Macromolecules **1992,** *25,* 2351–2358

Perturbed Markovian Probability Models[†]

H. N. Cheng

Research Center, Hercules Incorporated, Wilmington, Delaware 19894

Received August 20, 1991; Revised Manuscript Received January 19, 1992

ABSTRACT: A new class of reaction probability models is formulated to account for compositional heterogeneity in polymers. These models are based on perturbations of the Markovian reaction probabilities and are called "perturbed Markovian probability models". The necessary mathematical expressions are derived. Four different sources of composition heterogeneity and their relationships to the perturbed Markovian models are discussed. The model can be used to analyze NMR data on copolymer sequence distribution and tacticity. In suitable cases compositional heterogeneity can be detected and quantified from the NMR data. Computer programs have been written to facilitate the analysis.

Introduction

The use of Markovian statistics in polymers is widespread.[1–4] Such statistical models form the basis of copolymerization theory and can be used to fit polymerization kinetics data[4,5] as well as NMR spectral intensities.[3,4] A possible complication of such a copolymerization model is the compositional heterogeneity of the copolymers. For polymer samples where the heterogeneity is large, the use of a single set of Markovian parameters may be insufficient to describe the entire system. A modification of the standard reaction probability formulation may be necessary.

As part of an ongoing effort to use statistical models to describe polymerization,[6–12] a new approach is devised in this work called "perturbed Markovian probability models". These models are applicable to most free-radical and ionic polymerizations, as well as some Ziegler–Natta systems. The mathematical formulations of the perturbed models are fairly general and are readily adaptable to higher order Markovian statistics.

Numerous other approaches have been previously devised to describe compositional heterogeneity. The classic work of Stockmayer considered the effect of statistical fluctuation on copolymer composition.[13] This is variously called "statistical heterogeneity", "instantaneous heterogeneity", or "compositional heterogeneity of the first kind". Over the years Stockmayer's treatment has been modified several times for specific purposes.[14–17] Others have investigated the problem of chemical composition distribution in batch copolymerizations due to different reactivity ratios of the comonomers.[18–23] This compositional distribution is dependent on the degree of conversion and has been called "conversion heterogeneity" or "compositional heterogeneity of the second kind".

Apart from these two well-studied situations, other sources of heterogeneity exist. One commonly recognized problem occurs in Ziegler–Natta catalysis where multiple catalytic sites may occur,[24–26] giving rise to polymers that are in effect polymer mixtures or blends. Similarly, in some ionic polymerizations, it has been proposed that two propagating species may occur in equilibrium with each other.[27,28] The resulting polymers may be either blends or block copolymers, depending on the rates of equilibrium versus chain transfer. In some emulsion systems, more than one propagating center have been found.[29] For convenience in subsequent discussions in this work, this third kind of composition heterogeneity will be called "multistate heterogeneity".

In addition, compositional heterogeneity can also come about from practical limitations of industrial processes or changes in reaction conditions as polymerization proceeds. For example, problems with the reactor (inadequate agitation and/or dead space), catalyst (inadequate mixing or deactivation), reaction medium (gel effect and phase separation), and temperature fluctuations can also give rise to compositional heterogeneity. This fourth type of compositional heterogeneity will be referred to in this work as "process heterogeneity".

Since there are different sources of compositional heterogeneity, a unified treatment tends to be difficult. An advantage of the perturbed probability models presented in this work is that they are broadly applicable to statistical, conversion, and process heterogeneities. Only in multistate heterogeneity where discrete catalytic sites are noted will the perturbed probability models be inapplicable. The alternative, multistate probability models (multicomponent mixture analysis),[9,10] must then be used instead.

Perturbed Theory of Copolymerization

Formalism. The perturbed model for copolymerization will first be developed. Standard terminology[4,5] for chain copolymerization will be followed.

$$\begin{gathered}
-\mathrm{A}^* + \mathrm{A} \xrightarrow{k_{\mathrm{AA}}{}^0} -\mathrm{A}\,\mathrm{A}^* \\
-\mathrm{A}^* + \mathrm{B} \xrightarrow{k_{\mathrm{AB}}{}^0} -\mathrm{A}\,\mathrm{B}^* \\
-\mathrm{B}^* + \mathrm{A} \xrightarrow{k_{\mathrm{BA}}{}^0} -\mathrm{BA}^* \\
-\mathrm{B}^* + \mathrm{B} \xrightarrow{k_{\mathrm{BB}}{}^0} -\mathrm{BB}^* \qquad (1)
\end{gathered}$$

where A and B refer to the comonomer units, and the asterisk indicates the point of monomer addition (e.g., free radical, ion, or catalytic site). In the nonperturbed

---

[†] Hercules Research Center Contribution No. 2048. Part of this work was presented at the IUPAC Macro 90 Conference in Montreal in July 1990.

0024-9297/92/2225-2351$03.00/0

case, each of the above monomer addition reactions is associated with a rate constant $k_{ij}{}^0$, a reaction probability $P_{ij}{}^0$, and a reactivity ratio $r_i{}^0$:

$$r_A{}^0 = \frac{k_{AA}{}^0}{k_{AB}{}^0}, \quad r_B{}^0 = \frac{k_{BB}{}^0}{k_{BA}{}^0} \tag{2}$$

$$P_{AA}{}^0 = \frac{r_A{}^0}{r_A{}^0 + x^{-1}}, \quad P_{AB}{}^0 = \frac{1}{r_A{}^0 x + 1}$$

$$P_{BA}{}^0 = \frac{1}{1 + r_B{}^0 x^{-1}}, \quad P_{BB}{}^0 = \frac{r_B{}^0}{r_B{}^0 + x} \tag{3}$$

where $x = f_A/f_B$ (molar ratio of concentrations of monomer feed) and the superscript 0 indicates the unperturbed (intrinsic) value.

In the presence of compositional heterogeneity, a *perturbation* is felt by the reaction probabilities. We assume that instead of specific values, the reaction probabilities take on a range of values. Let $\pm\epsilon$ be the range of values that the reaction probabilities may take on. The perturbed reaction probabilities (P_{ij}) can be defined as follows:

$$P_{AA} = \langle P_{AA} \rangle \pm \epsilon, \quad P_{AB} = \langle P_{AB} \rangle \mp \epsilon$$

$$P_{BA} = \langle P_{BA} \rangle \pm \epsilon, \quad P_{BB} = \langle P_{BB} \rangle \mp \epsilon \tag{4}$$

where the symbol $\langle\ \rangle$ represents the average values. In effect, we are expressing[30] each reaction probability as a rectangular distribution function centered on $\langle P_{ij} \rangle$ with width 2ϵ. For this symmetrical distribution function, $\langle P_{ij} \rangle = P_{ij}{}^0$.

Copolymer Sequence Distribution. We shall proceed to derive the copolymer composition and the sequence expressions for the perturbed first-order Markovian model. The Bernoullian model can be readily deduced from the first-order Markovian expressions.

The derivation can be simplified by using the following substitutions:

$$P_{BA} = z$$

$$P_{AB} = y = s - z$$

$$P_{AA} = 1 - y = 1 - s - z$$

$$P_{BB} = 1 - z$$

Since $P_{AB} + P_{BA} = P_{AB}{}^0 + P_{BA}{}^0 =$ constant, we can define two constants, k and s, where $k = s^{-1} = (z + y)^{-1}$.

