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A versatile approach for modeling and simulating the tacticity of polymers

Massoud J. Miri · Benjamin P. Pritchard · H. N. Cheng

Abstract We are introducing a versatile computerized approach to model and simulate polymer tacticities using seven single-stage statistical models. The theory behind the models, e.g., Bovey's versus Price's, Bernoullian, 1st or 2nd order Markovian, enantiomeric types, and combinations thereof is explained. One of the models, "E-B gen", which can be used to produce four types of enantiomorphically controlled tacticities, and the pentad distribution for the model "E-M1" are reported here for the first time. The relations of chain-end controlled models to binary copolymerizations are discussed in detail, and equations for the conversion of tacticity based probabilities to reactivity ratios to obtain related n-ad distributions are presented. The models were applied to 20 polymers with exemplary tacticities found in the literature. A related software program ("Polytact") based on Microsoft's Excel has been designed to calculate all relevant characteristics of the polymer tacticity and to present them in graphical form in a user-friendly manner. The program can be used to produce graphs of the triad, pentad and sequence length distributions and a simulation of 50 monomer repeat units in the polymer for each of the seven models. One of the main

intended uses of the program is to compare the computed n-ad distributions to those of experimental polymers obtained from NMR spectroscopy and to gain insight into the polymerization mechanisms.

Introduction

Tacticity refers to the relative spatial arrangement of substituents along a polymer chain. We will discuss here polymers that are formed mainly from monomers representing a mono-substituted ethylene, e.g., propylene, or a 1,1-disubstituted ethylene with different groups, e.g., methyl methacrylate, as represented in the general reaction scheme shown in Fig. 1.

The tacticity of polymers is relevant industrially because polymer crystallinity and important macroscopic properties such as the density, glass and melting temperatures, clarity, and stiffness of a polymer depend on it. Moreover, a detailed knowledge of polymer tacticity can reveal insight into polymerization mechanism. The basic concepts of tacticity were developed more than 50 years ago on homopolymers of monosubstituted ethylene made with different types of polymerization initiators, such as radical, ionic or coordinative species [1–17]. At that time, three main types of tacticities were distinguished: isotactic, syndiotactic and atactic, shown in Fig. 2. The remaining forms of tacticities in Fig. 2 were introduced during the advent of the polymerization of propylene with various types of metallocene catalysts discussed below [18–29]. NMR spectroscopy is the usual technique employed to quantify tacticity, although IR and fractionation methods are often applied as well.

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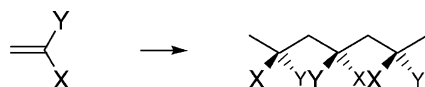New Orleans, LA 70124, USA

Fig. 1 Scheme for the polymerization of monomers that can lead to polymers with different tacticities; X and Y are substituents, Y=H for monosubstituted ethylene, e.g., propylene, vinyl chloride or styrene, Y=R in disubstituted ethylene, e.g., methyl methacrylate, methacrylamide

For depiction of configurations, we prefer to use Fischer projections, in which the substituents are portrayed up and down, over the zig-zag notation, because they are easier to apply and more efficient. In addition, the direction of adjacent methyl groups, or a dyad, needs to be compared with subsequent dyads. If both neighboring methyl groups in a dyad point in the same direction, they are meso or "m" to each other. If they point in opposite directions, they are racemic or "r" to each other. These notations were introduced by Bovey [1–3] and are the dominant nomenclature in the literature. The alternative nomenclature uses the absolute configurations "d" and "l" and is preferred by some authors, such as Price [4, 5], but this terminology is more relevant only when the polymer is chiral or when related mechanistic questions are of interest. We will elucidate the differences between these two nomenclatures

further below, under the more detailed discussion of statistical models.

Most commercial polypropylene is isotactic; this form is the most crystalline and has a melting temperature of ca. 165 °C. A much smaller fraction of polypropylene produced is syndiotactic, which has a melting temperature about 10 degrees lower than isotactic polypropylene. However, small changes or repetitive errors in the polymer's tacticity can influence crystallinity and melting temperature significantly [23]. Atactic polypropylene is completely amorphous and is used for more limited applications, e.g., as a hot melt adhesive and a viscosity index improver for lubricants. Isotactic stereoblock copolymers are similar in their crystallinity as regular isotactic polypropylene. A typical hemi-isotactic polypropylene is actually amorphous [25]. However, the crystallinity and melting temperature can also be lower for a polymer at a higher degree of isotacticity. For example, the melting temperature for isotactic polystyrene is 240 °C, while that of the syndiotactic polystyrene is 270 °C [30]. Similarly for polymethyl methacrylate the isotactic polymer has a lower melting temperature than the syndiotactic form ($T_{m, \text{ it-PMMA}} \approx 160$ °C, and $T_{m, \text{st-PMMA}} \approx 200$ °C) [1].

Fig. 2 Different types of tacticities

As will be mentioned in more detail later, we will use primarily polypropylene as an example of a polymer of which most types of tacticities shown in Fig. 2 can be produced. We will exclude regioselectivity, i.e., combinations of primary and secondary monomer additions resulting in head-to-head and tail-to-tail sequences. Only single-state models are discussed in this work. We exclude for example isotactic-atactic block copolymers of propylene, which had been developed by Waymouth and Coates, because it would require a two-state model [31, 32]. For the most part, we will not consider polymerizations with conventional heterogeneous Ziegler-Natta catalysts, because these catalysts contain multiple sites and therefore require more complex multi-state models to simulate their tacticities [33, 34]. Finally, we also will neglect any influences on tacticity due to molecular weight properties or process fluctuations [34].

The various models and their applications to NMR, IR and fractionation data can be challenging particularly for polymers where the catalyst used is unknown or where the reaction mechanism is not clear. We have developed a software program that incorporates all the models proposed together with many convenient features. The approach can be used as a tool in synthetic chemistry to target a desired polymer tacticity, or in analytical chemistry to test models based on data from NMR spectroscopy. The combination of choices for data input, calculations provided by the program, and output of results in visual form is intended to make the program user friendly and efficient as an analytical and learning tool. We hope the computer program is helpful to researchers dealing with polymer tacticity, particularly relating to polymers obtained with single-site catalysts.

Statistical models for formation of polymers with different tacticities

Chain-end versus site control

There are two types of propagation mechanism: "chain-end control" and "enantiomorphic site control" as shown in Fig. 3. These are caused by the different types of stereogenic centers including the catalyst site and the tertiary carbon atom closest to the active center. A more realistic view of tacticities should include the occurrence of natural errors during propagation. There are also two types of propagation errors. If during polymerization only one error occurs and the pendant methyl-groups are placed continuously on the opposite side of the chain compared to before the error, it can be assumed that this error was caused by the addition of monomer to the growing chain or an error in the chain end-control (see Fig. 3, right). If, however, the error is followed by a subsequent self-correcting monomer addition, so that the tacticity essentially remains the same, this error is caused by the active catalytic species, or an error in the enantiomorphic site control (Fig. 3, left). The stereoerrors are shown for primary insertions only.

