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NMR Characterization of Copolymers That Exhibit Nonsymmetric Compositional Heterogeneity*

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ABSTRACT: The perturbed first-order Markovian model has been developed for copolymers that exhibit nonsymmetric chemical compositional distribution. An exponentially modified Gaussian function is first used to approximate the distribution. The theoretical probability expressions for the comonomer diads, triads, and tetrads are derived. Using these expressions, one can analyze the observed NMR data and fit them to the perturbed Markovian model. The formalism given herein is next extended to the general case of an arbitrary chemical composition distribution. Computer programs have been written to facilitate the analyses, and examples are given to illustrate the use of these computer-assisted approaches.

Introduction

It is well-known that many commercial copolymers exhibit compositional heterogeneity. This heterogeneity may originate from different sources (Table 1). First, the instantaneous fluctuations in the composition of the copolymers formed during polymerization may lead to *statistical* (or instantaneous) heterogeneity.[1,2] Secondly, if the comonomers have different reactivity ratios, they would polymerize at different rates and the polymers generated in a batch polymerization process would have different compositions at different conversions. This has been called *conversion* heterogeneity.[3−7] Thirdly, in some polymerizations, polymers may be produced by different catalytic sites (e.g., in Ziegler-Natta catalyzed polymerizations), at different polymerization centers or at different phases (e.g., in some emulsion processes). Alternatively, the polymer may be made in a multistage process, each stage with different comonomer feeds. In all these cases, the copolymers made are in-situ blends of polymers with different compositions. This situation has been termed *multistate* heterogeneity.[8−13] Finally, fluctuations in polymerization process conditions (e.g., temperature, initiator concentration, incomplete mixing, and sample workup) may also lead to compositional fluctuations. This has been called *process* heterogeneity.[14−16] The various kinds of heterogeneity have been previously reviewed.[15,16] Other forms of heterogeneity have also been reported.[17,18]

Compositional heterogeneity may be directly visualized through chemical compositional distribution (CCD) curves. In general, multistate heterogeneity often provides the most complex CCD curves. Depending on the nature of the multiple states, for a given copolymer one may get a multi-modal distribution, a slightly skewed Gaussian, or anywhere in between. Conversion heterogeneity may give CCD curves with different shapes depending on the reactivity ratios and the conversion; these are usually nonsymmetric. Statistical and process heterogeneities mostly broaden the CCD curves symmetrically; however, some polymerization processes may lead to skewed distributions. For example, the polymerization may be terminated by slowly ramping down the temperature and/or venting away the unreacted monomers. The copolymer during workup may be washed in a solvent that has partial solubility toward one range of copolymer composition. Phase separation may occur during polymerization such that the monomer-rich phase decreases whereas the polymer-rich phase increases as polymerization proceeds. These situations may variously lead to some degree of asymmetry in the CCD curve.

Compositional heterogeneity also influences polymer microstructure (which is usually studied by NMR). In the analysis of NMR data of copolymers, compositional heterogeneity is often ignored. A number of workers have nevertheless recognized the problem and formulated analytical approaches. For example, Ross,[10] Cheng,[14] and Turcsanyi[19] have devised methods to analyze (or to fit) the NMR data directly. Particularly useful are the perturbed models.[10,14] It has been found[14,16] that statistical and process heterogeneities can be treated with the use of perturbed models. The problem of multistate heterogeneity has been addressed by a number of workers. For copolymers containing two components, several approaches have been proposed,[8−11] including the well-known Coleman−Fox model.[8] For multicomponent copolymerization, a computer-assisted mixture analysis has been reported.[11−13] As for conversion heterogeneity, less attention has been paid with respect to NMR methodology; this subject has been addressed recently.[7]

In NMR analysis, it is useful to take the observed NMR data and fit them to an appropriate statistical model. The model rationalizes the data and affords a suitable theoretical framework for analysis. Furthermore, the model parameters (e.g., reactivity ratios or reaction probabilities) often provide information on propagation mechanism and serve to characterize the copolymer system. For most vinyl polymers, the terminal copolymerization (first-order Markovian, **M1**) model is a good starting point for analysis.[20−23] In the presence of compositional heterogeneity, the perturbed Markovian model has been devised.[14] Whereas this model has been successful in treating many polymer data,[14,15] it assumes a symmetric CCD curve. In a separate work,[24] Ross has derived the general equations correlating sequence distributions of heterogeneous copolymers that conform to the first-order Markovian model. The equations are based on power series expansions and contain many variables. Whereas they are mathematically sound, those expressions cannot be easily used to fit the observed NMR data.

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Table 1. Different Kinds of Compositional Heterogeneity

kind	possible origin of heterogeneity	CCD curve
statistical	instantaneous copolymer composition fluctuation	symmetric
conversion	different comonomer reactivities	"tent"-shaped
multistate	1. polymerization occurring at different sites or phases 2. programmed monomer feeds	skewed to multimodal
process	fluctuations in polymerization process conditions	symmetric or slightly skewed

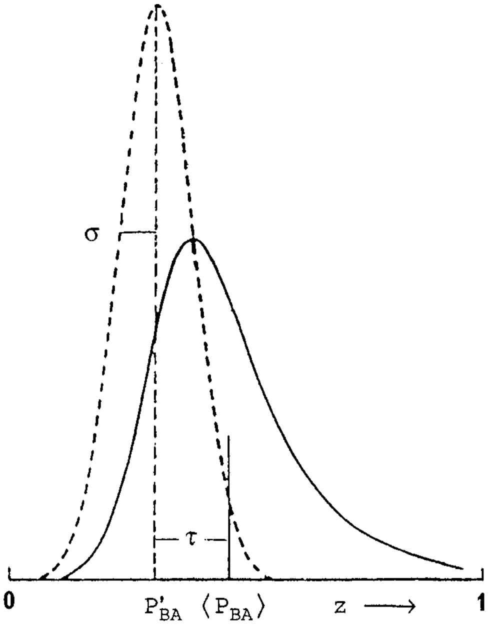

Figure 1. Exponential modified Gaussian function:

$$f(z) = \frac{N}{\tau\sigma\sqrt{(2\pi)}}\int_0^{\infty} \exp\left[-\frac{(z - P'_{\mathrm{BA}} - t')^2}{2\sigma^2} - \frac{t'}{\tau}\right] \mathrm{d}t'$$

In this work, the perturbed Markovian statistical model described previously[14] has been extended to generalized CCD curves. For convenience, the CCD curve is first approximated by the exponentially modified Gaussian function. A general approach is given next that can be used for any arbitrary CCD curves. The theoretical expressions for copolymer diad, triad, and tetrad sequences have been obtained, and appropriate computer programs have been written in order to facilitate the analysis of NMR data.

