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Improved increments for characterization of comonomer sequencing in binary copolymers

Wojciech K. Czerwinski*
Deutsches Kunststoff-Institut, Schloßgartenstr. 6, D-64289 Darmstadt, Germany
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The degree of randomness of higher order than first order was proposed to characterize the alternating structure of binary copolymers. The introduced parameter describes the alternating structure more precisely than the degree of alternation already proposed in the literature. Furthermore, the new parameter can be used in connection with standard copolymerization models where the need for such parameters is especially high. In this domain the degree of alternation fails. The usefulness of the degree of randomness was tested on model chains and two standard copolymerization models: the terminal and simplified penultimate model. This examination proves that more precise information on comonomer sequencing can be obtained when sequences longer than diads are described by means of the degree of randomness. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The simultaneous polymerization of two monomers yields polymers with a random distribution of monomeric units along the polymer chains if copolymerizability is given. In such cases statistical increments are an efficient tool for describing this distribution as well as other phenomena such as tacticity and cotacticity and/or its relation to the chemical distribution. The subject of the present paper is the comonomer distribution along the polymer chain. It can affect such properties of polymers as polarity, morphology, miscibility, optical, electrical and a number of other properties and is, therefore, of special interest. In this regard several parameters, some of them 'one-number' parameters, have been proposed for a simple characterization of copolymers. Such parameters frequently used are: average block length, run number (overall number of sequences per 100 consecutive monomeric units)[1,2], degree of randomness[3], degree of blockiness[4] and degree of alternation of nth order or degree of blockiness of nth order[4].

Most of these parameters were developed by workers investigating the microstructure of polycondensates[3–5] by means of n.m.r. spectroscopy. The problem of the randomness of those polymers was discussed more efficiently taking these parameters into account.

Less attention was paid to these parameters in connection with the vinyl copolymerization known to be in the nature of things random. As will be shown in the following sections, degrees of randomness, alternation or blockiness of higher orders than first order are especially relevant and allow a look into the sequence structuring by means of simple parameters. Higher order degrees of alternation (blockiness) already proposed[4] do not describe the alternating (blocked) structure of copolymers efficiently enough. Furthermore, the parameters proposed are insensitive to the relative reactivity ratios defined for the classical copolymerization model.

These disadvantages are overcome when the modified degree of randomness of higher order is used. The aim of the present paper is to introduce these parameters and to demonstrate their usefulness in the characterization of the alternation in copolymers either taken as model chains or calculated in terms of two different copolymerization models.

THEORETICAL PART

In the following $FX_1X_2\ldots X_n$ will designate the number fraction of a particular sequence $X_1X_2\ldots X_n$ among all sequences with the length n, where X is monomer unit A or B. $FX_1X_2\ldots X_n$ corresponds to the unconditional probability P_n $(X_1X_2\ldots X_n)$ of finding the above sequence in a polymer chain.

$P_{X_1X_2\ldots X_nX_{n+1}}$ defines conditional probability with which a growing polymer chain with the terminal sequence $X_1X_2\ldots X_n$ adds the particular monomer X_{n+1}

$$P_{X_1X_2\ldots X_nX_{n+1}} = \frac{P_{n+1}(X_1X_2\ldots X_nX_{n+1})}{P_n(X_1X_2\ldots X_n)} \qquad (1)$$

The concentrations of reactants and selectivities of growing species decide upon the distribution of monomer units along the polymer chain. In this regard three polymerization models are of special interest:

(a) growing species are not selective: copolymerization takes random shape and can be conveniently described in terms of the Bernoulli statistics[6]; the

* Present address: Silcherstrasse 22, D-22761 Hamburg, Germany

distribution of monomer units in the polymer depends on the concentration $[A]$ and $[B]$ of monomers only or on the ratio $x = [A]/[B]$;

(b) the selectivity of growing species is determined by the reactivity of the terminal growing unit; this case corresponds to the terminal model and can be described by means of Markov 1 statistics; The distribution of monomer units in the polymer depends on the selectivities of the growing species: $r_A = k_{aa}/k_{ab}$ and $r_B = k_{bb}/k_{ba}$ and x (k_{ij}, propagation rate constant of radical i with monomer j)

$$P_{ab} = \frac{1}{1 + r_A x}, \quad P_{aa} = 1 - P_{ab} \tag{2}$$

$$P_{ba} = \frac{1}{1 + r_B/x}, \quad P_{bb} = 1 - P_{ba} \tag{3}$$

(under point (a) equations (2) and (3) are valid with $r_A = r_B = 1$);

