-P_{mb})$ $+(1-P_{ma})^2P_{mb}(1-P_{mb})+P_{ma}(1-P_{ma})^2(1-P_{mb})$	$(1-P_{ma})P_{mb}(1-P_{mb})^2+P_{ma}(1-P_{ma})(1-P_{mb})^2$ $+(1-P_{ma})P_{mb}(1-P_{mb})^2+(1-P_{ma})^2P_{mb}(1-P_{mb})$	$P_{mb}(1-P_{mb})^3+(1-P_{ma})P_{mb}(1-P_{mb})^2$ $+P_{mb}(1-P_{mb})^3+(1-P_{ma})P_{mb}(1-P_{mb})^2$
(rmrm)	$2P_{ma}^2(1-P_{ma})^2$	$2P_{mb}^2(1-P_{mb})^2$	$P_{ma}(1-P_{ma})^2P_{mb}+P_{ma}^2(1-P_{ma})^2$ $+P_{ma}^2(1-P_{ma})(1-P_{mb})+P_{ma}^2(1-P_{ma})^2$	$P_{ma}(1-P_{ma})P_{mb}(1-P_{mb})+P_{ma}(1-P_{ma})^2P_{mb}$ $+P_{ma}(1-P_{ma})P_{mb}(1-P_{mb})+P_{ma}^2(1-P_{ma})(1-P_{mb})$	$(1-P_{ma})P_{mb}^2(1-P_{mb})+P_{ma}(1-P_{ma})P_{mb}(1-P_{mb})$ $+P_{ma}P_{mb}(1-P_{mb})^2+P_{ma}(1-P_{ma})P_{mb}(1-P_{mb})$	$P_{mb}^2(1-P_{mb})^2+(1-P_{ma})P_{mb}^2(1-P_{mb})$ $+P_{mb}^2(1-P_{mb})^2+P_{ma}P_{mb}(1-P_{mb})^2$
(rrrr)	$(1-P_{ma})^4$	$(1-P_{mb})^4$	$(1-P_{ma})^3(1-P_{mb})+(1-P_{ma})^4$	$(1-P_{ma})^2(1-P_{mb})^2+(1-P_{ma})^3(1-P_{mb})$	$(1-P_{ma})(1-P_{mb})^3+(1-P_{ma})^2(1-P_{mb})^2$	$(1-P_{mb})^4+(1-P_{ma})(1-P_{mb})^3$
(mrrr)	$2P_{ma}(1-P_{ma})^3$	$2P_{mb}(1-P_{mb})^3$	$P_{ma}(1-P_{ma})^2(1-P_{mb})+P_{ma}(1-P_{ma})^3$ $+(1-P_{ma})^3P_{mb}+(1-P_{ma})^3P_{ma}$	$P_{ma}(1-P_{ma})(1-P_{mb})^2+P_{ma}(1-P_{ma})^2(1-P_{mb})$ $+(1-P_{ma})^2(1-P_{mb})P_{mb}+(1-P_{ma})^3P_{mb}$	$P_{ma}(1-P_{mb})^3+P_{ma}(1-P_{ma})(1-P_{mb})^2$ $+(1-P_{ma})(1-P_{mb})^2P_{mb}+(1-P_{ma})^2(1-P_{mb})P_{mb}$	$P_{mb}(1-P_{mb})^3+P_{ma}(1-P_{mb})^3$ $+(1-P_{mb})^3P_{mb}+(1-P_{ma})(1-P_{mb})^2P_{mb}$
(mrrm)	$P_{ma}^2(1-P_{ma})^2$	$P_{mb}^2(1-P_{mb})^2$	$P_{ma}(1-P_{ma})^2P_{mb}+P_{ma}^2(1-P_{ma})^2$	$P_{ma}(1-P_{ma})P_{mb}(1-P_{mb})+P_{ma}(1-P_{ma})^2P_{mb}$	$P_{ma}(1-P_{mb})^2P_{mb}+P_{ma}(1-P_{ma})(1-P_{mb})P_{mb}$	$P_{mb}^2(1-P_{mb})^2+P_{ma}(1-P_{mb})^2P_{mb}$

$$\begin{array}{lccccccccccccccccccc}
\text{direction} & \multicolumn{9}{c}{\longrightarrow} & & \multicolumn{9}{c}{\longleftarrow} \\
\text{P(−1) structure} & 1 & & 1 & & 1 & - & 1 & & 1 & & \bar{1} & & \bar{1} & & \bar{1} & - & \bar{1} & & \bar{1} \\
\text{mechanism} & & A & & A & & B & & B & & & & A & & A & & A & & B & \\
\text{probability} & \multicolumn{9}{c}{P_{ma}^{2}P_{mb}^{2}} & & \multicolumn{9}{c}{P_{ma}^{3}P_{mb}}
\end{array}$$

$$\begin{array}{lccccccccccccccccccc}
\text{direction} & \multicolumn{9}{c}{\longrightarrow} & & \multicolumn{9}{c}{\longleftarrow} \\
\text{P(1) structure} & 1 & & 1 & - & 1 & & 1 & & 1 & & \bar{1} & & \bar{1} & - & \bar{1} & & \bar{1} & & \bar{1} \\
\text{mechanism} & & A & & B & & B & & B & & & & A & & A & & B & & B & \\
\text{probability} & \multicolumn{9}{c}{P_{ma}P_{mb}^{3}} & & \multicolumn{9}{c}{P_{ma}^{2}P_{mb}^{2}}
\end{array}$$

$$\begin{array}{lccccccccccccccccccc}
\text{direction} & \multicolumn{9}{c}{\longrightarrow} & & \multicolumn{9}{c}{\longleftarrow} \\
\text{P(2) structure} & 1 & - & 1 & & 1 & & 1 & & 1 & & \bar{1} & - & \bar{1} & & \bar{1} & & \bar{1} & & \bar{1} \\
\text{mechanism} & & B & & B & & B & & B & & & & A & & B & & B & & B & \\
\text{probability} & \multicolumn{9}{c}{P_{mb}^{4}} & & \multicolumn{9}{c}{P_{ma}P_{mb}^{3}}
\end{array}$$

