match no. 22 pp. 3-32 1987

# MATHEMATICAL MODELING OF POLYMERS. PART I. ENUMERATION OF NON REDUNDANT (IRREDUCIBLE) REPEATING SEQUENCES IN STEREOREGULAR POLYMERS, ELASTOMERS, OR IN BINARY COPOLYMERS

Alexandru T. Balaban and Cristian Artemi

Polytechnic Institute, Department of Organic Chemistry,
Splaiul Independentei 313, 76206 Bucharest, Roumania

(Received: December 1986)

*Abstract.* *Irreducible repeating sequences of binary symbols define all possibilities for the stereochemistry of steroregular homopolymers or of polyalkenamers, and for the constitution of binary copolymers formed from symmetrical monomers. A theorem is demonstrated for the number $N(n)$ of chemically non-equivalent irreducible sequences of $n$ binary symbols, coding R/S enantiomeric centers in stereoregular polymers, E/Z geometries in polyalkenamers, or the two comonomers in binary copolymers. The formula for $N(n)$ makes use of the Möbius function of the lattice of divisors, and is based upon Möbius's inversion theorem. Irreducibility is defined with respect to decomposition into smaller repeating subsequences, cyclic permutation of the binary symbols within the sequence or interchange between the two binary symbols. A computer program implements the algorithm for computing the numbers $N(n)$ up to a maximal selected $n$ value and displays the irreducible sequences. The asymptotic behavior of numbers $N(n)$ is described.*

Notation

$A_n$ : the set of words (sequences) with length n in the binary alphabet

$A_{n,p}$ : the set of words with length n, which are decomposed into n/p identical subsequences of length p ($p \leqslant n$) and p is minimal with this property

$A_{n,n}$ : the set of words of length n which are not decomposable into identical subsequences (are non-periodic)

A, B : notation for cis/trans substituents in cycloalkanes

a,b,n,p, q,s,t : are natural numbers

$C_n$ : the set of sequences with length n which are cyclically equivalent to their complement

d : the length of a sequence or a subsequence

E, Z : notation for diastereoisomers

F(n) : the n'th term of the Fibonacci series

f(x), g(x) : the functions from the Möbius's inversion theorem

$I_n$ : the set of sequences with length n which have the property that their inverse and complement are cyclically equivalent

$K_n$ : the set of sequences with length n which are cyclically equivalent to their inverse

M(d) : the cardinal of the set $(K_n \cap A_{n,d})$

N(n) : the number of irreducible chemically nonequivalent sequences with length n

m, r : abbreviated from *meso* and *racemic*

P(d) : the cardinal of the set $(I_n \cap A_{n,d})$

$p_i$ : a prime number

Q(d) : is the cardinal of the set $\{\alpha \in A_{n,d} \mid \alpha$ has the property (*) that $\alpha$ may be decomposed into two subsequences with the same length, being complementary to one another $\}$

R, S : denote chirality (rectus, sinister)

X : a partially ordered set

Y : a decimal digit

x,y,u : arguments of the functions f, g, $\mu$

$\alpha, \alpha', \alpha'', \alpha''', \alpha^\circ$, $\beta$ or $\gamma$ : are words (sequences) in binary alphabet

$\alpha_i$, $\beta_i$ : binary digits
$\lambda$ : the null sequence
$\mu(x,y)$ : Möbius's function
$\simeq$ : denotes cyclical equivalence
$\div$ : denotes chemical equivalence
$\bar{\alpha}$ : the bar symbol indicates the complement of $\alpha$
$\hat{\alpha}$ : this symbol indicates the inverse of $\alpha$

## 1. Introduction

The mathematical modeling of polymers has been successfully developed beginning with Flory.[1] Graph theoretical methods have been applied more recently to polymers by Gordon.[2] There still remain, however, interesting and challenging problems.

Depending upon the nature of the monomer, the polymer chain may possess various features. TABLE 1 presents types of monomer units with corresponding examples ; some of these types will be of interest for the following discussion.

TABLE 1. Types of monomer units in homopolymers and corresponding examples.

| Monomer units | Symmetrical | Non-symmetrical |
|---|---|---|
| Achiral | $-H_2C-CH_2-$ | $-H_2C-CMe_2-$ |
| Chiral | -CH——CH-<br>\|　　\|<br>COOMe COOMe | $-H_2C-CH-$<br>\|<br>OCOMe |

The present paper enumerates all possible repeating sequences in infinite linear chains composed of two kinds of units, which can be modelled by binary numbers. Such linear chains correspond to one of the following types of polymers :

1.1 *Stereoregular polymers* : Natta[3] and Ziegler[4] showed that the sequence of stereochemical configurations in head-to-tail vinylic homopolymers e.g. poly(propene) $-(-CH_2-CHMe-)_n-$ may give rise to several types of stereoregularities. They distinguished isotactic polymers with all chiral centers having the same configuration (either R or S, e.g. ...RRR...), syndiotactic polymers with alternating configurations, e.g. ...RSRS..., and irregular (atactic) polymers. The first above example has R as repeating sequence ; the second example has the dyad RS as repeating sequence.

An alternative description, generally adopted by polymer chemists, uses a different notation, namely m (for meso, when two adjacent stereocenters have the same configuration, e.g. the dyads RR or SS) and r (for racemic, when two adjacent stereocenters have opposite configurations, e.g. the dyads RS or SR); this notation can be obtained from the previous one according to the above rules and ends up in a different string of binary symbols. Thus the octad R.R.R.S.S.S.R.S corresponds to the heptad mmrmmrr since each pair of adjacent capital letters is replaced by m when the capital letters are identical, or by r when they are different. In the latter notation, there are n-1 symbols (m and/or r) for an n-ad of R/S symbols, in most cases ; the situation is, however, rather complicated in the m/r notation because in some cases (depending on the number and parity of r, m, and r + m numbers) on repeating the sequence of m/r symbols it results that a string of n-1 symbols m and r corresponds actually to (2n)-ad of R/S symbols.

Even journals and books have not yet adopted a unified approach.[16-30] According to theory, for an n-ad of R/S symbols there are $2^n$ possible sequences ; this number is halved on imposing one fixed starting configuration or on agreeing to consider together sequences derived from one another by R/S interconversion. This is actually what the m/r notation represents ; however, the $2^{n-1}$ sequences still have redundancies.

To avoid these complications we prefer to use the simpler R/S notation.