Polymerizations of monomers representing a monosubstituted ethylene, such as acrylates, with radical or ionic initiators entail mostly chain-end controlled mechanism,

Fig. 3 Two types of errors that can occur during polymerization caused at different stereogenic centers
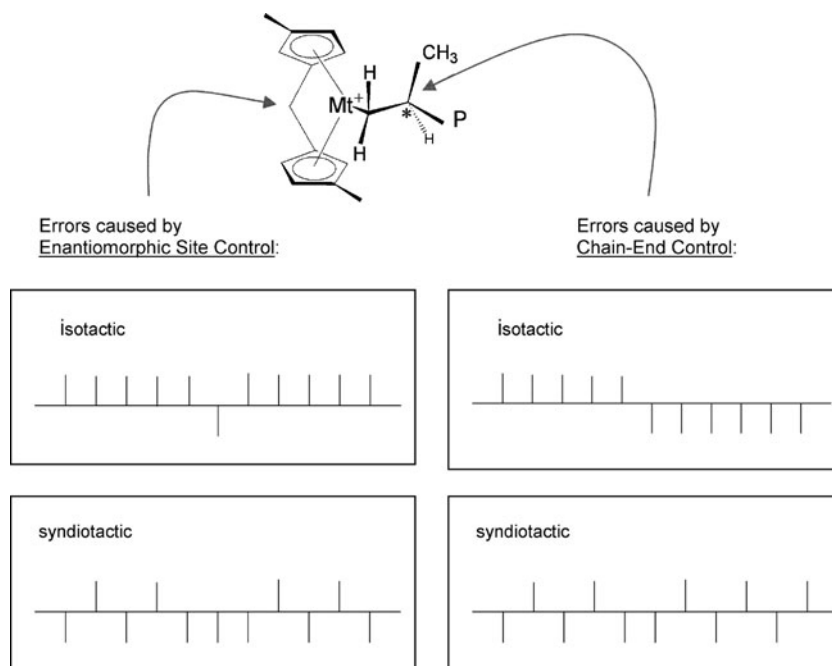
while coordinative initiators typically induce a site controlled mechanism.

Models with chain-end control

Although polymers of a monosubstituted ethylene are strictly speaking homopolymers, they can be treated mathematically as copolymers when it comes to the explanation of the processes leading to their tacticity. We will start with the case of chain-end control by the terminal monomer residue in the growing polymer chain, shown in Fig. 4. This can be regarded as a copolymerization of two configurations with an "up-monomer" (with the methyl group pointing up in the Fischer projections during the addition step) and a "down monomer" (using the same analogy). This would be a kinetic model with a terminal effect of the last monomer residue in the growing polymer chain on the polymerization, or in the parlance of probability theory, a 1st order Markovian model. As was described by Price, it has four reactions with four reaction probabilities, P_{dd}, P_{dl}, P_{ld}, and P_{ll}, or two independent reaction probabilities, P_{dl} (= $1 - P_{dd}$) and P_{ld} (= $1 - P_{ll}$).

However, one can view the same process through pairwise relative tacticity (Bovey's approach). Thus, instead of considering the configuration of individual monomers, one observes the relative configuration of the last two monomer residues, i.e., dyads. Bovey's approach is based on dyad units, whereas Price's approach is based on single units. If we neglect absolute configuration, the products of the reactions (1) and (4) shown in Fig. 4 have identical relative configuration (meso) and identical reaction probabilities, i.e., $P_m = P_{dd} = P_{ll}$. Similarly, the reactions (2) and (3) in Fig. 4 have the same relative configuration (racemic), with the same reaction probabilities $P_r = P_{dl} = P_{ld}$. Thus, Bovey's approach for the above case defaults to a Bernoullian model with only one independent probability, let's say P_m, and $P_r = 1 - P_m$. This is the simplest case of chain-end control and we designate it as model "B" [12].

We can extend this concept to the next higher models, i.e., the 2nd order Markovian model according to Price (for absolute configuration) or the 1st order Markovian model according to Bovey (for relative configuration). In this case there would be eight reactions with four independent probabilities for the copolymerization with absolute configurations for the Price approach (non-symmetric case), but they default to a 1st order Markovian case with only two independent probabilities, P_{mm} and P_{rr}, for the relative configurations in the Bovey approach. This model involves a penultimate effect because the last two monomer residues have an influence on the configuration of the incoming monomer. We will use the abbreviation "M1" for this model. With the same analogy, the next higher case is a penpenultimate model in the Bovey approach or 3rd order Markovian model in the Price approach (non-symmetric case), which defaults to a 2nd order Markovian model with four independent probabilities, P_{mmm}, P_{mrm}, P_{mrr}, and P_{rmm} in the Bovey approach. In our notation this model is abbreviated as "M2".

To test if a Bernoullian model according to Bovey is valid or not, an analysis of the triads is sufficient if the

Fig. 4 1st order Markov model of formation of polymer according to Price, equivalent to the Bernoullian model according to Bovey
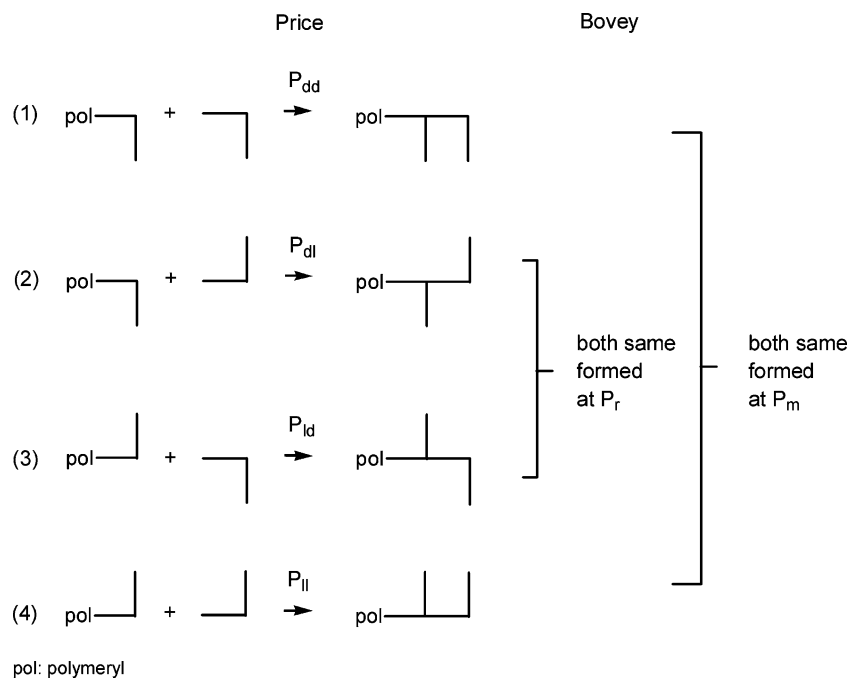
NMR data have enough precision and accuracy. However, to test if a 1st Markov model according to Bovey is valid or not tetrads must be determined at the minimum. Since we are discussing different chain-end controlled models up to Bovey's 2nd order Markovian, we will consider in more detail pentads as the representative n-ad sequences.

General relationships between the n-ads

The n-ads that are chemically equivalent are summarized into simpler n-ads. For example, triads with reversible sequences, such as the mr-triad and rm-triad, are equal and therefore are summed up to one triad, which is twice as large as each of related sequences.

$$[mr] = mr + rm = 2mr = 2rm \tag{1}$$

Similarly as an example for reversible sequences of pentads:

$$[mmrm] = mmrm + mrmm = 2mmrm = 2mrmm \tag{2}$$

The intensities of all n-ad groups must add up to unity; for example, for the sum of all three triads,

$$[mm] + [mr] + [rr] = 1 \tag{3}$$

In addition, certain relationships exist between the different types n-ads. For example, between dyads and triads,

$$[m] = [mm] + 0.5[mr] \tag{4}$$

and

$$[r] = [rr] + 0.5[mr] \tag{5}$$

or among pentads,

$$[mmmm] + 2[rmmr] = [mmrm] + [mmrr] \tag{6}$$

and

$$[mrrr] + 2[mrrm] = [rrmr] + [rrmm] \tag{7}$$

Further relations between the different n-ads have been established, which are based on the same straightforward methodology [11].