The overall probability expression for the (mmmm) pentad in the two-state B/B model is given as the sum of all the terms:

$$(\text{mmmm}) = k\{(\alpha-4)P_{ma}^{4} + (\beta-4)P_{mb}^{4} + P_{ma}^{3}P_{mb} + P_{ma}^{4} + P_{ma}^{2}P_{mb}^{2} + P_{ma}^{3}P_{mb} + P_{ma}P_{mb}^{3} + P_{ma}^{2}P_{mb}^{2} + P_{mb}^{4} + P_{ma}P_{mb}^{3}\} \quad (3)$$

Similar derivations have been carried out on all the other pentads. The probability expressions are summarized in Table II.

E/B Model. Let the reaction probabilities in the E and the B models be P_l and P_m, respectively. In this case, we need to consider both the absolute configuration and the direction of propagation. An example is again shown for the (mmmm) pentad.

$$\begin{array}{lccccccccccccc}
\text{direction} & \multicolumn{6}{c}{\longrightarrow} & & \multicolumn{6}{c}{\longleftarrow} \\
 & & & * & & & & & & & * & & & \\
\text{P(−2) structure} & 1 & 1 & 1 & 1 & - & 1 & & 1 & 1 & 1 & 1 & - & 1 \\
\text{mechanism} & E & E & E & E & B & & & E & E & E & E & s & \\
\text{probability} & \multicolumn{6}{c}{P_l^{4}P_m} & & \multicolumn{6}{c}{P_l^{4}s}
\end{array}$$

$$\begin{array}{lccccccccccccc}
\text{direction} & \multicolumn{6}{c}{\longrightarrow} & & \multicolumn{6}{c}{\longleftarrow} \\
\text{P(−2) structure} & 1 & 1 & 1 & 1 & - & 1 & & 1 & 1 & 1 & 1 & - & 1 \\
\text{mechanism} & E & E & E & E & B & & & E & E & E & E & s & \\
\text{probability} & \multicolumn{6}{c}{(1 - P_l)^{4}P_m} & & \multicolumn{6}{c}{(1 - P_l)^{4}s}
\end{array}$$

The junction probability for P(−2) is the sum of all four terms. Note that for the two structures on the right (corresponding to the B → E case) a factor called s appears. This is because the Bernoullian model refers to the relative configuration. If the chain propagation starts with the B block or if the block is very long, then at the end of the block just before B switches to E, the monomer residue can be either in the 1 or $\bar{1}$ configuration. In this case, $s = 0.5$.

If the B block is relatively short and is sandwiched between two E blocks, i.e., $-(\mathrm{E})(\mathrm{B})_{\beta}(\mathrm{E})-$:

$$\begin{array}{lcccccccccccccc}
\text{structure} & \ldots 1 & 1 & 1 & - & 1 & 1 & 1 & 1 & \ldots\ldots & 1 & 1 & - & 1 & 1\ldots \\
\text{block} & E & E & E & & B & B & B & B & & B & B & & E & E \\
\text{label} & & & & & 1 & 2 & 3 & 4\ldots n\ldots & \beta & -\ 1 & \beta & & &
\end{array}$$

then as the mechanism switches from E to B, a memory of the E model persists in the B block. If the last unit in the E block has a propagation probability P_l for the levo configuration, then by induction we can derive the propagation probability that the nth unit in the B block is in the levo configuration

$$\mathrm{P}(\text{at position } n) = \frac{(2P_l - 1)(2P_m - 1)^n + 1}{2} \quad (4)$$

At the end of the B block, $n = \beta$, and the propagation probability of levo configuration is then $^1/_2[(2P_l - 1)(2P_m - 1)^{\beta} + 1]$. In this case

$$s = {}^1/_2[(2P_l - 1)(2P_m - 1)^{\beta} + 1] \quad (5)$$

Note that s departs significantly from 0.5 only if P_m is close to 1.0 (or 0.0) and if β is small.

Similar considerations hold for the P(−1) structures:

$$\begin{array}{lccccccccccccccc}
\text{direction} & \multicolumn{7}{c}{\longrightarrow} & & \multicolumn{7}{c}{\longleftarrow} \\
\text{P(−1) structure} & 1 & 1 & 1 & - & 1 & & 1 & & 1 & 1 & 1 & - & 1 & & 1 \\
\text{mechanism} & E & E & E & B & & B & & & E & E & E & s & & B & \\
\text{probability} & \multicolumn{7}{c}{P_l^{3}P_m^{2}} & & \multicolumn{7}{c}{P_l^{3}P_m s}
\end{array}$$

$$\begin{array}{lccccccccccccccc}
\text{direction} & \multicolumn{7}{c}{\longrightarrow} & & \multicolumn{7}{c}{\longleftarrow} \\
\text{P(−1) structure} & \bar{1} & \bar{1} & \bar{1} & - & \bar{1} & & \bar{1} & & \bar{1} & \bar{1} & \bar{1} & - & \bar{1} & & \bar{1} \\
\text{mechanism} & E & E & E & B & & B & & & E & E & E & s & & B & \\
\text{probability} & \multicolumn{7}{c}{(1 - P_l)^{3}P_m^{2}} & & \multicolumn{7}{c}{(1 - P_l)^{3}P_m s}
\end{array}$$