Exponentially Modified Gaussian

The exponentially modified Gaussian (EMG) is defined by the following convolute integral:

$$f(t) = \frac{N}{\tau\sigma\sqrt{(2\pi)}}\int_0^{\infty} \exp\left[-\frac{(t - t_{\mathrm{R}} - t')^2}{2\sigma^2} - \frac{t'}{\tau}\right] \mathrm{d}t' \qquad (1)$$

where N is the area, τ the time constant for the exponential modifier, t_{R} the peak retention time (the center of gravity of the Gaussian), σ the standard deviation of the Gaussian, and t' the dummy variable of integration. The function is graphically depicted in Figure 1. A number of workers have explored its mathematical properties and applied it to gas chromatography, high-performance liquid chromatography, size exclusion chromatography, field flow fractionation, and flow injection analysis.[25-30] This subject has been reviewed periodically.[31-32]

The key advantage of the EMG is its ability to describe band broadening and skew. Grushka[26] and Yau[27] have described the mathematical relationships corresponding to these properties. For example, they obtained the statistical moments of the function:

$$\text{zeroth moment (area),} \qquad M_0 = \int_{-\infty}^{\infty} f(t)\, \mathrm{d}t = N \qquad (2)$$

1st moment (mean),

$$M_1 = \frac{1}{M_0}\int_{-\infty}^{\infty} t f(t)\, \mathrm{d}t = t_{\mathrm{R}} + \tau \qquad (3)$$

For moments higher than the first, only the central moments (i.e., moments about the mean) have been reported:[26,27]

$$M_{\mathrm{n,c}} = \frac{1}{M_0}\int_{-\infty}^{\infty} (t - M_1)^n f(t)\, \mathrm{d}t \qquad (4)$$

where $n \geq 2$. Thus,

$$M_{2,\mathrm{c}} = \sigma^2 + \tau^2 \qquad (5)$$

$$M_{3,\mathrm{c}} = 2\tau^3 \qquad (6)$$

In using this EMG function to describe the CCD curve, this author found it necessary to use the absolute moments (eq 7) instead of the central moments (eq 4):

$$M_{\mathrm{n}} = \frac{1}{M_0}\int_{-\infty}^{\infty} t^n f(t)\, \mathrm{d}t \qquad (7)$$

The moments can be derived by substituting eq 1 into eq 7:

$$M_{\mathrm{n}} = \frac{1}{M_0}\int_{-\infty}^{\infty} t^n \int_0^{\infty} \frac{N}{\sigma\tau\sqrt{(2\pi)}} \times \exp\left[-\frac{(t - t_{\mathrm{R}} - t')^2}{2\sigma^2} - \frac{t'}{\tau}\right] \mathrm{d}t'\, \mathrm{d}t \qquad (8)$$

Because both integrands in the convolution equation are well behaved throughout the integration region, one can interchange the order of integration. The derivation is straightforward but lengthy; only the answers are shown below:

$$M_2 = \sigma^2 + t_{\mathrm{R}}^2 + 2t_{\mathrm{R}}\tau + 2\tau^2 \qquad (9)$$

$$M_3 = 6\tau^3 + 6t_{\mathrm{R}}\tau^2 + 3(t_{\mathrm{R}}^2 + \sigma^2)\tau + t_{\mathrm{R}}^3 + 3\sigma^2 t_{\mathrm{R}} \qquad (10)$$

$$M_4 = 3\sigma^4 + 6\tau^2\sigma^2 + 9\tau^4 + 6(\sigma^2 + \tau^2)(t_{\mathrm{R}} + \tau)^2 + 8\tau^3(t_{\mathrm{R}} + \tau) + (t_{\mathrm{R}} + \tau)^4 \qquad (11)$$

For comparison, the various moments for Gaussian and EMG functions are summarized in Table 2.

Table 2. Moments for Gaussian and Exponentially Modified Gaussian

central moments	absolute moments
A. Gaussian	
$M_{1,c} = 0$	$M_1 = t_R$
$M_{2,c} = \sigma^2$	$M_2 = t_R^2 + \sigma^2$
$M_{3,c} = 0$	$M_3 = t_R^3 + 3t_R\sigma^2$
$M_{4,c} = 3\sigma^4$	$M_4 = t_R^4 + 6t_R^2\sigma^2 + 3\sigma^4$
B. Exponentially Modified Gaussian	
$M_{1,c} = 0$	$M_1 = t_R + \tau$
$M_{2,c} = \sigma^2 + \tau^2$	$M_2 = \sigma^2 + (\tau + t_R)^2 + \tau^2$
$M_{3,c} = 2\tau^3$	$M_3 = 2\tau^3 + 3\tau^2(\tau + t_R) + 3\sigma^2(\tau + t_R) + (\tau + t_R)^3$
$M_{4,c} = 3\sigma^4 + 6\sigma^2\tau^2 + 9\tau^4$	$M_4 = t_R^4 + 6t_R^2\sigma^2 + 3\sigma^4 + 4\tau t_R(3\sigma^2 + t_R^2) + 12\tau^2(\sigma^2 + t_R^2) + 24\tau^3(\tau + t_R)$

Perturbed Markovian Model with EMG Function

Standard terminologies will be used for the parameters of the first-order Markovian model. Thus, r_A and r_B = reactivity ratios, f_A and f_B = concentrations of comonomer feeds, F_A and F_B = copolymer composition, and P_{ij} is the reaction probability of comonomer j adding to a propagating chain that terminates in comonomer i. In addition, the superscript or subscript 0 indicates the unperturbed value (i.e., the value in the absence of compositional heterogeneity). The subscripts A and B refer to the comonomer A and B. Furthermore, the symbol ⟨ ⟩ represents the average value.

If the compositional heterogeneity is present, then instead of a discrete value, P_{ij} takes on a distribution of probability values.[14] In the nonsymmetric case, we approximate the distribution with the EMG function. Thus for P_{BA},

$$f(z) = \frac{N}{\tau\sigma\sqrt{(2\pi)}} \int_0^\infty \exp\left[-\frac{(z - P'_{BA} - t')^2}{2\sigma^2} - \frac{t'}{\tau}\right] dt' \quad (12)$$

where P'_{BA} is the average value of the Gaussian distribution without the exponential modification and $z = P_{BA}$. In a first-order Markovian model, the composition is proportional to the reaction probability, viz., for comonomer A, $F_A = kP_{BA}$, where k = proportionality constant. Thus, eq 12 implies that the CCD is also an EMG function. (It is assumed implicitly in this model that the compositional heterogeneity causes broadening and skewing of the CCD which is approximated by the EMG function.)