Sequence length distributions and averages

Another related and useful property representing the distribution of different monomer types in polymers with specific tacticities is the sequence length [7, 35]. We can distinguish hereby the length for a type of dyad, m or r. For example, the length of continuously isotactic sequences can be defined as the m dyads in the sequence r(m)$_n$r, whereby n is an integer. The actual number of dyads is however larger by one, i.e. $n+1$. We then can establish the following quantities.

The number fraction of the isotactic sequences can be expressed based on the meso dyad as:

$$N(n)_m = [r][m]^n[r] = (1 - [m])[m]^n(1 - [m]). \tag{8}$$

The corresponding weight fraction is:

$$W(n)_m = n[r][m]^n[r] = n(1 - [m])[m]^n(1 - [m]). \tag{9}$$

The average sequence length then can be obtained as:

$$\bar{n}_m = \frac{\sum W(n)_m}{\sum N(n)_m} \tag{11}$$

For an isotactic polymer $\bar{n}_m$ is larger than 2; for an atactic polymer it is close to 2; for a syndiotactic polymer it is close to 1, the minimal value.

Similarly, for the length of syndiotactic sequences based on the racemic dyad we can obtain the following equations:

$$N(n)_r = [m][r]^n[m] = (1 - [r])[r]^n(1 - [r]) \tag{12}$$

$$W(n)r = n[m][r]^n[m] = n(1 - [r])[m]^n(1 - [r]) \tag{13}$$

and

$$\bar{n}_r = \frac{\sum W(n)_r}{\sum N(n)_r}. \tag{14}$$

For the simple case of a Bernoullian polymer the average sequence lengths can be calculated as:

$$\bar{n}_m = \frac{1}{P_r} \text{ and } \bar{n}_r = \frac{1}{P_m} \tag{15}$$

Alternatively (or for non-Bernoullian models), the average sequence lengths can be calculated reliably by using Eqs. 11 and 14 for 1000 repeat units (i.e. n=1 to 1000).

Relationship between formation of polymers with different tacticities and binary copolymerization by chain end control

As mentioned above the polymerization of a homopolymer of a monosubstituted ethylene type monomer, such as propylene, can be considered as a binary copolymerization of a "down" and "up" propylene based on the Fischer projections. These two monomers can be represented as "A" and "B" in a binary copolymerization. We adopt for the chain-end models the more frequently used concept by Bovey, as mentioned earlier. Therefore, the probabilities leading to the *triad* distribution for a polymer with a certain tacticity, given as [mm], [mr], [mm] are related to reactivity ratios in binary copolymerizations that lead to a *dyad* distribution based on [AA], [AB], and [BB].

The theory of binary copolymerizations will not be discussed here, but can be readily found in the literature, for example in ref. [36]. Whereas for homopolymer tacticities

the reaction probabilities (e.g., P_{mm}) are used, for copolymerizations the comonomer fractions in the feed and reactivity ratios are needed as the model variables. When copolymerization theory is used for homopolymer tacticity, the fraction in the feed can be set as 0.5, because the two types of monomers ("up" and "down") can be considered to be the same and only the reactivity ratios remain as variables.

The following mathematical expressions can be used to obtain analogous n-ad distributions for both the tacticity chain-end models and binary copolymerizations. They were obtained by setting the n-ads, for example the triads [mm] and [rr], equal to the corresponding dyads, [AA and [BB], respectively. For a Bernoullian process the only independent probability is P_m and can be related to the independent reactivity ratio r_A:

$$\frac{P_m}{P_r} = \frac{P_m}{1 - P_m} = r_A. \qquad (16)$$

Similarly, the analogous n-ad distributions can be obtained for the 1st order Markovian processes with two independent probabilities:

$$\frac{P_{mm}}{P_{mr}} = \frac{P_{mm}}{P_{mm} - 1} = r_A \text{ and } \frac{P_{rr}}{P_{rm}} = \frac{P_{rr}}{P_{rr} - 1} = r_B. \qquad (17)$$

For example, if $r_A = 4$ and $r_B = 1.5$, then $P_{mm} = 0.8$ and $P_{rr} = 0.6$, according to Eq. 17. The same dyad distribution, [AA] = 0.5333, [AB] = 0.2667, and [BB] = 0.2000, and numerically the same triad distribution are obtained: [mm] = 0.5333, [mr] = 0.2667, and [rr] = 0.2000, when applying P_{mm} = 0.8 (i.e., P_{mr} = 0.2) and P_{rr} = 0.6 (i.e., P_{rm} = 0.4).

For processes that are 2nd order Markovian equivalent n-ads can be obtained based on the following relationships:

$$\frac{1}{P_{mmr}} - 1 = r_A \text{ and } \frac{1}{P_{rmm}} - 1 = r_B \qquad (18)$$

$$-\frac{P_{rmm}}{P_{rmm} - 1} = r'_A \text{ and } -\frac{P_{mrr}}{P_{mrr} - 1} = r'_B. \qquad (19)$$

Though the dyad distribution of a binary copolymer and the triad distribution representing a tacticity may be numerically equal, they can represent polymers with different monomer

Table 1 Comparison of polymers with equivalent monomer sequence distributions

Polymers based on stereospecificity of polymerization

No.	Probabilities				Monomer sequence	Description	Triad distribution			Average sequence length**	
	P_{mm}*	P_{rr}	–	–			mm	mr	rr	$\overline{n}_m$	$\overline{n}_r$
1a	0.99	0.01	–	–	⌐⌐⌐⌐⌐⌐⌐⌐ m m m r m m m	isotactic	0.98	0.02	0	100	1.01
2a	0.01	0.99	–	–	⌐⌐⌐⌐⌐⌐⌐⌐ r r r r r r r	syndiotactic	0	0.02	0.98	1.01	100
3a	0.50	0.50	–	–	⌐⌐⌐⌐⌐⌐⌐⌐ r m m r r r m	atactic	0.25	0.50	0.25	2	2
4a	0.01	0.01	–	–	⌐⌐⌐⌐⌐⌐⌐⌐ m r m r m r m	heterotactic	0.01	0.99	0.01	2	2

Polymers based on binary copolymerization

No.	Reactivity ratios				Monomer sequence	Description	Dyad distribution			Average sequence length	
	r_A	r_B	r_A'	r_B'			AA	AB	BB	l_A	l_B
1b	100	100	–	–	A A A A B B B B	block	0.50	≈0	0.50	100	100
2b	0.01	0.01	–	–	A B A B A B A B	alternating	0.01	0.99	0.01	1.01	1.01
3b	1	1	–	–	A B B B A B A A	perfectly random	0.25	0.50	0.25	2	2
4b	0.01	0.01	100	100	A A B B A A B B	alternating homodyads	0.25	0.50	0.25	2	2

*: or P_m for Bernoullian processes, except for 4a, for which both P_{mm} and P_{rr} have to be applied

**: calculated based on 1000 repeat units in the chain

sequence distributions. This is rooted in the basic definitions of the n-ads. For example, a high fraction of the [BB] dyad in a copolymer should be considered equivalent to high isotactic sequences. However, a high fraction of the algebraically equivalent [rr] triad means by definition predominantly syndiotactic sequences.

