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Hemiisotactic Polypropylene: A Key Point in the Elucidation of the Polymerization Mechanism with Metallocene Catalysts

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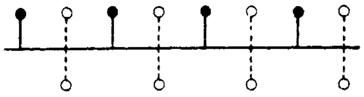
ABSTRACT: An analysis of propylene polymerization in the presence of metallocene complexes was carried out on the basis of the alternating mechanism and formulated in terms of fundamental stereochemistry. A statistical approach allowed the calculation of pentad distribution for polypropylenes produced in the presence of isospecific, syndiospecific, and hemiisospecific catalysts. Comparison with experimental data published for hemiisotactic polypropylene confirmed the validity of the alternating mechanism but showed also the presence of successive additions at the same catalyst face.

The structure of hemiisotactic polypropylene (hit-PP) was envisaged long ago in the course of our studies on the solid-state polymerization of substituted butadienes. The first example of hit-PP was obtained in our laboratory in 1982 by a two-step synthesis starting from *trans*-2-methylpentadiene:[1] the radical polymerization of this monomer, included as a guest in the channels of its inclusion compound with perhydrotriphenylene, yields a highly isotactic 1,4-trans polymer which converts into the desired product through a nonepimerizing hydrogenation. The spectroscopic behavior of hit-PP fully confirmed the expectation; its ^{13}C-NMR spectrum contains a large number of well-separated peaks and is a source of subtle stereochemical information.[2–6]

A new route to hit-PP has recently been published by Ewen and co-workers.[7] They were able to obtain it directly from propylene by using a carefully designed soluble catalyst based on an asymmetric metallocene complex. This exceptional result has renewed interest in hit-PP, which has become a central point in the elucidation of the mechanism of propylene polymerization.

As already reported in previous papers, ideal hemiisotactic polymers are characterized by an alternation of ordered and disordered stereogenic carbons as reported in I, where the open circles mean a 50% probability of finding a methyl group in a given position. In microtacticity terms hemiisotactic polymers contain a random succession of nonoverlapped mm and rr triads. Sequences containing isolated m or r diads or an odd number of equal diads flanked on both sides by opposite diads (such as rmr, mrm, rmmmr, mrrrrrm, etc.) are forbidden. As a consequence only four tetrads out of six and seven pentads out of ten can be observed. Simple statistical considerations predict for the seven allowed pentads the following intensity ratios: mmmm:mmmr:rmmr:mmrr:rrrr:mrrr:mrrm = 3:2:1:4:3:2:1. This distribution can be considered as the fingerprint of hemiisotactic polymers: it is easily recognized in the methyl region of the ^{13}C-NMR spectrum of hit-PP run at 135 °C.[1]



I

A different sequence distribution as well as the presence of small amounts of forbidden pentads (mmrm, rmrm, rmrr) can be accounted for with a probabilistic approach which takes into account the specific features of the polymerization mechanism. A statistical analysis of the two-step process has already been reported.[1,2,6,8] The aim of the present article is the stereochemical analysis of the Ewen one-step synthetic method and the comparison of this process with those which afford isotactic or syndiotactic polypropylene. A preliminary account of this study was presented recently.[9] In addition, new results concerning 1D- and 2D-NMR spectra of hit-PP will be reported in a forthcoming paper.[10]

A Stereochemical Analysis of the Polymerization Mechanism

A soluble metallocene catalyst, very active in isospecific propylene polymerization, was obtained by Ewen in 1984.[11] He arrived at this result by combining two independent lines of research, one concerning the synthesis of stereochemically rigid bridged metallocene compounds achieved by Brintzinger[12] and the other concerning the catalysts for ethylene polymerization developed by Kaminsky.[13] Later on, Ewen obtained a syndiospecific metallocene catalyst[14] and more recently a catalyst able to produce hemiisotactic polypropylene.[7] In this section we discuss the structure of the catalysts and some features of the polymerization mechanism in terms of general stereochemical concepts. Part of the following remarks have already been reported in other papers; here we try to give a general and unifying picture of all this matter.