For convenience, let

$$k = s^{-1} = (P_{AB} + P_{BA})^{-1} = (P'_{AB} + P'_{BA})^{-1} \quad (13)$$

Thus,

$$P_{AB} = s - P_{BA}, \qquad P_{AA} = 1 - s + P_{BA}, \qquad P_{BB} = 1 - P_{BA} \quad (14)$$

The average copolymer composition in the presence of heterogeneity is given by the first moments of the EMG functions:

$$\langle F_A\rangle = \langle A\rangle = \langle kP_{BA}\rangle = k(P'_{BA} + \tau) \quad (15)$$

$$\langle F_B\rangle = \langle B\rangle = \langle k(s - P_{BA})\rangle = 1 - k(P'_{BA} + \tau) \quad (16)$$

The diad sequences can be calculated in a similar fashion:

$$\begin{aligned}\langle AA\rangle &= \langle kP_{BA}P_{AA}\rangle \\ &= k\langle P_{BA}(1 - s + P_{BA})\rangle \\ &= k[(1 - s)\langle P_{BA}\rangle + \langle P_{BA}{}^2\rangle] \\ &= k(1 - s)(P'_{BA} + \tau) + k(P'_{BA}{}^2 + \sigma^2 + 2P'_{BA}\tau + 2\tau^2) \\ &= kP'_{BA} - P'_{BA} + kP'_{BA}{}^2 + (k - 1)\tau + k(\sigma^2 + 2P'_{BA}\tau + 2\tau^2)\end{aligned}$$

Since $\langle AA\rangle_o = k\,P'_{BA}\,P'_{AA} = k\,P'_{BA} - P'_{BA} + k\,P'_{BA}{}^2$, then

$$\langle AA\rangle = \langle AA\rangle_o + (k - 1)\tau + kK_2 \quad (17)$$

where $K_2 = \sigma^2 + 2P'_{BA}\tau + 2\tau^2$. In a similar way, it can be shown that

$$\langle AB\rangle = \langle AB\rangle_o + 2\tau - 2kK_2 \quad (18)$$

$$\langle BB\rangle = \langle BB\rangle_o - (k + 1)\tau + kK_2 \quad (19)$$

The calculation of triad sequences can be carried out in a likewise fashion. Only the ⟨BAB⟩ triad is illustrated here:

$$\begin{aligned}\langle BAB\rangle &= k\langle P_{AB}{}^2P_{BA}\rangle \\ &= k\langle (s - P_{BA})^2P_{BA}\rangle \\ &= k[s^2\langle P_{BA}\rangle - 2s\langle P_{BA}{}^2\rangle + \langle P_{BA}{}^3\rangle] \\ &= k[s^2(P'_{BA} + \tau) - 2s(\sigma^2 + P'_{BA} + 2P'_{BA}\tau + 2\tau^2) + \{6\tau^3 + 6P'_{BA}\tau^2 + 3(P'_{BA}{}^2 + \sigma^2)\tau + P'_{BA}{}^3 + 3\sigma^2P'_{BA}\}]\end{aligned}$$

Since $\langle BAB\rangle_o = kP'_{BA}{}^2P'_{BA} = k(s - P'_{BA})^2P'_{BA} = k(s^2P'_{BA} - 2sP'_{BA}{}^2 + P'_{BA}{}^3)$,

$$\begin{aligned}\langle BAB\rangle &= \langle BAB\rangle_o + ks^2\tau - 2s(\tau^2 + 2P'_{BA}\tau + 2\tau^2) + [6\tau^3 + 6P'_{BA}\tau^2 + 3(P'_{BA}{}^2 + \sigma^2)\tau + 3\sigma^2P'_{BA}] \\ &= \langle BAB\rangle_o + s\tau - 2K_2 + kK_3 \quad (20)\end{aligned}$$

where $K_3 = 6\tau^3 + 6P'_{BA}\tau^2 + 3(P'_{BA}{}^2 + \sigma^2)\tau + 3\sigma^2P'_{BA}$.

The expressions for all diads, triads, and tetrads are summarized in Table 3, column 2. In each expression, the first term corresponds to the unperturbed model (i.e., the conventional first-order Markovian model), and the subsequent term(s) are the perturbations. Note that the parameters K_2, K_3, and K_4 are related to the second,

Table 3. Probability Expressions for the Perturbed First-Order Markovian Model Using Exponentially Modified Gaussian

