

Theory of Markov chain copolymerization in terms of an intermonomer correlation coefficient and the arrangement of monomers along the polymer chain

Norbert Stribeck

*Institut für Technische und Makromolekulare Chemie, Universität Hamburg,
Bundesstr. 45, 0-2000 Hamburg 13, Germany*

(Received 19 June 1991; revised 19 August 1991; accepted 2 October 1991)

A binary copolymer chain is treated theoretically in the approximation of a first order Markov process. The microstructure of the chain is described in terms of the mole fraction of the dilute monomer and an intermonomer correlation coefficient. The resulting equation for the sequence distribution shows some symmetry in both parameters. It thus offers the possibility to separate influences of copolymer composition on one hand and the distribution of the monomer run lengths along the chain on the other hand. The connection of this formalism to n.m.r. dyad analysis and the classical copolymerization parameters is shown.

(Keywords: copolymerization theory; Markov chain; microstructure; sequence statistics)

INTRODUCTION

The classical theory of copolymer microstructure is described in a number of books¹⁻³. It was developed from the process of chemical synthesis and ends in a description of copolymer microstructure. This paper proceeds in the reverse direction and first describes the copolymer by its composition and order. Order, i.e. the arrangement of monomers along the polymer chain, is discussed in terms of a correlation coefficient, κ . The deduction ends in an equation for the sequence length distribution, which shows a way to separate the effects of composition and order on the properties of the copolymer. Following this deduction the correlation coefficient κ is connected to the classical theory by expressing it in terms of the copolymerization parameters.

The probability considerations of the deduction use the sum of the monomers in the polymer (degree of polymerization) as the basic entity. This leads to a straightforward construction principle for deduced probabilities. The corresponding steps can easily be translated into a computer simulation program. Additionally, if the mean degree of polymerization is given, this formalism allows simple computation of the frequencies of isolated sequences in the average chain.

NOMENCLATURE AND PREMISES

Let us consider a binary copolymer from two kinds of monomers, A and B. Effects of chain ends shall be neglected, but an intermonomer correlation shall be allowed, resulting in some kind of order along the chain. The letter A shall be used as a variable which can take one of the two values A or B.

Let (A) designate the number of monomers of the kind A from the ensemble of monomers in the polymer chain. Then the whole ensemble contains (A) + (B) members.

Because of the possible interdependence between both kinds of monomers it appears reasonable to carry out deductions with respect to this ensemble.

Let (AA) be defined as the number of sequences in the ensemble consisting of double A with both neighbours of the sequences being indeterminate (a dyad). The dyads (BB), (AB) and (BA) shall be written in analogy. Trivially for the ensemble the following equation holds:

$$(A) + (B) = (AA) + (AB) + (BA) + (BB) \quad (1)$$

The number of sequences in the ensemble consisting of n monomers A, which are delimited by its comonomer B at both ends, shall be written in brackets as $[A^n]$. These sequences shall be named isolated sequences.

The letter p shall denote a probability; the function $s_A(n)$ stands for the special probability of finding an isolated sequence $[A^n]$. Written in lower case letters, these quantities refer to the ensemble (A) + (B).

$S_A(n)$, in capital letters, shall be defined as the probability of finding one of the sequences $[A^n]$ with respect to all the sequences in the ensemble. Thus $S_A(n)$ is the common sequence distribution of the monomer A.

Let us consider the case in which the probability of monomer addition to the growing chain is merely controlled by the nature of its actual terminate monomer. This is the so-called first order Markov chain.

SEQUENCE DISTRIBUTIONS

Two groups of quantities, namely composition (amount of the monomers) and order (monomer placement) describe the copolymer. For the considered simple model the mole fraction φ_A of monomer A in the copolymer shall be chosen to describe the composition, while a correlation coefficient κ serves to describe the order. With

the above nomenclature, φ_A is given by:

$$\varphi_A = \frac{(A)}{(A) + (B)} \quad (2)$$

and

$$\varphi_B = 1 - \varphi_A$$

The simplest model for copolymerization is that of a random or Bernoulli process. For a given random chain the probability of adding any kind of monomer to the growing chain end has been independent from its predecessor. Thus the probability for the addition of a monomer A has been $p_A = \varphi_A$. The more complex model of a first order Markov chain can be described by four probabilities which are bound by two constraints^{4,5}.

