Isotactic Block Length Distribution in Polypropylene: Bernoullian vs Hemiisotactic

Stephen A. Miller[*]

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Received August 14, 2003; Revised Manuscript Received March 17, 2004

ABSTRACT: Derivation of the isotactic block length distribution is made for polypropylenes having Bernoullian (chain-end control) or hemiisotactic microstructures. For each of these tacticities, the isotactic block length distribution depends on a single stereochemical parameter and M_n, the number-average molecular weight. For polypropylene with Bernoullian statistics, the number of isotactic blocks of length n is given by $N_n = (1 - \sigma)^2(\sigma)^{(n-1)}(M_n/42.08)$. For hemiisotactic polypropylene, the number of isotactic blocks of length one is given by $N_1 = [(0.5)(1 - \alpha)^2 + (0.5)(1 - \alpha)](M_n/42.08)$ and the number of isotactic blocks of length n (where n is an odd integer greater than one) is given by $N_n = (0.5)(1 - \alpha)^2(\alpha)^{(n-1)/2}(M_n/42.08)$. The distributions are compared and contrasted for hypothetical polypropylenes and real polypropylenes for which σ, α (^{13}C NMR) and M_n (GPC) have been determined. For polypropylene with $M_n = 100\,000$ an elastomeric morphology is calculated to exist for $\sigma = 0.752-0.827$ (Bernoullian) and for $\alpha = 0.575-0.693$ (hemiisotactic). The lower limit defines the presence of at least two crystallizable isotactic segments ($n \geq 21$) per chain; the upper limit defines the point at which the calculated percent crystallinity exceeds 10%, and the properties are dominated by the crystalline phase at the expense of the amorphous phase. The elastomeric properties observed in hemiisotactic polypropylenes with $\alpha \approx 0.6$ are readily explained by the statistical presence of crystallizable isotactic blocks in the presence of an otherwise amorphous medium. In contrast, the calculations suggest that most elastomeric Bernoullian polymers (i.e., atactic with σ near 0.5) rely on chain entanglements rather than crystallization phenomena for their elastomeric properties since the calculated distributions do not render a sufficient number and arrangement of crystallizable isotactic blocks.

Introduction

The two primary strategies for synthesizing elastomers are chemical cross-linking of individual polymer chains (thermoset elastomers) and physical cross-linking of individual polymer chains (thermoplastic elastomers), most commonly achieved by ABA block copolymers.[1] Recent efforts to prepare elastomeric homopolymers have concentrated on propylene homopolymerization by discrete organometallic complexes.[2] Thus, the following approaches have proven successful for making elastomeric polypropylene (ePP) without the need for additional monomers or post-polymerization cross-linking or reformulation: polypropylene with an intermediate isotactic/atactic microstructure;[3] stereoblock isotactic−atactic polypropylene;[4] high molecular weight atactic polypropylene;[5] binary isotactic/atactic compatibilized polypropylene;[6] high molecular weight essentially atactic polypropylene with enhanced isotactic content;[7] isotactic polypropylene with controllable stereoerror sequences;[8] isotactic−hemiisotactic polypropylene.[9]

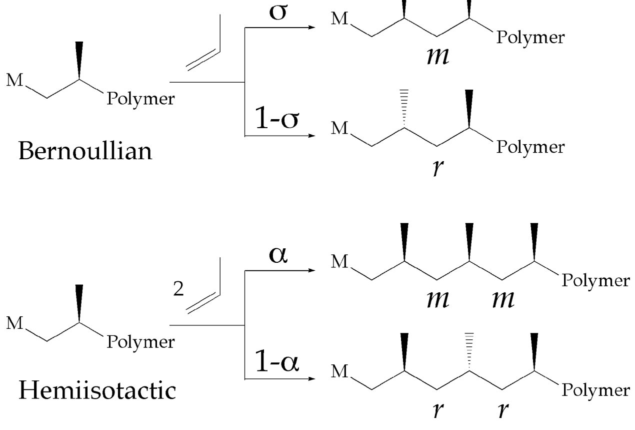


Figure 1. Bernoullian and hemiisotactic polypropylenes each described by a single stereochemical parameter. Atactic polypropylene is obtained when $\sigma = 0.5$, and perfectly hemiisotactic polypropylene is obtained when $\alpha = 0.5$.

