

# Stereochemistry of Vinyl Polymers and NMR Characterization\*

H. N. CHENG, *Hercules Incorporated, Research Center, Wilmington, Delaware 19894*

## Synopsis

The configuration of vinyl polymers has been conventionally described by either Bovey's or Price's formalism. In this work, the relationships between these two formalisms are derived, and their relevance to polymerization mechanisms is delineated. Experimental data for nuclear magnetic resonance (NMR) pertaining to either chain-end control or catalytic-site control are tested using the computerized "analytical approach." Suitable polymeric systems are illustrated.

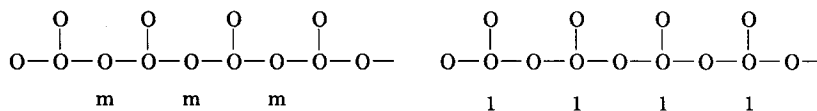
## INTRODUCTION

Tacticity in vinyl polymers is a major determinant of polymer properties.<sup>1-4</sup> The description of tacticity is conventionally made by either Bovey's<sup>2,5,6</sup> or Price's<sup>7</sup> formalism. Bovey's description is most commonly used in the literature.<sup>1-4</sup> The exact relationships between the two types of formalisms have never been reported, although the distinctive features of the separate formalisms are generally known. This article aims to fill that void, and in the process provide additional insight into the interesting phenomenon of polymer configuration and stereoregularity.

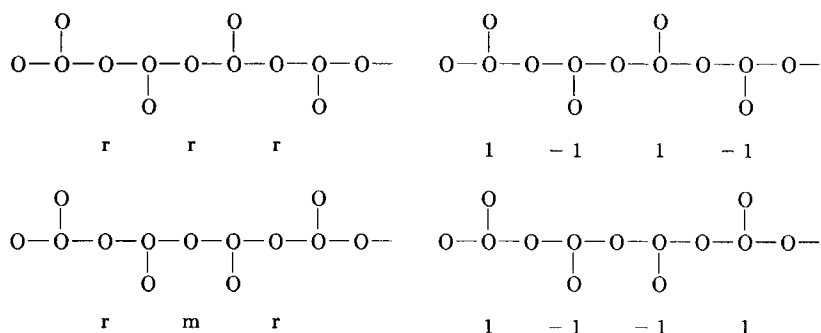
The measurement of tacticity can be most directly carried out by nuclear magnetic resonance (NMR) spectroscopy.<sup>1-6</sup> The application of NMR requires that the different tactic sequences be assigned properly and, preferably, be analyzed properly in the context of propagation statistics. Previously, computerized "analytical" approaches have been proposed for this purpose.<sup>8,9</sup> The use of this approach for both Bovey's and Price's formalisms is illustrated here for several polymer examples. The relevance of these formalisms to studies of polymerization mechanisms is also shown.

## THEORY

In the formalism devised by Bovey et al.,<sup>2,5,6</sup> tacticity is represented by the relative configuration of pairwise units (m or r). Some representative structures are shown below on the left side:

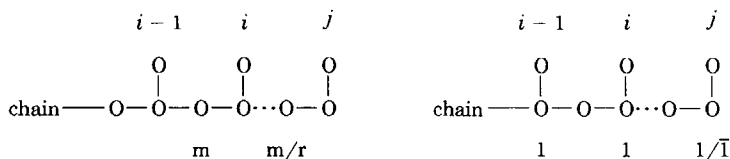


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In Price's formalism,<sup>7</sup> tacticity is depicted as a copolymer, with 1 for a configuration in the *dextro* direction, and  $-1$  or  $\bar{1}$  for the opposite *levo* direction (as above). For example, both (1111) and ( $\bar{1}\bar{1}\bar{1}\bar{1}$ ) sequences in Price's formalism are (mmm) tetrads in Bovey's formalism.

An important distinction between the two formalisms is that Bovey's formalism gives the relative configuration, whereas Price's gives the absolute configuration. The equivalence of Bovey's and Price's formalisms is best illustrated with reaction probability models. The use of these statistical models is fairly widespread and provides good illustrations of the formalisms.