The junction probabilities for P(1) are $P_l^2P_m^3 + P_l^2P_m^2s$ for all 1 configurations and $(1 - P_l)^2P_m^3 + (1 - P_l)^2P_m^2s$ for all $\bar{1}$ configurations. Similarly, the junction probabilities for P(2) are $P_lP_m^4 + P_lP_m^3s$ for 1 configurations and $(1 - P_l)P_m^4 + (1 - P_l)P_m^3s$ for $\bar{1}$ configurations. The overall probability expression for the (mmmm) pentad is the sum of all terms:

$$\begin{aligned}(\text{mmmm}) = k\{&(\alpha - 4)[P_l^5 + (1 - P_l)^5] + (\beta - 4)P_m^4 + P_l^4(P_m + s) + (1 - P_l)^4(P_m + s) + P_l^3P_m(P_m + s) + {} \\ &(1 - P_l)^3P_m(P_m + s) + P_l^2P_m^2(P_m + s) + (1 - P_l)^2 \times P_m^2(P_m + s) + P_lP_m^3(P_m + s) + (1 - P_l)P_m^3(P_m + s)\} \quad (6)\end{aligned}$$

Similar expressions can be derived for the other pentads. The derivations are tedious, and only the results are summarized in Table III.

Tetrad Tacticity

The derivations of the probability expressions for tacticity tetrads can be similarly carried out. As before, we assume that the polymer consists of polymer blocks $-(\mathrm{AB})_x-$. In the middle of each block (A or B), the enchainment of each monomer follows the propagation probability of the prevailing mechanism of that block. Near the block junctions the monomer residues again need special consideration (Figure 2). The propagation probabilities are given in Chart II. Note that all the propagation probabilities in Chart II represent the probabilities that a monomer unit is centered in a particular tetrad.

The overall probability expression for each tetrad is the average of all propagation probabilities related to that tetrad, i.e.

$$\mathrm{P(tetrad)} = \frac{(\alpha - 3)\mathrm{P_A} + (\beta - 3)\mathrm{P_B} + \sum \mathrm{P(j)}}{\alpha + \beta} \quad (7)$$

E/E Model. In the E model we again need to take into account the absolute configuration of the structures. The junction probabilities can be readily derived. As before,