Let us now introduce the correlation coefficient κ and write down the resulting probabilities. $p_{A+}(\kappa)$ shall be defined as the probability that at the growing polymer chain, actually ending in monomer A, a monomer of the same kind is added. $p_{A-}(\kappa)$ shall denote the probability for the other possible case, namely the addition of the comonomer B to the growing chain end.

Let us define κ in the way customary for correlation coefficients and demand that $\kappa = 0$ defines the Bernoulli chain without intermonomer correlations. Furthermore let $\kappa = 1$ describe perfect correlation. This means that positive values of κ describe a copolymer with a blocky tendency, while negative values of κ will result in a chain with alternating tendency.

Assuming $p_{A+}(\kappa)$ to be a linear function of κ one writes:

$$p_{A+}(\kappa) = \varphi_A + \kappa(1 - \varphi_A) \quad (3a)$$

$$\kappa \in \left[-\frac{\varphi_A}{1 - \varphi_A}, 1 \right] \quad (3b)$$

$$p_{A-}(\kappa) = 1 - p_{A+}(\kappa) \quad (3c)$$

This definition of p_{A+} is the simplest notation which assures that for $\kappa = 0$ and $\kappa = 1$ one obtains the necessary behaviour for a random chain ($p_{A+} = \varphi_A$) and a block copolymer ($p_{A+} = 1$), respectively. Beyond this, it appears natural to choose a formulation in which the statistical quantities (i.e. the probabilities for agglomeration or segregation) are linear functions of the controlling correlation coefficient. Finally, any definition has to be consistent in itself. For the present approach, self-consistency means that the number of (AB) dyads has to be equal to the number of (BA) dyads (after a transition into B, a transition back to A has to follow). The verification that the chosen definition implies this condition will be shown in the following (equation (9b)).

Without loss of generality φ_A may be chosen as the smaller mole fraction of the two, guaranteeing that κ will not be less than -1 . Restriction (3b) is necessary to obtain probabilities in the allowed range $[0, 1]$. As will be clear from the following treatment, the physical meaning of (3b) is that the average length of the isolated sequences of the dilute monomer fraction cannot be less than 1.

Let us now construct the probability $s_A(n)$ in order to obtain the sequence distribution. The construction proceeds in four steps:

1. find any comonomer B in the chain

$$s_A(n) = (1 - \varphi_A) \dots$$

2. at which a monomer A is coupled

$$s_A(n) = (1 - \varphi_A)p_{B-}(\kappa) \dots$$

3. with $(n - 1)$ trailing monomers A

$$s_A(n) = (1 - \varphi_A)p_{B-}(\kappa)[p_{A+}(\kappa)]^{n-1} \dots$$

4. and a terminator B

$$s_A(n) = (1 - \varphi_A)p_{B-}(\kappa)[p_{A+}(\kappa)]^{n-1}p_{A-}(\kappa)$$

With equation (3) one obtains:

$$s_A(n) = \varphi_A(1 - \varphi_A)^2(1 - \kappa)^2 \times [1 - (1 - \varphi_A)(1 - \kappa)]^{n-1}$$

and, with the shorthand notation:

$$\langle S_A \rangle_n = \frac{1}{1 - \varphi_A} \frac{1}{1 - \kappa} \quad (4)$$

we have

$$s_A(n) = \varphi_A \frac{1}{\langle S_A \rangle_n^2} \left(1 - \frac{1}{\langle S_A \rangle_n} \right)^{n-1} \quad (5)$$