The copolymer composition can be readily obtained:

$$\langle A \rangle = \langle k P_{BA} \rangle = k\langle z \rangle \tag{5a}$$

$$\langle B \rangle = \langle k P_{AB} \rangle = k\langle y \rangle = 1 - k\langle z \rangle \tag{5b}$$

We need the value of $\langle z^2 \rangle$ for the derivation of diad sequences. This can be obtained by integrating over all allowed values of z (i.e., $\langle z \rangle \pm \epsilon$).

$$\begin{aligned}\langle z^2 \rangle &= \frac{\int_{\langle z \rangle - \epsilon}^{\langle z \rangle + \epsilon} z^2 \, dz}{\int_{\langle z \rangle - \epsilon}^{\langle z \rangle + \epsilon} dz} = \frac{\left[\frac{1}{3} z^3\right]_{\langle z \rangle - \epsilon}^{\langle z \rangle + \epsilon}}{2\epsilon} \\ &= \frac{(\langle z \rangle + \epsilon)^3 - (\langle z \rangle - \epsilon)^3}{6\epsilon} \\ &= \langle z \rangle^2 + \epsilon^2/3\end{aligned}$$

$$\begin{aligned}\langle zy \rangle &= \langle z(s - z) \rangle \\ &= s\langle z \rangle - \langle z^2 \rangle \\ &= s\langle z \rangle - \langle z \rangle^2 - \epsilon^2/3\end{aligned}$$

The diad sequences for the perturbed model are given as follows:

$$\begin{aligned}\langle AA \rangle &= \langle k P_{AA} P_{BA} \rangle = k\langle z(1 - y) \rangle \\ &= k\langle z \rangle - k\langle zy \rangle \\ &= k\langle z \rangle (1 - s + \langle z \rangle) + k\epsilon^2/3 \\ &= k P_{AA}{}^0 P_{BA}{}^0 + k\epsilon^2/3 = \langle AA \rangle_0 + k\epsilon^2/3\end{aligned} \tag{6a}$$

$$\begin{aligned}\langle AB \rangle &= \langle 2k P_{AB} P_{BA} \rangle = 2k\langle zy \rangle \\ &= 2\langle z \rangle - 2k\langle z \rangle^2 - 2k\epsilon^2/3 \\ &= 2k P_{AB}{}^0 P_{BA}{}^0 - 2k\epsilon^2/3 \\ &= \langle AB \rangle_0 - 2k\epsilon^2/3\end{aligned} \tag{6b}$$

$$\begin{aligned}\langle BB \rangle &= \langle k P_{BB} P_{AB} \rangle = k\langle y(1 - z) \rangle \\ &= k\langle y \rangle - k\langle zy \rangle \\ &= 1 - k\langle z \rangle - \langle z \rangle + k\langle z \rangle^2 + k\epsilon^2/3 \\ &= k P_{BA}{}^0 P_{AB}{}^0 + k\epsilon^2/3 \\ &= \langle BB \rangle_0 + k\epsilon^2/3\end{aligned} \tag{6c}$$

where the subscript 0 indicates the unperturbed value.

The derivation of the triad sequences requires $\langle z^3 \rangle$. Following the same approach as above, we can obtain the following expression:

$$\langle z^3 \rangle = \frac{\int_{\langle z \rangle - \epsilon}^{\langle z \rangle + \epsilon} z^3 \, dz}{\int_{\langle z \rangle - \epsilon}^{\langle z \rangle + \epsilon} dz} = \langle z \rangle^3 + \langle z \rangle \epsilon^2$$

The derivation is straightforward but tedious. For illustration, only the derivation of $\langle BAB \rangle$ is given here.

$$\begin{aligned}\langle BAB \rangle &= \langle k P_{AB}{}^2 P_{BA} \rangle = 2k\langle (s - z)^2 z \rangle \\ &= k[s^2\langle z \rangle - 2s\langle z^2 \rangle + \langle z^3 \rangle] \\ &= k[s^2\langle z \rangle - 2s\langle z \rangle^2 + \langle z \rangle^3] + k\epsilon^2[\langle z \rangle - 2s/3] \\ &= k P_{AB}{}^{02} P_{BA}{}^0 + k\epsilon^2[\langle z \rangle - 2s/3] \\ &= \langle BAB \rangle_0 + k\epsilon^2[\langle z \rangle - 2s/3]\end{aligned} \tag{7}$$

The complete diad, triad, and tetrad expressions for the perturbed first-order Markovian model are summarized in Table I. Also given in Table I are the Bernoullian expressions. Note that, although the theoretical treatment is made for copolymer sequence distributions, exactly the same expressions can be used for homopolymer tacticity by using the substitutions A → m and B → r.

Bovey Plots. The effect of compositional heterogeneity on sequence distribution can be graphically shown for the simple case of Bernoullian diad sequences. Let $P_A{}^0$ and

Table I
Sequences and Theoretical Probabilities in the Perturbed Bernoullian and First-Order Markovian Model