(c) the reactivity of the growing terminal unit changes depending on what the penultimate unit is; this is known as the penultimate effect for which Markov 2 statistics are applicable[6]. In this case growing species are biselective. Let us consider that monomer B cannot homopropagate; then five conditional probabilities and x describe the monomer distribution in the polymer

$$P_{aab} = \frac{1}{1 + r_A x}, \quad P_{aaa} = 1 - P_{aab} \tag{4}$$

$$P_{bab} = \frac{1}{1 + r_{A'} x}, \quad P_{baa} = 1 - P_{bab} \tag{5}$$

$$P_{aba} = 1 \tag{6}$$

with $r_A = k_{aaa}/K_{aab}$ and $r_{A'} = k_{baa}/k_{bab}$ (k_{ijk} is the propagation rate constant of radical ij with monomer k).

In ref. 7 it was proposed to quantify the departure of the given reacting system from the Bernoullian statistics as

$$R_1 = \frac{R_f}{R_{f,\,\mathrm{random}}} = \frac{\mathrm{FAB} + \mathrm{FBA}}{2\mathrm{FA} \cdot \mathrm{FB}} = \frac{\mathrm{FAB}}{\mathrm{FA} \cdot \mathrm{FB}} \tag{7}$$

with R_1 = degree of randomness, R_f = sum of fractions of all A and B runs, and $R_{f,\,\mathrm{random}}$ = run fraction of a copolymer with Bernoullian (random) distribution of A and B.

For $R_1 > 1$ the polymer shows more alternating tendency and for $R_1 < 1$ it has a more block character than expected from random statistics. $R_1 = 2$ means a completely alternating copolymer and $R_1 = 0$ means a completely block copolymer or a mixture of homopolymers.

A similar idea was expressed in ref. 4 defining the degree of randomness R_1 as

$$R_1 = \frac{\mathrm{FAB} + \mathrm{FBA}}{2\mathrm{FAA} + \mathrm{FAB} + \mathrm{FBA}} + \frac{\mathrm{FAB} + \mathrm{FBA}}{2\mathrm{FBB} + \mathrm{FAB} + \mathrm{FBA}} \tag{8}$$

and further

$$R_1 = P_{ab} + P_{ba} \tag{9}$$

It can be shown that equations (7)–(9) are equivalent[7]. In ref. 4 it was found that information contained in R_1 is given from the analyses of diads, i.e. from very short sequences. Much more detailed information on the sequence structure is obtained when sequences longer than diads are considered. The author proposed to rename the degree of randomness R_1 as degree of alternation A_1 because he introduced an analogous degree of blockiness B_1 (not discussed here). The index '1' means that quantities under consideration are based on 1st order conditional probabilities [equation (9)].

For sequences longer than diads it was proposed to calculate the degree of alternation of higher orders as

$$A_2 = P_{aba} + P_{bab} \quad \text{2nd order degree of alternation} \tag{10}$$

$$A_3 = P_{baba} + P_{abab} \quad \text{3rd order degree of alternation} \tag{11}$$

.....

$$A_n = P_{aba\ldots ba} + P_{bab\ldots ab} \quad n\text{th order degree of alternation} \tag{12}$$

The usefulness of A_1, A_2 and A_3 was demonstrated on 16 model chains[4] with a wide scale of the sequence distribution.