The focus of this paper is the derivation and comparison of statistical models that describe the isotactic block length distributions in Bernoullian[10] and hemiisotactic[11,12] polypropylenes. In contrast to the other tacticities noted above, *each of these tacticities can be described by a single stereochemical parameter* (Figure 1). For polypropylene with Bernoullian statistics (simple chain-end control), $\sigma = P_m$, the probability of forming a *meso* (m) dyad. When $\sigma = 0.5$, atactic polypropylene is obtained and the *meso* (m) and *racemo* (r) dyads are formed in equal abundance. For hemiisotactic polypropylene, every other stereocenter has the same absolute stereochemistry and the intervening stereocenters are aligned with their neighbors with the probability of α. Thus, for perfectly hemiisotactic polypropylene, $\alpha = 0.5$ and the *mm* and *rr* triads are produced equally. For isotactic−hemiisotactic polypropylene,[9] $\alpha > 0.5$, and the intervening stereocenters are more likely to be aligned with their neighbors; in this case the *mm* triad is produced in excess of the *rr* triad. The relative simplicity of these tacticities should allow for a statistical analysis with a more definitive interpretation than that of complex tacticities which must be modeled by multiple stereochemical parameters.[3,4,6,8,13] The intent is to rationalize the elastomeric properties observed (or lacking)

---

[*] To whom correspondence should be addressed. E-mail: samiller@mail.chem.tamu.edu.

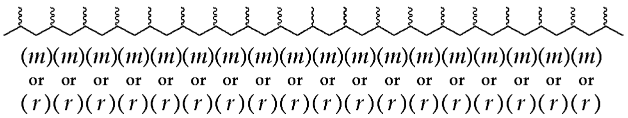
10.1021/ma035206+ CCC: $27.50

in these polypropylenes by calculating the statistical likelihood for the coexistence of crystallizable (isotactic) and amorphous (atactic or hemiisotactic) sequences, a necessary condition to achieve an elastomeric morphology.

Results and Discussion

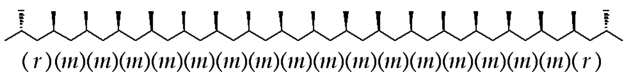
Derivation of the Isotactic Block Length Distribution for Bernoullian Polypropylene. A Bernoullian polymer can generally be represented by a sequence of *m* and *r* dyads.

Bernoullian polypropylene - general



An isotactic block is defined as a collection of *m* dyads terminated on either end by an *r* dyad. For Bernoullian polypropylene, an isotactic block will consist of a series of *m* dyads initiated and terminated with *r* dyads: $(r)(m)^{(s)}(r)$, where *s* is the number of repeating *m* dyads.

Bernoullian polypropylene - block length of 17



The probability P_n of obtaining an isotactic block of length *n* is given by eq 1 since $P_r = (1 - \sigma)$, $P_m = \sigma$, and $s = (n - 1)$.[14] Here σ is the Bernoullian stereochemical parameter, which indicates the likelihood of forming an *m* dyad.[10] For purely atactic polypropylene, $\sigma = 0.5$.

$$P_n = (1 - \sigma)(\sigma)^{(n-1)}(1 - \sigma) = (1 - \sigma)^2(\sigma)^{(n-1)} \quad (1)$$

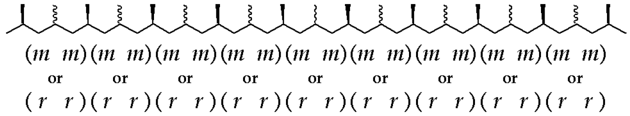
For a given polymer chain, the number of blocks of length *n* present is given by $N_n = P_n(\mathrm{DP})$, where DP is the degree of polymerization—the number of monomers in that chain—which equals the number-average molecular weight divided by the monomer molecular weight ($= M_n/\mathrm{MW}_{\mathrm{monomer}}$). Therefore, eq 2 describes the isotactic block length distribution as a function of exactly two experimental parameters: σ, a stereochemical parameter which is determined by ^{13}C NMR;[10,15] and M_n, a molecular weight parameter which is determined by gel permeation chromatography (GPC). For atactic polypropylene ($\sigma = 0.5$; $\mathrm{MW}_{\mathrm{monomer}} = 42.08$ for propylene), eq 2 reduces to eq 3.