Table III
Pentad Probability Expressions[a] in the Consecutive E/B Model

pentad	P_A	P_B	P(−2)	P(−1)	P(1)	P(2)
(mmmm)	$P_1^5+(1-P_1)^5$	P_m^4	$P_1^4v+(1-P_1)^4v$	$P_1^3P_mv+(1-P_1)^3P_mv$	$P_1^2P_m^2v+(1-P_1)^2P_m^2v$	$P_1P_m^3v+(1-P_1)P_m^3v$
(mmmr)	$2P_1^4(1-P_1)+2(1-P_1)^4P_1$	$2P_m^3(1-P_m)$	$P_1^4(1-v)+(1-P_1)^4(1-v)+(1-P_1)P_1^3v+P_1(1-P_1)^3v$	$P_1^3(1-P_m)v+(1-P_1)^3(1-P_m)v+(1-P_1)P_1^2P_mv+P_1(1-P_1)^2P_mv$	$P_1^2P_m(1-P_m)v+(1-P_1)^2P_m(1-P_m)v+(1-P_1)P_1P_m^2v+P_1(1-P_1)P_m^2v$	$P_1P_m^2(1-P_m)v+(1-P_1)P_m^2(1-P_m)v+(1-P_1)P_m^3(1-v)+P_1P_m^3(1-v)$
(rmmr)	$P_1^3(1-P_1)^2+P_1^2(1-P_1)^3$	$P_m^2(1-P_m)^2$	$(1-P_1)P_1^3(1-v)+P_1(1-P_1)^3(1-v)$	$(1-P_1)P_1(1-P_m)v$	$2P_1(1-P_1)P_m(1-P_m)v$	$(1-P_m)P_m^2(1-v)$
(mmrr)	$2P_1^4(1-P_1)+2(1-P_1)^4P_1$	$2P_m^2(1-P_m)^2$	$P_1^3(1-P_1)(1-v)+(1-P_1)^3P_1(1-v)+P_1^3(1-P_1)v+(1-P_1)^3P_1v$	$P_1^3(1-P_m)(1-v)+(1-P_1)^3(1-P_m)(1-v)+P_1^2(1-P_1)P_mv+(1-P_1)^2P_1P_mv$	$P_1^2(1-P_m)^2v+(1-P_1)^2(1-P_m)^2v+2P_1(1-P_1)P_m^2(1-v)$	$P_m(1-P_m)^2v+(1-P_m)P_m^2(1-v)$
(mmrm)	$2P_1^3(1-P_1)^2+2(1-P_1)^3P_1^2$	$2P_m^3(1-P_m)$	$P_1^3(1-P_1)v+(1-P_1)^3P_1v+2(1-P_1)^2P_1^2v$	$P_1^3P_m(1-v)+(1-P_1)^3P_m(1-v)+P_1(1-P_1)P_mv$	$P_1^2P_m(1-P_m)v+(1-P_1)^2P_m(1-P_m)v+(1-P_1)^2P_m^2(1-v)+P_1^2P_m^2(1-v)$	$P_m^2(1-P_m)v+P_m^2(1-P_m)v$
(rmrr)	$2P_1^2(1-P_1)^3+2P_1^3(1-P_1)^2$	$2P_m(1-P_m)^3$	$2(1-P_1)^2P_1^2(1-v)+P_1^3(1-P_1)(1-v)+(1-P_1)^3P_1(1-v)$	$(1-P_1)P_1(1-P_m)(1-v)+(1-P_1)P_1(1-P_m)v$	$2P_1(1-P_1)(1-P_m)^2v+2P_1(1-P_1)(1-P_m)P_m(1-v)$	$(1-P_m)^2P_m(1-v)+(1-P_m)^2P_m(1-v)$
(rmrm)	$2P_1^3(1-P_1)^2+2(1-P_1)^3P_1^2$	$2P_m^2(1-P_m)^2$	$2P_1^2(1-P_1)^2v+2P_1^2(1-P_1)^2(1-v)$	$(1-P_1)P_1P_m(1-v)+P_1(1-P_1)(1-P_m)v$	$2P_1(1-P_1)P_m(1-P_m)v+P_1^2(1-P_m)P_m(1-v)+(1-P_1)^2(1-P_m)P_m(1-v)$	$P_m^2(1-P_m)(1-v)+P_m(1-P_m)^2v$
(rrrr)	$P_1^3(1-P_1)^2+P_1^2(1-P_1)^3$	$(1-P_m)^4$	$2P_1^2(1-P_1)^2(1-v)$	$P_1(1-P_1)(1-P_m)(1-v)$	$2P_1(1-P_1)(1-P_m)^2(1-v)$	$(1-P_m)^3(1-v)$
(mrrr)	$2P_1^3(1-P_1)^2+2P_1^2(1-P_1)^3$	$2P_m(1-P_m)^3$	$P_1^3(1-P_1)(1-v)+(1-P_1)^3P_1(1-v)+2(1-P_1)^2P_1^2v$	$P_1(1-P_1)(1-P_m)(1-v)+P_1(1-P_1)P_m(1-v)$	$P_1^2(1-P_m)^2(1-v)+(1-P_1)^2(1-P_m)^2(1-v)+2(1-P_1)P_1(1-P_m)P_m(1-v)$	$(1-P_m)^3v+(1-P_m)^2P_m(1-v)$
(mrrm)	$P_1^4(1-P_1)+P_1(1-P_1)^4$	$P_m^2(1-P_m)^2$	$P_1^3(1-P_1)v+(1-P_1)^3P_1v$	$P_1(1-P_1)P_m(1-v)$	$P_1^2(1-P_m)P_m(1-v)+(1-P_1)^2(1-P_m)P_m(1-v)$	$P_m(1-P_m)^2v$

[a] $v = (P_m + s)/2$.

Table IV
Tetrad Probability Expressions in the Consecutive E/E Model

tetrad	P_A	P_B	P(−1)	P(0)	P(1)
(mmm)	$P_{1a}^4+(1-P_{1a})^4$	$P_{1b}^4+(1-P_{1b})^4$	$P_{1a}^3P_{1b}+(1-P_{1a})^3(1-P_{1b})$	$P_{1a}^2P_{1b}^2+(1-P_{1a})^2(1-P_{1b})^2$	$P_{1a}P_{1b}^3+(1-P_{1a})(1-P_{1b})^3$
(mmr)	$2P_{1a}^3(1-P_{1a})+2(1-P_{1a})^3P_{1a}$	$2P_{1b}^3(1-P_{1b})+2(1-P_{1b})^3P_{1b}$	$P_{1a}^3(1-P_{1b})+(1-P_{1a})^3P_{1b}+(1-P_{1a})P_{1a}^2P_{1b}+P_{1a}(1-P_{1a})^2(1-P_{1b})$	$P_{1a}^2P_{1b}(1-P_{1b})+(1-P_{1a})^2P_{1b}(1-P_{1b})+(1-P_{1a})P_{1a}P_{1b}^2+P_{1a}(1-P_{1a})(1-P_{1b})^2$	$P_{1a}P_{1b}^2(1-P_{1b})+(1-P_{1a})(1-P_{1b})^2P_{1b}+(1-P_{1a})P_{1b}^3+P_{1a}(1-P_{1b})^3$
(rmr)	$2P_{1a}^2(1-P_{1a})^2$	$2P_{1b}^2(1-P_{1b})^2$	$P_{1a}(1-P_{1a})^2P_{1b}+(1-P_{1a})P_{1a}^2(1-P_{1b})$	$2P_{1a}(1-P_{1a})P_{1b}(1-P_{1b})$	$P_{1a}(1-P_{1b})^2P_{1b}+(1-P_{1a})P_{1b}^2(1-P_{1b})$
(mrm)	$2P_{1a}^2(1-P_{1a})^2$	$2P_{1b}^2(1-P_{1b})^2$	$P_{1a}^2(1-P_{1a})(1-P_{1b})+(1-P_{1a})^2P_{1a}P_{1b}$	$P_{1a}^2(1-P_{1b})^2+(1-P_{1a})^2P_{1b}^2$	$P_{1a}P_{1b}(1-P_{1b})^2+(1-P_{1a})(1-P_{1b})P_{1b}^2$
(rrm)	$2P_{1a}^3(1-P_{1a})+2(1-P_{1a})^3P_{1a}$	$2P_{1b}^3(1-P_{1b})+2(1-P_{1b})^3P_{1b}$	$P_{1a}^2(1-P_{1a})P_{1b}+(1-P_{1a})^2P_{1a}(1-P_{1b})+P_{1a}^2(1-P_{1a})P_{1b}+(1-P_{1a})^2P_{1a}(1-P_{1b})$	$P_{1a}(1-P_{1a})P_{1b}^2+P_{1a}(1-P_{1a})(1-P_{1b})^2+P_{1a}^2(1-P_{1b})P_{1b}+(1-P_{1a})^2P_{1b}(1-P_{1b})$	$P_{1a}(1-P_{1b})P_{1b}^2+(1-P_{1a})P_{1b}(1-P_{1b})^2+P_{1a}P_{1b}^2(1-P_{1b})+(1-P_{1a})(1-P_{1b})^2P_{1b}$
(rrr)	$2P_{1a}^2(1-P_{1a})^2$	$2P_{1b}^2(1-P_{1b})^2$	$P_{1a}^2(1-P_{1a})(1-P_{1b})+(1-P_{1a})^2P_{1a}P_{1b}$	$2P_{1a}(1-P_{1a})P_{1b}(1-P_{1b})$	$P_{1a}P_{1b}(1-P_{1b})^2+(1-P_{1a})(1-P_{1b})P_{1b}^2$