sequence	expression based on P'_{ij}[a]	expression based on $\langle P_{ij}\rangle$[b]
$\langle A\rangle$	$k(P'_{BA} + \tau)$	$k\langle P_{BA}\rangle$
$\langle B\rangle$	$k(P'_{AB} - \tau)$	$k\langle P_{AB}\rangle$
$\langle AA\rangle$	$k(1 - P'_{AB})P'_{BA} + (k - 1)\tau + kK_2$	$k\langle P_{BA}\rangle(1 - \langle P_{AB}\rangle) + kK_2$
$\langle AB\rangle$	$2kP'_{AB}P'_{BA} + 2\tau - 2kK_2$	$2k\langle P_{BA}\rangle\langle P_{AB}\rangle - 2kK_2$
$\langle BB\rangle$	$k(1 - P'_{BA})P'_{AB} - (k + 1)\tau + kK_2$	$k\langle P_{AB}\rangle(1-\langle P_{BA}\rangle) + kK_2$
$\langle AAA\rangle$	$kP'_{BA}(1 - P'_{AB})^2 + (k - 2 + s)\tau + (2k - 2)K_2 + kK_3$	$k\langle P_{BA}\rangle(1 - \langle P_{AB}\rangle)^2 + (2k - 2)K_2 + kK_3$
$\langle AAB\rangle$	$2kP'_{BA}P'_{AB}(1 - P'_{AB}) + 2(1 - s)\tau + (4 - 2k)K_2 - 2kK_3$	$2k\langle P_{BA}\rangle\langle P_{AB}\rangle(1 - \langle P_{AB}\rangle) + (4 - 2k)K_2 - 2\mathrm{k}K_3$
$\langle BAB\rangle$	$kP'^{2}_{AB}P'_{BA} + s\tau - 2K_2 + kK_3$	$k\langle P_{AB}\rangle^2\langle P_{BA}\rangle - 2K_2 + kK_3$
$\langle ABA\rangle$	$kP'_{AB}P'^{2}_{BA} + K_2 - kK_3$	$k\langle P_{BA}\rangle^2\langle P_{AB}\rangle + K_2 - kK_3$
$\langle BBA\rangle$	$2kP'_{AB}P'_{BA}(1 - P'_{BA}) + 2\tau - (2k + 2)K_2 + 2kK_3$	$2\mathrm{k}\langle P_{AB}\rangle\langle P_{BA}\rangle(1 - \langle P_{BA}\rangle) - 2(k + 1)K_2 + 2kK_3$
$\langle BBB\rangle$	$kP'_{AB}(1 - P'_{BA})^2 - (k + 2)\tau + (2k + 1)K_2 - kK_3$	$k\langle P_{AB}\rangle(1 - \langle P_{BA}\rangle)^2 + (1 + 2k)K_2 - kK_3$
$\langle AAAA\rangle$	$kP'_{BA}(1 - P'_{AB})^3 + k(1 - s)^3\tau + 3k(1 - s)^2K_2 + (3k - 3)K_3 + kK_4$	$k\langle P_{BA}\rangle(1 - \langle P_{AB}\rangle)^3 + k[3(1 - s)^2K_2 + 3(1 - s)K_3 + K_4]$
$\langle AAAB\rangle$	$2kP'_{BA}P'_{AB}(1 - P'_{AB})^2 + 2(1 - s)^2\tau + (2k - 2)(3s - 1)K_2 + (6 - 4k)K_3 - 2kK_4$	$2k\langle P_{BA}\rangle\langle P_{AB}\rangle(1 - \langle P_{AB}\rangle)^2 + 2k[(1 - s)(3s - 1)K_2 + (3s - 2)K_3 - K_4]$
$\langle BAAB\rangle$	$kP'^{2}_{AB}P'_{BA}(1 - P'_{AB}) + s(1 - s)\tau + (3s - 2)K_2 + (k - 3)K_3 + kK_4$	$k\langle P_{AB}\rangle^2\langle P_{BA}\rangle(1 - \langle P_{AB}\rangle) + k[(3s^2 - 2s)K_2 + (1 - 3s)K_3 + K_4]$
$\langle AABA\rangle$	$2kP'^{2}_{BA}P'_{AB}(1 - P'_{AB}) + 2(1 - s)K_2 + (4 - 2k)K_3 - 2kK_4$	$2k\langle P_{BA}\rangle^2\langle P_{AB}\rangle(1 - \langle P_{AB}\rangle) + 2k[s(1 - s)K_2 + (2s - 1)K_3 - K_4]$
$\langle AABB\rangle$	$2kP'_{AB}P'_{BA}(1 - P'_{AB})(1 - P'_{BA}) + 2(1 - s)\tau + (2s + 2 - 2k)K_2 - 4K_3 + 2kK_4$	$2k\langle P_{AB}\rangle\langle P_{BA}\rangle(1 - \langle P_{AB}\rangle)(1 - \langle P_{BA}\rangle) + 2k[(s^2 + s - 1)K_2 - 2sK_3 + K_4]$
$\langle BABA\rangle$	$2kP'^{2}_{BA}P'^{2}_{AB} + 2sK_2 - 4K_3 + 2kK_4$	$2k\langle P_{BA}\rangle^2\langle P_{AB}\rangle^2 + 2k[s^2K_2 - 2sK_3 + K_4]$
$\langle BABB\rangle$	$2kP'^{2}_{AB}P'_{BA}(1 - P'_{BA}) + 2s\tau - (2s + 4)K_2 + (4 + 2k)K_3 - 2kK_4$	$2k\langle P_{AB}\rangle^2\langle P_{BA}\rangle(1 - \langle P_{BA}\rangle) + 2k[(-s^2 - 2s)K_2 + (2s + 1)K_3 - K_4]$
$\langle ABBA\rangle$	$kP'_{AB}P'^{2}_{BA}(1 - P'_{BA}) + K_2 - (k + 1)K_3 + kK_4$	$k\langle P_{AB}\rangle\langle P_{BA}\rangle^2(1 - \langle P_{BA}\rangle) + k[sK_2 - (s + 1)K_3 + K_4]$
$\langle BBBA\rangle$	$2kP'_{AB}P'_{BA}(1 - P'_{BA})^2 + 2\tau - (4 + 2k)K_2 + 2(1 + 2k)K_3 - 2kK_4$	$2k\langle P_{AB}\rangle\langle P_{BA}\rangle(1 - \langle P_{BA}\rangle)^2 + 2k[(-2s - 1)K_2 + (s + 2)K_3 - K_4]$
$\langle BBBB\rangle$	$kP'_{AB}(1 - P'_{BA})^3 - (k + 3)\tau + (3 + 3k)K_2 - (1 + 3k)K_3 + kK_4$	$k\langle P_{AB}\rangle(1 - \langle P_{BA}\rangle)^3 + k[3(s + 1)K_2 - (s + 3)K_3 + K_4]$

[a] Four parameters characterize this model: P'_{BA}, P'_{AB}, σ, and τ. The other variables are defined as follows:

$$K_2 = \sigma^2 + 2P'_{BA}\tau + 2\tau^2$$

$$K_3 = 6\tau^3 + 6P'_{BA}\tau^2 + 3(P'^{2}_{BA} + \sigma^2)\tau + 3\sigma^2P'_{BA}$$

$$K_4 = 3\sigma^4 + 6\tau^2\sigma^2 + 9\tau^4 + 6(\sigma^2 + \tau^2)(P'_{BA} + \tau)^2 + 8\tau^3(P'_{BA} + \tau) + (P'_{BA} + \tau)^4 - P'^{4}_{BA}$$

$$k^{-1} = s = P'_{AB} + P'_{BA}$$

[b] Four different parameters characterize this model: $\langle P_{BA}\rangle$, $\langle P_{AB}\rangle$, σ, and τ. The other variables are defined as follows:

$$K_2 = \sigma^2 + \tau^2$$

$$K_3 = 2\tau^3 + 3\tau^2\langle P_{BA}\rangle + 3\sigma^2\langle P_{BA}\rangle$$

$$K_4 = 3\sigma^4 + 6\tau^2\sigma^2 + 9\tau^4 + 8\tau^3\langle P_{BA}\rangle + 6(\sigma^2+\tau^2)\langle P_{BA}\rangle^2$$

$$k^{-1} = s = \langle P_{AB}\rangle + \langle P_{BA}\rangle$$

the third, and the fourth absolute moments of the EMG distribution:

$$K_2 = M_2 - P'^{2}_{BA} \tag{21}$$

$$K_3 = M_3 - P'^{3}_{BA} \tag{22}$$

$$K_4 = M_4 - P'^{4}_{BA} \tag{23}$$

In the expressions, there are only four independent parameters: P'_{BA}, P'_{AB}, σ, and τ. All other variables can be derived from these four parameters.

Some characteristics of the EMG distribution are summarized here for future reference:

$$\text{average probability } P_{BA} = \langle P_{BA}\rangle = P'_{BA} + \tau \tag{24}$$

$$\text{average probability } P_{AB} = \langle P_{AB}\rangle = P'_{AB} - \tau \tag{25}$$

$$\text{variance about the mean} = M_{2,c} = \sigma^2 + \tau^2 \tag{26}$$

$$\text{skew (about the mean)} = M_{3,c}/M_{2,c}^{3/2} = 2\tau^3/(\sigma^2 + \tau^2)^{3/2} \tag{27}$$

The expressions given in column 2 of Table 3 can be equivalently expressed as a function of $\langle P_{BA}\rangle$ and $\langle P_{AB}\rangle$, instead of P'_{BA} and P'_{AB} by using eqs 24 and 25. These expressions are given in column 3.