In Table 1 exemplary cases of polymers with different tacticities are placed on the top half (1a – 4a) and their counterparts from binary copolymerizations on the bottom half (1b – 4b).

It becomes obvious that the respective dyad and triad distributions for the pairs of polymers are actually not equal (except for the random cases 3a and b in Table 1). Also the corresponding average sequence lengths are not necessarily the same for these analog polymers. This difference becomes particularly apparent when comparing the perfectly atactic polymer (equivalent to the random copolymer, row 4a in Table 1) with the heterotactic polymer (equivalent to the polymer containing alternating homodyads, row 4b in Table 1). They both have the same triad distribution with 50% AB triads. However, while the value for the mr-dyad of the atactic polymer is still 50%, it is 99% for the heterotactic polymer.

The comparisons between sequence distributions of polymers with different tacticities with those obtained by binary copolymers can be easily and rapidly made by using a computer program for binary copolymerizations published earlier [36].

Enantiomorphic site controlled models

With coordinative catalysts such as metallocenes, site-controlled formation of polymer tacticities needs to be taken into account. In general, the degree of isotacticity (i.e., meso n-ads) is high, when a prochiral monomer like propylene is polymerized by a chiral catalyst, as already was found with heterogeneous Ziegler/Natta catalysts. In these cases Price's approach is superior to Bovey's, because the absolute configuration of the monomers is influenced by the catalyst site. In fact, the simplest catalytic site controlled case is a Bernoullian model according to Price (also known as enantio-morphic site model or E model), which has no counterpart in Bovey's models. No chain-end control takes effect; only the enantioface of the incoming monomer is relevant.

Two conventional models have been presented in the literature to separately model isotactic or syndiotactic polymers. To model an isotactic polymer, b is set as the probability that one enantioface of the monomer, typically the re-face, is being added to the R-site of the catalyst and into the growing chain. The notations re- and si-face are based on the Cahn-Ingold-Prelog analog definition, whereby one views the monomer from the coordinative center on to the double bonded C-atom with the substituent. Then if $b=1$, an isotactic polymer is formed. Likewise if $b=0$, only the si-face is added and isotactic polymer results. We therefore designate this model as

"E-B iso". If $b=0.5$, the two possible enantiofaces of the monomer are added randomly, resulting in atactic polymer.

For syndiotactic polymerization, one can define a model with the conventional term a as the probability for the addition of a monomer with a certain enantioface, e.g., the re-face, to only one of two enantiotopic faces of a syndiospecific catalyst. In the symmetric case, a will also be equal to the probability of adding the opposite monomer face, the si-face, to the other site of the catalyst. Consequently, in this case high syndiotacticity results from a being close to 1 or close to zero. We designate this model as "E-B syn".

We are introducing in this work a more comprehensive, single model that enables the modeling of four types of tacticities: isotactic, syndiotactic, atactic or hemisisotactic polymer, labeled as "E-B gen" model (with "gen" standing for general). Here we can use two probabilities, c and d, which now correspond to the addition of the monomer to one site, e.g., the left, or potentially the other site, the right, of the active catalyst species. An isotactic polymer is produced, if c and d are equal and close to zero or one. If c is close to zero or unity and equal to $(1-d)$, a syndiotacic polymer is produced. If c and d are both close to 0.5, an atactic polymer is produced. If either c is close to zero or unity and d is close to 0.5, or alternatively c is close to zero or unity and d is close to 0.5, a hemiisotactic polymer is produced.
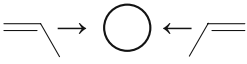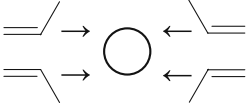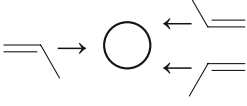
These dependencies are also shown in Table 2. The types of coordinative initiators (symbolized by a sphere) would be different for each type of tacticity. However, for the mathematical model this has not been taken directly into account and knowledge of the specific initiator is not required. Rather the tacticities are solely determined by the probabilities for the additions of the two possible types of monomer faces to each initiator site, i.e. from left and right, and symbolized by c and d. Not only does the "E-B gen" model represent a combination of two single-variable models, it makes the introduction of a third variable, such as α, as was previously done, unnecessary to model the hemiisotactic polymer [11].

The prescribed basis of the model elucidates how the symmetry of a coordinative initiator can be varied to obtain certain tacticities. Though hemiisotactic polymers (e.g., with $c=0.9999$ and $d=0.5000$) have formal similarity to both isotactic polymer and atactic polymer, based on the probabilities in the model they also can be considered a hybrid of an isotactic ($c=0.9999$, $d=0.9999$) and a syndiotactic polymer ($c=0.9999$, $d=0.0001$). The average sequence lengths for this type of a polymer with $\overline{n}_m = \overline{n}_r = 2$ are identical to those of an atactic polymer.

Combination of chain-end controlled and enantiomorphic models

Cheng introduced a model that is a hybrid of a site-controlled and a chain-end controlled model, with more emphasis on the

Table 2 The four types of tacticities which can be obtained by the E-B gen-model based on the probabilities c and d

Probabilities		Mode of subsequent additions of substituted ethylene[b] to coordinative initiator[c]	Resulting tacticity
c	d		
1 (or 0)[a]	1 (or 0)	re-face (or si-face)[d] re-face (or si-face)	isotactic
1 (or 0)	0 (or 1)	re-face (or si-face) si-face (or re-face)	syndiotactic
0.5	0.5	re-face and si-face re-face and si-face	atactic
1 (or 0)	0.5	re-face (or si-face) re-face and si-face	hemiisotactic

[a] : values or faces in brackets are for alternate cases

[b] : represented here as propylene

[c] : represented here by sphere

[d] : for simplicity monomer faces given in brackets are not shown in schematic illustrations

first type of control [13]. The "E-M1" model is based on two independent probabilities, P_{dl} and P_{ld}. Its pentad distribution is reported here for the first time (given below in Table 5). The model was originally applied to cases like the polymerization with a $TiCl_3$/$AlEt_2Cl$ catalyst [37]. However, this model could be also useful for polypropylene produced with some single-site catalysts, such as metallocenes [15]. If symmetric, the "E-M1" model would become equivalent to the 1st order Markovian ("M1") model. This model can be

extended to combinations of enantiomorphic and 2nd order Markovian ("E-M2"), or combinations of the enantiomorphic site model with higher order Markovian models.