sequence[a]	Bernoullian	first-order Markovian[b]
$\langle A\rangle$	$\langle A\rangle_0$	$\langle A\rangle_0$
$\langle B\rangle$	$\langle B\rangle_0$	$\langle B\rangle_0$
$\langle AA\rangle$	$\langle AA\rangle_0 + \epsilon^2/3$	$\langle AA\rangle_0 + k\epsilon^2/3$
$\langle AB\rangle$	$\langle AB\rangle_0 - 2\epsilon^2/3$	$\langle AB\rangle_0 - 2k\epsilon^2/3$
$\langle BB\rangle$	$\langle BB\rangle_0 + \epsilon^2/3$	$\langle BB\rangle_0 + k\epsilon^2/3$
$\langle AAA\rangle$	$\langle AAA\rangle_0 + \epsilon^2 P^0{}_A$	$\langle AAA\rangle_0 + k\epsilon^2[2(1-s)/3 + P_{BA}{}^0]$
$\langle AAB\rangle$	$\langle AAB\rangle_0 + \epsilon^2(2/3 - 2P_A{}^0)$	$\langle AAB\rangle_0 + 2k\epsilon^2[(2s-1)/3 - P_{BA}{}^0]$
$\langle BAB\rangle$	$\langle BAB\rangle_0 + \epsilon^2(P_A{}^0 - 2/3)$	$\langle BAB\rangle_0 + k\epsilon^2[P_{BA}{}^0 - 2s/3]$
$\langle ABA\rangle$	$\langle ABA\rangle_0 + \epsilon^2(1/3 - P_A{}^0)$	$\langle ABA\rangle_0 + k\epsilon^2[s/3 - P_{BA}{}^0]$
$\langle BBA\rangle$	$\langle BBA\rangle_0 + \epsilon^2(2P_A{}^0 - 4/3)$	$\langle BBA\rangle_0 + 2k\epsilon^2[P_{BA}{}^0 - (1+s)/3]$
$\langle BBB\rangle$	$\langle BBB\rangle_0 + \epsilon^2(1 - P_A{}^0)$	$\langle BBB\rangle_0 + k\epsilon^2[(2+s)/3 - P_{BA}{}^0]$
$\langle AAAA\rangle$	$\langle AAAA\rangle_0 + \epsilon^2[2P_A{}^{0\,2}] + \epsilon^4/5$	$\langle AAAA\rangle_0 + k\epsilon^2[(1-s)^2 + 3P_{BA}{}^0(1-s) + 2P_{BA}{}^{0\,2}] + k\epsilon^4/5$
$\langle AAAB\rangle$	$\langle AAAB\rangle_0 + 2\epsilon^2[P_A{}^0 - 2P_A{}^{0\,2}] - 2\epsilon^4/5$	$\langle AAAB\rangle_0 + 2k\epsilon^2[-1/3(1-s)(1-3s) + P_{BA}{}^0(3s-2) - 2P_{BA}{}^{0\,2}] - 2k\epsilon^4/5$
$\langle BAAB\rangle$	$\langle BAAB\rangle_0 + \epsilon^2[1/3 - 2P_A{}^0 + 2P_A{}^{0\,2}] + \epsilon^4/5$	$\langle BAAB\rangle_0 + k\epsilon^2[1/3(-2s + 3s^2) + P_{BA}{}^0(1-3s) + 2P_{BA}{}^{0\,2}] + k\epsilon^4/5$
$\langle AABA\rangle$	$\langle AABA\rangle_0 + 2\epsilon^2[P_A{}^0 - 2P_A{}^{0\,2}] - 2\epsilon^4/5$	$\langle AABA\rangle_0 + 2k\epsilon^2[1/3(s - s^2) + P_{BA}{}^0(2s-1) - 2P_{BA}{}^{0\,2}] - 2k\epsilon^4/5$
$\langle AABB\rangle$	$\langle AABB\rangle_0 + 2\epsilon^2[1/3 - 2P_A{}^0 + 2P_A{}^{0\,2}] + 2\epsilon^4/5$	$\langle AABB\rangle_0 + 2k\epsilon^2[1/3(s^2 + s - 1) - 2sP_{BA}{}^0 + 2P_{BA}{}^{0\,2}] + 2k\epsilon^4/5$
$\langle BABA\rangle$	$\langle BABA\rangle_0 + 2\epsilon^2[1/3 - 2P_A{}^0 + 2P_A{}^{0\,2}] + 2\epsilon^4/5$	$\langle BABA\rangle_0 + 2k\epsilon^2[1/3s^2 - 2sP_{BA}{}^0 + 2P_{BA}{}^{0\,2}] + 2k\epsilon^4/5$
$\langle BABB\rangle$	$\langle BABB\rangle_0 + 2\epsilon^2[-1 + 3P_A{}^0 - 2P_A{}^{0\,2}] - 2\epsilon^4/5$	$\langle BABB\rangle_0 + 2k\epsilon^2[-1/3(2s + s^2) + P_{BA}{}^0(1+2s) - 2P_{BA}{}^{0\,2}] - 2k\epsilon^4/5$
$\langle ABBA\rangle$	$\langle ABBA\rangle_0 + \epsilon^2[1/3 - 2P_A{}^0 + 2P_A{}^{0\,2}] + \epsilon^4/5$	$\langle ABBA\rangle_0 + k\epsilon^2[1/3s - P_{BA}{}^0(1+s) + 2P_{BA}{}^{0\,2}] + k\epsilon^4/5$
$\langle BBBA\rangle$	$\langle BBBA\rangle_0 + 2\epsilon^2[-1 + 3P_A{}^0 - 2P_A{}^{0\,2}] - 2\epsilon^4/5$	$\langle BBBA\rangle_0 + 2k\epsilon^2[-1/3(1+2s) + P_{BA}{}^0(2+s) - 2P_{BA}{}^{0\,2}] - 2k\epsilon^4/5$
$\langle BBBB\rangle$	$\langle BBBB\rangle_0 + \epsilon^2[2 - 4P_A{}^0 + 2P_A{}^{0\,2}] + \epsilon^4/5$	$\langle BBBB\rangle_0 + k\epsilon^2[(1+s) - P_{BA}{}^0(s+3) + 2\,P_{BA}{}^{0\,2}] + k\epsilon^4/5$

[a] Expressions for tacticity can be derived by substituting m (meso) for A and r (rac) for B. [b] $s = P_{BA} + P_{AB} = k^{-1}$.

$P_B{}^0$ = Bernoullian (unperturbed) probabilities of A and B addition, respectively; $P_A{}^0 + P_B{}^0 = 1$. From Table I, we get

$$(AA) = (P_A{}^{02} + \epsilon^2/3)$$

$$(AB) = 2(P_A{}^0 P_B{}^0 - \epsilon^2/3) \qquad (8)$$

$$(BB) = (P_B{}^{02} + \epsilon^2/3)$$

In a typical case, the diad distribution curves (Bovey plots[3]) for different values of $P_A{}^0$ are shown in Figure 1. A comparison of the perturbed model versus the unperturbed model indicates that compositional heterogeneity causes observable departure from the Bernoullian diad distribution. The most sensitive test of heterogeneity in this case appears to be near the maximum value of the (AB) diad, which occurs at $P_A{}^0 = P_B{}^0 = 0.5$ in Figure 1.

The Bernoullian triad distribution will be similarly modified by compositional heterogeneity. The following triad expressions (in the perturbed Bernoullian model) can be derived from the expressions given in Table I:

$$(AAA) = k[P_A{}^{03} + \epsilon^2(P_A{}^0)]$$

$$(AAB) = 2k[P_A{}^{02}P_B{}^0 + \epsilon^2(2/3 - 2P_A{}^0)]$$

$$(BAB) = k[P_A{}^0 P_B{}^{02} + \epsilon^2(P_A{}^0 - 2/3)]$$

$$(ABA) = k[P_A{}^{02}P_B{}^0 + \epsilon^2(1/3 - P_A{}^0)]$$

$$(BBA) = 2k[P_A{}^0 P_B{}^{02} + \epsilon^2(2P_A{}^0 - 4/3)]$$

$$(BBB) = k[P_B{}^{03} + \epsilon^2(1 - P_A{}^0)] \qquad (9)$$

The distribution curves of B-centered triads for different values of $P_A{}^0$ are shown in Figure 2. Note that the perturbed and the unperturbed curves cross over at $P_A{}^0$ = 0.67 for (BBA) and at $P_A{}^0$ = 0.33 for (ABA).

Compositional Heterogeneity

Thus far, the nature of ϵ has not been specified. The magnitude of ϵ obviously depends on the copolymer composition. In the limiting case where (A) = 1.0 or (B) = 1.0 (i.e., homopolymer), $\epsilon = 0$ by definition. In general, we can relate ϵ to the second moment of the chemical composition distribution (CCD) curve. For convenience, we can use the second moment about the mean value as

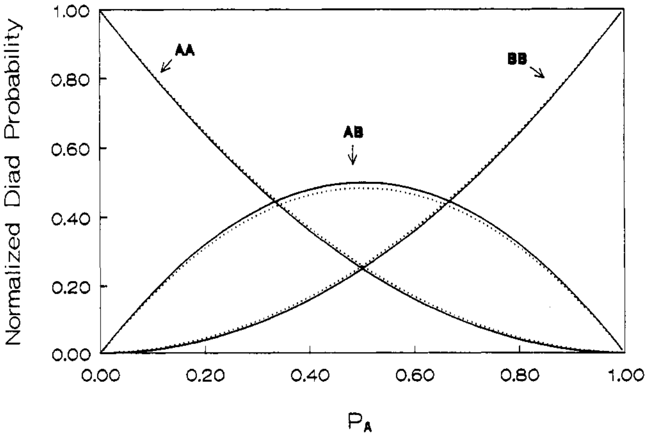

Figure 1. Bernoullian copolymer diad distribution curves as a function of P_A. (Solid lines) Unperturbed case. (Broken lines) Perturbed model with $\epsilon^2 = P_A P_B/10$ (corresponding to statistical heterogeneity with a degree of polymerization of 30).