It can be verified that equation (4) introduces not only a shorthand notation, but also has the physical meaning of the number average sequence length. Only an outline of the verification shall be given here. Since the number average sequence length is the first momentum of $s_A(n)$, it can be computed using the mathematical definition of the first momentum of $s_A(n)$

$$\left[\sum_{n=1}^{\infty} n s_A(n) \right] / \left[\sum_{n=1}^{\infty} s_A(n) \right]$$

One only has to insert equation (5) and use a well known mathematical technique¹. Equation (5) describes the amount of isolated sequences of length n with respect to the ensemble of polymerized monomers (A) + (B). For $\kappa = 0$ we obtain the known mean sequence length of a Bernoulli chain:

$$\langle S_A \rangle_n = 1/(1 - \varphi_A)$$

The sequence length distribution $S_A(n)$ with respect to the number of isolated sequences can now be easily obtained from $s_A(n)$. From the definition of both distributions, it follows that:

$$S_A(n) = s_A(n) / \sum_{n=1}^{\infty} s_A(n)$$

is valid. Carrying out this computation yields:

$$S_A(n) = \frac{1}{\langle S_A \rangle_n} \left(1 - \frac{1}{\langle S_A \rangle_n} \right)^{n-1} \quad (6)$$

Or, in a more intuitive approach: let $M = (A) + (B)$ be the number of monomers in the chain, then for any fixed n , $M s_A(n) = [A^n]$ gives the number of isolated sequences of run length n . The basic entity for $S_A(n)$, on the other hand, is the total number of isolated sequences:

$$\sum_{n=1}^{\infty} [A^n] = M \varphi_A / \langle S_A \rangle_n$$

Thus, with respect to $\langle S_A \rangle_n$:

$$[A^n] = (M \varphi_A / \langle S_A \rangle_n) S_A(n)$$

Combination of both formulations for $[A^n]$ leads to equation (6).

$\langle S_A \rangle_n$ is the first momentum of the sequence

distribution. For completeness the next two higher momenta of $S_A(n)$, the weight average $\langle S_A \rangle_w$ and the 'z-average' $\langle S_A \rangle_z$ shall be given here, although there is no difference to the known equations for a random chain, if these equations are expressed recursively in terms of $\langle S_A \rangle_n$:

$$\langle S_A \rangle_w = 2\langle S_A \rangle_n - 1 \quad (7)$$

$$\langle S_A \rangle_z = \frac{6\langle S_A \rangle_n^4 - 6\langle S_A \rangle_n - 1}{\langle S_A \rangle_w} \quad (8)$$

These equations can also be deduced using the general definitions of the momenta, equation (5) and the well known mathematical technique of Koenig¹.

DYAD PROBABILITIES

The method usually applied for analysis of the sequence distributions in a copolymer is ¹³C n.m.r. This method gives access to the frequencies of dyads and other parameters.

With equation (3) and the evident simple construction principle we find:

$$p_{AA} = \varphi_A p_{A-} = \varphi_A^2 + \varphi_A(1 - \varphi_A)\kappa \quad (9a)$$

for the probability of finding an (AA) dyad in the chain. The corresponding probability p_{BB} follows after exchanging the letter A by the letter B in equation (9a). For the mixed dyads we obtain:

$$\begin{aligned} p_{AB} &= \varphi_A p_{A-} = \varphi_A(1 - \varphi_A)(1 - \kappa) \\ p_{BA} &= \varphi_B p_{B-} = \varphi_A(1 - \varphi_A)(1 - \kappa) \end{aligned} \quad (9b)$$

The identity $p_{AB} = p_{BA}$, resulting without additional assumption, is the necessary steady-state condition⁶ for the first order Markov chain.

If one knows at least the probability of the mixed dyads and one of the probabilities of the plain dyads, it is possible to compute the correlation parameter κ and thus the complete sequence distribution, if the copolymer follows a first order Markov process.