$$N_n = (1 - \sigma)^2(\sigma)^{(n-1)}(M_n/\mathrm{MW}_{\mathrm{monomer}}) \quad (2)$$

$$N_n = (0.5)^{(n+1)}(M_n/42.08) \quad (3)$$

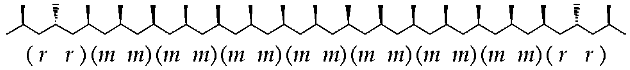
Derivation of the Isotactic Block Length Distribution for Hemiisotactic and Isotactic—Hemiisotactic Polypropylene. For a hemiisotactic architecture, every other stereocenter is of the same stereochemistry and the intervening stereocenters are of variable stereochemistry. Therefore, a hemiisotactic polymer can generally be represented by a sequence of *mm* and *rr* triads.

hemiisotactic polypropylene - general



For a given triad, if the probability of obtaining an *mm* triad is defined as α, then the probability of obtaining an *rr* triad is (1 − α). Of course *mr* and *rm* triads will also be present, but only at the *junction* of sequential *mm* and *rr* triads as in *m**mr**r*. (The idealized sequence of *mm* and *rr* triads will be disrupted when there are stereoerrors in the hemiisotactic polymer—vide infra.) An isotactic block is defined as a collection of *m* dyads terminated on either end by an *r* dyad. Since only sequential *mm* and *rr* triads are allowed for hemiisotactic polypropylene, an isotactic block must be a collection of *mm* triads terminated on either end by an *rr* triad: $(rr)(mm)^{(s)}(rr)$, where *s* is the number of repeating *mm* triads.

hemiisotactic polypropylene - block length of 15



In a hemiisotactic polymer, half of the monomers are at the start of a “sequential” triad and half of the monomers reside in the middle of a “sequential” triad. Therefore, the probability that a randomly selected monomer *begins* a string of sequential triads is 0.5 (Figure 2b). The probability that the initial triad is *rr* is given by (1 − α) (Figure 2c). The probability of then finding a sequence of *mm* triads is given by $\alpha^{(s)}$ (Figure 2d), where *s* is the number of repeating triads. Finally, the probability of terminating the isotactic sequence with an *rr* triad is (1 − α) (Figure 2e). Since the variables *s* and *n* are related as $s = (n - 1)/2$, eq 4 provides the generalized probability of obtaining an isotactic block containing *n* repeating monomer units. This is simply the probability of obtaining the structures shown in parts b, c, d, and e (Figure 2). It should be emphasized that *this derivation is only valid for odd numbers of n* since integral values of *s* are not obtained when *n* is even. Equivalently, the hemiisotactic model only allows for isotactic blocks of odd length since every other monomer has the same stereochemistry.

$$P_n = (0.5)(1 - \alpha)(\alpha)^{(n-1)/2}(1 - \alpha) = (0.5)(1 - \alpha)^2(\alpha)^{(n-1)/2} \quad (4)$$

A special situation arises for $n = 1$. In addition to $P_1 = (0.5)(1 - \alpha)(\alpha)^{(1-1)/2}(1 - \alpha) = (0.5)(1 - \alpha)^2$, an isotactic block of length one occurs with the central monomer of every *rr* triad. The probability of this occurrence is (0.5)(1 − α) because half of all monomers reside at the center of a sequential triad and (1 − α) of these provide the *rr* triad. Therefore, eq 4 is strictly valid for $n \geq 3$ (*n* is odd) and eq 5 holds for $n = 1$. Table 1 provides a description of the possible isotactic blocks for *n* = 1, 3, 5, 7, and 9 for hemiisotactic polypropylene. Since $N_n = P_n(\mathrm{DP})$ (vide supra), the isotactic block length distribution for hemiisotactic polypropylene is fully described by eqs 6 and 7. These apply only to odd values of *n* and are dependent on two experimentally determined parameters: α and M_n.

$$P_1 = (0.5)(1-\alpha)^2 + (0.5)(1-\alpha) \quad (5)$$

$$N_1 = [(0.5)(1-\alpha)^2 + (0.5)(1-\alpha)](M_n/\mathrm{MW}_{\mathrm{monomer}}) \quad (6)$$

$$N_n = (0.5)(1-\alpha)^2(\alpha)^{(n-1)/2}(M_n/\mathrm{MW}_{\mathrm{monomer}}) \quad (7)$$

