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Characterization of Copolymer Chains Based on Probabilities of Sequences Longer than Diads

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SUMMARY

A degree of alternation has been introduced in the paper as a useful "one-number" parameter characterizing the microstructure of a copolymer chain and replacing the degree of randomness. Based on a concept of alternation of comonomer units along the macromolecular chain the degree of alternation can be calculated for experimentally accessible sequences of any length.

INTRODUCTION

Physical properties of polymers depend among other factors on the macromolecular chain microstructure which can be statistically described using sequence probabilities (HAM 1964) experimentally obtained predominantly by NMR spectroscopy (BOVEY 1969,1972, HARWOOD 1972, KLESPER and SIELAFF 1974, SLONIM and URMAN 1982). At a given level of sequence determination a polymer can be shown to be consistent or inconsistent with a given statistical model. However, there is always the possibility that examination of higher sequences may reveal inconsistencies with a proposed model and ambiguities in copolymer characterization may arise. The knowledge of probabilities for all sequences provides a full description of the chain, nevertheless, several "one-number" parameters are useful and sometimes sufficient for a simple characterization of copolymers. Such parameters frequently used are: average block length, run number (HARWOOD and RITCHEY 1964), persistence ratio (COLEMAN and FOX 1963a,b), and degree of randomness (YAMADERA and MURANO 1967). The latter is commonly used for characterizing sequence distribution in condensation copolymers (YAMADERA and MURANO 1967, HAMB 1972, KORSHAK et al. 1973, MATLENGIEWICZ et al. 1979) and was defined by YAMADERA and MURANO (1967) as follows:

$$R = \frac{P(\overleftrightarrow{AB})}{2P(AA) + P(\overleftrightarrow{AB})} + \frac{P(\overleftrightarrow{AB})}{2P(BB) + P(\overleftrightarrow{AB})}$$

where:

R - degree of randomness (B instead R has been used in the original paper by YAMADERA and MURANO 1967)

$P(\overleftrightarrow{AB}) = P(AB) + P(BA)$ (For notation cf. KLESPER and SIELAFF 1974)

Numerical values of R, ranging from 0.0 to 2.0 , provide information about the distribution of comonomer units. For a mixture of homopolymers R = 0; for a random distribution of comonomer units R = 1.0 and for alternating chain R = 2.0 , The degree of randomness cannot precisely describe a chain because it is calculated using diad probabilities only, and even for significantly different chains, identical values of R can be obtained. An antepenultimate effect (FRISCH et al. 1965) is a good example of ambiguities which may arise when only diad probabilities are observed. For a "bialternating" copolymer chain

-AABBAABBAABBAABBAABBAABB-

the degree of randomness, which is equal to 1.0 , indicates random distribution of comonomer units while the chain is highly ordered. Only examination of sequences longer than diads can indicate the difference.

As long as only diads were experimentally accesible to investigations, the degree of randomness was sufficient to characterize the chain of condensation copolymer. But since NMR spectroscopy provides signals of longer sequences, i.e. triads and tetrads (MATLENGIEWICZ and TURSKA 1982) there is a possibility to extend the characterization introducing a parameter based on the probabilities of higher sequences.

DEGREE OF ALTERNATION AND DEGREE OF BLOCKINESS

Let's consider for example the model chains of an equimolar copolymer choosen to cover the whole range of degree of randomness from 0.0 to 2.0 (Figure 1). It can be seen from Fig.1 that for a given degree of randomness it is possible to create several quite different chains. A cyclic chain can be taken as a model of indefinitely long polymer chain, because there is

no end effect, hence, probabilities of sequences of various lengths can be readily calculated from Fig. 1 as fractions of respective sequences. Using the sequence probabilities the conditional probabilities can be calculated (KLESPER and SIELAFF 1974). First, second and third order conditional probabilities calculated for the model chains have been presented in Table I, overleaf.