As an example, in the Bovey-Bernoullian case, the tacticity of the monomer  $j$  adding to a propagating polymer does not depend at all on the last observable tacticity on the polymer chain (i.e., the relative configuration between units  $i$  and  $i-1$ ). However, the addition of monomer  $j$  can still depend on the absolute configuration of the last unit ( $i$ ) in the propagating chain (i.e., whether it is 1 or  $\bar{1}$ ), and in Price's formalism this would correspond to the first-order Markovian model. Thus, Bovey-Bernoullian case is equivalent to Price's first-order Markovian. Bovey's expressions are first given (where  $P_m$  = probability of m addition between  $i$  and  $j$ ):

*Diads:*

$$\begin{aligned} (\text{m}) &= P_m \\ (\text{r}) &= 1 - P_m \end{aligned}$$

*Triads:*

$$\begin{aligned} (\text{mm}) &= P_m^2 \\ (\text{mr}) &= 2P_m(1 - P_m) \\ (\text{rr}) &= (1 - P_m)^2 \end{aligned}$$

Price's expressions are based on first-order Markovian probabilities,  $P_{11}$ ,  $P_{\bar{1}\bar{1}}$ ,  $P_{1\bar{1}}$ , and  $P_{\bar{1}1}$ , out of which only two parameters are independent:  $P_{11} + P_{\bar{1}\bar{1}} = 1$ ,

$P_{\bar{1}\bar{1}} + P_{\bar{1}\bar{1}} = 1$ . (Standard definition is used here; thus,  $P_{\bar{1}\bar{1}}$  is the probability of the addition of an incoming  $\bar{1}$ -unit to a propagating chain terminating in a 1 unit.) The probability expressions are similar to those for copolymer sequences with 1 and  $\bar{1}$  as the comonomers.

$$\text{Diads:} \quad (m) = (11) + (\bar{1}\bar{1}) = k(P_{11}P_{\bar{1}\bar{1}} + P_{\bar{1}\bar{1}}P_{11})$$

$$(r) = (1\bar{1}) + (\bar{1}1) = k(2P_{1\bar{1}}P_{\bar{1}1})$$

$$\text{Triads:} \quad (mm) = (111) + (\bar{1}\bar{1}\bar{1}) = k(P_{11}^2P_{\bar{1}\bar{1}} + P_{\bar{1}\bar{1}}P_{11}^2)$$

$$(mr) = (11\bar{1}) + (\bar{1}11) + (\bar{1}\bar{1}1) + (1\bar{1}\bar{1})$$

$$= k(2P_{1\bar{1}}P_{11}P_{\bar{1}\bar{1}} + 2P_{\bar{1}\bar{1}}P_{\bar{1}1}P_{11})$$

$$(rr) = (\bar{1}\bar{1}\bar{1}) + (1\bar{1}\bar{1}) = k(P_{\bar{1}\bar{1}}P_{11}^2 + P_{11}^2P_{\bar{1}\bar{1}})$$

where  $k = (P_{1\bar{1}} + P_{\bar{1}1})^{-1}$ . Thus, Price's formalism needs two parameters and Bovey's only one. Price's formalism reduces to Bovey's if the constraint of absolute configuration (of the  $i$ th unit) is lifted; in this case,

$$P_{11} = P_{\bar{1}\bar{1}} = P_m$$

$$P_{1\bar{1}} = P_{\bar{1}1} = P_r$$

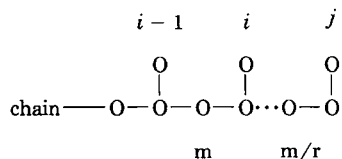
The expressions above are clearly equivalent, e.g.,

$$(mm) = P_{11}^2$$

$$(mr) = 2P_{1\bar{1}}P_{11}$$

$$(rr) = P_{\bar{1}\bar{1}}^2$$

Similar derivations hold for Bovey's first-order Markovian model. In this case the tacticity of incoming monomer  $j$  depends on the previous tacticity (between units  $i$  and  $i - 1$  on the propagating chain). In Price's formalism, this is equivalent to a second-order Markovian model because two previous units ( $i$  and  $i - 1$ ) are involved in the stereo control.