In Table 3 the relationships between Bovey's and Price's approaches are described. The absolute configurations of Price's models are not detected in regular, achiral polymers when observed in the NMR spectra, and therefore only the relative configurations described in Bovey's models are observed. As noted earlier, Bovey's

Table 3 Relationships between the approaches by Bovey and Price

	Bovey equivalent		Price equivalent	
Chain end control models	Bernoullian (0th order Markov)	B	1st order Markov terminal effect	
	1st order Markov	M1	2nd order Markov penultimate effect	
	2nd order Markov	M2	3rd order Markov penpenultimate effect	
Site control models	None		Bernoullian isotactic	E-B-iso
	None		Bernoullian syndiotactic	E-B syn
	None		Bernoullian general	E-B gen
Mixed model	None		1st order Markov and enantiomorphic	E-M1

Table 4 Dyad, triad and tetrad distributions for the described models

Dyads / Triads / Tetrads	m (M)	r	mm	mr	rr	mmm	mmr	mrm	rmr	rrm	rrr
B	P_m	$P_r=(1-P_m)$	P_m^2	$2P_mP_r=2P_m(1-P_m)$	$P_r^2=(1-P_m)^2$	P_m^3	$2P_m^2P_r$	$P_m^2P_r$	$P_mP_r^2$	$2P_mP_r^2$	P_r^3
M1 x k	P_m	P_{mr}	P_{mm}	$2P_{mr}$	$P_{rr}P_{mr}$	P_{mm}^2	$2P_{mm}P_{mr}$	$P_{mr}P_{rm}$	P_{mr}^2	$2P_{rm}P_{rr}$	P_{rr}^2
M2 x s	$(P_{mmr}+P_{rmm})P_{rm}$	$(P_{mmr}+P_{rmm})P_{rm}$	$P_{rmm}P_{mm}$	$2P_{mmr}P_{rm}$	$P_{mmr}P_{mrr}$	$P_{mmm}P_{rmm}P_{mmr}P_{rmr}$	$2P_{mmr}P_{mrm}P_{rmm}$	$P_{mmr}P_{rmr}^2$	$P_{mrr}P_{rmr}^2$	$2P_{mrr}P_{rm}P_{rrm}$	$P_{mrr}P_{mmr}P_{rrm}$
E-B iso	$b^2+(1-b)^2$	$2b(1-b)$	$1-3b(1-b)$	$2b(1-b)$	$b(1-b)$	$b^4+(1-b)^4$	$2[b^3(1-b)+b(1-b)^3]$	$2[b^2(1-b)^2]$	$2[b^2(1-b)^2]$	$2[b^3(1-b)+b(1-b)^3]$	$2[b^2(1-b)^2]$
E-B syn	$2a(1-a)$	$a^2+(1-a)^2$	$a^2(1-a)+a(1-a)^2$	$2a(1-a)^2+a^2(1-a)$	$a^3+(1-a)^3$	$2a^2(1-a)^2$	$2a^3(1-a)+2a^2(1-a)^3$	$2a^2(1-a)^2$	$2a^2(1-a)^2$	$2a^3(1-a)+a(1-a)^3$	$a^4+(1-a)^4$
E-B gen x 2	$2[cd+(1-c)(1-d)]$	$2[c(1-d)+d(1-c)]$	$c^2d+cd^2+(1-c)^2(1-d)+(1-c)(1-d)^2$	$2[cd(1-c)+cd(1-d)+c(1-c)(1-d)+d(1-c)(1-d)]$	$c^2(1-d)+d^2(1-c)+(1-c)d+(1-c)^2c+(1-d)^2$	$2[c^2d^2+(1-c)^2(1-d)^2]$	$2[c^2d(1-d)+d(1-c)(1-d)^2+c(1-c)^2d]$	$4[cd(1-c)(1-d)]$	$4[cd(1-c)(1-d)]$	$2[c^2d(1-d)+d(1-c)(1-d)^2+c(1-c)^2(1-c)]$	$2[c^2(1-d)^2+d^2(1-c)^2]$
E-M1 x k'	$(P_{dd}P_{ld}+P_{dl}P_{ll})$	$(2P_{dl}P_{ld})$	$(P_{dd}^2P_{ld}+P_{dl}P_{ll}^2)$	$2(P_{dl}P_{dd}P_{ld}+P_{dl}P_{ld}P_{ll})$	$(P_{dl}^2P_{ld}+P_{dl}^2P_{ld})$	$P_{dd}^3P_{ld}+P_{dl}P_{ll}^3$	$2(P_{dl}P_{dd}^2P_{ld}+P_{dl}P_{ld}P_{ll}^2)$	$2P_{dl}P_{dd}P_{ld}P_{ll}$	$P_{dl}^2P_{dd}P_{ld}+P_{dl}P_{ld}^2P_{ll}$	$2(P_{dl}P_{ld}P_{dd}+P_{dl}P_{ld}^2P_{ll})$	$2P_{dl}^2P_{ld}^2$

k = (P_mr + P_rm); P_m = 1 – P_r, P_mr = 1 – P_rr, P_rm = 1 – P_mm; s = P_mmr P_mrr = 1 – P_mmm; P_mrr = 1 - P_mmr, P_rrr = 1 – P_rrm, P_rmr = 1 – P_rrm; k' = (P_dl + P_ld), P_dl = 1 – P_dd, P_ld = 1 – P_ll; b = probability of an R or re monomer unit adding at the R site = probability of an S or si monomer unit adding at the S site;

a = probability of a monomer with a given enantioface adding at one catalyst site = probability of the monomer with the opposite enantioface adding at the other catalyst site; c = probability of monomer adding to one reaction site of catalyst, d = probability of monomer adding to the other site of the catalyst