Computer-Assisted Analytical Approach

In order to facilitate analysis, the computer-assisted analytical approach described previously[33−35] has been adopted to fit the NMR data. Thus, a simplex algorithm is used that compares the observed triad intensities (from the NMR data) to the triad intensities calculated via the expressions given in Table 3, column 2. The four parameters (P'_{BA}, P'_{AB}, σ, and τ) are then systematically varied in order to minimize the deviations between the observed and the calculated triad values. After an appropriate number of iterations (controlled by the user), the optimal values of the four parameters are obtained.

A computer program has been written in QuickBasic (called PERTEMG) that encodes the above operations for copolymer triads. The observed triad values are first entered. The user next enters the initial (guess) values of the four parameters, and also an operative range of values assigned to each parameter ($\delta P'_{AB}$, $\delta P'_{BA}$, $\delta\sigma$, and $\delta\tau$). The user can choose to fix a given parameter by simply assigning 0 to the operative range. In the program, P'_{AB} and P'_{BA} are allowed to take on any value between 0 and 1. The parameter σ is constrained to be positive. However, τ can be positive or negative, depending on the direction of skew.

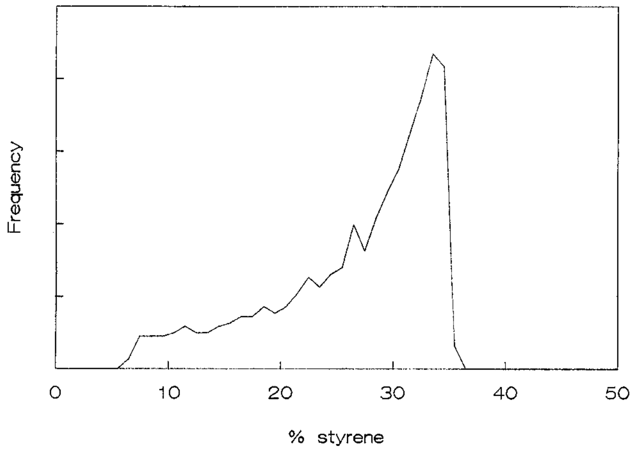

Figure 2. Simulated chemical compositional distribution (CCD) curve for the styrene (A)/ethyl methacrylate (B) copolymer. The following parameters have been used:[36] $r_A = 0.46$; $r_B = 0.38$; initial feed = 24.8% A, 75.2% B; batch polymerization, conversion = 92%. Simulation obtained via the program PODIS3.[16]

Table 4. Fitting the Computer-Generated Triad Data for the Styrene (A)/Ethyl Methacrylate (B) Copolymer by the EMG Perturbed First-Order Markovian Model[a]

	I_{comp}[b]	I_{calc} (1)	I_{calc} (2)	I_{calc} (3)
AAA	0.279	0.257	0.580	0.405
AAB	4.723	4.715	4.521	4.723
BAB	22.036	21.662	22.036	21.993
ABA	9.031	7.864	8.931	9.031
BBA	30.730	32.311	30.730	30.647
BBB	33.201	33.191	33.201	33.201
P'_{AB}		0.9019	0.9287	0.9247
P'_{BA}		0.3274	0.3459	0.3492
σ		0	0.1074	0.0938
τ		0	0	−0.0037
MD[c]		0.527	0.101	0.042

[a] Fitted with the program PERTEMG. [b] Computer-generated intensities produced via the program PODIS3[16] with the following parameters (taken from ref 36): conversion = 92%, $r_A = 0.46$, $r_B = 0.38$, and $f_A = 0.248$. [c] Mean deviation.

Examples of Perturbed Model with EMG Function

The NMR data of several samples reported to have compositional heterogeneity have been analyzed by the approach described above.

Styrene/Ethyl Methacrylate Copolymers. Tacx et al.[36] studied the copolymerization of styrene and ethyl methacrylate using different polymerization techniques. They developed a thin layer chromatography/flame ionization detection method to measure the compositional heterogeneity. For such a copolymer made at 92% conversion and polymerized in bulk, they reported $f_A = 0.248$, $f_B = 0.752$, $r_A = 0.46$, and $r_B = 0.38$ (where A = styrene, B = ethyl methacrylate). Because the reactivity ratios for the two comonomers are different, conversion heterogeneity is potentially present. The reported CCD is indeed broad and nonsymmetric.[36] The copolymerization has been simulated through a computer method with the program PODIS3, reported earlier.[16] The simulated CCD is given in Figure 2. It resembles the observed CCD curves reported by Tacx et al.[36] In addition, the predicted NMR triad data for this copolymer can be obtained (Table 4, column 2). As a test case, these simulated triad data have been analyzed by the program PERTEMG.

Three ways have been used to analyze the triad data: (1) no perturbation ($\sigma = \tau = 0$), i.e., no compositional heterogeneity, (2) symmetric perturbation ($\sigma > 0$, $\tau = 0$), and (3) EMG perturbation ($\sigma, \tau \neq 0$).

The symmetric perturbed model ($\sigma > 0$, $\tau = 0$) gives a large improvement over the unperturbed model (mean deviations 0.101 vs 0.527). The introduction of τ improves the fit even further (mean deviation = 0.042). Thus, the EMG perturbed model can be used as a suitable description of this copolymerization. In effect, we are approximating the CCD curve (Figure 2) with the EMG function.

Styrene/Butyl Acrylate Copolymers. Llauro et al.[37] have copolymerized styrene and butyl acrylate at various conversions in the batch mode and obtained the NMR triad data. It has been shown that the conversion heterogeneity is present in these samples.[15,37] As examples, two of the observed data sets have been fitted with the program PERTEMG (Table 5). Again, the data have been analyzed in three ways. The best results are obtained when both σ and τ are non-zero (providing the lowest mean deviations).

The examples given in Tables 4 and 5 suggest that the present methodology can be used at least for some copolymer samples that exhibit conversion heterogeneity. It may be cautioned, however, that the EMG function is only an approximation of the real CCD curve. Whereas we can use this methodology as a means to detect conversion heterogeneity and to estimate the CCD curve, the $\{P'_{ij}\}$ obtained are specific to the EMG functional form and in general may not be equal to the theoretical unperturbed probabilities $\{P^o_{ij}\}$.

Isobutylene/Isoprene Copolymers. Corno et al.[38] have copolymerized isobutylene and isoprene using cationic means. They made several samples at different conversions and different comonomer feed ratios and obtained the triad intensities from both ^{1}H and ^{13}C NMR spectra. It has been shown earlier by using the symmetric perturbed model[14] that these samples exhibit compositional heterogeneity. This problem has now been revisited using the (nonsymmetric) EMG perturbed Markovian model.

The observed and the calculated triad data for two samples of the isobutylene/isoprene copolymer are given in Table 6. In both samples, large improvements have been observed through the use of τ. The mean deviation (MD) decreases to 0.05−0.06 when the skew is introduced.

Whereas the EMG perturbation model appears to be a good description of the copolymerization system, the nature of the compositional heterogeneity is not known. All four kinds of heterogeneity (Table 1) can contribute toward σ. In view of the low conversion used for these copolymers, the asymmetry (τ) is likely the result of process and/or multistate heterogeneities.