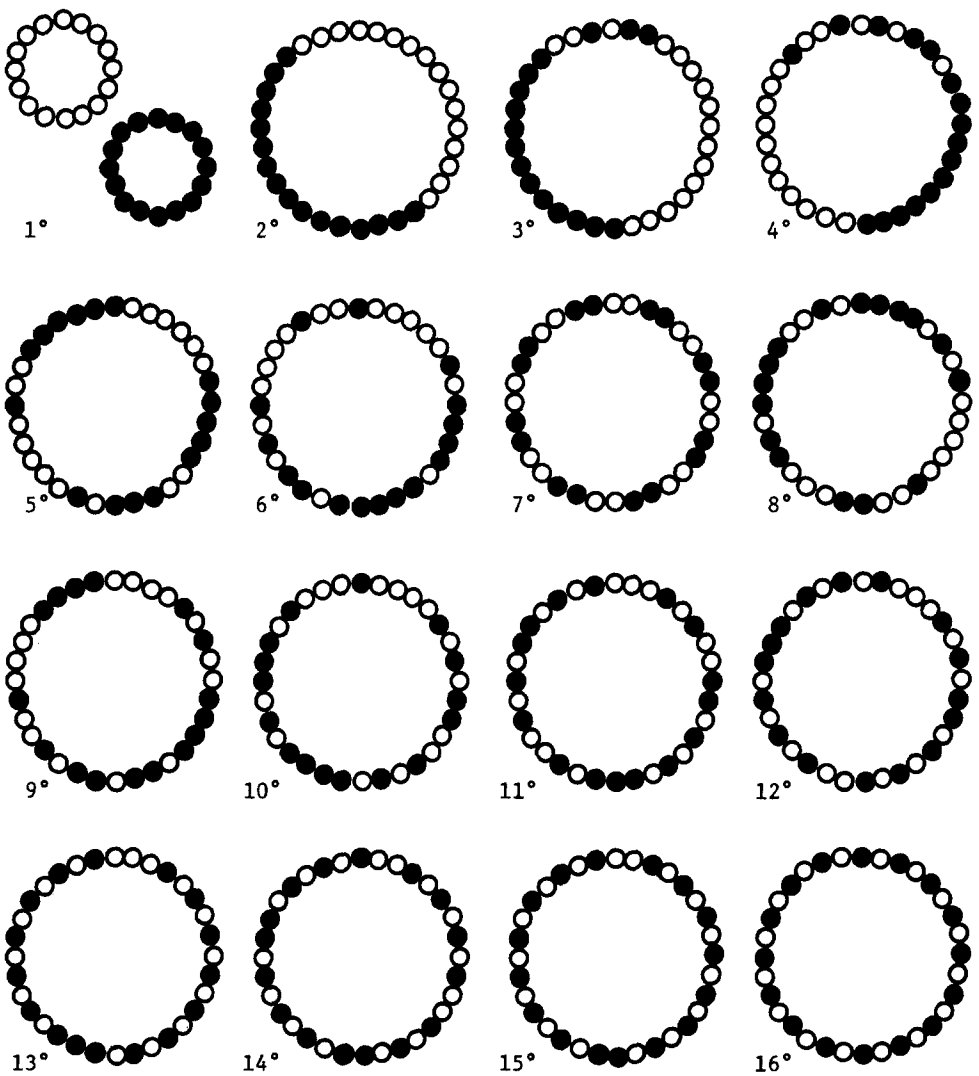

Fig. 1 Model chains of an equimolar copolymer - 16 A [○] + 16 B [●]