For application in our working group we refer to the work of McFarlane⁷. For this method the dyad frequencies p_{AA} and $2p_{AB}$ have to be determined. McFarlane defines a primary correlation factor α :

$$\alpha = \frac{p_{AA}}{p_{AA} + 2p_{AB}} \quad (10)$$

With this α he defines his final correlation factor Ψ by:

$$\Psi = \frac{\alpha - \alpha^0}{\alpha^1 - \alpha^0} = \frac{\alpha - \alpha^0}{1 - \alpha^0} \quad (11)$$

Here the superscripts denote the limiting cases for a random copolymer (α^0) and a totally blocky one (α^1). While the copolymer varies from random to blocky, Ψ , as well as the correlation coefficient κ , runs from 0 to 1. α^1 is 1, because in this case $p_{AB} = 0$. With equation (9) and the definitions of McFarlane we find for the dependence of these correlation parameters:

$$\Psi = \frac{\kappa}{1 + (1 - \varphi_A)(1 - \kappa)} \quad (12)$$

and vice versa:

$$\kappa = \frac{\varphi_B + 1}{\varphi_B + 1/\Psi} \quad (13)$$

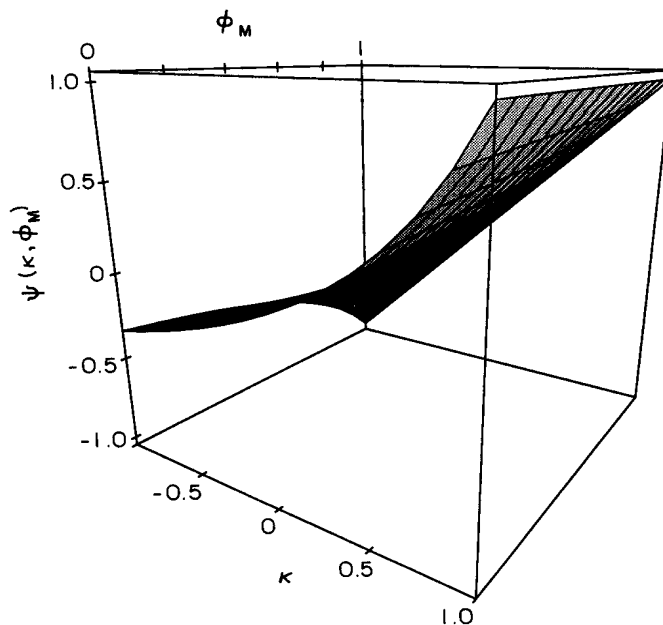


Figure 1 Order parameter, $\Psi(\kappa, \varphi_A)$, from dyad analysis (according to McFarlane⁷) of a copolymer generated by a first order Markov process. Ψ is a function of the intermonomer correlation κ and the mole fraction φ_A . Copolymers with negative κ and Ψ tend towards alternation of the monomers. Positive κ or Ψ denotes blocky character of the copolymer

For positive values of Ψ one can obtain the correlation parameter κ with almost the same precision as the precision of the measured Ψ . If, on the other hand, Ψ is negative, one should be careful in the determination of κ from Ψ . Let us consider the case where the determined value of Ψ is negative, and the mole fraction of the monomer corresponding to the measured plain dyad is smaller than 0.4. In this case we do not only have a small n.m.r. signal, but also $\kappa(\Psi)$ is a slowly varying function. A determination of κ with sufficient precision should be rather difficult.

Thus Ψ is a good experimental basis for the computation of κ , if the copolymer is ranging from random to blocky. In the case of an alternating tendency, we have to demand $\varphi_A > 0.4$. If this is not the case, measurement of the (BB) dyad frequency is needed. The function $\Psi(\kappa, \varphi_A)$ is plotted in Figure 1.