Table 5 Pentad distributions for the described models

Dyads	mmmm	mmmr	rmmr	mmrm	mmrr	rmrm	mrmr	mrrm	mrrr	rrrr
B	P_m^4	$2P_m^3(1-P_m)$	$P_m^2(1-P_m)^2$	$2P_m^3(1-P_m)$	$2P_m^2(1-P_m)^2$	$P_m^2(1-P_m)^2$	$2P_m^2(1-P_m)^2$	$P_m^2(1-P_m)^2$	$2P_m(1-P_m)^3$	$(1-P_m)^4$
M1 x k	P_{mm}^3	$2P_{mm}^2P_{mr}$	$P_{mm}P_{mr}^2$	$2P_{mm}^2P_{mr}$	$2P_{mm}P_{mr}P_{rm}$	$P_{mr}^2P_{rm}$	$2P_{mr}^2P_{rm}$	$P_{mr}^2P_{rm}$	$2P_{mr}P_{rr}^2$	P_{rr}^3
M2 x s	$P_{mmm}^2P_{mmr}P_{rmm}$	$2P_{mmm}P_{mmr}P_{rmm}$	$P_{mmr}P_{mrr}P_{rmm}$	$2P_{mmm}P_{mmr}P_{rmm}$	$2P_{mmr}P_{mrm}P_{rmm}P_{rrm}$	$P_{mmr}P_{rmr}P_{rrm}$	$2P_{mmr}P_{mrm}P_{rmr}$	$P_{mmr}P_{mrr}P_{rmr}$	$2P_{mmr}P_{mrr}P_{rrm}$	$P_{mmr}P_{mrr}P_{rrr}$
E-B iso	$b^5+(1-b)^5$	$2[b^4(1-b)+b(1-b)^4]$	$b^3(1-b)^2+b^2(1-b)^3$	$2[b^4(1-b)+b(1-b)^4]$	$2[b^3(1-b)^2+b^2(1-b)^3]$	$b^3(1-b)^2+b^2(1-b)^3$	$2[b^3(1-b)^2+b^2(1-b)^3]$	$2[b^3(1-b)^2+b^2(1-b)^3]$	$2[b^3(1-b)^2+b^2(1-b)^3]$	$b^3(1-b)^2+b^2(1-b)^3$
E-B syn	$a^3(1-a)^2+a^2(1-a)^3$	$a^3(1-a)^2+a^2(1-a)^3$	$a^4(1-a)+a(1-a)^4$	$2a^3(1-a)^2+2a^2(1-a)^3$	$2a^4(1-a)+2a(1-a)^4$	$a^4(1-a)+a(1-a)^4$	$2a^3(1-a)^2+2a^2(1-a)^3$	$2a^3(1-a)^2+2a^2(1-a)^3$	$2a(1-a)^4+2a^4(1-a)$	$a^5+(1-a)^5$
E-B gen x 2	$2[c^3d^2+c^2d^3+(1-c)^3(1-d)^2+(1-c)^2(1-d)^3]$	$2[c^2d^2(1-c)+c^2d^2(1-d)+(1-c)^2(1-d)^2c+(1-c)^2d(1-d)^2]$	$c^3d(1-d)+cd(1-c)^2(1-d)+(1-d)^2c(1-c)+(1-d)^3$	$2[c^2d(1-c)(1-d)+cd^2(1-c)(1-d)+cd(1-c)^2(1-d)+cd(1-c)(1-d)^2]$	$c^2d(1-c)(1-d)+cd^2(1-c)(1-d)+(1-d)^2c(1-c)+cd(1-c)(1-d)^2$	$c^2d(1-c)(1-d)$	$2a^3(1-a)^2+2a^2(1-a)^3$	$c^2(1-c)(1-d)+cd^2(1-c)(1-d)+cd(1-c)^2(1-d)+cd(1-c)(1-d)^2$	$c^3(1-c)^2+c^2d+d^3(1-c)^2+d^2(1-c)^3+c^2(1-d)^3$	$c^3(1-d)^2+d^3(1-c)^2+d^2(1-c)^3+c^2(1-d)^3$
E-M1 x k'	$P_{dd}^4P_{ld}+P_{dl}P_{ll}^4$	$2(P_{dd}^3P_{dl}P_{ld}+P_{dl}^2P_{ld}P_{ll}^3)$	$2(P_{dd}^2P_{dl}P_{ld}^2P_{ll}+P_{dl}^2P_{ld}^2P_{ll}^2)$	$2(P_{dd}^3P_{dl}P_{ld}+P_{dl}^2P_{ld}P_{ll}^3)$	$2(P_{dd}^2P_{dl}P_{ld}^2P_{ll}+P_{dl}^2P_{ld}^2P_{ll}^2)$	$P_{dd}^2P_{dl}^2P_{ld}+P_{dl}^2P_{ld}^2P_{ll}^2$	$2(P_{dl}^3P_{dd}P_{ld}+P_{dl}^2P_{ld}^2P_{ll}^2)$	$2(P_{dl}^2P_{dd}P_{ld}P_{ll}+P_{dl}^2P_{ld}^2P_{ll})$	$2(P_{dd}P_{dl}^2P_{ld}P_{ll}+P_{dl}^2P_{ld}^2P_{ll}^2)$	$P_{dl}^3P_{ld}^2+P_{dl}^2P_{ld}^3$

k = (P_mr + P_rm); P_m = 1 – P_r, P_mr = 1 – P_rr, P_rm = 1 – P_mm; s = P_mmr P_mrr = 1 – P_mmm; P_mrr = 1 - P_mmr, P_rrr = 1 – P_rrm, P_rmr = 1 – P_rrm; k' = (P_dl + P_ld), P_dl = 1 – P_dd, P_ld = 1 – P_ll; b = probability of an R or re monomer unit adding at the R site = probability of an S or si monomer unit adding at the S site;

a = probability of a monomer with a given enantioface adding at one catalyst site = probability of the monomer with the opposite enantioface adding at the other catalyst site; c = probability of monomer adding to one reaction site of catalyst, d = probability of monomer adding to the other site of the catalyst.

Table 6 Group symmetries of metallocene catalysts and resulting tacticities

Symmetry	Metallocene Structure	Sites	Polymer Tacticity Type of Control	Metallocene Example
C_{2v} achiral		A,A homotopic	Atactic CE	Cp_2ZrCl_2
C_2 chiral		E,E homotopic	Isotactic ES	rac-$Me_2Si(Ind)_2ZrCl_2$
C_s achiral		A,A diastereotopic	Atactic CE	meso-$Me_2Si(Ind)_2ZrCl_2$
C_s prochiral		E,-E enantiotopic	Syndiotactic ES	$Me_2Si (Cp)(9-Flu)_2ZrCl_2$
C_1 chiral		E,A diastereotopic	Hemiisotactic ES	$Me_2Si (3-Me-Cp)(9-Flu)_2ZrCl_2$

A: aselective, *E*: enantioselective, *CE*: Chain-end control, *ES*: Enantiomorphic site-control

models are more frequently used in determining polymer tacticities for chain-end controlled polymerizations. Price's models are used for site-controlled polymerizations.

In Tables 4 and 5 the mathematical expressions for the n-ads in various models are given. These same expressions have been entered in the related software program, described further below, to facilitate calculations and comparisons.

Tacticities of polypropylene obtained with single-site catalysts

A variety of single-site catalysts, in particular achiral and chiral metallocene catalysts originally developed by Kaminsky, Brinztinger and Ewen have been applied to obtain polypropylenes with different tacticities [19, 28, 38].
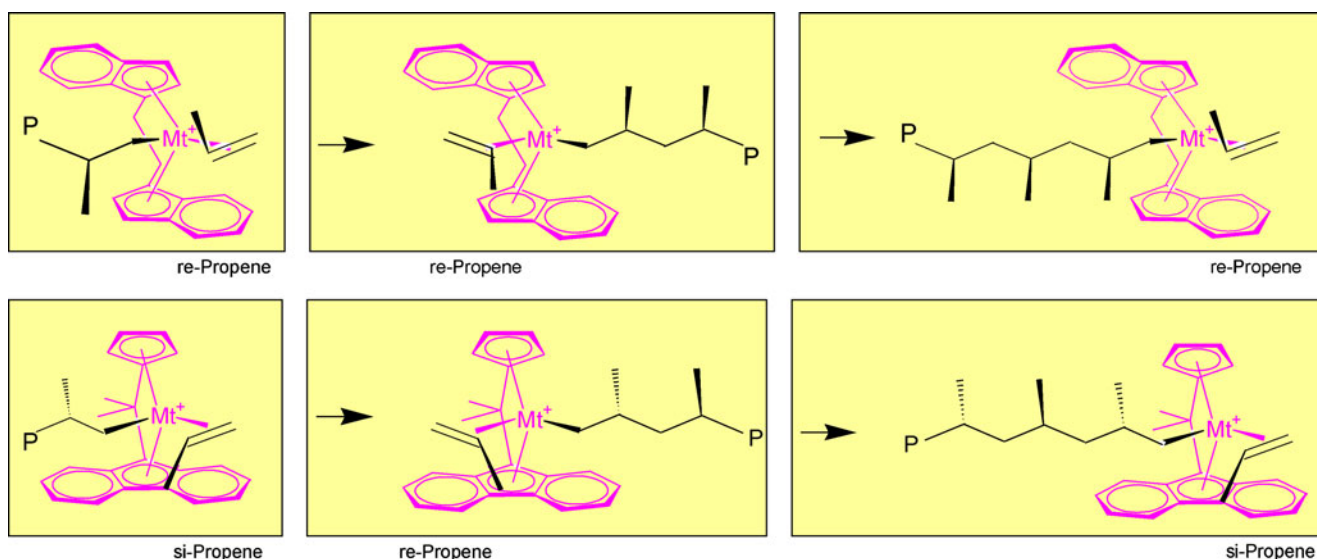

Fig. 5 Isospecific polymerization of propene by a metallocene catalyst with a C_2-symmetry (top) and syndiospecific polymerization by a metallocene catalyst bearing a C_s-symmetry (bottom)

Details of the polymerization mechanism of propylene with various single-site catalysts, predominantly metallocene catalysts, have been described abundantly in the literature [19, 21–24, 27–29, 38]. A relationship between the group symmetries of many metallocene catalysts and their tacticities was established by Ewen and is given Table 6 [19].