From equations (9)–(12) it is obvious that parameters A_1–A_n can be used for model discriminations

$$A_0 = 1 = A_1 = A_2 = A_3 = \ldots A_n$$

Bernoulli process (13)

$$A_0 \neq A_1 = A_2 = A_3 \ldots A_n$$

Markov 1 process (14)

$$A_0 \neq A_1 \neq A_2 = A_3 = \ldots A_n$$

Markov 2 process (penultimate effect) (15)

.....

$$A_0 \neq A_1 \neq A_2 \neq A_3 \neq \ldots A_n$$

$(n-1)$ – ante penultimate effect (16)

Radical copolymerizations are mainly Markov 1 processes[8,9] (classical copolymerizartion model) for which

$$A_1 = P_{ab} + P_{ba} \tag{17}$$

$$A_2 = P_{bab} + P_{aba} = P_{ab} + P_{ba} \tag{18}$$

$$A_3 = P_{abab} + P_{baba} = P_{ab} + P_{ba} \tag{19}$$

.....

$$A_n = P_{ab} + P_{ba} \tag{20}$$

As a result the degree of alternation A of higher order than 2 is independent of sequence length and does not allow a more precise characterization of the sequence distribution.

Let us consider Markov 2 processes (effect of penultimate units) in copolymerization of monomers A and B

$$A_1 = P_{ab} + P_{ba} \tag{21}$$

$$A_2 = P_{bab} + P_{aba} \tag{22}$$

$$A_3 = P_{abab} + P_{baba} = P_{bab} + P_{aba} \tag{23}$$

$$A_4 = P_{babab} + P_{ababa} = P_{bab} + P_{aba} \tag{24}$$

.....

$$A_n = P_{bab} + P_{aba} \tag{25}$$

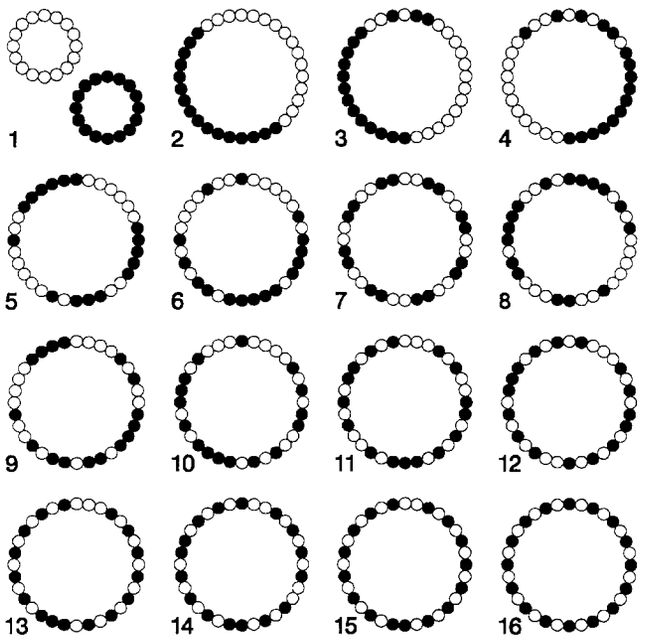

Figure 1 Model chains cited from ref. 4; equimolar copolymers with 16 units of *A* (○) and 16 units of *B* (●)

For this model it follows that the degree of alternation of higher order than 3 does not contribute new information on the sequence structure. Generally it must be stated that the need for higher order degree of alternation increases for higher order models, but exactly in this domain the degree of alternation fails.

To overcome this dilemma it is proposed to make use of degree of randomness formulated in ref. 4 and given in equation (8). In application to the second and third order degree of randomness one obtains:

$$R_2 = \frac{\mathrm{FABA} + \mathrm{FBAB}}{2\mathrm{FAAA} + \mathrm{FABA} + \mathrm{FBAB}} + \frac{\mathrm{FABA} + \mathrm{FBAB}}{2\mathrm{FBBB} + \mathrm{FABA} + \mathrm{FBAB}} \quad (26)$$

$$R_3 = \frac{\mathrm{FBABA} + \mathrm{FABAB}}{2\mathrm{FAAAA} + \mathrm{FBABA} + \mathrm{FABAB}} + \frac{\mathrm{FBABA} + \mathrm{FABAB}}{2\mathrm{FBBBB} + \mathrm{FBABA} + \mathrm{FABAB}} \quad (27)$$

and successively higher order degree of randomness can be formulated. It can be shown that:

$$R_1 = A_1$$

$$R_2 \neq A_2$$

$$R_3 \neq A_3$$

$$\cdots\cdots\cdots$$

$$R_n \neq A_n$$

i.e. the *R* series does not have the properties of the *A* series.

In the following sections the properties of both series are compared.