$$\text{Bovey} \quad (m) = kP_{rm}$$

$$(r) = kP_{mr}$$

$$\text{Price} \quad (m) = (11) + (\bar{1}\bar{1}) = k'(cd + \bar{a}\bar{b})$$

$$(r) = (1\bar{1}) + (\bar{1}1) = k'(2\bar{a}d)$$

where  $k = (P_{mr} + P_{rm})^{-1}$ , and  $k' = (\bar{a}\bar{b} + 2\bar{a}\bar{d} + cd)^{-1}$ , and

$$a = P_{111}, \quad c = P_{\bar{1}\bar{1}\bar{1}}$$

$$b = P_{1\bar{1}\bar{1}}, \quad d = P_{\bar{1}\bar{1}1}$$

Thus, in Bovey's relative configurational scheme, two parameters are needed, whereas in Price's absolute configurational scheme, four parameters are used. To relax the constraints of absolute configuration, one sets

$$a = \bar{d}, \quad \bar{a} = d$$

$$b = \bar{c}, \quad \bar{b} = c$$

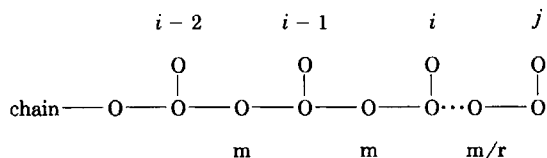
In this case,

$$(m) = k'c = k'(1 - b)$$

$$(r) = k'd = k'(1 - a)$$

Thus, by using the absolute configurational scheme (Price), we gained two extra degrees of freedom (i.e., two additional parameters). If we set  $a + d = 1$ , and  $b + c = 1$ , then in effect we are using the relative configurational scheme of Bovey, where  $c = P_{rm}$ ,  $d = P_{mr}$ . Price's second-order Markov is therefore a generalization of Bovey's first-order Markov.

Analogous arguments can be used for Bovey's second-order Markov. Here the tacticity of incoming monomer  $j$  depends on two previous tacticities. In Price's formalism, this is equivalent to a third-order Markovian model, as three previous units ( $i, i - 1, i - 2$ ) are involved in the stereo-control.



The second-order Markovian model in Bovey's formalism would require four reaction probabilities<sup>2,6</sup>:  $\alpha = P_{mmm}$ ,  $\beta = P_{mrm}$ ,  $\gamma = P_{rmm}$ ,  $\delta = P_{rrm}$ . In Price's

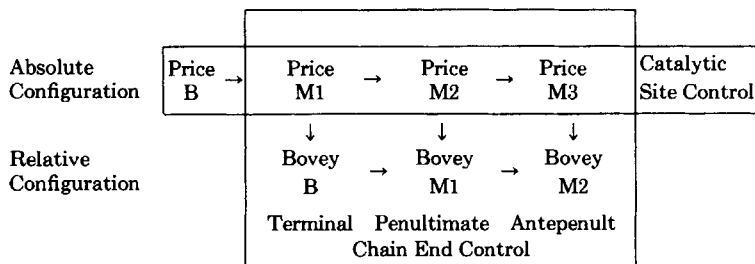


Fig. 1. Logical relationships between Bovey's and Price's models: B = Bernoullian, M = Markovian, and 1, 2, 3 refer to first-, second-, and third-order.

third-order Markovian model, this would require 8 parameters. The logical relationship between the two formalisms is shown in Figure 1.

### POLYMERIZATION MECHANISM

In studies of polymerization, two general kinds of mechanisms have been identified; one is chain-end controlling, and the other is catalytic-site controlling. Usually free radical, anionic, and most cationic polymerizations are chain-end controlled, whereas many Ziegler-Natta polymerizations are considered to be catalytic-site controlled. The features of both chain-end and catalytic-site controlling mechanisms have recently been reviewed.<sup>10</sup>

In a purely chain controlling mechanism, the absolute configuration is not needed, and Bovey's formalism works well. For polymerizations wherein the catalytic sites have a major influence, differentiation by the absolute configuration is necessary. Price's formalism may be used in this latter case.