RELATIONS TO THE CLASSICAL APPROACH

The classical approach to copolymerization theory^{1,2} is deduced from the chemical process and finally describes the copolymer in terms of mole fraction and chain statistics. According to the classical approach the first order Markov chain is described by two parameters: $f = \varphi_A/\varphi_B$ is the molar ratio in the copolymer and $r_A r_B$ is the product of the copolymerization parameters (reactivity ratios). f is a common composition parameter, while $r_A r_B$ determines the order within the copolymer from the point of view of the synthesizing chemist. Let us now deduce the relation between the correlation coefficient κ and the product of reactivity ratios. The following deduction is based on the equations given by Tosi⁸, who has used the equations of Fineman and Ross⁹ for numerical calculations of sequence distributions.

For the probability p_{A+} (p_{11} in the notation of Tosi⁸) the following equation is valid:

$$p_{A+} = \frac{r_A F}{r_A F + 1} \quad (14)$$

Equation (3a) links κ to equation (14). The product $r_A F$ in the above equation is given by:

$$r_A F = \frac{1}{2} [f - 1 + \sqrt{(f - 1)^2 + 4r_p f}] \quad (15)$$

where $r_p = r_A r_B$ is defined for ease of writing. A combination of equations (3a), (14) and (15) results in:

$$\kappa = \frac{\sqrt{1 + 4\varphi_A(1 - \varphi_A)(r_p - 1)} - 1}{\sqrt{1 + 4\varphi_A(1 - \varphi_A)(r_p - 1)} + 1} \quad (16)$$

and *vice versa*:

$$r_p = 1 + \frac{\kappa}{\varphi_A(1 - \varphi_A)(1 - \kappa)^2} \quad (17)$$

The function $r_p(\varphi_A, \kappa)$, given in equation (17), describes the relation between synthesis and the resulting structure under the assumption of a first order Markov process. Only for positive values of r_p is it of physical sense. For negative values of r_p the average sequence length of the dilute monomer drops below 1. If we are synthesizing a copolymer using a first order Markov process with a well defined structure, we should fix r_p during synthesis and, furthermore, should be able to reproduce it. In practice, these demands can only be fulfilled approximately. An impression of the influence of small variations of r_p on the resulting structure can be gained by partial derivation of equation (17) with respect to κ , yielding:

$$\partial\kappa = \varphi_A(1 - \varphi_A) \frac{(1 - \kappa)^3}{1 + \kappa} \partial r_p \quad (18)$$

From this equation the influence of a variation of r_p on the order parameter κ can be determined, if we assume that φ_A can be controlled perfectly.

CONCLUSIONS

The approach presented in this paper offers the possibility to determine a well defined correlation coefficient κ from

dyad analysis of a given copolymer, if the composition of the copolymer is known. κ is a measure of the order in the copolymer. Data analysis based on this approach can be carried out to describe the arrangement of the monomers along the chain by a number, which is closely connected to the process of monomer addition in a first order Markov process.

In this paper the sequence distribution for the first order Markov chain has been expressed in terms of the parameters φ_A and κ , resolving an interesting symmetry. Since the sequence distribution is a function of only the product $(1 - \varphi_A)(1 - \kappa)$, the shape of the function remains the same, if only this product remains constant. Thus it may be possible to separate the influence of composition (φ_A) and order (distribution $S_A(n, \varphi_A, \kappa)$) on the properties of the copolymer material. To achieve this, one would have to study series of copolymers, where the product $(1 - \varphi_A)(1 - \kappa)$ varies from series to series.

Since the sequence distribution has been deduced in analytical form, it is possible to develop it into the series of its momenta. If one concerns a copolymer where monomer A is deuterated, the second momentum of the sequence distribution, $\langle S_A \rangle_w$ (see equation (7)) can be measured directly by neutron scattering¹⁰. Thus if we have measured $\langle S_A \rangle_w$, we can compute κ using equations (7), (4) and φ_A . So the neutron scattering experiment can give quantitative information on the arrangement of monomers along the copolymer chain. If κ has been determined independently by n.m.r. measurement and dyad analysis, even the assumption of a first order Markov process can be tested.

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