In Fig. 5 the simplified polymerization mechanisms for two metallocenes with different symmetries are shown. The prochirality of propene with the catalyst of different symmetries ultimately results in the formation of polypropylene with different tacticities. The assignments of re- and si-propene are derived from the Cahn-Ingold-Prelog rules. With every insertion step, the chain migrates. With the bis(indenyl) catalyst, the propylene is inserted from both sides (left and right in Fig. 5) under the same spatial constellation. In the case of the fluorenyl catalyst with its two different enantiotopic sites, however, syndiospecific polymerization is induced.

An exceptional case of a catalyst with a C_{2v} symmetry is titanocene diphenyl, which leads to the formation of isotactic stereoblock polymer as was initially described by Ewen [19]. There are also many exceptions to the stereochemistry with catalysts having a C_1-symmetry, which can form (besides hemiisotactic) isotactic, atactic or isotactic stereoblock polypropylene [23]. It can be generally critical as to how fast the monomer insertion takes place compared to the chain migration. If several insertions can take place before the chain migration occurs, a stereoblock polymer is formed.

To simulate atactic polypropylene produced by a coordinative catalyst it is more realistic to use the "E-B gen" model instead of the simpler "B" model, because chain end control should be less relevant with these initiators. Indeed, the errors caused by site control are also well reflected by this model if the values of c and d are smaller than about 0.95. Heterotactic polypropylene, which should not be confused with a predominantly atactic polymer according to older nomenclature, is the least observed tacticity. So far, it has not been found for

Table 7 Overview of cases of stereoregular polymerizations from the literature to which probability values of the presented models have been applied

Monomer	Type of initiator	Initiator	Applied model	Probability values[a]				Dominant type of tacticity	[mmmm] or ([rrrr])[b] in%	Ref.
				1st	2nd	3rd	4th			
MMA	Radical	$(C_6H_5COO)_2$	B	0.22	–	–	–	st	(36.6)	[2]
MMA	Radical	$C_8H_{12}N_4$ (AIBN)	B	0.25	–	–	–	st	(31.5)	[2]
MMA	Anionic	n-C_4H_9Li	B	0.83	–	–	–	it	46.3	[2]
MMA	Anionic	C_6H_5MgBr	M2	0.97	0.25	0.06	0.32	it	29.7	[3]
MMA	Coord.	t-Bu-Li/MeAl(ODBP)$_2$	M1	0.255	0.375	–	–	het	0.8	[41]
MA	Coord.	[2,6-(2,6-iPrC$_6$H$_3$N═ CCH$_3$)$_2$C$_5$H$_3$N]FeCl$_2$	E-B gen	0.50	0.50	–	–	at	6.25	[40]
MA	Coord.	rac-Me$_2$Si (H$_4$-Ind)$_2$ZrCl$_2$	E-B iso	0.932	–	–	–	it	70.3	[40]
Styrene	Radical	$(C_6H_5COO)_2$	B	0.48	–	–	–	at	5.3	[29]
Styrene	Coord.	CpTiCl$_3$	E-B syn	0.996	–	–	–	st	(98)	[42, 43]
Propene	Coord.	Cp$_2$ZrCl$_2$	E-B gen	0.55	0.55	–	–	at	7.0	[28]
Propene	Coord.	rac-Eth(Ind)$_2$ZrCl$_2$	E-B iso	0.974	–	–	–	it	87.4	[23]
Propene	Coord.	rac-Me$_2$Si (Ind)$_2$ZrCl$_2$	E-B iso	0.980	–	–	–	it	90.3	[23]
Propene	Coord.	rac-Me$_2$Si (H$_4$-Ind)$_2$ZrCl$_2$	E-B iso	0.990	–	–	–	it	94.9	[23]
Propene	Coord.	Me$_2$C(Cp)(Flu)ZrCl$_2$	E-B syn	0.97	–	–	–	st	(86)	[44]
Propene	Coord.	Me$_2$C(3-MeCp)(Flu)ZrCl$_2$	E-B-gen	0.92	0.50	–	–	hit	14	[45]
Propene	Coord.	Cp$_2$TiPh$_2$ (at 0 °C)	B	0.67	–	–	–	it-stereo	20	[19]
Propene	Coord.	Me$_2$C(t-Bu-Cp)(9-Flu)ZrCl$_2$	E-B iso	0.977	–	–	–	it	89	[46]
Propene	Coord.	Me$_2$C(Cp)(3-CH$_2$SiMe-2-Me-Ind)Zr	E-B-syn	0.9	–	–	–	st	(68.5)	[47]
Propene	Coord.	TiCl$_3$/AlEt$_2$Cl	E-M1	0.98	0.98	–	–	it	92	[37]
Propene	Coord	[2,6-(2,6-iPrC$_6$H$_3$N═CCH$_3$)$_2$ C$_5$H$_3$N]FeCl$_2$	B	0.86	–	–	–	it	55	[48]