A good example of catalytic-site controlled mechanism is demonstrated by the special case of Price's Bernoullian model. This model has no equivalence in the Bovey formalism. The catalytic site will have a reaction probability  $P_1$  for *d*-configuration and  $P_{\bar{1}}$  (or  $1 - P_1$ ) for the *l*-configuration. The various n-ad sequences are given as follows:

$$(m) = (11) + (\bar{1}\bar{1}) = P_1^2 + (1 - P_1)^2$$

$$(r) = (1\bar{1}) + (\bar{1}1) = 2P_1(1 - P_1)$$

$$(mm) = (111) + (\bar{1}\bar{1}\bar{1}) = P_1^3 + (1 - P_1)^3$$

$$(mr) = (1\bar{1}\bar{1}) + (\bar{1}\bar{1}1) + (\bar{1}11) + (11\bar{1}) = 2P_1(1 - P_1)^2 + 2P_1^2(1 - P_1)$$

$$(rr) = (1\bar{1}1) + (\bar{1}\bar{1}1) = P_1(1 - P_1)^2 + P_1^2(1 - P_1)$$

The above expressions may be compared to the enantiomeric-site model<sup>11,12</sup> found to be suitable for the highly isotactic portions of Ziegler-Natta polymers.<sup>13,14</sup>

$$(mm) = fP_1^3 + fP_{\bar{1}}^3 + \bar{f}P_1^3 + \bar{f}P_{\bar{1}}^3$$

$$(mr) = 2fP_1P_{\bar{1}}^2 + 2fP_{\bar{1}}^2P_1 + 2\bar{f}P_1P_{\bar{1}}^2 + 2\bar{f}P_{\bar{1}}^2P_1$$

$$(rr) = fP_1P_{\bar{1}}^2 + fP_{\bar{1}}^2P_1 + \bar{f}P_1P_{\bar{1}}^2 + \bar{f}P_{\bar{1}}^2P_1$$

where  $f$  is the probability that the catalytic site will show *d*-preference, and  $\bar{f}$  is a probability for *l*-preference, and the  $P_1$  and  $P_{\bar{1}}$  are the probabilities of *d* catalytic site adding *d*-monomer and *l*-monomer to the propagating chain, respectively, and  $\bar{P}_1$  and  $\bar{P}_{\bar{1}}$  are the corresponding probabilities of *l* catalytic site adding *d*-monomer and *l*-monomer. For *symmetrical* enantiomeric sites,  $P_1 = \bar{P}_1$ ,  $f + \bar{f} = 1$ ,  $P_1 + P_{\bar{1}} = 1$ , and the n-ad expressions are identical to the Price's expressions for the Bernoullian model.

TABLE I  
Second-Order Markovian<sup>a</sup> Expressions in Bovey's and Price's  
Formalisms for the n-ad Sequences