Vinyl Chloride/Vinylidene Chloride Copolymers. Final examples are given for this copolymer system. Schlothauer et al.[39] have reported the triad data for several commercial samples of vinyl chloride/vinylidene chloride copolymers. The polymerization process and the reaction conditions for these samples have not been reported. In this work the data for several of these samples have been analyzed through the program PERTEMG. The results for samples A and C (from B. F. Goodrich) are given in Table 7. In these cases, the benefit of introducing σ is apparent, but τ appears not to improve the fit. These are examples

Table 5. Fitting of the Triad Data for the Styrene (S)/Butyl Acrylate (A) Copolymers by the EMG Perturbed First-Order Markovian Model[a]

	sample 1 (conversion = 5%)				sample 3 (conversion = 63%)			
	I_{obsd}	I_{calc} (1)	I_{calc} (2)	I_{calc} (3)	I_{obsd}	I_{calc} (1)	I_{calc} (2)	I_{calc} (3)
SSS	1.5	1.3	2.1	1.5	0	0.5	0.9	0.1
SSA	12.2	12.4	12.0	11.8	7.0	7.0	6.4	7.0
ASA	29.1	29.1	28.7	29.1	24.8	24.8	24.8	24.8
SAS	21.8	21.8	21.8	22.2	12.6	11.8	12.3	12.6
AAS	25.8	27.0	25.8	25.7	31.4	32.9	31.4	31.4
AAA	9.7	8.4	9.7	9.7	24.2	22.9	24.2	24.2
P'_{SA}		0.824	0.833	0.839		0.876	0.900	0.890
P'_{AS}		0.616	0.622	0.626		0.418	0.425	0.432
σ		0	0.118	0.095		0	0.106	0.0016
τ		0	0	−0.004		0	0	−0.0107
MD[b]		0.49	0.20	0.16		0.68	0.29	0.02

[a] Observed intensities adapted from ref 37; the calculated intensities obtained by fitting with the program PERTEMG. [b] Mean deviation.

Table 6. Fitting of the Triad Data for the Isobutylene (A)/Isoprene (B) Copolymers by the EMG Perturbed First-Order Markovian Model[a]

	sample 5[b]				sample 6[c]			
	I_{obsd}	I_{calc} (1)	I_{calc} (2)	I_{calc} (3)	I_{obsd}	I_{calc} (1)	I_{calc} (2)	I_{calc} (3)
AAA	22.5	22.5	22.5	22.5	18.9	18.9	18.9	18.9
AAB	25.8	27.4	25.8	25.8	24.7	26.5	24.7	24.6
BAB	9.3	8.4	9.0	9.4	10.6	9.3	10.5	10.7
ABA	11.7	11.7	11.7	11.7	11.2	11.2	12.2	11.3
BBA	20.8	20.8	20.4	21.3	23.2	22.6	21.5	23.2
BBB	9.2	9.2	10.5	9.2	11.3	11.4	12.2	11.3
P'_{AB}		0.379	0.403	0.404		0.418	0.454	0.446
P'_{BA}		0.530	0.542	0.542		0.498	0.537	0.513
σ		0	0.107	0.096		0	0.129	0.107
τ		0	0	0.005		0	0	0.006
MD[d]		0.54	0.44	0.05		0.63	0.60	0.06

[a] Observed data taken from ref 38; calculated intensities analyzed via the program PERTEMG. [b] Feed, $f_A = 0.500$ and conversion = 6.6%. [c] Feed, $f_A = 0.455$ and conversion = 8.0%. [d] Mean deviation between the observed and the calculated intensities.

Table 7. Fitting of the Triad Data for Vinyl Chloride (A)/Vinylidene Chloride (B) Copolymers by the EMG Perturbed First-Order Markovian Model[a]

	sample A				sample C			
	I_{obsd}	I_{calc} (1)	I_{calc} (2)	I_{calc} (3)	I_{obsd}	I_{calc} (1)	I_{calc} (2)	I_{calc} (3)
AAA	2.1	0.6	0.8	0.7	68.8	68.8	68.8	68.8
AAB	3.6	4.8	5.0	4.6	14.4	17.6	14.4	14.4
BAB	9.1	9.1	9.1	9.5	2.5	1.1	3.6	3.6
ABA	2.4	1.6	2.2	2.4	9.6	7.9	8.8	8.8
BBA	18.8	19.9	18.9	18.8	4.0	4.0	4.0	4.0
BBB	63.9	64.0	63.9	64.0	0.7	0.5	0.4	0.4
P'_{AB}		0.791	0.825	0.863		0.114	0.152	0.153
P'_{BA}		0.135	0.145	0.147		0.799	0.998	0.996
σ		0	0.083	0.101		0	0.164	0.164
τ		0	0	0.003		0	0	0.002
MD[b]		0.77	0.51	0.46		1.08	0.37	0.37

[a] Observed data from ref 39; calculated data fitted via the program PERTEMG. [b] Mean deviation.

where the EMG is not needed; the regular (symmetric) perturbed model appears to be sufficient.

Similar analysis has been carried out for samples B1 and B2 (from Buna factories). The observed and the calculated data are shown in Table 8. It is of interest that neither the (unperturbed) first-order Markovian model ($\sigma = \tau = 0$) nor the symmetric perturbed model ($\tau = 0$) fit the data well. However, when $\sigma,\tau > 0$, the mean deviations decrease noticeably. In view of the large values of σ, the two copolymers are chemically very heterogeneous.

Schlothauer et al.[39] reported that several copolymers prepared in the laboratory conform well to the conventional (unperturbed) first-order Markovian model. Thus, there is a difference between the lab-prepared samples and commercial copolymers as far as chemical heterogeneity is concerned.

General-Case Model: Arbitrary Composition Distributions

Sometimes the CCD curves do not conform to a simple mathematical function, such as rectangular, Gaussian, or EMG. For example, in conversion heterogeneity, the CCD curves are complex[4] and often become shaped like a “tent”. Similarly, in many multistate heterogeneous polymers (especially those made with Ziegler−Natta catalysts), the CCD curves are multi-modal and may be more properly treated as the sum of several components.[8−13]

The theoretical formalism presented in this work may be extended to any functional form of the CCD curve. In the general case, instead of the EMG function (eq 12), we use a general function $g(F_A,q_i)$ for the distribution of the molar composition of A, where q_i represents