MODEL CHAINS TAKEN OUTSIDE OF STANDARD POLYMERIZATION MODELS

Model chains proposed in ref. 4 were used to compare how both degree of randomness and degree of alternation of first to third order describe the sequence distribution in a binary copolymer. These chains are presented in *Figure 1*. The cyclic structure was chosen to exclude any chain end effects on chain statistics and stands for infinite chain length.

Degrees of randomness of first to third order (R_1–R_3) and degrees of alternation of first to third order (A_1–A_3) taken from ref. 4 are summarized in *Table 1*.

From comparison of *R* with *A* values in *Table 1* the following conclusions may be drawn.

(1) For $R_n = 0$ no alternating sequences at the sequence length level $n+1$ are contained in the polymer. For chain No. 2 only a low content of alternating diads, but no alternating triads or tetrads are given. In chain No. 3 only few alternating triads and tetrads are represented (in each case one) in the polymer.

(2) The *R* values describe in much more nuanced manner the blocked character of polymers 3–6. A_3 values suggest a very random (not predominantly blocked or alternating) structure of polymers 3 and 4, $A_3 = 1$ (and equally 5 and 6). Without any doubt these structures have predominantly blocked structure. This fact is well accentuated by *R* values rapidly decreasing with increasing order. This means that long blocks predominate in the polymer under consideration.

Table 1 Degree of randomness of first to third order and degree of alternation of first to third order calculated for model chains Nos 1–16 presented in *Figure 1*

	Chain No.															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Degree of randomness																
R_1	0.	0.125	0.375	0.625	0.625	1.000	1.000	1.000	1.000	1.250	1.500	1.625	1.750	1.750	1.875	2.000
R_2	0.	0.	0.167	0.500	0.334	1.000	–	1.000	1.000	1.400	1.800	1.833	1.857	2.000	2.000	2.000
R_3	0.	0.	0.182	0.250	0.182	0.583	–	1.000	0.667	1.636	2.000	2.000	2.000	2.000	2.000	2.000
Alternation																
A_1	0.	0.126	0.376	0.626	0.626	1.000	1.000	1.000	1.000	1.250	1.500	1.624	1.750	1.750	1.874	2.000
A_2	0.	0.	0.666	1.200	0.600	1.250	–	1.000	1.000	1.400	1.500	1.692	1.858	1.714	1.866	2.000
A_3	0.	0.	1.000	1.000	0.750	0.800	–	1.000	0.750	1.286	1.444	1.636	1.846	1.666	1.858	2.000

Table 2 Chain statistics for three binary copolymers calculated in terms of the terminal and simplified penultimate ($r_2 = 0$) copolymerization models

Quantity or parameter	System		
	Monomer A: St[10] Monomer B: AN	*p*-ClSt[11] i-butylene	St[12] FN
Monomer feed mol fraction:			
A	0.24	0.85	0.619
B	0.76	0.15	0.381
Polymer composition mol fraction:			
A	0.50	0.50	0.60
B	0.50	0.50	0.40
r_A	0.40	0.7	$r_A = 0.054$
r_B	0.04	22.5	$r'_A = 0.524$
Run number	88.77	20.13	80.00
Average sequence length			
l_A	1.126	4.969	1.500
l_B	1.126	4.969	1.000
Degree of randomness:			
$R_1 = A_1$	1.775	0.403	1.667
R_2	1.968	0.119	1.950
R_3	1.913	0.031	1.994
Degree of alternation			
A_2	1.775	0.403	1.540
A_3	1.775	0.403	1.540

(3) The alternating structure of polymer chains increases from structures 10 to 16 successively reaching full alternation for chains No. 16. All A values increase simultaneously departing from 1 and reaching 2 for the last structure. However, there are practically no differences between A_1, A_2 and A_3 within one particular model chain suggesting that there are no differences in alternation (blockiness) when longer sequences are considered.

Conversely, R values increase in succession R_1, R_2, R_3 for each chain rapidly and indicate an almost total absence of blocks longer than 4.

If the degree of randomness of nth order reaches the value 2.00, that means that blocks of length $n+1$ or longer are not more contained in the polymer, i.e. we obtain detailed information on the sequence structuring in a polymer chain when a series of R values is available.