Both the practical importance of stereoregular homopolymers obtained first by Ziegler[4] and then by Natta,[3] and the experimental detection of repeating sequences ( dyads, triads, etc.) by $^1$H-NMR,[5-8], $^{13}$C-NMR and other methods pointed out the fact that other types of stereoregularity, in addition to isotacticity and syndiotacticity are possible, e.g. with repeating triad sequences RRS. $^{19}$F-NMR spectroscopy for poly(fluorethylene) and poly(1,1-difluorethene)[10,11] and especially cross-polarization magic angle spinning for NMR of solid (crystalline) polymers have been extremely helpful.[12-15] In solid state the molecules are coiled in regular fashion, e.g. isotactic poly(propene) has just one kind of $CH_3$, $CH_2$, and CH groups, whereas the syndiotactic polymer has one kind each of CH and $CH_3$ groups, but two kinds of $CH_2$ groups. In solution the NMR spectra of stereoregular polymers are much more complicated owing to various conformations (transoid, gauche) which coexist for each stereoregularity.

The problem is to enumerate and generate explicitly all possible regular infinite chains having repeating sequences : how many pentads, hexads, etc. are possible, and which are they?

1.2. *Stereoregular elastomers (polyalkenamers)* :[31,32] natural rubber is *cis*--poly(isoprene) with all-Z configuration, Guttapercha is *trans*-poly(isoprene) with all-E configuration, but synthetic poly(isoprene) has various contents -and sequences- of *cis/trans* (Z/E) configurations at the double bonds. The same is true for poly(1,3-butadiene) i.e. for polybutenamer (which can be obtained either by polymerization of 1,3-butadiene or by ring-opening polymerization of 1,5-cyclooctadiene) and for polypentenamer (which can be obtained by ring--opening polymerization of cyclopentene). The sequence of *cis* and *trans* configurations along the ideal infinite chain of a polyalkenamer can give rise to regularities if repeating sequences exist. Thus *all-cis*-poly(isoprene) has Z as repeating sequence (monad).

In real poly(1,3-butadiene), in addition to the E/Z configurations of 1,4-polyaddition products, one may encounter 1,2-addition products. The situation for poly(isoprene) or poly(chloroprene) is much more complex because 1,4-addition products may be formed with different regioselectivities : tail--to-tail, head-to-head, or head-to-tail, each in E/Z configurations ; the 1,2-addition products again may have also various regioselectivities. We shall only consider for elastomers the E/Z configurations of 1,4-poly(butadiene).

1.3. *Binary copolymers* :[33] the constitution of binary copolymers formed from symmetrical monomers (such as ethylene, tetrahaloethene, etc. which cannot yield regioselective polyadditions) in linear macromolecules is dictated by the copolymerization mechanism. Homopolymers $A_n$ correspond to a monadic repeating sequence, alternating copolymers have a dyad $(AB)_n$ as the repeating sequence, etc. Of course, the problem is more complicated if there is the possibility of regioselectivity e.g. with isobutene (head-to-head, head-to-tail, etc.) and/or if the monomer(s) lead to chiral centers, e.g. for vinyl chloride or acetate. However, in the present context all regio- and stereochemical considerations in copolymers will be ignored, so as to reduce the problem to that discussed for the other two above cases. Future parts of this series will consider both the problem of stereochemistry in copolymer sequences, and that of ternary and n-nary copolymer sequences.

1.4. *Regioselectivity in vinylic homopolymers (or in polymers from non-symmetrical olefinic monomers).* When a vinylic monomer $CH_2$=CHR such as vinyl chloride (R=Cl) gives rise to a linear homopolymer, most monomer units become attached head-to-tail but a few may be linked in the opposite fashion. We may generalize the problem, and ask whether one may enumerate all irreducible possibilities for regularly repeating sequences, wherein the head-to-tail monomer units are symbolized by digit 0, and the reverted monomer unit is symbolized by digit 1. The resulting repeating sequence is a binary number, e.g. a strictly head-to-tail polymer chain has 0 as irreducible repeating sequence; by interchanging the binary symbols we obtain 1 as the sequence for a strictly head-to-head and tail-to-tail polymer chain. It is interesting to note that the latter chain can also be described as an alternating binary copolymer of ethene and 1,2-dichloroethene : more generally for other regularities, such chains may also be viewed as ternary copolymers involving three monomers : $CH_2$=$CH_2$, $CH_2$=CHR, and CHR=CHR.

## 2. Formulation of the problem

The mathematical modeling of the problem under discussion in the present paper consists in determining all possible sequences of given length n which define by repetition chemically different infinite strings and which are not themselves decomposable into smaller repeating subsequences.

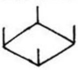
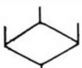
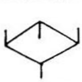
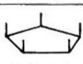
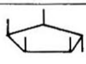
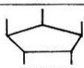
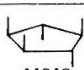
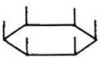
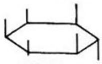
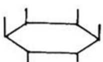
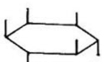
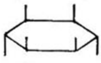
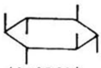
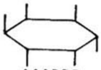
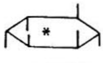
We shall call such sequences *irreducible ;* they are not redundant in the sense that they contain all the information on the sequence and nothing but this information.

Although there exists a rich bibliography in this area, till now no attempt has been made to enumerate and list these irreducible sequences. We mention that for binary copolymers obtained from symmetrical monomers the numbers of possible n-ads are quoted to be : 3 dyads (AA, AB and BB), 6 triads (AAA, BAA, BBA, BAB, ABA, BBB), 10 tetrads, 20 pentads, etc. Likewise the numbers of possible stereosequences are quoted to be 3 triads (mm, mr, rr), 6 tetrads, 10 pentads, 20 hexads, 36 heptads, etc. It is easy to see that these numbers include three types of redundancies : (a) redundancy with respect to reducibility to a lower n-ad e.g. AA and AAA are reducible to monad A ; (b) redundancy with respect to cyclic permutation, i.e. to the starting point of the n-ad, e.g. the triads BAA and ABA lead to the same infinite chain on repetition ; (c) redundancy with respect to interchange of the two symbols, e.g. the triads BAA and BBA.