Table 8. More Fitting of the Triad Data for Vinyl Chloride (A)/Vinylidene Chloride (B) Copolymers by the EMG Perturbed First-Order Markovian Model[a]

	sample B1				sample B2			
	I_{obsd}	I_{calc} (1)	I_{calc} (2)	I_{calc} (3)	I_{obsd}	I_{calc} (1)	I_{calc} (2)	I_{calc} (3)
AAA	16.2	4.7	7.5	16.2	36.0	36.0	36.0	36.0
AAB	9.9	16.7	16.5	10.3	13.0	20.6	20.6	13.0
BAB	14.9	14.9	14.9	15.2	9.3	3.0	3.0	9.0
ABA	8.6	8.5	10.7	7.9	6.7	4.4	4.4	7.1
BBA	24.8	29.5	24.8	24.8	16.8	17.8	17.8	16.8
BBB	25.7	25.7	25.7	25.7	18.2	18.2	18.2	18.2
P'_{AB}		0.640	0.678	0.714		0.223	0.226	0.443
P'_{BA}		0.365	0.430	0.423		0.329	0.334	0.593
σ		0	0.188	0.324		0	0.031	0.324
τ		0	0	0.050		0	0	0.007
MD[b]		3.86	2.91	0.22		2.89	2.85	0.12

[a] Observed data from ref 39; calculated data fitted via the program PERTEMG. [b] Mean deviation.

the parameters that define the CCD shape and normalization. In this way, $g(F_A,q_i)$ can be a mathematical function or an experimentally observed distribution. We may characterize this composition distribution function through the absolute moments:

$$M_n(F_A) = \frac{\int_0^1 F_A^n g(F_A,q_i)\,dF_A}{\int_0^1 g(F_A,q_i)\,dF_A} \tag{28}$$

In the probability model, we translate the CCD curve to a probability distribution, $g(z,q_i)$, where z is the probability variable (viz., P_{BA}). The two distributions are related by the simple relationship, $g(F_A,q_i) = kg(z,q_i)$. The absolute moments in the probability distribution are given by

$$M_n(z) = \frac{\int_0^1 z^n g(z,q_i)\,dz}{\int_0^1 g(z,q_i)\,dz} \tag{29}$$

It is obvious that $M_n(F_A) = k^n M_n(z)$. In the following derivation, only the probability distribution is used; for simplicity, $M_n = M_n(z)$. As in eq 13, let $s = k^{-1} = P_{AB} + P_{BA} = \langle P_{AB}\rangle + \langle P_{BA}\rangle$. The probabilities P_{AB}, P_{AA}, and P_{BB} are obtained via eq 14. The composition is again given by the first moment:

$$\langle A\rangle = \langle kP_{BA}\rangle = kM_1 \tag{30}$$

$$\langle B\rangle = \langle kP_{AB}\rangle = 1 - kM_1 \tag{31}$$

The diads and the triads can be calculated in the same way as in eqs 17−23. As an example, the derivation of the ⟨BBA⟩ triad is given below:

$$\begin{aligned}\langle BBA\rangle &= \langle 2kP_{AB}P_{BB}P_{BA}\rangle = 2k\langle (s - P_{BA})(1 - P_{BA})P_{BA}\rangle \\ &= 2k\langle sP_{BA} - (1 + s){P_{BA}}^2 + {P_{BA}}^3\rangle \\ &= 2\langle P_{BA}\rangle - 2(k + 1)\langle {P_{BA}}^2\rangle + 2k\langle {P_{BA}}^3\rangle \\ &= 2M_1 - 2(k + 1)M_2 + 2kM_3 \end{aligned} \tag{32}$$

For convenience, the entire sequences up to tetrads are given in Table 9. In this generalized model, four parameters characterize the triad sequences: k, M_1, M_2, and M_3. Since $k^{-1} = \langle P_{AB}\rangle + \langle P_{BA}\rangle$ and $M_1 = \langle P_{BA}\rangle$, the four parameters are equivalent to $\langle P_{AB}\rangle$, $\langle P_{BA}\rangle$, M_2, and M_3. For tetrads, five parameters are needed: k, M_1, M_2, M_3, and M_4 or equivalently $\langle P_{AB}\rangle$, $\langle P_{BA}\rangle$, M_2, M_3, and M_4.

Table 9. Probability Expressions[a] **for the General-Case Perturbed First-Order Markovian Model**

sequence	model expression[b]
⟨A⟩	kM_1
⟨B⟩	$1 - kM_1$
⟨AA⟩	$(k - 1)M_1 + kM_2$
⟨AB⟩	$2M_1 - 2kM_2$
⟨BB⟩	$1 - (1 + k)M_1 + kM_2$
⟨AAA⟩	$(k - 2 + s)M_1 + (2k - 2)M_2 + kM_3$
⟨AAB⟩	$2(1 - s)M_1 + (4 - 2k)M_2 - 2kM_3$
⟨BAB⟩	$sM_1 - 2M_2 + kM_3$
⟨ABA⟩	$M_2 - kM_3$
⟨BBA⟩	$2M_1 - 2(k + 1)M_2 + 2kM_3$
⟨BBB⟩	$1 - (2 + k)M_1 + (1 + 2k)M_2 - kM_3$
⟨AAAA⟩	$k[(1 - s)^3M_1 + 3(1 - s)^2M_2 + 3(1 - s)M_3 + M_4]$
⟨AAAB⟩	$2k[s(1 - s)^2M_1 + (1 - s)(3s - 1)M_2 + (3s - 2)M_3 - M_4]$
⟨BAAB⟩	$k[s^2(1 - s)M_1 + (3s^2 - 2s)M_2 + (1 - 3s)M_3 + M_4]$
⟨AABA⟩	$2k[s(1 - s)M_2 + (2s - 1)M_3 - M_4]$
⟨AABB⟩	$2k[s(1 - s)M_1 + (s^2 + s - 1)M_2 - 2sM_3 + M_4]$
⟨BABA⟩	$2k[s^2M_2 - 2sM_3 + M_4]$
⟨BABB⟩	$2k[s^2M_1 - (s^2 + 2s)M_2 + (2s + 1)M_3 - M_4]$
⟨ABBA⟩	$k[sM_2 - (s + 1)M_3 + M_4]$
⟨BBBA⟩	$2k[sM_1 - (2s + 1)M_2 + (s + 2)M_3 - M_4]$
⟨BBBB⟩	$1 + k[-(1 + 3s)M_1 + 3(s + 1)M_2 - (s + 3)M_3 + M_4]$

[a] Four parameters characterize the first-order Markovian general-case triads: k, M_1, M_2, and M_3. Since $k^{-1} = s = \langle P_{AB}\rangle + \langle P_{BA}\rangle$, and $M_1 = \langle P_{BA}\rangle$, four equivalent parameters are $\langle P_{AB}\rangle$, $\langle P_{BA}\rangle$, M_2, and M_3. For tetrads, an additional parameter is needed: M_4. [b] Bernoullian general-case model can be obtained by setting $k = s = 1$. Three parameters characterize the triads: $\langle P_A\rangle$, M_2, and M_3. Four parameters characterize the tetrads: $\langle P_A\rangle$, M_2, M_3, and M_4, where $\langle P_A\rangle = \langle P_{BA}\rangle = 1 - \langle P_{AB}\rangle$.