N-ad	Price	Bovey
m	$cd + \bar{a}\bar{b}$	$(\bar{\alpha} + \gamma)\delta$
r	$2\bar{a}\bar{d}$	$(\bar{\beta} + \delta)\bar{\alpha}$
mm	$acd + \bar{a}\bar{b}\bar{d}$	$\gamma\delta$
mr	$2\bar{a}\bar{c}\bar{d} + 2\bar{a}\bar{b}\bar{d}$	$2\bar{\alpha}\delta$
rr	$\bar{a}\bar{b}\bar{d} + \bar{a}\bar{c}\bar{d}$	$\bar{\alpha}\bar{\beta}$
mmm	$a^2\bar{c}\bar{d} + \bar{a}\bar{b}\bar{d}^2$	$\alpha\gamma\delta$
mmr	$2\bar{a}\bar{a}\bar{c}\bar{d} + 2\bar{a}\bar{b}\bar{d}\bar{d}$	$2\bar{\alpha}\gamma\delta$
rmr	$\bar{a}\bar{b}\bar{d}^2 + \bar{a}^2\bar{c}\bar{d}$	$\bar{\alpha}\gamma\delta$
mrn	$2\bar{a}\bar{b}\bar{c}\bar{d}$	$\bar{\alpha}\bar{\beta}\delta$
rrm	$2\bar{a}\bar{b}\bar{c}\bar{d} + 2\bar{a}\bar{b}\bar{c}\bar{d}$	$2\bar{\alpha}\bar{\beta}\delta$
rrr	$2\bar{a}\bar{b}\bar{c}\bar{d}$	$\bar{\alpha}\bar{\beta}\delta$
mmmm	$a^3\bar{c}\bar{d} + \bar{a}\bar{b}\bar{d}^3$	$\alpha^2\gamma\delta$
mmmr	$2\bar{a}\bar{a}^2\bar{c}\bar{d} + 2\bar{a}\bar{b}\bar{d}\bar{d}^2$	$2\bar{\alpha}\bar{\alpha}\gamma\delta$
rmmr	$\bar{a}\bar{a}^2\bar{c}\bar{d} + \bar{a}\bar{b}\bar{d}\bar{d}^2$	$\bar{\alpha}^2\gamma\delta$
mmrr	$2\bar{a}\bar{a}\bar{b}\bar{c}\bar{d} + 2\bar{a}\bar{b}\bar{c}\bar{d}\bar{d}$	$2\bar{\alpha}\bar{\beta}\gamma\delta$
mrmm	$2\bar{a}\bar{a}\bar{b}\bar{c}\bar{d} + 2\bar{a}\bar{b}\bar{c}\bar{d}\bar{d}$	$2\bar{\alpha}\bar{\beta}\gamma\delta$
rmrr	$2\bar{a}\bar{b}\bar{c}\bar{d}^2 + 2\bar{a}^2\bar{b}\bar{c}\bar{d}$	$2\bar{\alpha}\bar{\beta}\gamma\delta$
mrrr	$2\bar{a}\bar{b}\bar{c}\bar{d}^2 + 2\bar{a}^2\bar{b}\bar{c}\bar{d}$	$2\bar{\alpha}\bar{\beta}\gamma\delta$
rrrr	$\bar{a}\bar{b}\bar{c}^2\bar{d} + \bar{a}\bar{b}^2\bar{c}\bar{d}$	$\bar{\alpha}\bar{\beta}\delta^2$
rrrm	$2\bar{a}\bar{b}\bar{c}\bar{c}\bar{d} + 2\bar{a}\bar{b}\bar{b}\bar{c}\bar{d}$	$2\bar{\alpha}\bar{\beta}\delta\bar{\delta}$
mrrm	$\bar{a}\bar{b}\bar{c}^2\bar{d} + \bar{a}\bar{b}^2\bar{c}\bar{d}$	$\bar{\alpha}\bar{\beta}\delta^2$
k	$(\bar{a}\bar{b} + 2\bar{a}\bar{d} + \bar{c}\bar{d})^{-1}$	$(\bar{\alpha}\bar{\beta} + 2\bar{\alpha}\delta + \gamma\delta)^{-1}$

<sup>a</sup>Corresponding expressions for the first-order Markov can be obtained by substituting (for Price's formalism)  $a = c = P_{11}$ ,  $\bar{a} = \bar{c} = P_{\bar{1}\bar{1}}$ ,  $b = d = P_{\bar{1}1}$ , and  $\bar{b} = \bar{d} = P_{1\bar{1}}$ , and (for Bovey's formalism)  $\alpha = \gamma = P_{mm}$ ,  $\bar{\alpha} = \bar{\gamma} = P_{mr}$ ,  $\beta = \delta = P_{rm}$ ,  $\bar{\beta} = \bar{\delta} = P_{rr}$ . Similarly, Bernoullian expressions may be readily deduced: (for Price)  $P_{11} = P_{\bar{1}\bar{1}} = P_1$ ,  $P_{1\bar{1}} = P_{\bar{1}1} = P_1$ , and (for Bovey)  $P_{mm} = P_{rm} = P_m$ ,  $P_{mr} = P_{rr} = P_r$ .

A problem of considerable interest is the description of a polymerization which is controlled by *both* the catalyst sites and the chain ends. It is significant to note that Price's formalism with its emphasis on absolute configuration is a suitable description for such hybrid models. The various mechanisms of stereochemical control and the suitable models are summarized below.