Metallocene complexes can be represented by the general formula L_2MtX_2, where L_2 is a rigid bidentate metallocene ligand, Mt is a group IV transition metal (Ti, Zr, Hf), and X is a chlorine atom or an organic radical. The structure of the active center obtained after reaction with a large excess of methylaluminoxane (MAO) or MAO–trimethylaluminum mixtures is usually described as a cation $[L_2Mt^{IV}MP]^+$, where M is an η_2-coordinated monomer molecule and P is the growing chain σ-bonded to the metal.[15,16]

Modulation of the catalytic ability was obtained by a careful choice of the structure of the organic ligand. The isospecific catalyst (II) contains the dianion derived from diindenylethane, the syndiospecific one (III) the dianion derived from cyclopentadienylfluorenyldimethylmethane, and the hemiisotactic-specific one (IV) the dianion derived from (3-methylcyclopentadienyl)fluorenyldimethylmethane. According to Brintzinger,[12] diindenylethane can give rise to two diastereomeric metallocene complexes: the one reported as II is chiral, while the other is meso and lacks steric control. The recognition

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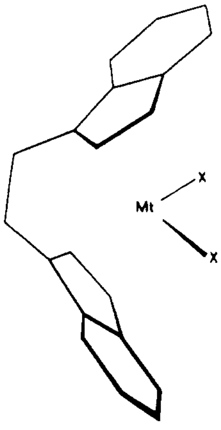
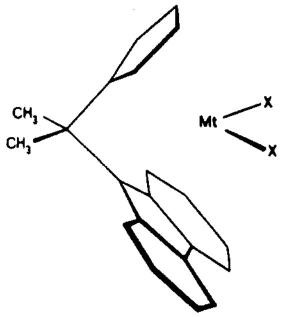
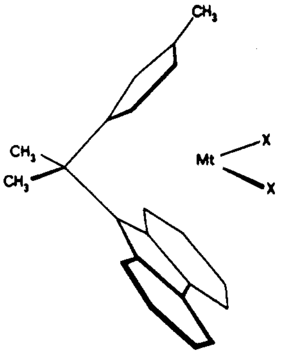


II



III



IV

that their different catalytic behavior depends on their different symmetry is one of the major results obtained by Ewen.[11]

For the purpose of the present discussion we prefer to describe the catalyst structure in a schematic way as shown in Table I, where the (deformed) tetrahedral coordination around the metal is projected on the plane as in the Fischer projection. The idealized molecular symmetry of the complexes with formula L_2MtX_2 is C_2 for II, C_s for III, and C_1 for IV. In agreement with the nomenclature used in organic stereochemistry,[17] the two X groups, or the two Mt–X bonds, are defined as homotopic, enantiotopic, and diastereotopic, respectively; in other words, the two chlorine atoms are equivalent in all respects in II, mirror images of each other in III, and different in IV.

For the catalytic center of formula $[L_2MtMP]^+$ it should be noted that in IIa (IIa, IIIa, and IVa refer to the catalytic centers derived from II, III, and IV) the exchange of any pair of substituents does not change the configuration of the central metal atom: according to Mislow,[18] this atom is defined as chirotopic but not stereogenic, contrary to cases IIIa and IVa, where the metal atom is both chirotopic and stereogenic.

Several authors have already pointed out that the stereochemical control exerted by these catalysts agrees, on the whole, with the hypothesis of a mechanism, often referred to as the *alternating* or *migratory mechanism*, in which at each step the growing chain shifts to the position previously occupied by the coordinated monomer,[7,15,16] a mechanism already proposed for heterogeneous $TiCl_3$ catalysts.[19] From the above reported analysis it follows that the alternating mechanism is consistent with the experimental results in all cases. However, formation of isotactic PP in case II is not diagnostic for this mechanism; the nonstereogenic nature of the metal atom makes the two complementary parts of the catalyst completely equivalent, and we cannot distinguish between alternate addition on both faces, successive addition on the same face, and random addition on both faces.

The alternating mechanism is supported by the results obtained with catalyst III, where a clear correspondence exists between the alternate configuration of successive monomer units in the polymer and the presence of enantiotopic catalytic sites. The presence of other mechanisms such as the chain-end controlled addition cannot be excluded, although it should be considered rather unlikely.

The evidence in favor of the alternating mechanism becomes even stronger in the case of catalyst IV, as already pointed out by Ewen.[7] The presence of ordered and disordered stereogenic carbons in hit-PP requires in fact a polymerization mechanism where a regular succession of two different reaction steps occurs, a process for which an explanation in general terms is not a simple task. The alternating mechanism however passes all the tests: formation of hit-PP is easily explained if we assume that the diastereomeric faces have a different steric control, in particular if one of the faces possesses a steric control analogous to that observed in case III, while on the opposite face control is practically nil.