One may establish a connection between this problem and the number of diastereomers of substituted cycloalkanes having the same type of substituent bonded to each carbon atom (this is related to the "necklace problem" for beads of two colors, if the above redundancy restrictions are applied). In this case from the preceding three redundancies we eliminate the second and third ones. Thus, for (1,2...n)-*n-cis*-chlorocycloalkanes $C_nH_nCl_n$ the diastereomers are shown in TABLE 2, ignoring the ring puckering ; symbols A/B indicate "up" or "down" (or E/Z) configurations. From the numbers of diasteromers (which can be easily obtained by using Polya's theorem [34]) one has to subtract the redundant or reducible sequences if one imagines that the n-ad corresponding to each diastereoisomer is repeated over and over again. Such redundant sequences, decomposable into repeated subsequences, are indicated by brackets in TABLE 2. The numbers of irreducible sequences whose notation is bracket-free are indicated in the last column of TABLE 2. As an extension, for n = 2 one may include in TABLE 2 the two diastereomeric 1,2-dichloroethenes, *cis (AA)*, and *trans (AB)* ; the former is reducible while the latter is irreducible. Thus we obtain for n = 2 through 6 the following numbers N(n) of irreducible sequences : 1, 1, 2, 3, 5, ... . One might wonder if we are to obtain the Fibonacci sequence also for larger n values ; as it will be seen, the answer is : No.

As a final remark, in TABLE 2 the first chiral polychlorocycloalkane is the last formula marked with an asterisk. In the present paper we shall ignore the chirality of binary copolymer sequences.

TABLE 2. Diastereomers of substituted cycloalkanes.

| n | Diastereoisomers | Nos. of sequences | |
|---|---|---|---|
| | | Diastereomers | N(n) |
| 3 |  (AAA)  AAB | 2 | 1 |
| 4 |  (AAAA)  AAAB  AABB  (ABAB) | 4 | 2 |
| 5 |  (AAAAA)  AAAAB  AAABB  AABAB | 4 | 3 |
| 6 |  (AAAAAA)  AAAAAB  AAAABB  AAABAB<br> (AABAAB)  (ABABAB)  AAABBB  AABABB | 8 | 5 |

Two sequences of n binary digits (or letters R/S, A/B, etc.) define by repetion the same infinite string from a chemical viewpoint if :
(i) they belong to the same class of cyclic permutations ; or
(ii) one is the symmetrical of the other relative to the middle of the sequence (i.e. one is obtained from the other by reading it from right to left) ; or
(iii) one is obtained from the other by permuting the binary digits.

For modeling consistently all three types of polymers mentioned in the preceding section, we shall denote by the binary alphabet R/S : the binary digits 0/1 corresponding to letters R/S symbolize either tridimensional configurations in stereoregular polymers, or E/Z (cis-trans) configurations in elastomers, or finally the two mers of binary copolymers.

## 3. Number of chemically nonequivalent (irreducible) sequences of given length n in the binary alphabet.

### 3.1. Möbius's function $\mu$ and the number of non-periodic sequences.

Let X be a partially ordered set. If for any $x, y \in X$ the interval $[x, y] = \{u \mid u \in X, u \geqslant x$ and $u \leqslant y$ (namely, the set of elements between x and y) is a finite set, then X is called a locally finite ordered set.

Möbius's function $\mu : X \times X \rightarrow N$ is defined in the following way :

$$\mu(x, x) = 1$$

$$\mu(x, y) = -\sum_{x \leqslant u < y} \mu(x, u) \quad \text{for } x < y$$

$$\mu(x, y) = 0 \quad \text{for } x > y$$

### 3.2. Möbius's inversion theorem.

If X is a locally finite ordered set and if f(x) and g(x) are functions defined on X such that :

$$f(x) = \sum_{0 \leqslant u \leqslant x} g(u) \quad \text{for any } x \in X,$$

then

$$g(x) = \sum_{0 \leqslant u \leqslant x} \mu(u, x) f(u) \quad \text{for any } x \in X.$$

### 3.3. Möbius's function of the lattice of divisors.

Let X be the set of natural numbers {1, 2, ...} with the order relationship $a \leqslant b$ if a divides into b (denoted by $a|b$). This set is partially ordered because the divisibility relation is reflexive, antisymmetric and transitive ; the universal minorant is number 1 which divides any number. This ordered set is locally finite and is a lattice because for two natural numbers, the smallest majorant with respect to the divisibility relationship is their smallest common multiple, and the largest minorant is their largest common divisor.

The Möbius function of the lattice of divisors $\mu(d, n)$ equals 1 for $n = d$;

$\mu(d, n) = (-1)^k$ if $n = p_1p_2 \dots p_k \cdot d$ with $p_i$ being different mutually prime numbers (without considering number 1 as a prime number), and $\mu(d, n) = 0$ otherwise, i.e. when d does not divide into n or if in the expression of n, at least two of the prime numbers $p_i$ and $p_j$ are equal.

The function defined above and denoted by $\mu$ was introduced in 1832 by Möbius for studying the repartition of prime numbers. In the following, we shall denote by $\mu$ only Möbius's function of the divisor lattice.

## 3.4. Number N(n) of non-periodic sequences.

Let $n \in N \setminus \{0\}$, and let $A_n = \{\alpha_0, \alpha_1, \dots \alpha_{n-1} | \alpha_i \in \{0, 1\} \; \forall \; i \in [0,n-1]\}$ be the set of words with length n in the binary alphabet. The void word is $A_0 = \{\lambda\}$.

*Definition 1.* Let $\alpha, \beta \in A_n$, where $\alpha = \alpha_0\alpha_1 \dots \alpha_{n-1}$, $\beta_0\beta_1 \dots \beta_{n-1}$. We define an equivalence relationship between the two words $\alpha$, $\beta$ of length n in the binary alphabet and we say that $\alpha$ is cyclically equivalent to $\beta$ (denoted by $\alpha \simeq \beta$) if there exists $p \in [1,n]$ such that $\alpha_i = \beta_{i \oplus p} \; \forall \; i \in [0,n-1]$, $\oplus$ is the addition modulo n operation.

*Definition 2.* We say that $\alpha = \alpha_0\alpha_1 \dots \alpha_{n-1} \in A_n$ admits period p ($p \in [1,n]$) if $\alpha_i = \alpha_{i \oplus p} \forall \; i \in [0,n-1]$. The smallest period of $\alpha$ is called the primitive period of $\alpha$.

*Remark 1.* A cyclically reducible sequence $\alpha \in A_n$ is decomposed into n/p identical subsequences of length p if $p < n$, where p is the primitive period of $\alpha$ (p is a divisor of n).

*Remark 2.* Two cyclically reducible words belonging to the same class of $(\simeq)$-equivalence have the same primitive period p ; each class of $(\simeq)$-equivalence, formed from words of primitive period p, contains exactly p words.

If we denote by $A_{n.p}$ the set of cyclically reducible words of primitive period p, we may write

$$|A_n| = 2^n = \sum_{p|n} |A_{n,p}|$$

*Remark 3.* The number $|A_{n,p}|$ of elements in the set $A_{n,p}$ does not depend on n.