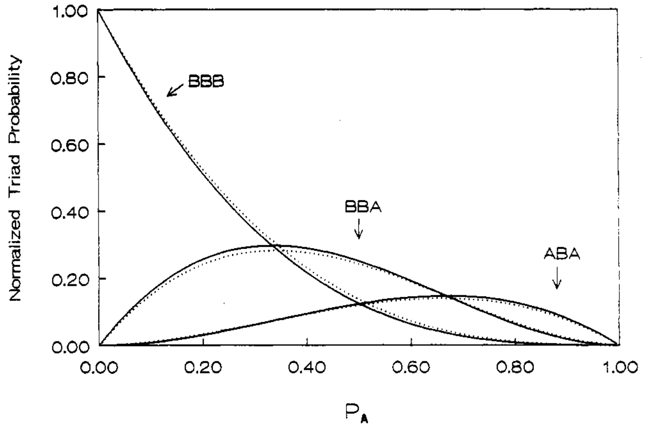

Figure 2. Bernoullian copolymer triad distribution curves as a function of P_A. (Solid lines) Unperturbed case. (Broken lines) Perturbed model with $\epsilon^2 = P_A P_B/10$ (corresponding to statistical heterogeneity with a degree of polymerization of 30).

a measure of the extent of chemical heterogeneity:

$$\langle F^2\rangle_{\text{mean}} = \frac{\int_0^1 (F-\bar{F})^2 g(F)\,\mathrm{d}F}{\int_0^1 g(F)\,\mathrm{d}F} \qquad (10)$$

where F is the copolymer composition, $\bar{F}$ is the average composition, and g is the composition distribution function.

In the perturbed Markovian model, we have used a distribution of reaction probabilities. The second moment about the mean in this case ($z = P_{\text{BA}}$) is

$$\langle z^2\rangle_{\text{mean}} = \frac{\int_0^1 (z-\langle z\rangle)^2 g(z)\,\mathrm{d}z}{\int_0^1 g(z)\,\mathrm{d}z} \qquad (11)$$

For a rectangular distribution function with width $2\sigma_z$, eq 11 becomes

$$\langle z^2\rangle_{\text{mean}} = \frac{\int_{\langle z\rangle-\sigma_z}^{\langle z\rangle+\sigma_z} (z-\langle z\rangle)^2\,\mathrm{d}z}{\int_{\langle z\rangle-\sigma_z}^{\langle z\rangle+\sigma_z} \mathrm{d}z} \qquad (12)$$

The probability and the composition distributions are proportional to each other; e.g. $\langle F\rangle = \langle z\rangle/s$, and

$$\langle F^2\rangle_{\text{mean}} = \langle z^2\rangle_{\text{mean}}/s^2 \qquad (13)$$

where $s = P_{\text{AB}} + P_{\text{BA}}$, as before. The perturbation (ϵ) to the reaction probabilities can be defined such that

$$\epsilon^2 = 3s^2\langle F^2\rangle_{\text{mean}} \qquad (14)$$

For a rectangular probability distribution with width $2\sigma_z$, $\langle z^2\rangle_{\text{mean}} = \sigma_z^2/3$. Thus, $\epsilon^2 = 3s^2\langle F^2\rangle_{\text{mean}} = \sigma_z^2$. This result is consistent with the definition of the perturbation ϵ in eq 4.

For any composition distribution function $g(F)$, ϵ can be evaluated using eq 14. For example, in the case of a Gaussian distribution of probabilities where σ_z is the probability standard deviation, $\langle z^2\rangle_{\text{mean}} = \sigma_z^2$ because the second moment is the standard deviation. The composition has a proportional Gaussian distribution with σ_F as the composition standard deviation ($\sigma_z = s\sigma_F$). In eq 14, then $\langle F^2\rangle_{\text{mean}} = \sigma_F^2$, and $\epsilon^2 = 3\sigma_z^2 = 3s^2\sigma_F^2$.

According to eq 14, the perturbation ϵ depends directly on the second moment of the CCD curve, which in turn depends on the nature of the compositional heterogeneity. For *statistical* compositional heterogeneity, the composition distribution (g_s) due to statistical fluctuation where termination occurs by disproportionation was derived by Stockmayer in his classic paper:[13]

$$g_s(d,Y) = \left(\frac{d}{d_n^{\,2}}e^{-d/d_n}\right)\left[\frac{1}{\sigma(2\pi)^{1/2}}\exp\left(-\frac{Y^2}{2\sigma^2}\right)\right] \qquad (15)$$

where d is the degree of polymerization, d_n is the number-average degree of polymerization, Y is the deviation of a given composition (F) from the average copolymer composition ($\bar{F}$)

$$Y = (F - \bar{F})$$

$$K = [1 + 4\bar{F}(1-\bar{F})(r_Ar_B - 1)]^{1/2}$$

and

$$\sigma^2 = \bar{F}(1-\bar{F})K/d$$

Because the composition distribution function is Gaussian, $\langle F^2\rangle_{\text{mean}} = \sigma^2$. From eq 14, we get

$$\epsilon^2 = 3s^2\bar{F}(1-\bar{F})[1 + 4\bar{F}(1-\bar{F})(r_Ar_B - 1)]^{1/2}/d \qquad (16)$$

For copolymerizations obeying Bernoullian statistics, $P_A = \bar{F}$, $P_B = 1 - \bar{F}$, $s = 1$, $r_Ar_B = 1$, and

$$\epsilon^2 = 3P_AP_B/d \qquad (17)$$

Thus ϵ^2 depends on the degree of polymerization and is a constant for a given polymer.

In the case of *conversion* heterogeneity, the compositional distribution (g_c) as a function of the weight fraction (F) of component A in the copolymer has been derived by Myagchenkov and Frenkel[19] and reviewed by Stejskal and Kratochvil.[22]

$$g_C(F) = \left|\left(\frac{f}{f_0}\right)^{k_1}\left(\frac{f-1}{f_0-1}\right)^{k_2}\left(\frac{f-k_4}{f_0-k_4}\right)^{k_3}\left(\frac{k_1}{f}+\frac{k_2}{f-1}+\frac{k_3}{f-k_4}\right)\times \frac{[f^2(r_Bt + r_A - 1 - t) + f(1 + t - 2r_Bt) + r_Bt]^2}{f^2(r_A + r_Bt^2 - 2r_Ar_Bt) + 2ftr_B(r_A - t) + r_Bt^2}\right| \qquad (18)$$

where f_0 and f are the compositions of the monomer mixture, expressed as the weight fraction of monomer A at the beginning and at a given time of copolymerization, respectively, and

$$k_1 = \frac{r_B}{1-r_B},\quad k_2 = \frac{r_A}{1-r_A}$$

$$k_3 = \frac{1-r_Ar_B}{(r_A-1)(1-r_B)},\quad k_4 = \frac{t(1-r_B)}{t(1-r_B) + (1-r_A)}$$

and t is the ratio of monomer molecular weights. The monomer composition (f) and the copolymer composition (F) are related by the copolymerization equation

$$F = \frac{f^2(r_A - t) + ft}{f^2[t(r_B-1) + r_A - 1] + f(1 - 2r_Bt + t) + r_Bt} \qquad (19)$$

The perturbation (ϵ) is again related to the second moment of the composition distribution (eq 14). Thus

$$\epsilon^2 = \frac{3s^2\int_0^1 (F-\bar{F})^2 g_c(F)\,\mathrm{d}F}{\int_0^1 g_c(F)\,\mathrm{d}F} \qquad (20)$$

It may be noted that the ϵ value in this type of heterogeneity depends on the extent of conversion and is not constant throughout the course of a copolymerization.