This behavior is consistent with the general scheme proposed by Corradini,[16] who assumes that the catalyst structure influences directly the conformation of the growing chain and through it the stereochemistry of monomer insertion. In the stereospecific polymerization step the chain is bonded at the less crowded part of the catalyst (left side in Table I) and assumes a rather rigid, low-energy conformation; as a consequence propylene coordination occurs exclusively (or mostly) with a defined face (*re* or *si*). In the nonspecific step the chain is bonded at the opposite, more crowded face and experiences in almost the same way the presence of the fluorenyl group on one side and that of the methylcyclopentadienyl ring on the other. Two conformations exist for the chain, with about the same energy, which exert an opposite influence on monomer coordination, thus explaining the lack of steric control.

The above stereochemical discussion is summarized in Table I.

A Probabilistic Approach

A more detailed and quantitative description of the polymerization mechanism can be obtained when considering the type and amount of the "forbidden" sequences. This concept was used by us to describe those structures which are incompatible with the definition of hit-PP.[2] The term can be extended to cover all the structures which are incompatible with the proposed mechanism for all the cases discussed in the present article. If we take the alternating mechanism for granted, forbidden sequences can mainly derive from a noncomplete or nonideal stereocontrol at the catalytic sites or from the occurrence of successive additions on the same catalyst face. This second kind of error has also been named *skipped insertion*[7] or *isomerization without monomer insertion*.[20,21] Other sources of stereochemical defects are not considered in the present discussion.

From these premises we derived a statistical description of polymer stereosequences and compared the predicted pentad distribution with the experimental results. For this purpose we have introduced four probability parameters, defined as follows (more details are reported in Appendix A): a = probability that at a *given catalytic face* the stereogenic carbon of the entering monomeric

Table I
Propylene Polymerization with Soluble Catalysts

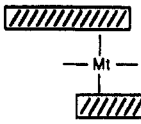
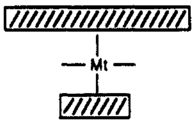
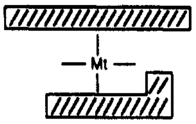
	catalyst		
	II	III	IV
idealized (tetrahedral) geometry of the catalyst			
symmetry of the L_2MtX_2 complex	C_2	C_s	C_1
relationship between Mt–X bonds (or X atoms) in L_2MtX_2	homotopic	enantiotopic	diastereotopic
stereochemical notation for Mt in $[L_2MtMP]^+$	chirotopic nonstereogenic	chirotopic stereogenic	chirotopic stereogenic
polymer	isotactic	syndiotactic	hemiisotactic
alternating mechanism	possible	highly probable	highly probable
reactivity of successive steps	equivalent	equivalent	different
relationships between probability parameters	$a = b$ $c = d$	$a = 1 - b$ $c = d$	$a \neq b$ $c \neq d$ ($d = 0$)
values of parameters for ideal structures	$a = b = 1$ $c = d$ = any value	$a = 0, b = 1$ $c = d = 0$	$a = 0.5, b = 1$ $c = 0$

Table II
Pentad Distribution for Catalyst II (mol %)

a	*b*	*c*	*d*	mmmm	mmmr	rmmr	mmrr	mmrm	rmrr	rmrm	rrrr	mrrr	mrrm
1.0	1.0	0	0	100.00	0	0	0	0	0	0	0	0	0
1.0	1.0	0.1	0.1	100.00	0	0	0	0	0	0	0	0	0
0.95	0.95	0	0	77.38	8.15	0.22_5	8.15	0.45	0.45	0.45	0.22_5	0.45	4.07
0.95	0.95	0.1	0.1	77.38	8.15	0.22_5	8.15	0.45	0.45	0.45	0.22_5	0.45	4.07
0.9	0.9	0	0	59.05	13.14	0.81	13.14	1.62	1.62	1.62	0.81	1.62	6.57
0.7	0.7	0	0	17.05	15.54	4.41	15.54	8.82	8.82	8.82	4.41	8.82	7.77
0.5	0.5	0	0	6.25	12.50	6.25	12.50	12.50	12.50	12.50	6.25	12.50	6.25