The computer program PERTEMG has been modified for this general case. The triad expressions in Table 9 have been coded using the four parameters, $\langle P_{AB}\rangle$, $\langle P_{BA}\rangle$, M_2, and M_3. The resulting program is called PERTGEN. As before, the triad data, the initial (guess) values of the average probabilities $\langle P_{AB}\rangle$ and $\langle P_{BA}\rangle$, and their operating ranges are first entered. Three options are available for the input of the initial values of M_2 and M_3:

(1) Manually input M_2 and M_3 and their operating ranges (δM_2,δM_3).

(2) Assume initially that no perturbation exists. The program has been coded to compute M_2, M_3, δM_2, and δM_3 automatically.

(3) Use the EMG function as a starting point, and enter the initial σ and τ values. The program will compute M_2 and M_3 from the following equations:

$$M_2 = \sigma^2 + \tau^2 + \langle P_{BA}\rangle^2 \tag{33}$$

$$M_3 = 2\tau^3 + 3(\sigma^2 + \tau^2)\langle P_{BA}\rangle + \langle P_{BA}\rangle^3 \tag{34}$$

Table 10. Fitting of the Triad Data of Two Vinyl Chloride (A)/Vinylidene Chloride (B) Copolymers by the General-Case Perturbed First-Order Markovian (M1) Model[a]

	sample C				sample B2			
sequence	I_{obsd}	I_{calc} (1)	I_{calc} (2)	I_{calc} (3)	I_{obsd}	I_{calc} (1)	I_{calc} (2)	I_{calc} (3)
AAA	68.8	68.8	68.8	68.8	36.0	36.0	36.0	36.0
AAB	14.4	17.4	14.4	14.5	13.0	21.0	21.5	13.0
BAB	2.5	1.2	3.5	3.3	9.3	2.8	2.6	8.9
ABA	9.6	7.8	8.8	8.6	6.7	4.6	4.9	7.0
BBA	4.0	4.1	3.8	4.0	16.8	17.3	16.8	16.9
BBB	0.7	0.7	0.7	0.7	18.2	18.2	18.2	18.2
Fitted to General-Case Perturbed **M1** Model								
$\langle P_{\mathrm{AB}}\rangle$		0.116	0.153	0.150		0.223	0.225	0.433
$\langle P_{\mathrm{BA}}\rangle$		0.799	0.996	0.977		0.332	0.338	0.596
M_2		0.640	1.022	0.982		0.111	0.115	0.455
M_3		0.513	1.073	1.010		0.036	0.037	0.397
MD[b]		1.06	0.33	0.33		2.88	2.83	0.13
Calculated for Conventional (Unperturbed) **M1** Model								
M_2		0.638	0.993	0.955		0.110	0.114	0.356
M_3		0.510	0.989	0.933		0.037	0.039	0.212

[a] Observed data from ref 39; calculated data fitted via the program PERTGEN. [b] Mean deviation.

The operating ranges can likewise be obtained for the above equations:

$$\delta M_2 = 2\sigma(\delta\sigma) + 2\tau(\delta\tau) + 2\langle P_{\mathrm{BA}}\rangle\delta\langle P_{\mathrm{BA}}\rangle \qquad (35)$$

$$\delta M_3 = 6\tau^2(\delta\tau) + 6[\sigma(\delta\sigma) + \tau(\delta\tau)]\delta\langle P_{\mathrm{BA}}\rangle + 3[\sigma^2 + \tau^2 + \langle P_{\mathrm{BA}}\rangle^2]\delta\langle P_{\mathrm{BA}}\rangle \qquad (36)$$

These three options have been incorporated into the program as a convenience feature. In the next step, all four initial parameters, $\langle P_{\mathrm{AB}}\rangle$, $\langle P_{\mathrm{BA}}\rangle$, M_2, and M_3, are optimized through the simplex algorithm which produces the best fit to the observed data.

As an illustration, the generalized approach has been attempted on two sets of vinyl chloride/vinylidene chloride copolymer data: sample B2 (from Table 8) and sample C (from Table 7). As before, the observed data have been taken from Schlothauer et al.;[39] the analysis has been carried out using the program PERTGEN. The results are summarized in Table 10.

In fitting the data, we found it advisable to use a stepwise approach, whereby the observed data are fitted in at least three ways. First, little or no perturbation is assumed and approximate values of $\langle P_{\mathrm{AB}}\rangle$ and $\langle P_{\mathrm{BA}}\rangle$ are obtained. Secondly, symmetric broadening of the CCD curve is permitted. The use of the EMG function (as option 3 in the program input) is useful in this regard. Finally, all parameters are allowed to float, and the optimal values of the four parameters (in the general case) are obtained. The results of these steps are given in Table 10 for each of the two samples. For comparison, the M_2 and the M_3 values for the corresponding first-order Markovian (unperturbed) model are shown in the last two rows of Table 10.

It is apparent that the generalized model is indeed useful for the analysis of copolymers that exhibit compositional heterogeneity. Some comments concerning the uses and the limitations of this model are provided below.

(1) The generalized approach is potentially applicable to copolymers that exhibit all forms of compositional heterogeneity. Information available (for triad analysis) includes the average Markovian reaction probabilities ($\langle P_{\mathrm{BA}}\rangle$,$\langle P_{\mathrm{AB}}\rangle$) and the moments ($M_2$,$M_3$) of the CCD.

(2) In the generalized approach no specific functional form is assumed for the CCD curve. Instead, the CCD is characterized by the moments (M_{n}). While this feature permits a general treatment of heterogeneity, it is often difficult to visualize the CCD curve from the moments alone. If the exact functional form of the CCD is desirable, additional data (e.g., fractionation and chromatography) may be needed.

(3) Although only examples of the analysis of triad sequences have been shown, a similar treatment can be made for higher *n*-ad sequences. For tetrads, the fourth moment (M_4) is involved, and for pentads the fifth moment (M_5). It is obvious that if we know more about the higher moments then we have more information on the CCD curve.

(4) Sometimes, through other analytical techniques, we know the shape (or the functional form) of the CCD curve. We can then calculate (or derive) the moments (M_n). Since the copolymer sequences are functions of the moments and the constant k (Table 9), we can then predict the intensities of all *n*-ad sequences if we know the copolymer composition. If the NMR data are also available, we can compare the predicted sequence intensities with the observed NMR values.

(5) The symmetric perturbed model that was previously reported[14] and the EMG model (vide supra) may be considered special cases of the general-case model.

Conclusion

In this work the methodology has been developed to treat NMR triad data of compositionally heterogeneous copolymers. Two approaches have been considered: a general formalism applicable to any arbitrary CCD curve as well as a special formalism that pertains to copolymers that exhibit exponentially modified (skewed) Gaussian CCD curves. Both approaches have been shown to be useful in the analysis of NMR data. Through these methods, it is possible to obtain not only the first-order Markovian probabilities but also (in suitable cases) information on the CCD curves.

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