Pure Chain-end Control: Bovey's B, M1, M2 Models

Pure Catalyst-site Control: Price's B Model

Both Catalyst-site and Chain-end Control: Price's M1, M2 Models

The simplest case of catalyst-site control occurs when the catalytic enantiomorphic sites are symmetric. In this case, the n-ad expressions for Price's formalism (Table I) can be used without modification. For example, in a polymer system which exhibits both catalyst-site control and chain-end control in the second order (i.e., propagation influenced by both the catalyst-site and the last two units of the propagating polymer chain), Price's M2 model is



TABLE II  
Tacticity of Poly(Methyl Vinyl Ether) Prepared with  $\text{Al}_2(\text{SO}_4)_3\text{-H}_2\text{SO}_4^a$

Sample	Obsd intensity			Price's M1	
	mm	mr	rr	$P_{\bar{1}\bar{1}}$	$P_{\bar{1}1}$
1	50.7	32.5	16.8	0.809	0.208
2	69.9	21.0	9.1	0.816	0.111
3	54.2	30.7	15.1	0.804	0.188
4	55.8	29.2	15.0	0.836	0.180
5	59.6	27.2	13.2	0.825	0.160
4-1	45.5	36.0	18.5	0.775	0.239
4-2	67.5	22.1	10.4	0.847	0.123

<sup>a</sup>Data from Ref. 15.

### HOMOPOLYMER TACTICITY

Hagashimura et al.<sup>15</sup> have shown earlier from <sup>1</sup>H NMR data that the polymerization of methyl vinyl ether with  $\text{Al}_2(\text{SO}_4)_3\text{-H}_2\text{SO}_4$  is catalyst-site controlled, and the configuration of the polymer conforms to enantiomorphoic-site model statistics. Their observed tacticity values are summarized in Table II. Analysis can be repeated using Price's first-order Markov expressions (Table I):

$$(\text{mm}) = k(P_{11}^2 P_{\bar{1}\bar{1}} + P_{\bar{1}\bar{1}} P_{11}^2)$$

$$(\text{mr}) = 2k(P_{\bar{1}\bar{1}} P_{11} P_{\bar{1}\bar{1}} + P_{11} P_{\bar{1}\bar{1}} P_{11})$$

$$(\text{rr}) = k(P_{\bar{1}\bar{1}} P_{11}^2 + P_{11}^2 P_{\bar{1}\bar{1}})$$

The reaction probabilities can be readily obtained through the computerized optimization procedure. The results are shown in Table II. It can be seen that in all cases  $P_{\bar{1}\bar{1}} + P_{11} \sim 1$ . Thus, the data tend to support the symmetrical enantiomorphoic-site model (equivalent to Price's Bernoullian model). The overall  $P_1$  is approximately 0.2 for all the samples. The result is in sharp contrast to the  $\text{BF}_3$ -initiated polymerization<sup>16-19</sup> of the same monomer where first-order Markovian statistics were found.<sup>19</sup> Unfortunately, only the triad sequences are available in Hagashimura's work<sup>15</sup> which do not provide enough variables to discriminate between Bovey's and Price's first-order Markovian models. Perhaps these samples should be re-examined with <sup>13</sup>C NMR which, with its sensitivity to longer sequence lengths, would be a better technique to test their conformity to different propagation statistics.

Another case where the problem of chain-end control versus catalyst-site control has been investigated is polypropylene. Owing to its industrial importance, this polymer has been repeatedly studied by NMR,<sup>9,13,14,20-23</sup> and the relationship between stereoregularity and polymerization mechanism delineated, most notably by Zambelli et al.,<sup>14,20</sup> and Doi et al.<sup>13,22</sup> The consensus is that the polymerization of isotactic polypropylene (usually involving titanium



TABLE III  
Observed Intensities and Calculated Reaction Probabilities of  
Polypropylenes Made With Isospecific Catalysts

	Wolfsgruber <sup>a</sup>	A-5	Pavan <sup>b</sup>	
			A-4	A-3
mmmm	90	96.5	93.6	76.5
mmmr	4	1.7	2.7	6.2
rmmr	0	0	0	0
mmrr	4	1.7	2.7	8.7
rrmr + mrrm	0	0	0	2.0
rmmr	0	0	0	0
rrrr	0	0	0	0
rrrm	0	0	0	0
mrrm	2	0	1.0	5.0
Price/Markov I				
$P_{1\bar{1}}$	0.021	0.007	0.013	0.050
$P_{\bar{1}1}$	0.995	0.818	0.947	0.985
$R^c$	0.07	0.23	0.12	0.65
Bovey/Markov II				
$\alpha$	0.979	0.993	0.987	0.945
$\beta$	0.015	0.016	0.013	0.098
$\gamma$	0.979	0.987	0.984	0.960
$\delta$	0.999	0.986	0.985	0.988
$R^c$	0.05	0.16	0.09	0.67

<sup>a</sup>Data from Ref. 24, Table 1, Res. 7 fractions.