In *process* heterogeneity, fluctuations in reaction conditions usually show up as errors in the values of monomer feeds or reactivity ratios. Using the definition of reaction probabilities

$$P_{\text{AB}} = \frac{1}{1 + r_Ax},\quad P_{\text{BA}} = \frac{1}{1 + r_B/x} \qquad (21)$$

one can apply standard propagation-of-error treatment to estimate ϵ.

$$\begin{aligned}\epsilon \propto \delta P_{\text{AB}} &= \left|\frac{\partial P_{\text{AB}}}{\partial r_A}\right|\delta r_A + \left|\frac{\partial P_{\text{AB}}}{\partial f_A}\right|\delta f_A \\ &= \left|\frac{x}{(1 + r_Ax)^2}\right|\delta r_A + \left|\frac{r_A}{[(1 + f_A) + r_Af_A]^2}\right|\delta f_A \qquad (22)\end{aligned}$$

The proportionality constant in eq 22 is $s\sqrt{3}$ for fluctuations in P_{ij} that have Gaussian or near-Gaussian distributions. We can also estimate ϵ from P_{BA}:

$$\epsilon \propto \delta P_{\mathrm{BA}} = \left|\frac{\partial P_{\mathrm{BA}}}{\partial r_{\mathrm{B}}}\right|\delta r_{\mathrm{B}} + \left|\frac{\partial P_{\mathrm{BA}}}{\partial f_{\mathrm{A}}}\right|\delta f_{\mathrm{A}}$$

$$= \left|\frac{1}{x}\frac{1}{(1 + r_{\mathrm{B}}/x)^2}\right|\delta r_{\mathrm{B}} + \left|\frac{r_{\mathrm{B}}}{[f_{\mathrm{A}} + r_{\mathrm{B}}(1 - f_{\mathrm{A}})]^2}\right|\delta f_{\mathrm{A}} \quad (23)$$

In the above equations, linear propagation of errors is assumed. Alternatively, one can use the square root of the sum of squares which will decrease the estimate of the ϵ value somewhat. In any case, the size of ϵ will depend on δr_i and δf_i (the fluctuations in the values of the reactivity ratios and comonomer concentrations, respectively).

In *multistate* heterogeneity, if the individual catalytic sites produce very different compositions, then the perturbation approach breaks down altogether. However, if the catalytic sites are similar, each producing copolymers with a slightly different composition, then we can still use the present approach. In this case ϵ is simply an empirical parameter that envelopes the range of compositions and provides a measure of the extent of compositional heterogeneity.

Equivalent Reactivity Ratios

In copolymerization, it is customary to obtain reactivity ratios from comonomer feed concentrations (f_{A} and f_{B}) and copolymer compositions (F_{A} and F_{B}). For example, the following relationship[31] can be used to evaluate r_{A} and r_{B}:

$$F_{\mathrm{A}} = \frac{r_{\mathrm{A}}f_{\mathrm{A}}^2 + f_{\mathrm{A}}f_{\mathrm{B}}}{r_{\mathrm{A}}f_{\mathrm{A}}^2 + 2f_{\mathrm{A}}f_{\mathrm{B}} + r_{\mathrm{B}}f_{\mathrm{B}}^2} \quad (24)$$

Equation 24 has been recast to give linear plots, the common ones being devised by Fineman–Ross[32] and Kelen–Tudos.[33]

Since the copolymer composition is not affected by the perturbation (i.e., $\langle \mathrm{A}\rangle = \langle \mathrm{A}\rangle_0$), the use of eq 24 or the plots by Fineman–Ross and Kelen–Tudos will not be affected. The intrinsic reactivity ratios (r_{A}^0 and r_{B}^0) are obtained in all cases.

In the analysis of NMR data, it is useful to define "equivalent reactivity ratios". Rearranging eq 3, we get

$$r_{\mathrm{A}} = \frac{1 - P_{\mathrm{AB}}}{P_{\mathrm{AB}}}\frac{1}{x}, \quad r_{\mathrm{B}} = \frac{1 - P_{\mathrm{BA}}}{P_{\mathrm{BA}}}x \quad (25)$$

Let the reactivity ratio averaged over all values of P_{ij} be $\langle r_i\rangle$; then

$$\langle r_{\mathrm{A}}\rangle = \frac{\int_{P_{\mathrm{AB}}^0-\epsilon}^{P_{\mathrm{AB}}^0+\epsilon}\left(\frac{1 - P_{\mathrm{AB}}}{P_{\mathrm{AB}}}\frac{1}{x}\right)\mathrm{d}P_{\mathrm{AB}}}{\int_{P_{\mathrm{AB}}^0-\epsilon}^{P_{\mathrm{AB}}^0+\epsilon}\mathrm{d}P_{\mathrm{AB}}}$$

$$= \frac{1}{2\epsilon}\frac{1}{x}[\ln (P_{\mathrm{AB}}) - P_{\mathrm{AB}}]_{P_{\mathrm{AB}}^0-\epsilon}^{P_{\mathrm{AB}}^0+\epsilon}$$

$$= \frac{1}{x}\left[\frac{1}{2\epsilon}\ln\left(\frac{P_{\mathrm{AB}}^0 + \epsilon}{P_{\mathrm{AB}}^0 - \epsilon}\right) - 1\right] \quad (26)$$

We can use series expansion:

$$\ln\left(\frac{1 + n}{1 - n}\right) = 2\left[n + \frac{n^3}{3} + \frac{n^5}{5} + ...\right] \quad (27)$$

$$\langle r_{\mathrm{A}}\rangle = \frac{1}{x}\left[\frac{1}{P_{\mathrm{AB}}^0} + \frac{\epsilon^2}{3P_{\mathrm{AB}}^{03}} + \frac{\epsilon^4}{5P_{\mathrm{AB}}^{05}} + ...\right] - \frac{1}{x}$$

$$= r_{\mathrm{A}}^0 + \frac{\epsilon^2}{3xP_{\mathrm{AB}}^{03}} + \frac{\epsilon^4}{5xP_{\mathrm{AB}}^{05}} + ... \quad (28)$$

Similarly, it can be shown that

$$\langle r_{\mathrm{B}}\rangle = r_{\mathrm{B}}^0 + \frac{\epsilon^2 x}{3P_{\mathrm{BA}}^{03}} + \frac{\epsilon^4 x}{5P_{\mathrm{BA}}^{05}} + ... \quad (29)$$

As an illustration, we assume $P_{\mathrm{AB}}^0 = 0.20$, $P_{\mathrm{BA}}^0 = 0.25$, and a perturbation of $\epsilon = 0.1$. Then from eqs 25, 28, and 29

$$\langle r_{\mathrm{A}}\rangle = \frac{1 - P_{\mathrm{AB}}^0}{P_{\mathrm{AB}}^0}\frac{1}{x} + \frac{\epsilon^2}{3P_{\mathrm{AB}}^{03}}\frac{1}{x} + \frac{\epsilon^4}{5P_{\mathrm{AB}}^{05}}\frac{1}{x} + ...$$

$$= \frac{1}{x}(4 + 0.417 + 0.0625 + ...) \quad (30)$$

$$\langle r_{\mathrm{B}}\rangle = \frac{1 - P_{\mathrm{BA}}^0}{P_{\mathrm{BA}}^0}x + \frac{\epsilon^2}{3P_{\mathrm{BA}}^{03}}x + \frac{\epsilon^4}{5P_{\mathrm{BA}}^{05}}x + ...$$

$$= x(3 + 0.213 + 0.0205 + ...) \quad (31)$$

In this example, the equivalent reactivity ratios, $\langle r_i\rangle$, are roughly 10% higher than the intrinsic values, r_i^0. The product of the equivalent reactivity ratios $\langle r_{\mathrm{A}}\rangle\langle r_{\mathrm{B}}\rangle$ is about 20% higher than the product of the intrinsic reactivity ratios ($r_{\mathrm{A}}^0 r_{\mathrm{B}}^0$).