Note that other factors influencing tacticity, e.g., type of cocatalysts, catalyst/cocatalyst ratio, polymerization temperature and monomer concentration are not included here, but typically are mentioned in given references. MMA: methyl methacrylate; MA: methyl acrylate, Coord.: coordinative; it: isotactic, st: syndiotactic, at: atactic, hit: hemisotactic, het: heterotactic, sterep: steroblock. [a] Depending on the model the parameters are: for B: P_m, for M1: P_{mm} and P_{rr}; for E-M2: P_{mmmm}, P_{mrm}, P_{rmm}, and P_{rrm}; for E-B iso: b; for E-B syn: a; for E-B gen: c and d; for E-M1: P_{dd} and P_{ll}, resp.., [b]: [rrrr] given in brackets, if polymer is syndiotactic
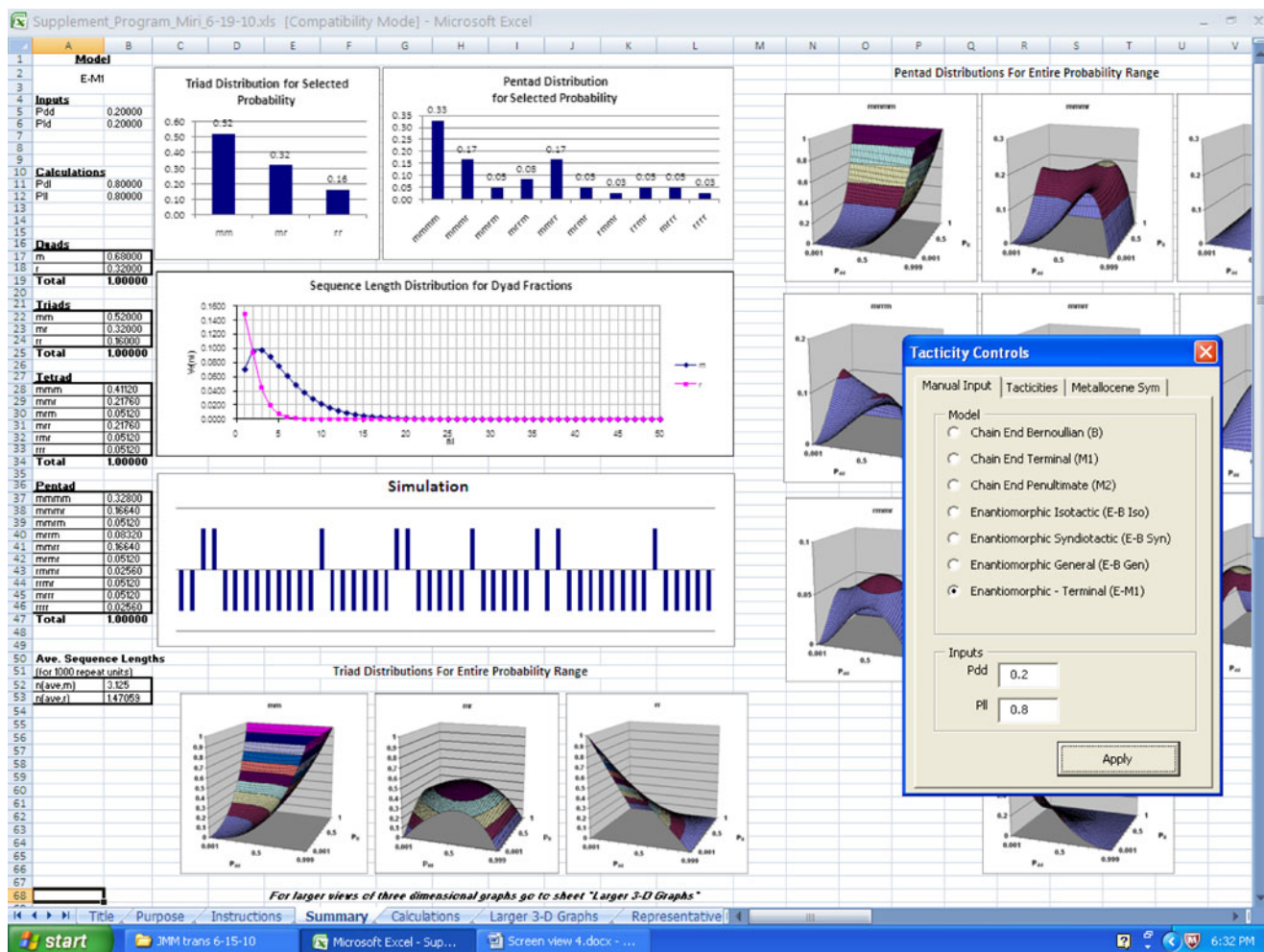
Fig. 6 Screenview of summary sheet of the "Polytact" program showing one set of results of applying the model "E-M1" with the input window towards the bottom right

polypropylene made from single-site catalysts but only with a couple of heterogeneous Ziegler/Natta catalysts [39] and more typically with methyl methacrylate as monomer [41].

In Table 7 different types of tacticities obtained by a variety of initiators and monomers mentioned in the literature and suitable statistical models are summarized.

Short description of related software program ("Polytact")

We have developed a related software program, "Polytact", based on Microsoft's Excel®, thereby making it user-friendly and widely applicable. A Macro is used to link

Table 8 Examples of calculated pentad intensities for given probabilities applying different models

Model Pentad	B[a]	M1[b]	M2[c]	E-B iso[d]	E-B syn[e]	E-B gen[f]	E-M1[g]
mmmm	0.65610	0.64303	0.80222	0.59050	0.00810	0.44070	0.74138
mmmr	0.14580	0.06769	0.08444	0.13140	0.01620	0.15620	0.11036
mmrm	0.14580	0.01069	0.08000	0.01620	0.01620	0.02880	0.10901
mrrm	0.00810	0.00478	0.00418	0.06570	0.00810	0.07810	0.00643
mmrr	0.01620	0.06056	0.00889	0.13140	0.13140	0.16360	0.01286
mrmr	0.01620	0.00056	0.01412	0.01620	0.01620	0.02880	0.01211
rmmr	0.00810	0.00178	0.00222	0.00810	0.06570	0.01810	0.0576
rrmr	0.00180	0.00319	0.00157	0.01620	0.01620	0.02880	0.00101
mrrr	0.00180	0.05419	0.00209	0.01620	0.13410	0.03620	0.00101
rrrr	0.00010	0.15353	0.00026	0.00810	0.59050	0.02070	0.00006

[a] reaction probability $P_m = 0.9$,
[b] reaction probability $P_{mm} = 0.95$ and $P_{rr} = 0.85$, [c] reaction probability $P_{mmm} = 0.95$, $P_{mrm} = 0.90$, $P_{rmm} = 0.85$, $P_{rrm} = 0.80$,
[d] reaction probability $b = 0.9$,
[e] reaction probability $a = 0.9$,
[f] reaction probabilities: $c = 0.9$ and $d = 0.8$, [g] reaction probabilities $P_{ll} = 0.95$, $P_{dd} = 0.85$

data on different sheets based on input data and to initiate calculations and creations of graphs. The user of the program only needs to supply the choice of a particular tacticity, a metallocene group symmetry, or enter the reaction probabilities for a particular model. Figure 6 shows the worksheet "Summary" with the input window located towards the bottom right. The input window can be moved around on the screen.

Based on the applied formulas, the following output is produced: the values of the dyads, triads, tetrads, pentads, and average sequence lengths the specific triad and pentad distributions as bar diagrams, two- or three-dimensional plots of the triad and pentad distributions over the entire probability range, the sequence length distributions, and a simulation of 50 monomer units along the polymer chain.

The pentad intensities calculated by the "Polytact" for several models are shown in Table 8.

This could represent the case of polypropylene samples made with different metallocene catalysts. On the Excel spreadsheet, it takes literally seconds to obtain these numbers. More details on the features of the software program are described in the Supplement.

Conclusions

We have provided a set of models that describe and allow us to model and simulate a variety of polymer tacticities. The theories behind each of the seven models and the relations among the models have been explained. For each model the calculations of n-ads have been provided. A new model, "E-B gen" was introduced, which can be used to obtain up to four types of enantiomorphically controlled tacticities. The quantitative relations between polymer tacticity and the monomer sequence distribution of binary copolymers have been provided and their similarities and differences between them have been elucidated. The seven models were applied on 20 types of polymerizations mentioned in the literature involving different monomers or initiators. A user-friendly and versatile software program, "Polytact", is presented that facilitates the use of these models and provides all relevant data related to polymer tacticity with a few "clicks". Types of tacticities or group symmetries of coordinative initiators can be selected, or values for the probabilities for each model entered. The values for n-ads up to pentads, and the triad, pentad, and sequence length distributions in graphical form are produced by the program. The program also enables simulations of 50 repeat units along a polymer chain. Calculations of these quantities are provided in additional worksheets. This computer-based approach should make it easier to interpret NMR tacticity data, to compare polymers made at different compositions, or from different catalysts.

Above all, this approach permits analysis and simulation of NMR data with pertinent statistical models and provides useful information on chain propagation mechanisms.

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