Comparison of Hypothetical Bernoullian and Hemiisotactic Polypropylenes with $M_n = 100\,000$. Consider a hypothetical collection of polypropylenes having a number-average molecular weight of 100 000 and stereochemical parameters of $\sigma = 0.5$ (atactic), $\sigma = 0.6$, $\sigma = 0.7$, $\sigma = 0.8$, $\sigma = 0.9$ (Bernoullian statistics/chain-end control), $\sigma = 1.0$ (isotactic), $\alpha = 0.5$ (hemiisotactic), $\alpha = 0.6$, $\alpha = 0.7$, $\alpha = 0.8$, $\alpha = 0.9$ (isotactic−hemiisotactic), and $\alpha = 1.0$ (isotactic). Table 2 presents the calculated isotactic block length distributions for these 12 polymers. The numbers shown are the average number of blocks of length *n* that the polymer chains possess. Of course, this is only a statistical average and real polymers will contain a *varying distribution* of isotactic blocks of length *n*, where *n* is a positive integer.

These distributions become more meaningful once it has been considered how long an isotactic block must be before it is capable of participating in a crystallite. The lamellar thickness of the isotactic crystallites in certain elastomeric polypropylene samples has been estimated by transmission electron microscopy (TEM) at 3.0 to 4.0 nm.[16] This length corresponds to 14−18 monomer units since the repeat distance along the polymer helix is 0.65 nm/three monomers for isotactic I (monoclinic).[17] But, Collette et al. concluded that cocrystallization requires isotactic blocks with a minimum of 11−15 monomer units because TEM estimates are probably biased toward larger lamellar thicknesses.[16] Extensive modeling of crystallization phenomena in stereoblock isotactic−atactic polypropylene has invoked a minimum length of 14 monomer units.[18] However, Chien et al. have pointed out that a few monomer units in each isotactic sequence are likely located in diffuse phase boundaries and thus, while necessary, do not participate directly in the cocrystallization. A reasonable assumption was advanced that crystallites are made of isotactic sequences approximately 20 propylene units or longer.[3e] For much of this discussion, a minimum length of 21 monomer units will be considered since only isotactic blocks of odd length are present in hemiisotactic polypropylene.

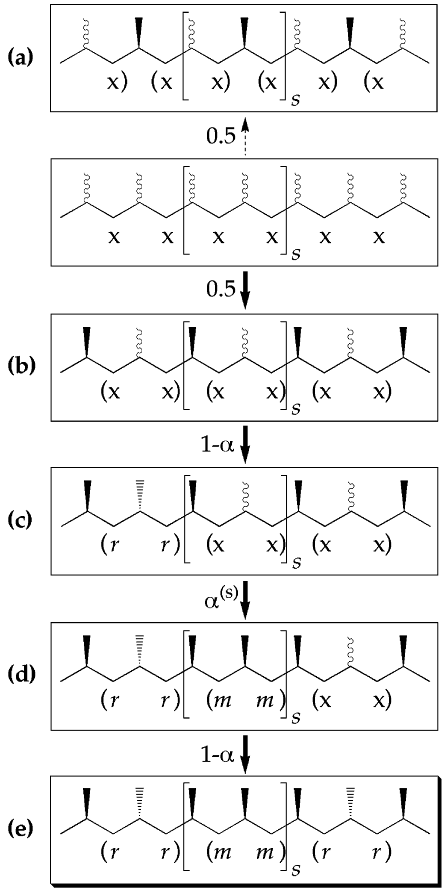
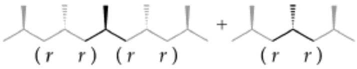
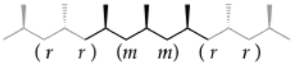
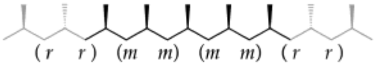
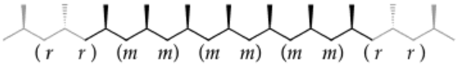
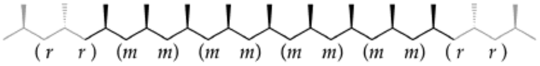


Figure 2. Probability of obtaining an isotactic block, $(rr)(mm)^{(s)}(rr)$, in hemiisotactic polypropylene. This can be conceptualized as the probability of obtaining the structures in parts b, c, d, and e.