Alternative ways to express eqs 30 and 31 can be made by reverting the series:

$$\frac{1}{P_{\mathrm{BA}}^0} = \left[1 + \frac{\langle r_{\mathrm{B}}\rangle}{x}\right] - \frac{\epsilon^2}{3}\left[1 + \frac{\langle r_{\mathrm{B}}\rangle}{x}\right]^3 + \frac{2\epsilon^4}{15}\left[1 + \frac{\langle r_{\mathrm{B}}\rangle}{x}\right]^5 + ... \quad (32)$$

$$\frac{1}{P_{\mathrm{AB}}^0} = [1 + \langle r_{\mathrm{B}}\rangle x] - \frac{\epsilon^2}{3}[1 + \langle r_{\mathrm{B}}\rangle x]^3 + \frac{2\epsilon^4}{15}[1 + \langle r_{\mathrm{B}}\rangle x]^5 + ... \quad (33)$$

Equations 28 and 29 provide a means to relate the *perturbed* NMR analysis ($\epsilon > 0$) to the *apparent* NMR analysis where compositional heterogeneity is ignored (i.e., $\epsilon = 0$). In the latter case, we would fit the data to the conventional Markovian models ($\epsilon = 0$) and obtain the apparent reaction probabilities (P_{ij}^{app}), from which we can determine the apparent reactivity ratios, r_i^{app}. Because the NMR sequence intensities depend on the product of the reactivity ratios, if satisfactory fits to the NMR data have been achieved using both the apparent and the perturbed NMR analysis, then $\langle r_{\mathrm{A}}\rangle\langle r_{\mathrm{B}}\rangle \approx r_{\mathrm{A}}^{\mathrm{app}}r_{\mathrm{B}}^{\mathrm{app}}$.

One use of eqs 28 and 29 is to estimate the error incurred when the apparent NMR analysis ($\epsilon = 0$) is made on samples exhibiting compositional heterogeneity. In the example given in eqs 30 and 31 there would be an error of approximately 20% between $r_{\mathrm{A}}^{\mathrm{app}}r_{\mathrm{B}}^{\mathrm{app}}$ and $r_{\mathrm{A}}^0 r_{\mathrm{B}}^0$. Equations 28 and 29 would also be useful if the polymer involved is fractionated and the NMR data on the polymer fractions are available. The reaction probabilities (and

Table II
Analysis of the Tacticity Data[a] of Poly(methyl α-chloroacrylate)

tacticity	I_{obsd}	I_{calc}	I_{calc}
mmm	7	5.8	6.5
mmr	19	19.0	19.0
rmr	16	15.6	15.5
mrm	11	10.6	11.0
rrm	27	29.1	28.0
rrr	20	20.0	20.0
	First-Order Markovian Model		
	P_{mr}	0.621	0.625
	P_{rm}	0.421	0.434
	ϵ	0	0.143
	mean dev	0.69	0.34

[a] Data taken from ref 34.

the reactivity ratios) of the fractions can be compared with the reaction probabilities and the reactivity ratios of the overall polymer sample using these two equations.

NMR Analysis

The perturbed Markovian model can be used as the theoretical framework for the analysis of the NMR data. We can use NMR to study compositional heterogeneity in two ways. In some copolymerizations, enough knowledge about the mechanism, the process, and the conversion is available such that ϵ can be estimated a priori. The NMR data from such a copolymer can be treated with the perturbed model using the known ϵ value. In many other copolymers, there is insufficient knowledge about the compositional heterogeneity. We can then use the model fitting approach[11,12] and rely on the goodness of fit as a criterion for the presence (or the absence) of compositional heterogeneity. This latter approach can only be applied for very precise and accurate NMR data.

NMR analysis has been carried out for a free-radical, a cationic, and an anionic copolymer. The data are first presumed not to have compositional heterogeneity ($\epsilon = 0$) and analyzed by Bernoullian or first-order Markovian models to give the apparent reaction probabilities (P_{ij}^{app}). The data are then analyzed using the perturbation treatment. Specific computer programs called PERT have been written for this purpose. In this approach, the triad intensities are fed into the computer. Guess values of reaction probabilities $\{P_{ij}^0\}$ and ϵ are also entered. The theoretical intensities (as given in Table I) are generated for the given values of $\{P_{ij}^0\}$ and ϵ and compared with the observed intensities. Through a simplex algorithm,[11,12] iterations were carried out to minimize deviations between observed and theoretical intensities and to produce the optimal values of P_{AB}^0, P_{BA}^0, and ϵ.

An example is first shown for an anionic polymer. Lenz[34] has made low-molecular-weight poly(methyl α-chloroacrylate) by anionic polymerization and determined the tacticity through ^{1}H NMR at 300 MHz. His result for one of the polymers is shown in Table II. We can treat tacticity as a copolymer problem with meso (m) and racemic (r) configurations as comonomers. The reactivity ratios for meso and racemic addition are then r_m and r_r, respectively. If we ignore compositional heterogeneity, the tacticity data can be readily fitted to a first-order Markovian model with $P_{mr}^{app} = 0.621$ and $P_{rm}^{app} = 0.421$. Using eq 3, we get

$$r_m^{app} = 0.61/x, \quad r_r^{app} = 1.38x, \quad r_m^{app} r_r^{app} = 0.84$$

We need to examine possible sources of compositional heterogeneity in poly(methyl α-chloroacrylate). There is no conversion heterogeneity because we are dealing with tacticity. The samples have been made on a small scale in the laboratory; thus, process heterogeneity is also small. The molecular weight is indeed low ($M_n \sim 4200$), and statistical heterogeneity is significant. Using eq 16 and $d \sim 33$, we can estimate ϵ to be 0.143.

We now introduce this known perturbation ($\epsilon = 0.143$) into the first-order Markovian model (program PERT.TRIAD). The result (Table II, last column) does show an improvement in the goodness of fit; the mean deviation decreases to 0.34. From the perturbed probabilities ($P_{mr}^0 = 0.625$, $P_{rm}^0 = 0.434$), we can determine the equivalent reactivity ratios (eqs 28 and 29)

$$\langle r_m \rangle = 0.63/x, \quad \langle r_r \rangle = 1.39x, \quad \langle r_m \rangle \langle r_r \rangle = 0.88$$

Thus, $\langle r_m \rangle \langle r_r \rangle \approx r_m^{app} r_r^{app}$, as expected.