Table III
Pentad Distribution for Catalyst III (mol %)

a	*b*	*c*	*d*	mmmm	mmmr	rmmr	mmrr	mmrm	rmrr	rmrm	rrrr	mrrr	mrrm
0	1	0	0	0	0	0	0	0	0	0	100.00	0	0
0.05	0.95	0	0	0.22_5	0.45	4.07	8.15	0.45	0.45	0.45	77.38	8.15	0.22_5
0.1	0.9	0	0	0.81	1.62	6.57	13.14	1.62	1.62	1.62	59.05	13.14	0.81
0.3	0.7	0	0	4.41	8.82	7.77	15.54	8.82	8.82	8.82	17.05	15.54	4.41
0	1	0.05	0.05	0	0.02_5	0.22_5	0.45	0.02_5	8.57_5	0.45	81.45	8.57_5	0.22_5
0	1	0.1	0.1	0.01	0.18	0.81	1.62	0.18	14.58	1.62	65.61	14.58	0.81
0.1	0.9	0.1	0.1	0.96_5	3.51	5.16_5	11.06_5	2.77	11.99	3.69_5	40.00	18.62_5	2.21_5
0.3	0.7	0.3	0.3	5.08_5	11.16	6.19_5	12.72	10.83_5	13.52_5	11.64	8.58	14.28	5.98

unit assumes a *certain configuration*; b = probability that at *the complementary catalytic face* the new stereogenic carbon assumes the *same configuration*; c = probability of two successive additions at the catalytic face related to parameter b; d = probability of two successive additions at the catalytic face related to parameter a.

A similar approach has been independently developed by Fink[20,21] in the frame of a kinetic study on propylene polymerization with homogeneous metallocene catalysts.

The definition of four parameters is necessary to cover all the cases (II, III, and IV), but for a specific case, at least as a first approximation, only two or at most three independent parameters will be used. The probabilities of existence of diads, triads, tetrads, and pentads have been calculated for the general case with the method briefly described in Appendix A. Application to specific cases is obtained by a proper choice of the probability parameters.

For catalyst II symmetry considerations impose that $b = a$ and $d = c$; it can be easily shown that sequence distribution is independent of c and d (see Table II). As a consequence, for isospecific polymerization a single parameter (a or b) describes the polymer structure, and the distribution coincides with that obtained by the usual enantiomeric site control scheme. Pure isotactic polymers are obtained when a equals 1 or 0. For values slightly lower than 1 (or slightly higher than 0), three pentads stand out: mmmr, mmrr, and mrrm in the 2:2:1 ratio, in agreement with experiment.[11] We note that the same result was obtained long ago by Zambelli[22] in the case of heterogeneous catalysts, proving for the first time that the stereochemical control is due to the catalyst chirality. a values approaching 0.5 correspond to a lower stereochemical control; for $a = 0.5$ an ideal atactic polymer is obtained (see Table II).

In the case of catalyst III, the symmetry conditions are $b = 1 - a$ and $d = c$. Pure syndiotactic polymers require that a equals 0 (or 1) and $c = 0$. Deviation from ideal conditions has a different effect depending on which are the defective parameters: if a is different from 0, an mm triad forms; if c differs from 0, an isolated m diad is observed. At the pentad level for an almost pure syndiotactic polymer we observe in the first instance a 2:2:1 ratio between pentads mrrr, mmrr, and rmmr, while in the second the two pentads mrrr and rmrr are present in the same amount (Table III). Hence, the analysis of forbidden sequences is a diagnostic tool of the degree of migration of the growing chain.

Case IV is more complex. Here no symmetry condition exists and all four parameters are independent. However, one can suppose that probability of successive insertions at the nonstereospecific face is quite negligible. Hence we put at the beginning $d = 0$. Other parameters for pure hit-PP are $a = 0.5$, $b = 1$, and $c = 0$. These values give the classical 3:2:1:4:3:2:1 pentad distribution with the complete absence of the forbidden pentads mmrm, rmrm, and rmrr. This distribution coincides with that already reported in the first paper concerning hit-PP.[1]