These values are, therefore, of special interest in application to the classical and penultimate models since the A series cannot provide any supplementary information on alternation for sequences longer than diads.

CHAINS CALCULATED IN TERMS OF THE CLASSICAL MODEL

In the following section, the degree of randomness of first to third order is discussed. Interested users should, however, take into consideration higher degrees of randomness if needed. For all calculations the assumption of infinite chain length is valid.

Starting from equations (8), (26) and (27) and applying conditional probabilities given in equations (2) and (3) one obtains analytical expressions for R_1, R_2 and R_3 with $a = 1 + r_A x$ and $b = 1 + r_B/x$

$$R_1 = A_1 = \ldots = A_n = \frac{1}{a} + \frac{1}{b} \tag{28}$$

$$R_2 = \frac{a+b}{2b(r_A x)^2 + a + b} + \frac{a+b}{2a(r_B/x)^2 + a + b} \tag{29}$$

$$R_3 = \frac{a}{b(r_A x)^3 + a} + \frac{b}{a(r_B/x)^3 + b} \tag{30}$$

A typical copolymer with a prevalent alternating sequence structure will be compared with a copolymer having a blocked sequence structure. For simplification copolymers with the 1/1 mol ratio of both comonomers in the polymer are considered. Under this condition the distribution of A and B sequence lengths are equal to each other and both comonomers do not need to be considered separately.

Terminal model/alternating system

The system styrene (St, A)/acrylonitrile (AN, B) with $r_A = 0.40$ and $r_B = 0.04$ was chosen from the literature[10] as a system yielding alternating copolymers. As it mainly follows from *Table 2*, very short sequence length of A and B is obtained in polymers consisting of equimolar amounts of A and B. The run number about 90 lies near the maximum value of 100 and suggests a very progressed alternation of comonomer units in the polymer. This is very well underlined in terms of the degree of randomness which increases rapidly passing from R_1 to R_2 and R_3. The last two values are greater than 1.9, which means that only a few A or B block triads or tetrads are given in the polymer, i.e. the polymer has a predominant alternating structure.

The A_i values do not change.

Terminal model/system with blocked structure

Changes in higher order R than 1 for a polymer with blocked structure are discussed on the system *p*-chloro styrene (*p*-ClSt, *A*)/iso-butylene (*B*) polymerized in the presence of $AlBr_3$ at 0°C[11]. For a polymer consisting of equimolar amounts of comonomers average sequence length of nearly 5 and a low run number ≈ 20 are obtained (see chain statistics in *Table 2*, third column). Both numbers suggest a blocked character of the copolymer. The degree of randomness decreases markedly with increasing order. $R_3 = 0.031$ means that only a few strictly alternating tetrads can be found in the polymer. All these numbers agree with each other.

The A_i values do not change.

Simplified penultimate model/alternating system

In cases where B cannot homopolymerize a simplified penultimate model can be used, since the relative reactivity ratios corresponding to monomer B, r_B and r'_B are equal to zero[12,13].

Using definitions (8), (26) and (27) and conditional probabilities given in equations (4)–(6) equations for R_1 to R_3 are obtained with $a = 1 + r_A x$ and $c = 1 + r'_A x$ as

$$R_1 = \frac{c}{r'_A x \cdot a + c} + 1 \tag{31}$$

$$R_2 = \frac{c + 1}{2 r_A x \cdot r'_A x + c + 1} + 1 \tag{32}$$

$$R_3 = \frac{a}{r'_A x (r_A x)^2 + a} + 1 \tag{33}$$

Equations (31)–(33) are tested on the system St/fumaronitrile (FN)[14] assuming that the copolymer consists of 60 mol% of styrene. Calculated chain statistics including R-values are listed in *Table 2*, last column. It follows from a relatively high run number (80.0) and low values of average sequence length that the copolymer has a predominantly alternating structure. This fact is expressed by R-values very well. They increase markedly with order and reach the value of 1.994 at the level of the third order. It means that blocks of four identical monomer units (and longer) are practically not represented in the copolymer.

Calculations of the sequence length distribution show that only 2.7 mol% of A are contained in four-unit-blocks and only 0.2 mol% in five-unit-blocks. B is bound in the polymer as isolated units.

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