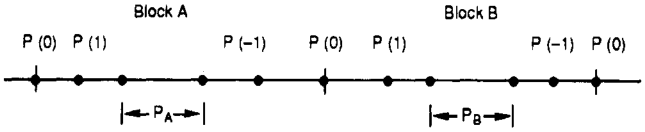

Figure 2. Chain propagation probabilities for tacticity tetrads in the consecutive two-state model. P_A, P_B, and P(i) correspond to the probabilities that a monomer unit is centered in a particular tetrad.

Chart II

block	no. of monomer residues	propagation probability
A	$\alpha - 3$	P_A
B	$\beta - 3$	P_B
A (junction)	1	P(−1)
	1	P(0)
	1	P(1)
B (junction)	1	P(−1)
	1	P(0)
	1	P(1)

we shall derive the probability expression for the isotactic sequence (mmm) as illustration.

P(−1) structure	1 1 1 − 1	$\bar{1}$ $\bar{1}$ $\bar{1}$ − $\bar{1}$
mechanism	A A A B	A A A B
probability	$P_{la}{}^3P_{lb}$	$(1 - P_{la})^3(1 - P_{lb})$
P(0) structure	1 1 − 1 1	$\bar{1}$ $\bar{1}$ − $\bar{1}$ $\bar{1}$
mechanism	A A B B	A A B B
probability	$P_{la}{}^2P_{lb}{}^2$	$(1 - P_{la})^2(1 - P_{lb})^2$
P(1) structure	1 − 1 1 1	$\bar{1}$ − $\bar{1}$ $\bar{1}$ $\bar{1}$
mechanism	A B B B	A B B B
probability	$P_{la}P_{lb}{}^3$	$(1 - P_{la})(1 - P_{lb})^3$

The overall probability expression for the (mmm) tetrad is

$$(\mathrm{mmm}) = k\{(\alpha - 3)[P_{la}{}^4 + (1 - P_{la})^4] + (\beta - 3)[P_{lb}{}^4 + (1 - P_{lb})^4] + 2P_{la}{}^3P_{lb} + 2(1 - P_{la})^3(1 - P_{lb}) + 2P_{la}{}^2P_{lb}{}^2 + 2(1 - P_{la})^2(1 - P_{lb})^2 + 2P_{la}P_{lb}{}^3 + 2(1 - P_{la})(1 - P_{lb})^3\} \quad (8)$$

Similar derivations may be made with the other tetrads. Again, each of the nonsymmetrical tetrads (viz., mmr and rrm) comprises two individual tetrads (mmr/rmm, and rrm/mrr). The probability expressions for all six tetrads in the E/E model are given in Table IV.

B/B Model. In the B/B model we need to consider not the absolute configuration but the direction of propagation. The junction probability P(−1) of the (mmm) tetrad is calculated as follows:

direction	$\longrightarrow$	$\longleftarrow$
P(−1) structure	1 1 1 − 1	1 1 1 − 1
block	A A B	A A A
probability	$P_{ma}{}^2P_{mb}$	$P_{ma}{}^3$

Similarly, for P(0) the junction probability is $P_{ma}P_{mb}{}^2 + P_{ma}{}^2P_{mb}$, and for P(1) the junction probability is $P_{ma}{}^2P_{mb} + P_{mb}{}^3$. The overall probability expression for the (mmm) tetrad is as follows:

$$(\mathrm{mmm}) = k\{(\alpha - 3)P_{ma}{}^3 + (\beta - 3)P_{mb}{}^3 + P_{ma}{}^2P_{mb} + P_{ma}{}^3 + P_{ma}P_{mb}{}^2 + P_{ma}{}^2P_{mb} + P_{ma}{}^2P_{mb} + P_{mb}{}^3\} \quad (9)$$

The probability expressions for all six tetrads in the B/B model are shown in Table V.