This example also illustrates the accuracy requirement in using NMR data to determine compositional heterogeneity. Although compositional heterogeneity is present in the NMR data (as is the case here), we need accurate NMR data to extract the information. In this case, the accuracy in the NMR triad values should be 0.34 mol % or better.

A second example can be shown for free-radically polymerized vinyl chloride/vinylidene chloride copolymers. Schlothauer et al.[35] have compiled the triad NMR data for a number of commercial copolymers as well as samples made at low conversions in the laboratory. The NMR triad results for four samples are shown in Table III. Samples A and C refer to commercial polymers, and W2 and U2 are laboratory samples.

Table III
Reaction Probability Model Calculations for Vinyl Chloride (A)/Vinylidene Chloride (B) Copolymers (Observed[a] versus Calculated[b] Intensities)

	A			C			W2			U2		
	obsd	calc	calc	obsd	calc	calc	obsd	calc	calc	obsd	calc	calc
AAA	2.1	0.6	0.8	68.8	68.8	68.8	7.0	7.0	7.1	23.0	23.0	23.0
AAB	3.6	4.8	4.9	14.4	17.6	14.4	16.0	16.0	16.0	22.0	22.4	22.3
BAB	9.1	9.1	9.3	2.5	1.1	3.6	9.0	9.1	9.1	5.5	5.5	5.5
ABA	2.4	1.6	2.3	9.6	7.9	8.8	4.5	4.3	4.3	6.0	5.6	5.7
BBA	18.8	19.9	18.8	4.0	4.0	4.0	25.5	25.6	25.5	22.0	22.0	22.0
BBB	63.9	64.0	64.0	0.7	0.5	0.4	38.0	38.0	38.0	21.5	21.5	21.5
					M1 Model							
P_{AB}		0.791	0.840		0.114	0.152		0.532	0.532		0.327	0.330
P_{BA}		0.135	0.148		0.799	0.998		0.252	0.253		0.339	0.342
ϵ		0	0.158		0	0.284		0	0.035		0	0.047
mean dev		0.77	0.48		1.08	0.37		0.07	0.06		0.14	0.11

[a] Observed triad data from ref 35. [b] Calculated intensities on the basis of the perturbed first-order Markovian model (program PERT.TRIAD). Computation was carried out with $\epsilon = 0$ and $\epsilon > 0$.

The analysis is carried out by first fitting the data to a first-order Markovian model ($\epsilon = 0$) and then repeating the fitting with an adjustable perturbation ϵ. The results for both the apparent case ($\epsilon = 0$) and the perturbed case ($\epsilon > 0$) are given in Table III. It is clear by observing the mean deviations that the addition of ϵ improves the fit in every case. Note that ϵ is very large for commercial samples. These samples have been made at very high conversions in an industrial process, and their compositions may include contributions from process and conversion heterogeneities, and (perhaps) even multistate heterogeneity if blending or multistage synthesis has been used.

For the two laboratory samples, although ϵ improves the fit, the improvement is small. A comparison of the observed and the calculated values for $\epsilon = 0$ and $\epsilon > 0$ indicates that all three sets of numbers are probably within the limits of experimental error. Whereas it is reasonable to expect some compositional heterogeneity, exact determination again requires very accurate NMR data.

The third example is taken from cationic copolymerization. Corno et al.[36] have studied the copolymerization of isobutylene/isoprene copolymer. They made several samples at different conversions with different comonomer feed ratios. They then carried out comonomer sequence determination using both ^{1}H and ^{13}C NMR. Their data for six low-conversion samples are shown in Table IV (A = isobutylene, B = isoprene). A detailed analysis of their data was carried out using first-order Markovian model with or without the perturbation. In each of the six cases, there is an improvement using a perturbation. However, the ϵ value (as determined by the goodness-of-fit criterion) is found to vary with the samples.

In order to extract more information, a different approach is taken. Instead of solving for P_{AB}^0 and P_{BA}^0 for individual samples, we use eq 21 in conjunction with the theoretical expressions given in Table I. We can then take the NMR triad data for all six samples at once and solve for r_A and r_B. The ϵ value is allowed to depend on polymer composition: $\epsilon = c_0 + c_1F_B + c_2F_B^2$, where $F_B = P_{AB}^0/(P_{AB}^0 + P_{BA}^0)$. The fitting was accomplished with the program MINSQ.[37] The process was carried out twice, once with $\epsilon = 0$ (solving for r_A and r_B) and once with $\epsilon > 0$ (solving for r_A, r_B, c_0, c_1, and c_2). An advantage of this fitting approach is the improved statistics (36 data points, 2 or 5 parameters).

Through this means, the apparent reactivity ratios ($\epsilon = 0$) are found to be

$$r_A^{app} = 1.58, \quad r_B^{app} = 0.93$$

These numbers compare well with the results given by Corno et al.[36] ($r_A^{app} = 1.56$, $r_B^{app} = 0.94$). The inclusion of a perturbation improves the fit. The perturbed model gives

$$r_A^0 = 1.47, \quad r_B^0 = 0.80$$

$$\epsilon = 0.103 + 0.154F_B$$

(The quadratic term, c_2, was found to be negligible.) The calculated ϵ values for the six samples are given in Table IV. Note that r_A^0 and r_B^0 are slightly different from the apparent r_A and r_B. This procedure is one of the methods whereby the intrinsic reactivity ratios (r_A^0 and r_B^0) can be estimated from the NMR data.

A reviewer pointed out the distinction[38] between chemical heterogeneity (i.e., the compositions of different polymer chains being different) and sequential heterogeneity (i.e., the sequence distribution within each chain

Table IV

^{13}C NMR Data[36] and Model Fitting Results of Isobutylene (A)/Isoprene (B) Copolymers

	sample 1			sample 2			sample 3			sample 4			sample 5			sample 6		
	obsd	calc	calc	obsd	calc	calc	obsd	calc	calc	obsd	calc	calc	obsd	calc	calc	obsd	calc	calc
feed f_a	33.0			65.0			61.0			55.5			50.0			45.5		
conv	2.3			8.2			5.5			7.0			6.6			8.0		
AAA	71.2	71.2	71.2	34.7	34.7	34.7	36.9	36.9	37.0	28.3	28.3	28.3	22.5	22.5	22.5	18.9	18.9	18.9
AAB	17.1	16.7	16.7	26.3	28.0	26.3	25.6	27.5	26.3	27.3	28.3	27.9	25.8	27.4	26.5	24.7	26.5	24.7
BAB	1.3	1.0	1.0	6.6	5.7	6.5	6.3	5.1	6.0	7.3	7.1	7.4	9.3	8.4	8.7	10.6	9.3	10.5
ABA	7.2	7.8	7.8	12.3	12.2	12.3	12.2	11.7	12.2	12.6	12.3	12.6	11.7	11.7	11.7	11.2	11.2	12.2
BBA	3.1	3.1	3.1	15.5	14.9	14.7	14.6	14.4	13.9	18.2	17.7	17.4	21.4	20.8	20.6	13.2	22.6	21.5
BBB	0.3	0.3	0.3	4.5	4.5	5.3	4.4	4.4	4.7	6.4	6.4	6.4	9.2	9.2	10.0	11.3	11.4	12.2
Markovian I Model (Individual Fit)																		
P_{AB}		0.105	0.105		0.287	0.310		0.272	0.292		0.333	0.341		0.378	0.393		0.418	0.454
P_{BA}		0.835	0.836		0.622	0.648		0.619	0.658		0.582	0.596		0.529	0.537		0.498	0.537
ϵ		0	0.02		0	0.19		0	0.18		0	0.10		0	0.14		0	0.22
mean dev		0.22	0.22		0.56	0.27		0.64	0.35		0.33	0.25		0.54	0.47		0.63	0.60
Markovian I Model (Global Fit)[a]																		
ϵ			0.12			0.15			0.15			0.16			0.17			0.17