<sup>b</sup>Data representing successive fractions, with A-5 least soluble, from Ref. 25, intensities normalized.

<sup>c</sup>Mean deviation between observed and calculated intensities.

catalysts) is catalytic-site controlled, whereas the polymerization of syndiotactic polymer (e.g., with vanadium catalysts) is chain-end controlled.

In order to examine this problem, the computerized analytical approach<sup>9</sup> (FITCO program) has been adapted to accommodate both Bovey's and Price's formalisms. As usual, the <sup>13</sup>C NMR data on the methyls are used for the analysis. The theoretical expressions for the pentad intensities are the same ones as shown in Table I.

A lot of spectral data have been published in the literature on titanium-catalyzed polypropylene. The results must be treated with care since it is now commonly accepted that these samples contain mixtures of polymers made at different catalytic sites. In order to ensure that such inherent polymer blending had not occurred, only data on fractionated samples were chosen for analysis. Zambelli et al.<sup>24,25</sup> had previously published such data, and these are shown in Table III.

The use of Price's M1 model readily provides the reaction probabilities which are also given in Table III. The fit is excellent. (In order to accomplish similarly good agreement, one needs to use Bovey's Markovian model up to the second order.) In addition,  $P_{1\bar{1}} + P_{\bar{1}1} \sim 1$ . Thus, the effect of chain-end control is small, and the polymerization is mostly catalytic-site controlled, in agreement with previous findings.<sup>20,24,25</sup>

TABLE IV  
Observed Pentad Intensities<sup>a</sup> and Calculated Probabilities of  
Polypropylenes Made With Soluble Vanadium Catalysts

	Sample a	Sample s
mmmm	8.4	1.1
mmmr	10.8	3.3
rmmr	4.0	3.1
mmrr	9.3	3.7
rrmr + mrrm	22.6	23.9
rmm	13.3	10.9
rrrr	7.9	25.4
rmmm	16.6	21.7
mrrm	7.2	6.9
Bovey/Markov I		
$P_{mr}$	0.536	0.830
$P_{rm}$	0.471	0.298
$R^c$	1.74	1.21
Bovey/Markov II		
$\alpha$	0.606	0.408
$\beta$	0.430	0.312
$\gamma$	0.367	0.183
$\delta$	0.479	0.291
R	0.75	0.96
Price/Markov I		
$P_{\bar{1}\bar{1}}$	0.659 <sup>b</sup>	0.711
$P_{\bar{1}1}$	0.427 <sup>b</sup>	0.709
R	1.59	1.42

<sup>a</sup>Data from Ref. 26.

<sup>b</sup>Same fit observed by reversing these two numbers.

<sup>c</sup>See footnote c in Table III.

Similar analysis can be carried out on vanadium-catalyzed polypropylene. Detailed tacticity information is surprisingly rare in the literature. Nevertheless, two data sets<sup>26</sup> are available (Table IV). Computerized analysis indicates that Bovey's first- or second-order Markovian model can be made to fit the data. The use of Price's models gives no substantial improvements. In fact, in sample s,  $P_{\bar{1}\bar{1}} \sim P_{\bar{1}1}$ ; and in sample a, equally good fits are obtained with  $P_{\bar{1}\bar{1}} = 0.659$ ,  $P_{\bar{1}1} = 0.427$  as well as  $P_{\bar{1}\bar{1}} = 0.427$ ,  $P_{\bar{1}1} = 0.659$ . The propagation reaction obviously depends primarily on the relative configuration. The effect of catalytic sites on configuration is therefore small.

It appears that polymerizations due to heterogeneous catalysts are often catalytic-site controlled, whereas homogeneous catalysis mostly gives chain-end stereo control. The choice (and the testing) of an appropriate formalism is therefore highly dependent upon the catalyst system in question.