TABLE I

1st, 2nd and 3rd Order Conditional Probabilities Calculated for the Model Chains

P()	1°	2°	3°	4°	5°	6°	7°	8°	9°	10°	11°	12°	13°	14°	15°	16°
P(A/A)	1.000	0.937	0.812	0.687	0.687	0.500	0.500	0.500	0.500	0.375	0.250	0.188	0.125	0.125	0.063	0.000
P(B/A)	0.000	0.063	0.188	0.313	0.313	0.500	0.500	0.500	0.500	0.625	0.750	0.812	0.875	0.875	0.937	1.000
P(A/B)	0.000	0.063	0.188	0.313	0.313	0.500	0.500	0.500	0.500	0.625	0.750	0.812	0.875	0.875	0.937	1.000
P(B/B)	1.000	0.937	0.812	0.687	0.687	0.500	0.500	0.500	0.500	0.375	0.250	0.188	0.125	0.125	0.063	0.000
P(AA/A)	1.000	0.933	0.846	0.818	0.636	0.625	0.000	0.500	0.500	0.500	0.250	0.333	0.500	0.000	0.000	-
P(AB/A)	-	0.000	0.333	0.600	0.400	0.625	0.000	0.500	0.500	0.700	0.750	0.846	0.929	0.857	0.933	1.000
P(BA/A)	-	1.000	0.667	0.400	0.800	0.375	1.000	0.500	0.500	0.300	0.250	0.154	0.071	0.143	0.067	0.000
P(BB/A)	0.000	0.067	0.154	0.182	0.273	0.375	1.000	0.500	0.500	0.500	0.750	0.667	0.500	1.000	1.000	-
P(AA/B)	0.000	0.067	0.154	0.182	0.364	0.375	1.000	0.500	0.500	0.500	0.750	0.667	0.500	1.000	1.000	-
P(AB/B)	-	1.000	0.667	0.400	0.600	0.375	1.000	0.500	0.500	0.300	0.250	0.154	0.071	0.143	0.067	0.000
P(BA/B)	-	0.000	0.333	0.600	0.200	0.625	0.000	0.500	0.500	0.700	0.750	0.846	0.929	0.857	0.933	1.000
P(BB/B)	1.000	0.933	0.846	0.818	0.727	0.625	0.000	0.500	0.500	0.500	0.250	0.333	0.500	0.000	0.000	-
P(AAA/A)	1.000	0.929	0.909	0.889	0.714	0.600	-	0.500	0.500	0.333	0.000	0.000	0.000	-	-	-
P(BAA/A)	-	1.000	0.500	0.500	0.500	0.667	0.000	0.500	0.500	0.667	0.333	0.500	1.000	0.000	0.000	-
P(ABA/A)	-	-	0.500	0.500	0.750	0.600	-	0.500	0.625	0.357	0.278	0.182	0.077	0.167	0.071	0.000
P(AAB/A)	-	0.000	0.250	0.750	0.375	1.000	0.000	0.500	0.625	0.833	0.833	1.000	1.000	1.000	1.000	-
P(BBA/A)	-	1.000	0.750	0.250	0.833	0.000	1.000	0.500	0.375	0.167	0.167	0.000	0.000	0.000	0.000	-
P(BAB/A)	-	-	0.500	0.500	0.500	0.400	-	0.500	0.375	0.643	0.722	0.818	0.923	0.833	0.929	1.000
P(ABB/A)	-	0.000	0.500	0.500	0.000	0.333	1.000	0.500	0.500	0.333	0.667	0.500	0.000	1.000	1.000	-
P(BBB/A)	0.000	0.071	0.091	0.111	0.375	0.400	-	0.500	0.500	0.667	1.000	1.000	1.000	-	-	-
P(AAA/B)	0.000	0.071	0.091	0.111	0.286	0.400	-	0.500	0.500	0.667	1.000	1.000	1.000	-	-	-
P(BAA/B)	-	0.000	0.500	0.500	0.500	0.333	1.000	0.500	0.500	0.333	0.667	0.500	0.000	1.000	1.000	-
P(ABA/B)	-	-	0.500	0.500	0.250	0.400	-	0.500	0.375	0.643	0.722	0.818	0.923	0.833	0.929	1.000
P(AAB/B)	-	1.000	0.750	0.250	0.625	0.000	1.000	0.500	0.375	0.176	0.167	0.000	0.000	0.000	0.000	-
P(BBA/B)	-	0.000	0.250	0.750	0.167	1.000	0.000	0.500	0.625	0.833	0.833	1.000	1.000	1.000	1.000	-
P(BAB/B)	-	-	0.500	0.500	0.500	0.600	-	0.500	0.625	0.357	0.278	0.182	0.077	0.167	0.071	0.000
P(ABB/B)	-	1.000	0.500	0.500	1.000	0.667	0.000	0.500	0.500	0.667	0.333	0.500	1.000	0.000	0.000	-
P(BBB/B)	1.000	0.929	0.909	0.889	0.625	0.600	-	0.500	0.500	0.333	0.000	0.000	0.000	-	-	-

TABLE II

1st, 2nd and 3rd Order Degree of Alternation, and Averaged Degree of Alternation Calculated for the Model Chains