Table 1. Relationship of *n* and *s* for Isotactic Blocks of Length *n* = 1, 3, 5, 7, and 9 for Hemiisotactic Polypropylene, Where an Isotactic Block of Length *n* Is Defined as $(rr)(mm)^{(s)}(rr)$ with $s = ((n-1)/2)$

n	*s*	Examples
1	0	 (*r r*) (*r r*) + (*r r*)
3	1	 (*r r*) (*m m*) (*r r*)
5	2	 (*r r*) (*m m*) (*m m*) (*r r*)
7	3	 (*r r*) (*m m*) (*m m*) (*m m*) (*r r*)
9	4	 (*r r*) (*m m*) (*m m*) (*m m*) (*m m*) (*r r*)

Additional statistics are included at the bottom of Table 2. Compiled are the longest isotactic blocks for which $N_n \geq 1$. These block lengths are the longest for which there exists one block *of exactly length n* per polymer chain, on average. For the Bernoullian polymer, σ must be 0.794 or greater to attain $N_{21} > 1$, while for the hemiisotactic polymer, α must be 0.589 or greater to attain $N_{21} > 1$. The quantity $N_{n\geq 21}$ provides the average number of isotactic blocks of length 21 *or greater* per chain. To achieve the morphology of a stereoblock elastomer, this value should be at least two, thereby allowing an average of two crystallizable segments per polymer chain. For the Bernoullian polymer, this minimum is reached with $\sigma = 0.753$; for the hemiisotactic polymer, this minimum is reached with $\alpha = 0.576$. The isotactic block length distributions are illustrated in Figure 3 for a Bernoullian polymer and in Figure 4 for a hemiisotactic polymer. The surfaces are plotted on the same scale and indicate the number of isotactic blocks (N_n) of length *n* than can be found, on average, in a polymer with $M_n = 100\,000$ (DP = 2376) for various values of σ and α. For example, in a Bernoullian polymer with $\sigma = 0.85$, one can expect an average of roughly 2.1 blocks of length 21, about 1.8 blocks of length 22, about 1.5 blocks of length 23 and so forth. If N_n is summed to large values of *n*, one will find that this polymer contains an average of 13.8 isotactic blocks of length 21 or greater. Similarly, one can expect a hemiisotactic polymer with $\alpha = 0.85$ to contain an average of roughly 5.3 blocks of length 21, about 4.5 blocks of length 23, about 3.8 blocks of length 25, and so forth. If N_n is summed to large values of *n*,

Table 2. Isotactic Block Length Distribution for Several Bernoullian Polymers (σ) and Several Hemiisotactic Polymers (α), All Having $M_n = 100\,000$