[a] For all six samples, $r_A^{app} = 1.58$, $r_B^{app} = 0.92$, $\epsilon = 0$, standard dev = 1.5; and $r_A^0 = 1.47$, $r_B = 0.80$, ϵ as indicated, standard dev = 1.3.

being different). NMR is potentially a tool to probe sequential heterogeneity. It is of interest to note that the perturbed Markovian formalism proposed in this work can serve to relate the chemical heterogeneity to sequential heterogeneity. Thus, an estimation of the chemical heterogeneity (viz., the second moment of the CCD curve) is incorporated into the perturbation model as ϵ. The reaction probabilities and ϵ are then related to the sequence distribution, which is reflected in the NMR data. The three examples shown in this section indicate that this perturbation formalism does permit the NMR data to be analyzed for the presence of chemical heterogeneity.

The relationships among chemical/sequential heterogeneity and the perturbation models are depicted as follows:

$$\begin{tikzcd}
\text{chemical heterogeneity} \arrow[d] & & \text{sequential heterogeneity} \arrow[d] \\
\text{second moment} \arrow[r, "\varepsilon"] & \text{perturbation model} \arrow[r, leftrightarrow, "P_{ij}^0 + \varepsilon", "\text{analysis}"'] & \text{NMR data}
\end{tikzcd}$$

Experimental Section. The computer programs PERT.TRIAD and PERT.TETRAD were written in QuickBASIC. They use a similar algorithm as before,[11,12] together with the expressions in Table I. Interested readers may write to the author for program listings.

Acknowledgment. I thank Kathleen Beutler, Michael Roland, and Leo Kasehagen for their assistance at various times during this work.

References and Notes

(1) Lowry, G. G., Ed. *Markov Chains and Monte Carlo Calculations in Polymer Science*; Marcel Dekker: New York, 1970.

(2) Provder, T., Ed. *Computer Applications in Applied Polymer Science II*; ACS Symposium Series 404; American Chemical Society: Washington, DC, 1989.

(3) Bovey, F. A. *High Resolution NMR of Micromolecules*; Academic: New York, 1972.

(4) Koenig, J. L. *Chemical Microstructure of Polymer Chains*; Wiley-Interscience: New York, 1980.

(5) Ham, G. E., Ed. *Copolymerization*; Wiley-Interscience: New York, 1964.

(6) Cheng, H. N. *J. Appl. Polym. Sci.* **1988**, *36*, 229.

(7) Cheng, H. N. In *Transition-Metal Catalyzed Polymerization: Ziegler–Natta and Metathesis Polymerization*; Quirk, R. P., Ed.; University of Cambridge Press: Cambridge, U.K., 1988; pp 599–623.

(8) Cheng, H. N. Bennett, M. A. *Anal. Chem.* **1984**, *56*, 2320.

(9) Cheng, H. N. *J. Appl. Polym. Sci.* **1988**, *35*, 1639.

(10) Cheng, H. N. Reference 2, pp 174–188.

(11) Cheng, H. N. *J. Chem. Inf. Comput. Sci.* **1987**, *27*, 8.

(12) Cheng, H. N. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1989**, *43*, 129.

(13) Stockmayer, W. H. *J. Chem. Phys.* **1945**, *13*, 199.

(14) Stejskal, J.; Kratochvil, P.; Strakova, D. *Macromolecules* **1981**, *14*, 150 and references cited therein.

(15) Stejskal, J.; Kratochvil, P.; Jenkins, A. D. *Macromolecules* **1987**, *20*, 181.

(16) Stejskal, J.; Kratochvil, P. *Macromolecules* **1987**, *20*, 2624.

(17) Tacx, J. C. J. F.; Linssen, H. N.; German, A. L. *J. Polym. Sci., Polym. Chem.* **1988**, *26*, 61.

(18) Meyer, V. E.; Lowry, G. G. *J. Polym. Sci., Part A* **1965**, *3*, 2843.

(19) Myagchenkov, V. A.; Frenkel, S. Y. *Vysokomol. Soedin, Ser. A* **1969**, *11*, 2348.

(20) Mirabella, F. M., Jr.; Barrall, E. M., II; Jordan, E. F., Jr.; Johnson, J. F. *J. Appl. Polym. Sci.* **1976**, *20*, 581.

(21) Stejskal, J.; Kratochvil, P. *J. Appl. Polym. Sci.* **1980**, *25*, 407.

(22) Stejskal, J.; Kratochvil, P.; Strakova, D.; Prochazka, O. *Macromolecules* **1986**, *19*, 1575 and references cited therein.

(23) Semchikov, Y. D.; Knyazeva, T. Y.; Smirnova, L. A.; Ryabov, S. A.; Slavnitskaya, N. N.; Modeva, S. I.; Bulgakova, S. A.; Sherstyanykh, V. I. *Vysokomol. Soedin.* **1987**, *A29*, 2625.

(24) Pino, P.; Mulhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857.

(25) Kissen, Y. V. *Isospecific Polymerization of Olefins with Heterogeneous Ziegler–Natta Catalysts*; Springer-Verlag: New York, 1985.

(26) Cozewith, C.; Ver Strate, G. *Macromolecules* **1971**, *4*, 482.

(27) Coleman, B. D.; Fox, T. G. *J. Chem. Phys.* **1963**, *38*, 1065.

(28) Coleman, B. D.; Fox, T. G.; Reinmoller, M. *J. Polym. Sci., Part B* **1966**, *4*, 1029.

(29) Doremaele, G. H. J.; Van Herk, A. M.; Ammerdorffer, J. L.; German, A. L. *Polym. Commun.* **1988**, *29*, 299.

(30) The rectangular distribution function is chosen because it has an intermediate shape between g_s (Gaussian) and g_c (frequently shaped like a tent). The exact form of the distribution should not affect the analysis because only the second moment of the distribution is used (eq 14). In fact, for a Gaussian distribution of probabilities (standard deviation σ_z), exactly the same expressions in Table I can be used, where $\epsilon^2 = 3\sigma_z^2$.

(31) For example: Odian, G. *Principles of Polymerization*, 2nd ed.; Wiley-Interscience: New York, 1981.

(32) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259.

(33) Kelen, T.; Tudos, F. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1.

(34) Lenz, R. W. In *Ionic Polymerization. Unsolved Problems*; Furukawa, J., Vogl, O., Eds.; Marcel Dekker: New York, 1976; pp 305–319.

(35) Schlothauer, K.; Keller, F.; Schneider, H.; Wandelt, B. *Polym. Bull. (Berlin)* **1985**, *13*, 473 and references cited therein.

(36) Corno, C.; Priola, A.; Cesca, S. *Macromolecules* **1980**, *13*, 1099.

(37) Available from MicroMath Scientific Software, Salt Lake City, UT.

(38) For example: Saudek, V.; Stejskal, J.; Schmidt, P.; Zimmermann, V.; Skarda, V.; Kratochvil, P.; Drobnik, J. *Biopolymers* **1987**, *26*, 705.

Registry No. Poly(methyl α-chloroacrylate), 25704-33-0.