Table IV
Pentad Distribution for Catalyst IV and Comparison with Experimental Data (mol %)

	a	*b*	*c*	*d*	mmmm	mmmr	rmmr	mmrr	mmrm	rmrr	rmrm	rrrr	mrrr	mrrm	*R″* (%)
	from ref 7, Table 18, run 8B				14	12	6	21	5		0	19	14	8	
A	0.4735	1	0	0	16.52	11.80	6.56	24.93	0	0	0	21.16	13.13	5.90	19.73
B	0.4695	0.9511	0	0	14.18	11.65	6.64	22.61	2.32	2.32	2.32	18.87	13.27	5.82	9.76
C	0.4076	0.9862	0.1644	0	13.92	12.86	5.03	22.26	0.67	4.86	0.69	19.36	13.59	6.76	6.31_5
D	0.4196	0.9811	0.1404	0	14.06	12.73	5.25	22.31	0.92	4.43	0.94	19.21	13.54	6.61	6.42
E	0.3950	0.9914	0.1893	0	13.81	12.99	4.82	22.21	0.42	5.31	0.44	19.44	13.61	6.95	6.42
F	0.4184	1	0.1301	0.0411	14.02	12.76	5.00	22.20	0.56	4.94	0.74	19.32	13.80	6.66	6.26
	from ref 7, Table 18, run 8A				20	14	8	21	5		2	11	10	7	
G	0.5586	0.9383	0	0	20.58	13.93	5.40	21.88	2.86	2.86	2.86	11.87	10.80	6.96	8.66

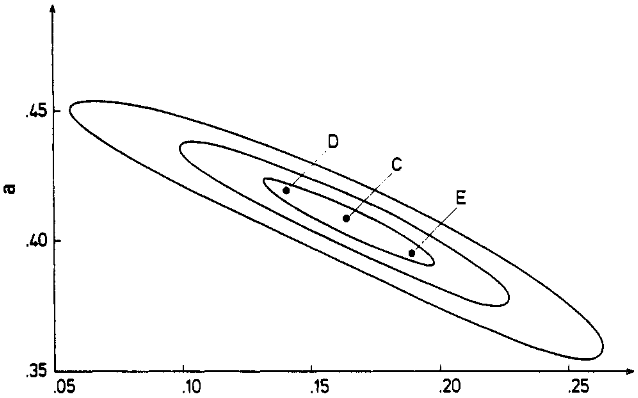


Figure 1. Map of the agreement factor *R″* as a function of *a* and *c* (*b* being optimized in each point, $d = 0$). Contour lines are drawn at $R'' = 6.5, 7.0,$ and 8.0%. Points C, D, and E correspond to the distribution reported in Table IV.

A deviation of *a* with respect to 0.5, other parameters being unchanged, alters the ratio among permitted sequences, a decrease of *a* producing both a decrease of the mm triad and an increase of rr, with only a minor influence on mr. A polymer of this type was obtained by Fink polymerizing propylene with catalyst IV at low temperature.[21]

When *b* differs from 1, the forbidden pentads form, but the ratio of their concentration is always 1:1:1, regardless of the *a* values.[23] As pentads mmrm and rmrr have the same chemical shift, we should observe two "forbidden" peaks in the ratio 2:1 in the NMR spectrum. If this does not occur, we must take parameter *c* into account; in other words, we are forced to assume the existence of some defect in the alternated reactivity of the catalyst faces. This conclusion is quite reasonable in view of the different energetic levels of the two faces of catalyst IV.

Comparison of the calculated pentad distribution with experimental data reported by Ewen[7] (catalyst IV + MAO without solvent, 65 °C) is very significant (Table IV). The two-parameter statistics gives a minimum at $a = 0.4695$ and $b = 0.9511$ with the Hamilton agreement factor[24]

$$R'' = \left(\sum_i (I_{ic} - I_{io})^2 / \sum_i (I_{io})^2\right)^{1/2}$$

equal to 9.76%. A much better agreement is obtained using three parameters *a*, *b*, and *c* (Table IV, line C). Figure 1 shows a map of the agreement factor *R″* as a function of *a* and *c*, *b* being optimized for every pair of *a* and *c* values. The contour lines define an elongated and flat hollow where the main axis has a slope of about −0.5. Inside the deepest contour line any pair of *a* and *c* fits almost equally well the experimental values (see lines D and E in Table IV).

Calculations carried out using parameters *a*, *b*, and *d* (instead of *c*) gave higher *R″* values; this result supports the hypothesis that consecutive insertions occur preferably at the stereospecific catalyst site.