E/B Model. In the two-state E/B model, we take into account the absolute configuration and the direction of propagation. The junction probability P(−1) of the (mmm) tetrad is as follows:

direction	$\longrightarrow$	$\longleftarrow$
P(−1) structure	1 1 1 − 1	1 1 1 − 1
mechanism	E E E B	E E E *s*
probability	$P_l{}^3P_m$	$P_l{}^3s$
direction	$\longrightarrow$	$\longleftarrow$
P(−1) structure	$\bar{1}$ $\bar{1}$ $\bar{1}$ − $\bar{1}$	$\bar{1}$ $\bar{1}$ $\bar{1}$ − $\bar{1}$
mechanism	E E E B	E E E *s*
probability	$(1 - P_l)^3P_m$	$(1 - P_l)^3s$

Thus, the total junction probability for the P(−1) structures is $P_l{}^3v + (1 - P_l)^3v$, where $v = (P_m + s)/2$. Similarly, P(0) can be shown to be $P_l{}^2P_mv + (1 - P_l)^2P_mv$, and P(1) can be shown to be $P_lP_m{}^2v + (1 - P_l)P_m{}^2v$. The overall probability expression for the (mmm) tetrad in the two-state E/B model is

$$(\mathrm{mmm}) = k\{(\alpha - 3)[P_l{}^4 + (1 - P_l)^4] + (\beta - 3)P_m{}^3 + P_l{}^3v + (1 - P_l)^3v + P_l{}^2P_mv + (1 - P_l)^2P_mv + P_lP_m{}^2v + (1 - P_l)P_m{}^2v\} \quad (10)$$

The probability expressions for the other tetrads can be derived in an analogous fashion. They are given in Table VI.

Computerized Analytical Approach

Methodology. The expressions given in Tables I–VI contain many terms and are very time-consuming to evaluate in practice. To facilitate their use, we have adopted the computerized analytical approach.[25,26] A family of programs (called EXCO) has been written for this purpose, viz.,

EXCO.TETRAD	for homopolymer tacticity tetrad analysis and for copolymer triad sequence analysis;
EXCO.PENTAD	for homopolymer tacticity pentad analysis and for copolymer tetrad sequence analysis.

Listings of these programs are available as Supplementary Material.

A simplified schematic of these programs is shown in Figure 3. The input data include the observed tetrad or pentad intensities and initial guess values of four parameters (conditional probabilities and block lengths for states 1 and 2). A range of reasonable values is also needed for each parameter. A random number generator then automatically produces five sets of parameters (vertices) from the initial guess values and the ranges indicated. For each parameter set, the theoretical intensities are calculated from eq 1 or 7 and the appropriate expressions in Tables I–VI. These intensities are compared with the observed intensities through the simplex algorithm. Further vertices are generated through the simplex procedure to minimize the mean deviation between the observed and the calculated intensities. When the mean deviation is equal to or less than the experimental precision in the NMR intensity determination, then an acceptable parameter set is obtained.

In both EXCO programs, the minimum length of each block (α or β) is set to two monomer residues. This is the minimum number we can call a "block". This is also the

Table V
Tetrad Probability Expressions[a] in the Consecutive B/B Model

tetrad	P_A	P_B	$P(-1)$	$P(0)$	$P(1)$
(mmm)	P_{ma}^3	P_{mb}^3	$P_{ma}^2P_{mc}$	$P_{ma}P_{mb}P_{mc}$	$P_{mb}^2P_{mc}$
(mmr)	$2P_{ma}^2(1-P_{ma})$	$2P_{mb}^2(1-P_{mb})$	$P_{ma}^2(1-P_{mc})$ $+(1-P_{ma})P_{ma}P_{mc}$	$P_{ma}(1-P_{mb})P_{mc}$ $+(1-P_{ma})P_{mb}P_{mc}$	$P_{mb}(1-P_{mb})P_{mc}$ $+(1-P_{mc})P_{mb}^2$
(rmr)	$P_{ma}(1-P_{ma})^2$	$P_{mb}(1-P_{mb})^2$	$(1-P_{ma})P_{ma}(1-P_{mc})$	$(1-P_{ma})P_{mc}(1-P_{mb})$	$(1-P_{mc})P_{mb}(1-P_{mb})$
(mrm)	$P_{ma}^2(1-P_{ma})$	$P_{mb}^2(1-P_{mb})$	$P_{ma}(1-P_{ma})P_{mc}$	$P_{ma}(1-P_{mc})P_{mb}$	$P_{mc}(1-P_{mb})P_{mb}$
(rrm)	$2P_{ma}(1-P_{ma})^2$	$2P_{mb}(1-P_{mb})^2$	$(1-P_{ma})^2P_{mc}$ $+P_{ma}(1-P_{ma})(1-P_{mc})$	$(1-P_{ma})(1-P_{mc})P_{mb}$ $+P_{ma}(1-P_{mc})(1-P_{mb})$	$(1-P_{mc})(1-P_{mb})P_{mb}$ $+P_{mc}(1-P_{mb})^2$
(rrr)	$(1-P_{ma})^3$	$(1-P_{mb})^3$	$(1-P_{ma})^2(1-P_{mc})$	$(1-P_{ma})(1-P_{mc})(1-P_{mb})$	$(1-P_{mc})(1-P_{mb})^2$

[a] $P_{mc} = (P_{ma} + P_{mb})/2$.