	N_n											
n	$\sigma = 0.5$	$\sigma = 0.6$	$\sigma = 0.7$	$\sigma = 0.8$	$\sigma = 0.9$	$\sigma = 1.0$	α = 0.5	α = 0.6	α = 0.7	α = 0.8	α = 0.9	α = 1.0
1	594.106	380.228	213.878	95.057	23.764	0.000	891.160	665.399	463.403	285.171	130.703	0.000
2	297.053	228.137	149.715	76.046	21.388	0.000						0.000
3	148.527	136.882	104.800	60.837	19.249	0.000	148.527	114.068	74.857	38.023	10.694	0.000
4	74.263	82.129	73.360	48.669	17.324	0.000						0.000
5	37.132	49.278	51.352	38.935	15.592	0.000	74.263	68.441	52.400	30.418	9.625	0.000
6	18.566	29.567	35.947	31.148	14.033	0.000						0.000
7	9.283	17.740	25.163	24.919	12.629	0.000	37.132	41.065	36.680	24.335	8.662	0.000
8	4.641	10.644	17.614	19.935	11.366	0.000						0.000
9	2.321	6.386	12.330	15.948	10.230	0.000	18.566	24.639	25.676	19.468	7.796	0.000
10	1.160	3.832	8.631	12.758	9.207	0.000						0.000
11	0.580	2.299	6.042	10.207	8.286	0.000	9.283	14.783	17.973	15.574	7.016	0.000
12	0.290	1.379	4.229	8.165	7.457	0.000						0.000
13	0.145	0.828	2.960	6.532	6.712	0.000	4.641	8.870	12.581	12.459	6.315	0.000
14	0.073	0.497	2.072	5.226	6.041	0.000						0.000
15	0.036	0.298	1.451	4.181	5.437	0.000	2.321	5.322	8.807	9.967	5.683	0.000
16	0.018	0.179	1.015	3.345	4.893	0.000						0.000
17	0.009	0.107	0.711	2.676	4.404	0.000	1.160	3.193	6.165	7.974	5.115	0.000
18	0.005	0.064	0.498	2.140	3.963	0.000						0.000
19	0.002	0.039	0.348	1.712	3.567	0.000	0.580	1.916	4.315	6.379	4.603	0.000
20	0.001	0.023	0.244	1.370	3.210	0.000						0.000
21	0.001	0.014	0.171	1.096	2.889	0.000	0.290	1.150	3.021	5.103	4.143	0.000
22	0.000	0.008	0.119	0.877	2.600	0.000						0.000
23	0.000	0.005	0.084	0.701	2.340	0.000	0.145	0.690	2.115	4.083	3.729	0.000
24	0.000	0.003	0.059	0.561	2.106	0.000						0.000
25	0.000	0.002	0.041	0.449	1.896	0.000	0.073	0.414	1.480	3.266	3.356	0.000
26	0.000	0.001	0.029	0.359	1.706	0.000						0.000
27	0.000	0.001	0.020	0.287	1.535	0.000	0.036	0.248	1.036	2.613	3.020	0.000
28	0.000	0.000	0.014	0.230	1.382	0.000						0.000
29	0.000	0.000	0.010	0.184	1.244	0.000	0.018	0.149	0.725	2.090	2.718	0.000
30	0.000	0.000	0.007	0.147	1.119	0.000						0.000
31	0.000	0.000	0.005	0.118	1.007	0.000	0.009	0.089	0.508	1.672	2.446	0.000
32	0.000	0.000	0.003	0.094	0.907	0.000						0.000
33	0.000	0.000	0.002	0.075	0.816	0.000	0.005	0.054	0.355	1.338	2.202	0.000
34	0.000	0.000	0.002	0.060	0.734	0.000						0.000
35	0.000	0.000	0.001	0.048	0.661	0.000	0.002	0.032	0.249	1.070	1.982	0.000
36	0.000	0.000	0.001	0.039	0.595	0.000						0.000
37	0.000	0.000	0.001	0.031	0.535	0.000	0.001	0.019	0.174	0.856	1.783	0.000
38	0.000	0.000	0.000	0.025	0.482	0.000						0.000
39	0.000	0.000	0.000	0.020	0.434	0.000	0.001	0.012	0.122	0.685	1.605	0.000
40	0.000	0.000	0.000	0.016	0.390	0.000						0.000
longest $N_n \geq 1$	10	12	16	21	31	2376	17	21	27	35	47	2376
$N_{n\geq 21}$	0.001	0.035	0.569	5.480	28.892	1.000	0.580	2.874	10.069	25.517	41.430	1.000
$\Sigma(N_n n)\|n \geq 21$	0.025	0.782	13.273	136.992	866.754	2376	13.344	68.973	258.443	739.984	1615.786	2376
% crystallinity	0.001	0.033	0.559	5.765	36.473	100	0.562	2.902	10.875	31.139	67.992	100

one will find that this polymer contains an average of 35.1 isotactic blocks of length 21 or greater. Note that N_n is linearly proportional to M_n (see eqs 2 and 7) and, therefore, a polymer with $M_\mathrm{n} = 200\,000$ will simply have N_n values twice those plotted in Figures 3 and 4.