### COPOLYMER SEQUENCE DETERMINATION

For copolymers where the effect of tacticity is either not present or not observed, one needs only to treat the copolymer sequence effects. Since the

consideration of absolute configuration does not enter in this case, the Bovey expressions (Table I, third column) can be used directly. For comonomer sequences through triads in the second-order Markovian model, the expressions for two comonomers A and B are shown<sup>2</sup> below ( $\alpha = P_{AAA}$ ,  $\beta = P_{ABA}$ ,  $\gamma = P_{BAA}$ ,  $\delta = P_{BBA}$ ):

$$\begin{aligned}
 (\text{A}) &= k(\bar{\alpha} + \gamma)\delta & (\text{AAA}) &= k \cdot \alpha\gamma\delta \\
 (\text{B}) &= k(\bar{\beta} + \delta)\bar{\alpha} & (\text{AAB}) &= k \cdot 2\bar{\alpha}\gamma\delta \\
 & & (\text{BAB}) &= k \cdot \bar{\alpha}\gamma\delta \\
 (\text{AA}) &= k \cdot \gamma\delta & (\text{ABA}) &= k \cdot \bar{\alpha}\beta\delta \\
 (\text{AB}) &= k \cdot 2\bar{\alpha}\delta & (\text{BBA}) &= k \cdot 2\bar{\alpha}\bar{\beta}\delta \\
 (\text{BB}) &= k \cdot \bar{\alpha}\bar{\beta} & (\text{BBB}) &= k \cdot \bar{\alpha}\bar{\beta}\delta
 \end{aligned}$$

where  $k = (\bar{\alpha}\bar{\beta} + 2\bar{\alpha}\delta + \gamma\delta)^{-1}$ .

The computerized model-fitting approach can also be applied to the analysis of comonomer sequences. A general program FITCO.TRIAD has been written, applicable to the analysis of triad sequence intensities observed in

TABLE V  
Computerized Analysis of the Triad Intensities for Selected  
Copolymers with First-Order Markovian Probabilities

A B	VDC <sup>b</sup> VC	VAc <sup>c</sup> VC	VAc <sup>d</sup> E	VAc <sup>e</sup> VA
AAA	63.9	0	0	8.74
AAB	18.8	1.0	4	6.27
BAB	2.4	5.5	10	3.99
ABA	9.1	0	0	2.43
BBA	3.6	12.1	20	12.15
BBB	2.1	81.4	66	66.42
Markov I				
P <sub>AB</sub>	0.135	0.918	0.883	0.343
P <sub>BA</sub>	0.791	0.066	0.130	0.087
R <sup>a</sup>	0.77	0.20	0.55	1.14
Markov II				
$\alpha$	—	—	—	0.719
$\beta$	—	—	—	0.209
$\gamma$	—	—	—	0.444
$\delta$	—	—	—	0.084
R	—	—	—	0.27

<sup>a</sup>See footnote in Table III.

<sup>b</sup>Data from Ref. 30.

<sup>c</sup>Data from Ref. 29.

<sup>d</sup>Data from Ref. 28.

<sup>e</sup>Data from Ref. 27.

NMR spectra. Selected data of copolymers involving vinyl chloride (VC), vinylidene chloride (VDC), vinyl acetate (VAc), vinyl alcohol (VA), and ethylene (E) are given in Table V.

Most of the triad sequence data fit fairly well to either Bernoullian or first-order Markovian models. The VAc-VA copolymer gives the best fit at the second-order Markov level. Since this copolymer was made by base hydrolysis of poly(vinyl acetate), the hydrolysis must not have been a random (Bernoullian) process.<sup>27</sup> The rather extreme probability values ( $\alpha = P_{AAA} = 0.719$ , and  $1 - \delta = P_{BBB} = 0.917$ ) suggest that neighboring alcohol groups greatly facilitate the hydrolysis of the acetate.

## CONCLUSION

Much has been published in the literature on statistical models in polymerization and NMR determination of tacticity. This work attempts to bring together the germane information and to provide a unified view. In particular, the conditions of equivalence of Bovey's and Price's formalisms are derived. The relevance of Price's formalism to catalytic-site-controlled polymerizations is pointed out, and Markovian expressions for n-ad sequences through pentads for Price's formalism are derived. In addition, the use of a computerized analytical approach in the analysis of NMR data as pertaining to both Bovey's and Price's formalisms is demonstrated.

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