Table VI
Tetrad Probability Expressions[a] in the Consecutive E/B Model

tetrad	P_A	P_B	$P(-1)$	$P(0)$	$P(1)$
(mmm)	$P_1^4+(1-P_1)^4$	P_m^3	$P_1^3v+(1-P_1)^3v$	$P_1^2P_mv+(1-P_1)^2P_mv$	$P_1P_m^2v+(1-P_1)P_m^2v$
(mmr)	$2P_1^3(1-P_1)$ $+2(1-P_1)^3P_1$	$2P_m^2(1-P_m)$	$P_1^3(1-v)+(1-P_1)^3(1-v)$ $+P_1^2(1-P_1)v+(1-P_1)^2P_1v$	$P_1^2(1-P_m)v+(1-P_1)^2(1-P_m)v$ $+2P_1(1-P_1)P_mv$	$P_1P_m(1-P_m)v+(1-P_1)P_m(1-P_m)v$ $+(1-P_1)P_m^2(1-v)+P_1P_m^2(1-v)$
(rmr)	$2P_1^2(1-P_1)^2$	$P_m(1-P_m)^2$	$(1-P_1)P_1^2(1-v)+P_1(1-P_1)^2(1-v)$	$(1-P_1)P_1(1-P_m)v+P_1(1-P_1)(1-P_m)v$	$(1-P_1)P_m(1-P_m)(1-v)+P_1P_m(1-P_m)(1-v)$
(mrm)	$2P_1^2(1-P_1)^2$	$P_m^2(1-P_m)$	$P_1^2(1-P_1)v+(1-P_1)^2P_1v$	$P_1^2P_m(1-v)+(1-P_1)^2P_m(1-v)$	$P_1P_m(1-P_m)v+(1-P_1)P_m(1-P_m)v$
(rrm)	$2P_1^3(1-P_1)$ $+2(1-P_1)^3P_1$	$2P_m(1-P_m)^2$	$P_1^2(1-P_1)v+(1-P_1)^2P_1v$ $+P_1^2(1-P_1)(1-v)+(1-P_1)^2P_1(1-v)$	$2P_1(1-P_1)P_m(1-v)$ $+P_1^2(1-P_m)(1-v)+(1-P_1)^2(1-P_m)(1-v)$	$P_1P_m(1-P_m)(1-v)+(1-P_1)P_m(1-P_m)(1-v)$ $+P_1(1-P_m)^2v+(1-P_1)(1-P_m)^2v$
(rrr)	$2P_1^2(1-P_1)^2$	$(1-P_m)^3$	$P_1^2(1-P_1)(1-v)+(1-P_1)^2P_1(1-v)$	$2P_1(1-P_1)(1-P_m)(1-v)$	$P_1(1-P_m)^2(1-v)+(1-P_1)(1-P_m)^2(1-v)$

[a] $v = (P_m + s)/2$.

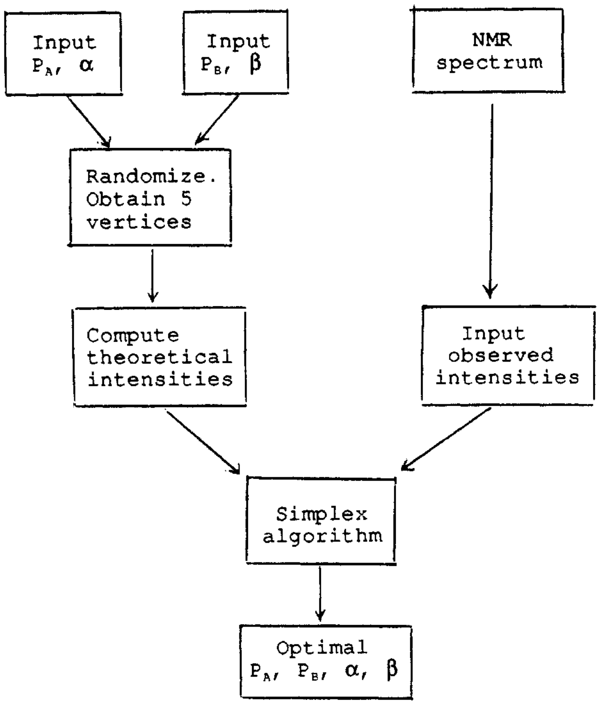

Figure 3. Schematic of program EXCO.

minimum number for the probability expressions in Tables I–VI to hold.

Illustrative Examples. As an example of the application of the computerized analytical approach to tetrad analysis, we treat the tetrad data for poly(methyl methacrylate) reported by Bovey[27] (designated Polymer II). The data have been analyzed previously[22,27] and shown to conform to the Coleman–Fox model. We can readily analyze the data with the one-state first-order Markovian model and the second-order Markovian model using the program FITCO reported earlier.[28] The fitted intensities and the conditional probabilities are shown in Table VII. The probabilities obtained by us are similar to the one-state conditional probabilities obtained by Frisch et al.,[22] as expected.