The quantity $\Sigma(N_n n)|n \geq 21$ reveals the number of monomers, on average, that reside in isotactic blocks of length 21 or greater. Therefore, when this number is divided by the degree of polymerization (DP), one obtains an approximation for the percentage of monomers presumably residing within crystalline domains. This is a *calculated percent crystallinity* and such numbers are reported on the last line of Table 2. Because these values are percentages, they are independent of molecular weight; in practice, they are valid only for DP $\gg$ 21. Moreover, these numbers are based on the assumed minimum threshold for crystallinity of 21 or more monomers per isotactic block. Figure 5 plots the calculated percent crystallinity as a function of σ (Bernoullian) and α (hemiisotactic) for a variety of threshold parameters (17, 19, 21, 23, and 25 monomers per isotactic block). Clearly the two tacticity models have different crystallinity profiles. For hemiisotactic polypropylene, α must be 0.603 to achieve 3% crystallinity, whereas σ must be 0.770 for Bernoullian polypropylene to achieve 3% crystallinity.

Further insight is gained by visualizing the crystalline and amorphous phases simultaneously in a series of simulated polymers with $M_\mathrm{n} = 100\,000$. Figure 6 shows such a simulation for statistically representative polymers with varying σ (Bernoullian) and α (hemiisotactic) values. Black regions depict isotactic segments of length 21 or greater and gray regions depict amorphous segments devoid of such lengthy isotactic blocks. The mechanical properties of many known polymers agree well with the morphology suggested by these simulated polymers. From reported work on hemiisotactic polypropylene, it is known that an α value of 0.50 typically results in an amorphous material, which exhibits no elastomeric properties.[12] Also, it has been demonstrated that α values near 0.75 result in a rigid polymer whose properties are dominated by the crystalline phase (19.0% calculated crystallinity). Indeed, normal melting endotherms have been observed for such samples (T_m = 91 or 98 °C). However, α values near 0.60 typically provide elastomeric polypropylene with an isotactic–hemiisotactic structure.[9] Accordingly, it is predicted that high molecular weight Bernoullian polypropylene with

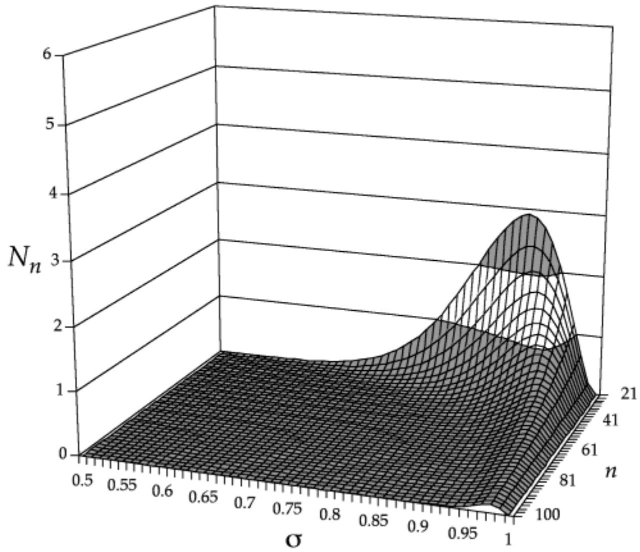


Figure 3. Number of isotactic blocks (N_n) of length n, which varies according to the Bernoullian parameter σ (M_n = 100 000).

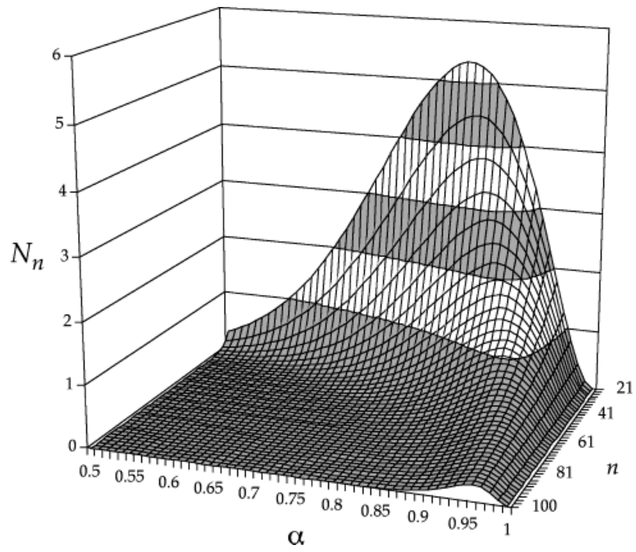


Figure 4. Number of isotactic blocks (N_n) of length n, which varies according to the hemiisotactic parameter α (M_n = 100 000).