Taking into account that $f(n) = 2^n$ and that $g(p) = |A_{n,p}|$ we obtain by using Möbius's inversion theorem:

$$|A_{n,p}| = \sum_{d|p} \mu(d,p) \cdot 2^d$$

The set $A_{n,n}$ of irreducible words which cannot be decomposed into smaller identical subsequences (this is equivalent to saying that the primitive period is n) contains $|A_{n,n}|/n$ classes of ($\simeq$)-equivalence having n elements each.

According to the preceding formula,

$$|A_{n,n}| = \sum_{d|p} \mu(d,n) \cdot 2^d$$

3.5. <u>A formula for computing the number N(n) of chemically non-equivalent sequences.</u>

Two sequences of length n are said to be chemically equivalent if they define the same infinite string ; otherwise they are called chemically non--equivalent. In the above statement, "same" means "indistinguishable" if the reading of the string is from left to right or vice-versa.

*Definition 3.* Let a sequence $\alpha \in A_n, \alpha = \alpha_0\alpha_1 \ldots \alpha_{n-1}$. The inverse of $\alpha$ is $\hat{\alpha} = \alpha'_0\alpha'_1\ldots\alpha'_{n-1}$ where $\alpha'_i = \alpha_{n-i-1}$ $\forall$ i $\in [0,n-1]$.

*Definition 4.* The complement of $\alpha$ is $\overline{\alpha} = \overline{\alpha}_0\overline{\alpha}_1\ldots\overline{\alpha}_{n-1}$ where $\overline{\alpha}_i = 1 - \alpha_i$ $\forall$ i $\in [0,n-1]$.

Thus inversion means the change in the direction of reading, and complementarity means the permutation of binary digits.

By definition 3 and 4 we have :

$\hat{\lambda} = \lambda$ ; $\overline{\lambda} = \lambda$ ; $\hat{\hat{\alpha}} = \alpha$ ; $\overline{\overline{\alpha}} = \alpha$

*Definition 5.* Chemical equivalence, denoted by $\div$, is defined on $A_{n,n}$ as follows :

(1) $\alpha \simeq \beta \rightarrow \alpha \div \beta; \forall\ \alpha, \beta \in A_{n,n}$ (a class of chemical equivalence is the union of several classes of cyclic equivalence).

(2) $\hat{\alpha} \div \alpha; \forall\ \alpha \in A_{n,n}$ (any sequence is chemically equivalent to its inverse).

(3) $\overline{\alpha} \div \alpha; \forall\ \alpha \in A_{n,n}$ (any sequence is chemically equivalent to its complement).

(4) $\alpha \div \beta$ and $\beta \div \gamma \rightarrow \alpha \div \gamma; \alpha, \beta, \gamma \in A_{n,n}$

*Remark.* The fact that the relationship $\div$ is an equivalence results from (1), (4) and from the fact that $\simeq$ is an equivalence relationship.

*Notation.*

$K_n = \{\alpha \in A_n | \hat{\alpha} \simeq \alpha\}$, ($K_n$ is the set of sequences which are cyclically equivalent to their inverse).

$C_n = \{\alpha \in A_n | \overline{\alpha} \simeq \alpha\}$, ($C_n$ is the set of sequences which are cyclically equivalent to their complement).

$I_n = \{\alpha \in A_n | \overline{\alpha} \simeq \hat{\alpha}\}$, ($I_n$ is the set of sequences which have the property that their inverse and complement are cyclically equivalent).

To determine the number of chemically non-equivalent sequences (irreducible sequences) means to compute the number of classes of (÷)-equivalence. We denote this cardinal :

$$N(n) = |A_{n,n} / \div|$$

The following lemmas and corollaries were demonstrated :

*Lemma 1.* Let $\alpha \in A_n$. Then $\alpha \in K_n$ iff there exist $\alpha' \in A_s$ and $\alpha'' \in A_t$ $(s + t = n)$ such that $\alpha = \alpha'\alpha''$, $\hat{\alpha}' = \alpha'$, and $\hat{\alpha}'' = \alpha''$.

*Corollary 1.* If $\alpha \in A_{n,d} \cap K_n$ $(d|n)$, then $\alpha$ admits exactly n/d decompositions described by lemma 1.

*Lemma 2.* Let $\alpha \in A_{n,d}$, $\alpha = (\alpha')^{n/d}$, $\alpha' \in A_{d,d}$. Then $\alpha \in K_n$ iff $\alpha' \in K_d$.

*Lemma 3.* If $M(d) = |K_n \cap A_{n,d}|$, then

$$M(d) = d \cdot \sum_{q|d} \mu(q,d) \frac{1}{q} \cdot \sum_{0 \leqslant s \leqslant q-1} 2^{\lceil s/2 \rceil} \cdot 2^{\lceil (q-s)/2 \rceil}$$

The demonstration is based on the fact that $\alpha \in A_s$ and $\hat{\alpha} = \alpha$ indicate a symmetric word relative to its midpoint. Therefore the number of such words is $2^{\lceil s/2 \rceil}$ where $\lceil s/2 \rceil$ means the smallest integer greater than, or equal to, s/2. The number of possible decompositions described by lemma 1 (for an n-digit word with primitive period d) is exactly n/d. The number of possible decompositions into two words invariant to transformation, of lengths s and n - s, is the product :

$$2^{\lceil s/2 \rceil} \cdot 2^{\lceil (n-s)/2 \rceil}$$

The Möbius's inversion theorem is applied and the lemma is demonstrated.

*Corollary 3 :*

$$M(n) = \sum_{d|n} \mu(d,n) \frac{n}{d} \cdot \sum_{0 \leqslant s \leqslant d-1} 2^{\lceil s/2 \rceil} \cdot 2^{\lceil (d-s)/2 \rceil}$$

*Lemma 4.* Let $\alpha \in A_n$. Then $\alpha \in I_n$ iff there exist $\alpha' \in A_s$, $\alpha'' \in A_t$ $(s + t = n)$ such that $\alpha = \alpha'\alpha''$, $\hat{\alpha}' = \overline{\alpha}'$ and $\hat{\alpha}'' = \overline{\alpha}''$.

*Corollary 4.* If $\alpha \in A_{n,d} \cap I_n$, $(d|n)$, then $\alpha$ admits exactly n/d decompositions described by lemma 4.

*Lemma 5.* Let $\alpha \in A_{n,d}$, $\alpha = (\alpha')^{n/d}$, $\alpha' \in A_d$. Then $\alpha \in I_n$ iff $\alpha' \in I_d$.