In an attempt to find a better agreement with the experiment, we optimized the calculation taking into account all four parameters *a*, *b*, *c*, and *d* (Table IV, line F). In this case *b* tends to 1 and the occurrence of forbidden sequences is completely assigned to the effect of the successive insertions at both catalyst sites. From a statistical point of view it is difficult to distinguish between such a scheme ($b = 1$ and $d \neq 0$) and the previous one ($b \neq 1$ and $d = 0$). A discussion on this point would require additional experimental data, preliminary tested with regard to the necessary pentad relationships.[25] A value of *b* different from 1, as observed with the syndiospecific catalyst III,[26] seems more realistic; hence at present we prefer an interpretation based on parameters *a*, *b*, and *c* only, leaving $d = 0$.

Experiments carried out at lower temperatures[21] indicate a notable decrease in the *c* value; below room temperature this kind of defect becomes quite negligible.

The extent of consecutive insertions at the same catalyst face appears to depend also on the nature of the cocatalyst. The best agreement between our calculations and the results reported by Ewen[7] using zirconocene (IV) in the presence of tetrakis(perfluorotetraphenyl)borate (F20) is obtained when parameter *c* tends to zero. A clue in this direction comes, as discussed above, from the inspection of the "forbidden" peaks, which are almost exactly in the 2:1 ratio. In Table IV we report the experimental data by Ewen[7] and our calculations (last two lines). Comparison of line G with C, which refers to a polymerization carried out in the same conditions but using MAO as a cocatalyst, shows that all three parameters *a*, *b*, and *c* are different in the two experiments. In energetic terms the difference in activation free energy between the two catalytic systems increases in absolute value, passing from ≃0.4 kcal/mol for the process related to parameter *a* (i.e., the stereochemical control at the nonspecific site) to ≃1 kcal/mol for *b* (stereochemical control at the specific site) to a value larger than 2 kcal/mol for *c* (consecutive addition at the stereospecific site).

Conclusions

The symmetry analysis of the metallocene catalysts and the statistical approach presented in this paper confirm the validity of the alternating mechanism of propylene polymerization in the presence of soluble catalysts. At the same time evidence is obtained for the occurrence of consecutive insertions at the stereospecific catalyst face, whose amount depends on the polymerization conditions and on the structure of the catalyst and cocatalyst. In particular, our approach may be used for a quantitative evaluation of stereospecificity in different catalytic systems and may give some suggestions about the specific role and interaction of the catalyst and cocatalyst.

Most of the preceding remarks would not be possible without a precise point of reference, namely the structure of hit-PP. It is noteworthy that this polymer, first synthesized within the frame of a stereochemical and spectroscopic research, has found an important application in a more practical field, such as the determination of the working mechanism of a new class of polymerization catalysts.

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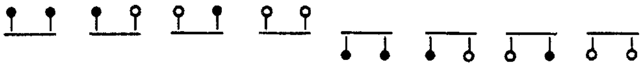
Appendix A

For statistical purposes, the polymer structure is described as a succession of black and white beads placed above or below the chain. The parameters already cited in the text are redefined as follows: a = probability of finding a white bead above the chain, b = probability of finding a black bead above the chain, c = probability of finding two adjacent black beads, and d = probability of finding two adjacent white beads. In addition, we put $e = 1 - a$, $f = 1 - b$, $g = 1 - c$, and $h = 1 - d$.

All the possible ways to form a given sequence are taken into account. Their number is 2 for palindromic sequences (the original sequence and its mirror image with respect to a plane containing the chain axis) and 4 for nonpalindromic sequences (in addition to the preceding ones, the inverted sequence and its mirror image).

The probability that a given sequence begins with a black bead (i.e., the total number of black beads) is $h/(g + h)$, and with a white bead $g/(g + h)$.

In the case of diad m we take into account the following structures:



The related probability of existence is

$$m = (ch(b^2 + f^2) + 2gh\ (ab + ef) + dg(a^2 + e^2))/(g + h)$$

In the case of pentads, the probability of each sequence is obtained as the product of a row vector containing 32 fifth-degree monomials in c, d, g, and h (common to all pentads) with a column vector containing 32 fifth-degree polynomials in a, b, e, and f (specific for each pentad), the normalization factor always being $(g + h)$. A few numerical results are listed in Tables II–IV.

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(23) It should be noted that parameter b differs from β of our previous paper.[2] In this regard we should correct the equations reported in Table III of ref 2: all the probability expressions should be divided by 2 and not only those concerning the palindromic sequences.

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