Table VII
Analysis of Tetrad Tacticity Data on Poly(methyl methacrylate)

tetrad	obsd[a]	1st-order Markov	2nd-order Markov	consec B/B model
(mmm)	70.7	70.7	70.7	70.7
(mmr)	9.1	11.5	9.1	10.0
(rmr)	3.0	0.5	2.8	2.1
(mrm)	4.0	2.2	4.3	4.0
(rrm)	6.1	8.0	6.1	6.1
(rrr)	7.1	7.1	7.1	7.1
		$P_{mr} = 0.075$	$P_{mmm} = 0.940$	$P_{ma} = 0.959$
		$P_{rm} = 0.361$	$P_{mrm} = 0.585$	$\alpha = 49$
			$P_{rmm} = 0.619$	$P_{mb} = 0.210$
			$P_{rrm} = 0.301$	$\beta = 11$
		MD[b] = 1.45	MD = 0.09	MD = 0.31

[a] Observed tetrad intensities taken from ref 22 and normalized.
[b] Mean deviation between observed and calculated intensities.

The data are next analyzed by the consecutive two-state B/B model. Through the program EXCO.TETRAD, we obtain the results shown in Table VII. To relate the parameters in our model with the rates as given by Coleman and Fox, we use the following definitions:[21,22]

λ_a = rate constant for state 2 (block B) → state 1 (block A);

λ_b = rate constant for state 1 (block A) → state 2 (block B);

k_{1i}, k_{1s} = rate constants for m and r placements in state 1;

k_{2i}, k_{2s} = rate constants for m and r placements in state 2;

$$k_1 = k_{1i} + k_{1s};$$

$$k_2 = k_{2i} + k_{2s}.$$

The four parameters in our model (P_{ma}, P_{mb}, α, β) are related to the rate constants thus: $P_{ma} = k_{1i}/k_1$, $P_{mb} =$

Table VIII
Analysis of Pentad Tacticity Data on Elastomeric Polypropylene Made with a Homogeneous Catalyst

pentad	obsd[a]	one-state B model	one-state E model	consec E/E model
(mmmm)	38.3	38.3	38.3	38.3
(mmmr)	15.5	20.8	16.4	15.7
(rmmr)	3.2	2.8	2.1	2.3
(mmrr)	16.1	5.6	16.4	15.6
(mmrm) + (rmrr)	8.5	22.3	8.3	9.1
(rmrm)	3.8	5.6	4.2	4.5
(rrrr)	2.5	0.2	2.1	2.2
(rrrm)	4.6	1.5	4.2	4.5
(mrrm)	7.4	2.8	8.2	7.8
			$P_1 = 0.825$	$P_1 = 0.844$
				$\alpha = 250$
		$P_m = 0.787$		$P_m = 0.500^c$
				$\beta = 30^c$
		$MD^b = 4.64$	$MD = 0.49$	$MD = 0.42$

[a] Data from ref 23. [b] Mean deviation between observed and calculated intensities. [c] These P_m and β values are presumed; they are not fitted.

k_{2i}/k_2; $\alpha = k_1/\lambda_b$, and $\beta = k_2/\lambda_a$. If w_1 = weight fraction of polymer produced in state 1, then

$$w_1 = \frac{\alpha}{\alpha + \beta} = \frac{k_1/\lambda_b}{k_1/\lambda_b + k_2/\lambda_a} = \frac{\lambda_a k_1}{\lambda_a k_1 + \lambda_b k_2} \tag{11}$$

From our values of α and β, we get $w_1 = 0.82$. This is close to the value obtained by Frisch et al.[22] Thus, our consecutive two-state B/B model gives the same results as the Coleman–Fox model, as indeed it should.

As an illustration of NMR pentad analysis, we take the data of polypropylene[23] made with the homogeneous catalysts *rac*-[*anti*-ethylidene(1-η^5-tetramethylcyclopentadienyl)(1-η^5-indenyl)titanium dimethyl[19a] and dichloride.[19b] The catalyst system appears to have two active states differing in polymerization rate constants and stereoselectivities,[20] and the polymer exhibits thermoplastic elastomeric properties. The pentad data for one such polymer[23] made at 25 °C are given in Table VIII.

Analysis by the one-site E model and the one-site B model can be readily made through the program PPTAC.[28,29] The B model gives a poor fit, but the E model gives reasonable agreement with a mean deviation = 0.49 (Table VIII). The use of the consecutive two-state E/E model with a random E-state ($P_l = 0.5$) gives a slightly better agreement with mean deviation = 0.42. The data can also be fitted (with similar mean deviation) with the concurrent E/E model. Thus, the analysis is compatible with the earlier results[19,20] from X-ray crystallinity and equilibrium modulus that the catalyst contains two (isomeric) active sites.

Comments. In the analysis of NMR data to obtain the relevant parameters, the importance of the precision and the accuracy of the available NMR data cannot be overemphasized. In the consecutive two-state models the junction points provide the means whereby the block sizes (α and β) are obtained. If the block sizes are large and the junction points are few, then the values of the tetrads or the pentads must be accurate enough for computer fitting to be made.

Although the expressions given in Tables II and V pertain to tacticity tetrads and pentads, the same expressions can be used for copolymer triads and tetrad sequence analysis. We only need to use the substitutions m → M_1 and r → M_2 (if the comonomers are M_1 and M_2).

Only tacticity tetrads and pentads are given in this work because they are most often encountered in NMR analysis. Similarly, only two-state models involving E and B statistics are treated because the E and B statistics are most often used in NMR analysis. The approach delineated in this work is, however, general and can be readily used for higher order *n*-ads (e.g., hexads and heptads) or for higher order Markovian statistical models. The same approach also applies to three-state (or multi state) models. The probability expressions do become more complex and require care and patience to derive.

Supplementary Material Available: Listings of programs EXCO.TETRAD and EXO.PENTAD used in this study (18 pages). Ordering information is given on any current masthead page.

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