*Lemma 6.* If $P(d) = |I_n \cap A_{n,d}|$ then

$$P(d) = \sum_{\substack{q|d \\ q \text{ even}}} \mu(q,d) \cdot d \cdot 2^{q/2-1}$$

The demonstration starts from the fact that when $I_n \neq \emptyset$, n and s are even. There exists a bijection between the set of $s/_2$-digit words and that of s-digit words having the property that they are invariant with respect to complementarity of the inverse. According to corollary 4 and applying Möbius's inversion theorem, lemma 6 results.

*Corollary 6.*

$$P(n) = \sum_{\substack{d|n \\ d \text{ even}}} \mu(d,n) \cdot n \cdot 2^{d/2-1}$$

*Lemma 7.* Let $\alpha \in A_{n,n}$ be a non-periodic word of length n in the binary alphabet. We have $\alpha \in C_n$ iff n is even and there exists $\alpha^\circ \in A_{n/2}$ such that $\alpha = \alpha^\circ\overline{\alpha}^\circ$.

The demonstration consists of two parts for the direct and inverse implication. In the former part, from the definition of the set $C_n$, it results there exists a natural number p, $1 \leqslant p \leqslant n$, such that $1 - \alpha_i = \alpha_{i \oplus p}$ for any i, $0 \leqslant i < n-1$ (we recall that $\alpha_i$ is the i-th letter of $\alpha$) ; on choosing the minimal number p having the above property, one shows that n is even and that $p = n/_2$ by reduction *ad absurdum*. One observes thus that on complementing the sequence, its two halves are permuted. The latter part of the demonstration is trivial.

*Lemma 8.* If for $\alpha \in A_n$, n even, we denote by (*) the property encountered in Lemma 7 ($\exists|\ \alpha^\circ \in A_{n/2}$ such that $\alpha = \alpha^\circ\overline{\alpha}^\circ$) then for $\alpha \in A_{n,d}$, $\alpha = (\alpha')^{n/d}$, $\alpha' \in A_d$ where $d|n$, the property (*) belongs to sequence $\alpha$ iff n/d is odd and each sequence $\alpha'$ has property (*).

The demonstration that n/d is odd (hence d is even) succeeds by reduction *ad absurdum* ; a consequence is the decomposition of sequence $\alpha$ into :

$\alpha^\circ = \alpha''(\alpha')^{(n-d)/2d}$

$\overline{\alpha}^\circ = \alpha'''(\alpha')^{(n-d)/2d}$ where $\alpha' = \alpha''\alpha'''$ ; $\alpha'', \alpha''' \in A_{d/2}$.

It results that $\alpha'' = \overline{\alpha}'''$. In other words, the subsequence in the middle of sequence $\alpha$ has the property (*). Therefore, any subsequence $\alpha'$ has this property (*).

*Lemma 9.* If $Q(d) = |\{\alpha \in A_{n,d} | \alpha \text{ has property } (*)\}|$, then

$$Q(d) = \sum_{\substack{q|d \\ d/q \text{ odd} \\ q \text{ even}}} \mu(q,d) \cdot 2^{q/2}$$

The demonstration starts with the observation that for odd d, Q(d) = 0. We shall therefore admit that d is even. The number of words from the set $A_n$ which have the property (*) is $2^{n/2}$. We have therefore

$$2^{n/2} = \sum_{\substack{d|n \\ n/d \text{ odd}}} Q(d)$$

and by applying Möbius's inversion theorem we obtain Lemma 9.

*Corollary 9.*

$$Q(n) = \sum_{\substack{d|n \\ n/d \text{ odd} \\ d \text{ even}}} 2^{d/2}$$

According to lemma 7, $Q(n) = |A_{n,n} \cap C_n|$.

*Theorem 1.* Let $n \in N$, $n > 1$.

$$N(n) = \frac{1}{4n}\Bigg( \sum_{d|n} \mu(d,n)\ 2^d + \sum_{\substack{d|n \\ n/d \text{ odd} \\ d \text{ even}}} \mu(d,n)\cdot 2^{d/2} +$$

$$+ \sum_{d|n} \mu(d,n)\cdot \frac{n}{d} \cdot \sum_{0 \leqslant s \leqslant d-1} 2^{\lceil s/2 \rceil} 2^{\lceil (d-s)/2 \rceil} + \sum_{\substack{d|n \\ d \text{ even}}} \mu(d,n) \cdot n \cdot 2^{d/2\ -1} \Bigg)$$

*Demonstration.*

On using set theory, the set $A_{n,n}$ of non-periodic words is decomposed into the following five subsets (complementation of set X is denoted as $\overline{X}$ and $|X|$ is the number of elements).

$S_1 = A_{n,n} \cap K_n \cap C_n$

$S_2 = A_{n,n} \cap K_n \cap \overline{C}_n$

$S_3 = A_{n,n} \cap \overline{K}_n \cap C_n$

$S_4 = A_{n,n} \cap \overline{K}_n \cap I_n$

$S_5 = A_{n,n} \cap \overline{K}_n \cap \overline{C}_n \cap \overline{I}_n$

One observes that any two subsets are disjoint.

The demonstration then considers in turn each of the five subsets. In $S_1$ the class of cyclic equivalence (ClCyE) coincides with the class of chemical equivalence (ChE). The class of chemical equivalence of a sequence in $S_2$ is the union between the cyclic equivalence class of the sequence, and the class of cyclic equivalence of its complement. In $S_3$ and $S_4$ the ClChE is the union between ClCyE of the sequence with the ClCyE of its inverse. Finally, in $S_5$

the ClChE is the union between the ClCyE of the sequence, the ClCyE of its complement, the ClCyE of its inverse, and the ClCyE of the inverse of its complement.

Taking into account that a ClCyE in $A_{n,n}$ contains exactly n words, one obtains the number of ClChE, N(n) :

$$N(n) = \frac{1}{n}\left(|S_1| + \frac{|S_2| + |S_3| + |S_4|}{2} + \frac{|S_5|}{4}\right)$$

After all operations have been completed one obtains

$$N(n) = \frac{1}{4n}\left[|A_{n,n}| + Q(n) + M(n) + P(n)\right]$$

and by means of corollaries associated to lemmas 3, 6 and 9 we obtain the formula presented in Theorem 1.