Parameter	1°	2°	3°	4°	5°	6°	7°	8°	9°	10°	11°	12°	13°	14°	15°	16°
$A_1 = F_1$	0,000	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
A_2	0,000	0,000	0,667	1,200	0,600	1,250	0,000	1,000	1,000	1,400	1,500	1,692	1,857	1,714	1,867	2,000
A_3	0,000	0,000	1,000	1,000	0,750	0,800	0,000	1,000	0,750	1,256	1,444	1,636	1,846	1,667	1,857	2,000
$F_1 = A_1$	0,000	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
F_2	0,000	0,063	0,521	0,913	0,613	1,125	0,500	1,000	1,000	1,325	1,500	1,659	1,804	1,732	1,857	2,000
F_3	0,000	0,042	0,681	0,942	0,658	1,017	0,333	1,000	0,917	1,312	1,481	1,651	1,818	1,710	1,867	2,000

Starting from triads and 2nd order conditional probabilities it can be noticed that only two kinds of copolymer chain can be clearly distinguished giving two opposite limiting cases, namely block sequences, i.e. AAAA and BBBB, and strictly alternating sequences, i.e. ABAB and BABA, while the reminder can be regarded as miscellaneous, e.g. AABA, ABBB, etc. Irrespective of the length of sequences there are always two, and only two, strictly block sequences, and only two strictly alternating ones. The longer the sequences concerned are the greater is the number of miscellaneous sequences hence, it seems reasonable to adopt only these four block and alternating sequences for a simple characterization of a copolymer.

It should be noted, however, that randomness is usually expressed in terms of discrepancy from alternation or blockiness. In fact, the degree of randomness by YAMADERA and MURANO (1967) should be called degree of alternation of the first order (A_1) since it is based on 1st order conditional probabilities describing the formation of a purely alternating chain

$$R = A_1 = P(A/B) + P(B/A)$$

Of course, one can calculate the degree of blockiness (B_1), based on 1st order conditional probabilities leading to a block chain

$$B_1 = P(A/A) + P(B/B)$$

but in this case the numerical values form a reverse scale with respect to the former parameter, i.e. $B_1 = 0.0$ for alternating copolymers; $B_1 = 1.0$ for random copolymers and $B_1 = 2.0$ for mixture of homopolymers. To preserve the physical meaning behind the numerical values, widely used in literature for characterizing the chain microstructure, it seems reasonable to prefere the degree of alternation, though both A_1 and/or B_1 can be used to distinguish a random copolymer, as far as diad probabilities and 1st order conditional probabilities are concerned.

For sequences longer than diads the degree of alternation and the degree of blockiness of higher orders can be calculated as follows:

$A_2 = P(AB/A) + P(BA/B)$ — 2nd order degree of alternation

$A_3 = P(BAB/A) + P(ABA/B)$ — 3rd order degree of alternation

. . . . . .

$A_n = P(\underbrace{ABAB...B}_{n}/A) + P(\underbrace{BABA...A}_{n}/B)$ — n-th order degree of alternation

$A_n = 0.0$ for a mixture of homopolymers
$A_n = 1.0$ for random copolymers
$A_n = 2.0$ for alternating copolymers

$B_2 = P(AA/A) + P(BB/B)$ 2nd order degree of blockiness

$B_3 = P(AAA/A) + P(BBB/B)$ 3rd order degree of blockiness

. . . . . .

$B_n = P(\underbrace{AA...A}_{n}/A) + P(\underbrace{BB...B}_{n}/B)$ n-th order degree of blockiness

$B_n = 0.0$ for alternating copolymers
$B_n = 1.0$ for random copolymers
$B_n = 2.0$ for a mixture of homopolymers

Numerical values of 1st, 2nd and 3rd order degree of alternation calculated for the model chains are presented in Table II. The data obtained indicate that degree of alternation of different orders complete each other i.e. those model copolymers which possess the same A_1 value but differ significantly in their structure, differ in their degrees of alternation of higher order. Therefore, the averaged degree of alternation can be used as a useful "one-number" parameter for a simple characterizing of copolymer chain

$$F_n = \frac{\sum_{i=1}^{n} A_i}{n}$$ n-th order averaged degree of alternation

$F_n = 0.0$ for a mixture of homopolymers
$F_n = 1.0$ for random copolymers
$F_n = 2.0$ for alternating copolymers

Numerical values of 2nd and 3rd order averaged degree of alternation are presented in Table II. It can be seen from this Table that the longer the sequences involved are the better is the differentiation between similar chains.

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