*Corollary 1.* When n is odd, $C_n = I_n = \emptyset$ and the above theorem reduces to

$$N(n) = \frac{1}{4n}\left[\sum_{d|n} \mu(d,n)\left(n \cdot 2^{(d+1)/2} + 2^d\right)\right]$$

*Corollary 2.* When n is even, the above theorem may be simplified to

$$N(n) = \frac{1}{4n}\left[\sum_{d|n} \mu(d,n) \cdot 2^d + \sum_{\substack{d|n \\ n/d\ \text{odd}}} \mu(d,n) \cdot 2^{d/2} + \right.$$

$$\left. + \sum_{\substack{d|n \\ d\ \text{even}}} n \cdot \mu(d,n) \cdot 2^{d/2+1} + \sum_{\substack{d|n \\ d\ \text{odd}}} n \cdot \mu(d,n) \cdot 2^{(d+1)/2}\right]$$

## 3.6. Asymptotic behavior of the numbers N(n) of irreducible sequences.

When the word length n increases indefinitely, the number N(n) also increases to infinity. According to Theorem 1 we obtain

*Corollary 3.* For $n \to \infty$, $N(n) \sim (2^{n-2})/n$, i.e. the number of classes of (÷)-equivalence (ClChE) tends asymptotically towards $(2^{n-2})/n$.

The demonstration consists in showing that

$$\lim_{n\to\infty} \frac{N(n)}{(2^{n-2})/n} = 1$$

## 4. Computer program for generating and enumerating irreducible chemically non--equivalent binary sequences

A FORTRAN-IV computer program was devised for generating irreducible chemically non-equivalent sequences consisting of n binary symbols. The input gives an integer upper limit NMAX for n. The output presents the (÷)-equivalence classes for increasing n values and within each class it prints the irreducible binary sequences in lexicographic order using R and S as binary symbols (letters R and S correspond to digits 0 and 1, respectively).

The algorithm generates sequences in the class of (÷)-equivalence, and tests them sequentially. If there exists a smaller sequence (with respect to lexicographic order) which is (÷)-equivalent with the tested sequence, the program goes on to test the next sequence ; otherwise the tested sequence is displayed as representing an irreducible member of this class of (÷)-equivalence. The program is based on the fact that a sequence which is (÷)-equivalent to a given sequence may be obtained from the latter by successive application of inversion, complementarity and/or cyclic permutation.

For minimizing the time and memory requirements of the program, we used the following observations :

(a) It is sufficient to test only those sequences whose last digit is 1.

Indeed, should $\alpha \in A_{n,n}$ and $\alpha_{n-1} = 0$, then the cyclically permuted word $\alpha' = \alpha_n \ \alpha_1 \ldots \alpha_n$ is lexicographically smaller than $\alpha$ (only in on case $\alpha = \alpha'$, namely when all digits are zero).

(b) It is sufficient to test only those sequences which have digits 0 in the first two positions. Indeed, for $\alpha \in A_{n,n}$ ; $n > 3$ ; $\alpha = \alpha_0 \ldots \alpha_n$ and $\alpha_0 \neq 0$ or $\alpha_1 \neq 0$, then we have two possibilities of lexicographic order < :

- $\alpha_0 = 1$, then $\overline{\alpha} < \alpha$
- if $\alpha_0 = 0$ and $\alpha_1 = 1$, then there exists no $i \in [0, n-2]$ such that $\alpha_i = \alpha_{i+1}$ (otherwise on effecting a cyclic permutation and possibly also a complementarity, we obtain a sequence having zeros on the first two positions). According to observation (a), $\alpha_{n-1} = 1$, therefore $\alpha$ is periodic with a period $\alpha' = 01$ so that it need not be tested. Thus, according to observation (b), one has to test only those sequences generated in the class of (÷)-equivalence whose first two positions have zeros.

(c) Since the (÷)-equivalence relationship is defined on $A_{n,n}$ (words of primitive period n), only the non-cyclic words need be tested, i.e. those words which cannot be decomposed into smaller identical subsequences. According to observation (b), should the given sequence be decomposable into identical subsequences of lengths 1 or 2, then these subsequences could only be 0 and 00, respectively. Therefore a given sequence undergoing testing cannot have a period smaller than, or equal to, 2. This fact is reflected in the program by considering only numbers larger than, or equal to, 3 as divisors of the sequence length.

The printing is effected with the help of an alphabetic vector ALPH implementing the binary correspondence 0 ↔ R and 1 ↔ S. For the sequence of length 1 the printing is effected before entering the first loop of the program. The notation for variables used by the program is explained in its initial comment. Labels have the following significance :

1Y - labels for FØRMAT statements

2Y, 4Y, 5Y, 6Y - usual labels

3Y - labels for statements indicating the end of a DO loop (Y is a decimal digit).

Figure 1 presents the listing of the program. The block diagram is presented in Fig. 2. A few variables in the program are abridged for convenience as follows: S ≡ SEQBIN ; S1 ≡ SEQ1 ; S2 ≡ SEQ2 ; A ≡ ALPH ; D ≡ DIV.

## 5. Discussion of the results

Fig. 3 presents the result for NMAX = 10. The same results, including also higher N values, may be presented as a counting series $\sum Nx^n$ :

$$x + x^2 + x^3 + 2x^4 + 3x^5 + 5x^6 + 8x^7 + 14x^8 + 21x^9 + 39x^{10} + 62x^{11} + 112x^{12} + 189x^{13} + 352x^{14} + 607x^{15} + 1144x^{16} + 2055x^{17} + 3885x^{18} + 7154x^{19} + \dots$$

It may be seen that N(n) deviates from the Fibonacci series for $n \geq 8$, and that for n = 3 through 6 we obtain the values indicated in Table 2 for N(n). It may be verified that for large n values the ratio between two successive N(n) values tends towards 2, in agreement with the asymptotic formula :

$$\lim_{n \to \infty} \left[N(n+1)/N(n)\right] = \lim_{n \to \infty} \left[2n/(n+1)\right] = 2$$

Thus the numbers N(n) of irreducible binary sequences increase faster *versus* n than the Fibonacci series, F(n), whose ratio between two successive terms is the Golden Ratio $(\sqrt{5} + 1)/2$.

FIGURE 1. The listing of the program

```
C    **************************************************************
C  * THE PROGRAM DISPLAYS SEQUENCES OF GIVEN LENGTH.              *
C  * VARIABLES ARE:                                               *
C  *   SEQBIN=VECTOR OF BINARY SEQUENCES                          *
C  *   SEQ1,SEQ2=VECTORS OF AUXILIARY SEQUENCES                   *
C  *   ALPH=VECTOR OF ALPHABETICALLY ORDERED SEQUENCES            *
C  *        FOR DISPLAY                                           *
C  *   DIV=VECTOR OF DIVISORS OF THE SEQUENCE LENGTH              *
C  *   N=LENGTH OF SEQUENCE BEING ANALYZED                        *
C  *   NMAX=MAXIMAL SEQUENCE LENGTH                               *
C  *   AUX,I,I1,J,K,L,M,N1,NL,NP,NR,NS,SP ARE AUXILIARY           *
C  *        VARIABLES AND COUNTERS.                               *
C    **************************************************************
      INTEGER SEQBIN(30),SEQ1(30),SEQ2(30),ALPH(36),
     *DIV(10),AUX
      DATA NS,NR,SP/'S','R',' '/
      READ(105,10)NMAX
   10 FORMAT(I2)
      WRITE(108,11)NR
   11 FORMAT(//11X,'POSSIBLE SEQUENCES OF LENGTH N = 1'
     *,' ARE:'//13X,A1)
      DO 30 N=2,NMAX
        WRITE(108,12)N
   12   FORMAT(///11X,'POSSIBLE SEQUENCES OF LENGTH ',
     *  'N =',I2,' ARE:'/)
        NL=1
        N1=0
        SEQBIN(N)=1
        I1=N-1
        DO 31 I=1,I1
          SEQBIN(I)=0
   31   CONTINUE
        K=0
        I1=N/2
        DO 32 I=1,I1
```

```
      IF(N.NE.(N/I)*I) GO TO 32
        K=K+1
        DIV(K)=I
32    CONTINUE
29    I=K
21    IF(I.LT.1) GO TO 40
        J=1
22      IF(J.GT.DIV(I)) GO TO 26
          M=1
24        IF(M.GE.N/DIV(I)) GO TO 23
            IF(SEQBIN(J).EQ.SEQBIN(J+M*DIV(I)))
   *        GO TO 25
              I=I-1
              GO TO 21
25          CONTINUE
              M=M+1
              GO TO 24
23        CONTINUE
            J=J+1
            GO TO 22
26      CONTINUE
          J=N-1
27        SEQBIN(J)=1-SEQBIN(J)
          IF(SEQBIN(J).NE.0) GO TO 28
            J=J-1
            GO TO 27
28        CONTINUE
          IF(J.GT.2) GO TO 29
            IF(N1.EQ.0) GO TO 30
              GO TO 55
40    CONTINUE
        L=0
        NP=0
        DO 33 I=1,N
          SEQ1(I)=SEQBIN(I)
```

```
33      CONTINUE
41      IF(L.EQ.0) GO TO 44
          L=0
45        IF(NP.EQ.N-1) GO TO 56
            NP=NP+1
            AUX=SEQ1(1)
            I1=N-1
            DO 34 I=1,I1
              SEQ1(I)=SEQ1(I+1)
34          CONTINUE
            SEQ1(N)=AUX
            IF(SEQ1(1).NE.SEQ1(2)) GO TO 41
              IF(SEQ1(1).EQ.0) GO TO 42
                DO 35 I=1.N
                  SEQ2(I)=1-SEQ1(I)
35              CONTINUE
                GO TO 43
42              CONTINUE
                DO 36 I=1.N
                  SEQ2(I)=SEQ1(I)
36              CONTINUE
43            CONTINUE
              GO TO 48
44      CONTINUE
          IF(SEQ1(N).NE.SEQ1(N-1)) GO TO 45
            IF(SEQ1(N).EQ.0) GO TO 46
              DO 38 I=1.N
                SEQ2(I)=1-SEQ1(N-I+1)
38            CONTINUE
              GO TO 47
46          CONTINUE
              DO 39 I=1.N
                SEQ2(I)=SEQ1(N-I+1)
39            CONTINUE
47          CONTINUE
```

```
              L=1
48            CONTINUE
              I=2
50            IF(I.GT.N) GO TO 41
                IF(SEQBIN(I)-SEQ2(I)) 41,49,26
49                I=I+1
                  GO TO 50
56      CONTINUE
        DO 37 I=1,N
          ALPH(N1+I)=NR*(1-SEQBIN(I))+NS*SEQBIN(I)
37      CONTINUE
        N1=N1+N+1
        M=NL*12
        DO 60 I=N1,M
          ALPH(I)=SP
60      CONTINUE
        N1=M
        IF(NL.NE.3) GO TO 51
55      CONTINUE
        WRITE(108,13)(ALPH(I),I=1,N1)
13      FORMAT(/13X,36A1)
        IF(N1.LT.36) GO TO 30
          N1=0
          NL=1
        GO TO 26
51      CONTINUE
        NL=NL+1
        GO TO 26
30    CONTINUE
      STOP
      END
```

FIGURE 2. Block diagram ; (S) is the decimal number corresponding to the binary sequence S ; : = indicates assignment ; ← indicates the transfer position by position, of elements belonging to one vector into another vector.

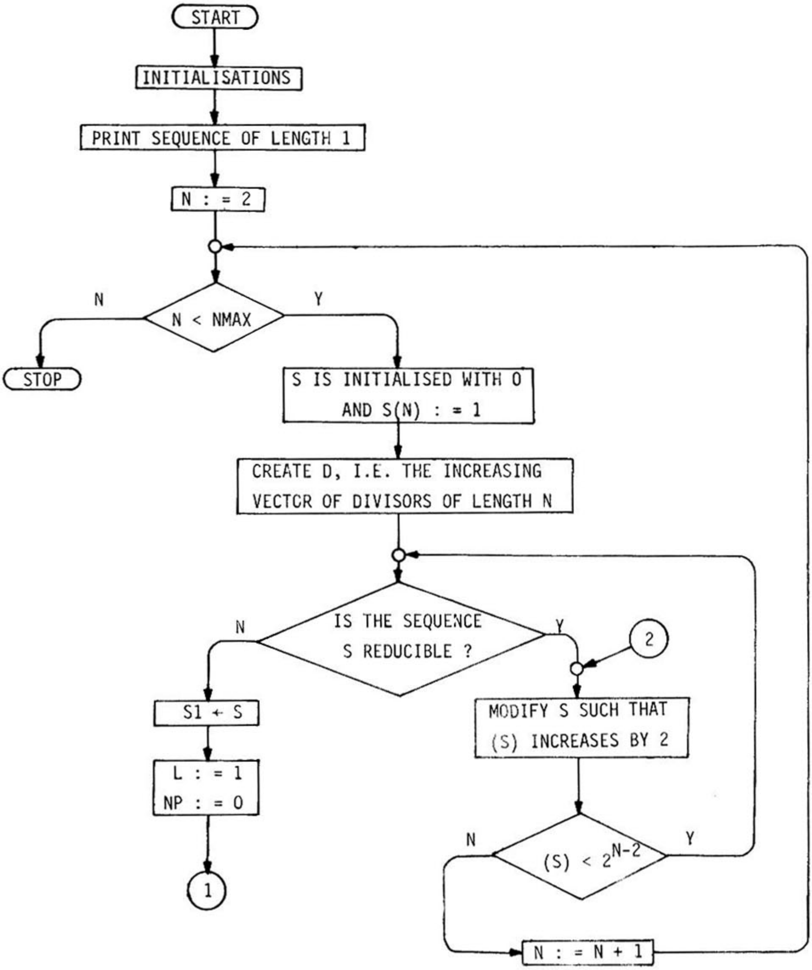


FIGURE 2 Continued.

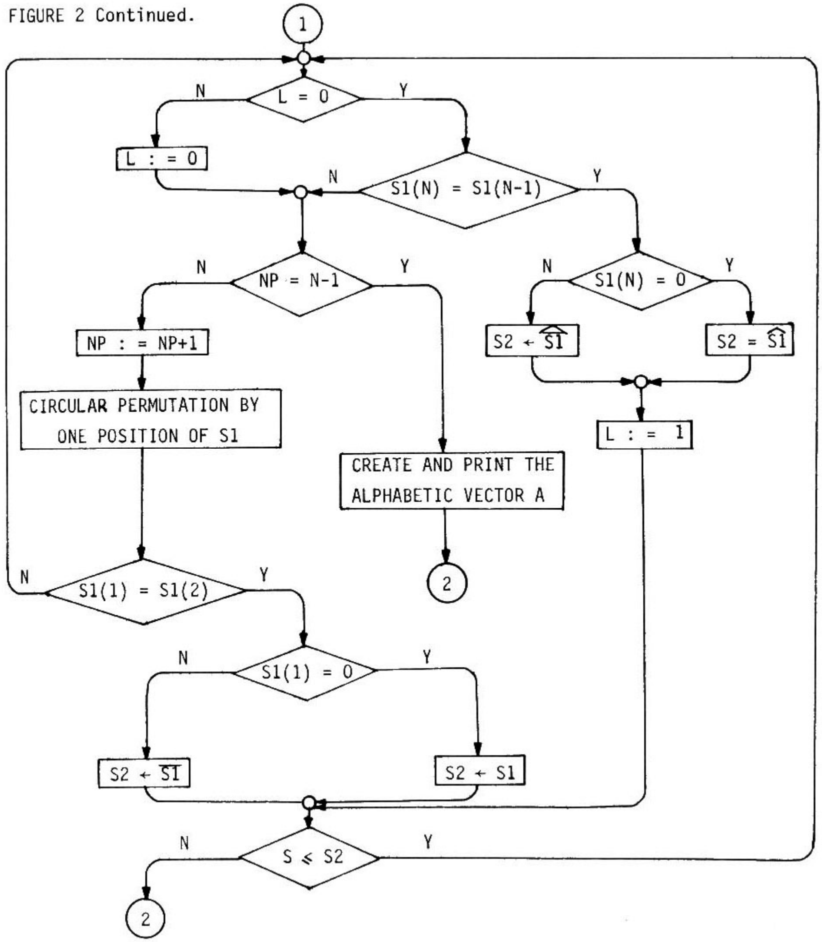


FIGURE 3. All irreducible sequences with $n \leqslant 10$

POSSIBLE SEQUENCES OF LENGTH N = 1 ARE:

R

POSSIBLE SEQUENCES OF LENGTH N = 2 ARE:

RS

POSSIBLE SEQUENCES OF LENGTH N = 3 ARE:

RRS

POSSIBLE SEQUENCES OF LENGTH N = 4 ARE:

RRRS    RRSS

POSSIBLE SEQUENCES OF LENGTH N = 5 ARE:

RRRRS    RRRSS    RRSRS

POSSIBLE SEQUENCES OF LENGTH N = 6 ARE:

RRRRRS RRRRSS RRRSRS

RRRSSS RRSRSS

POSSIBLE SEQUENCES OF LENGTH N = 7 ARE:

RRRRRRS RRRRRSS RRRRSRS

RRRRSSS RRRSRRS RRRSRSS

RRSRRSS RRSRSRS

POSSIBLE SEQUENCES OF LENGTH N = 8 ARE:

RRRRRRRS RRRRRRSS RRRRRSRS

RRRRRSSS RRRRSRRS RRRRSRSS

RRRRSSSS RRRSRRSS RRRSRSRS

RRRSRSSS RRRSSRSS RRSRRSRS

RRSRSRSS RRSRSSRS

POSSIBLE SEQUENCES OF LENGTH N = 9 ARE:

RRRRRRRRS    RRRRRRRSS    RRRRRRSRS

RRRRRRSSS    RRRRRSRRS    RRRRRSRSS

RRRRRSSSS    RRRRSRRRS    RRRRSRRSS

RRRRSRSRS    RRRRSRSSS    RRRRSSRSS

RRRSRRRSS    RRRSRRSRS    RRRSRRSSS

RRRSRSRSS    RRRSRSSRS    RRRSSRRSS

RRSRRSRSS    RRSRSRRSS    RRSRSRSRS

POSSIBLE SEQUENCES OF LENGTH N = 10 ARE:

RRRRRRRRRS    RRRRRRRRSS    RRRRRRRSRS

RRRRRRRSSS    RRRRRRSRRS    RRRRRRSRSS

RRRRRRSSSS    RRRRRSRRRS    RRRRRSRRSS

RRRRRSRSRS    RRRRRSRSSS    RRRRRSSRSS

RRRRRSSSSS    RRRRSRRRSS    RRRRSRRSRS

RRRRSRRSSS    RRRRSRSRSS    RRRRSRSSRS

RRRRSRSSSS    RRRRSSRRSS    RRRRSSRSSS

RRRRSRSSSS RRRRSSRRSS RRRRSSRSSS

RRRSRRRSRS RRRSRRRSSS RRRSRRSRRS

RRRSRRSRSS RRRSRRSSRS RRRSRSRRSS

RRRSRSRSRS RRRSRSRSSS RRRSRSSRSS

RRRSRSSSRS RRRSSRRSSS RRRSSRSRSS

RRSRRSRRSS RRSRRSRSRS RRSRRSSRSS

RRSRSRSRSS RRSRSRSSRS RRSRSSRRSS

*STOP*

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