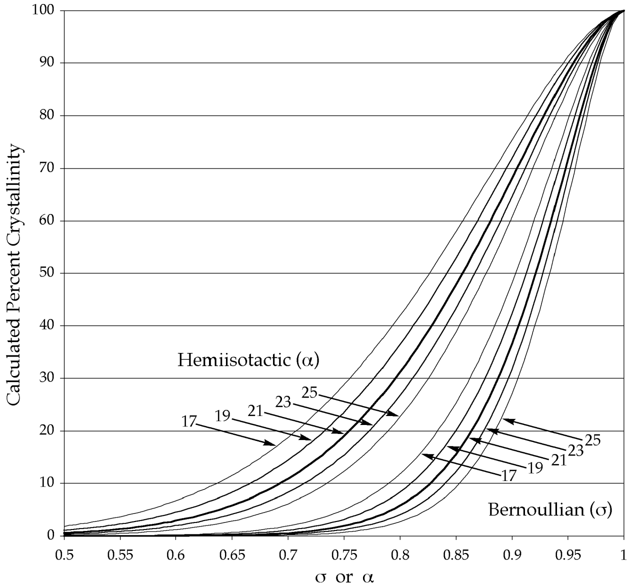


Figure 5. Variation of the calculated percent crystallinity as a function of σ (Bernoullian) and α (hemiisotactic), depending on the minimum threshold length (e.g., 17, 19, 21, 23, or 25) for which an isotactic block is considered capable of cocrystallization.

a σ value near 0.75 or 0.80 will exhibit elastomeric properties since such polymers are calculated to have a number of long isotactic blocks comparable to that for hemiisotactic polypropylene with α = 0.60. High molecular weight Bernoullian polymers with σ near 0.75 or 0.80 are essentially unknown.

An advantage of the derived equations is that they provide the explicit statistical distribution of isotactic blocks. Thus, one is not confined to the presumed threshold value of 21 monomeric units per crystallizable segment; other threshold values are readily considered. Figure 7 plots the total number of isotactic blocks of length n or greater as a function of σ (Bernoullian) and α (hemiisotactic) for polypropylene with a molecular weight of 100 000 (2376 monomeric units). The curves shown represent different possible threshold lengths—odd values from 11 to 31. Bernoullian and hemiisotactic polymers are readily compared, and a few points are noteworthy: (1) regardless of the specific threshold value invoked, approximately the same maximum number of crystallizable blocks can be achieved with either tacticity; (2) numerous isotactic blocks are more readily found with lower α parameters and with higher σ parameters; (3) the broader hemiisotactic curves indicate a wider stereochemical range for observing polymers with abundant isotactic blocks. The curves with threshold values of 21 correspond directly to the polymers depicted in Figure 6. Naturally, Figure 6 would appear markedly different if another threshold value were chosen. Figure 8 illustrates this difference for two randomly simulated polypropylenes with molecular weight of 100 000: one Bernoullian polymer with σ = 0.7846 and one hemiisotactic polymer with α = 0.6240. Each of these polymers is predicted to have an average of 4.00 isotactic blocks of length 21 or greater per chain. In comparing the two simulated polymers, note that the number of isotactic blocks remains approximately the same even if a different threshold value is considered. This is roughly true for the statistical average number of isotactic blocks (bottom of Figure 8), and thus, these two polymers are predicted to have very similar properties.

Comparison of Hypothetical Bernoullian and Hemiisotactic Polypropylenes with Varying Molecular Weights. The parameter $N_{n\geq 21}$ can be calculated for a polymer by summing the number of isotactic blocks of length 21 or greater. The calculated value is reported in Table 2 for selected Bernoullian and hemiisotactic polymers with M_n = 100 000. This parameter is linearly proportional to the number-average molecular weight (see eqs 2 and 7) and can be plotted on a contour map as a function of M_n and σ (Bernoullian) or α (hemiisotactic), as in Figures 9 and 10, respectively. These figures also include the percent crystallinity curves (from 0 to 100%) for a threshold length of n = 21 (see Figure 5).

For Bernoullian and hemiisotactic polymers, an elastomeric morphology is reasonably anticipated when the following two conditions are met: (1) the average polymer chain contains at least two crystallizable isotactic blocks; (2) the percent crystallinity does not surpass a value where the polymeric properties are

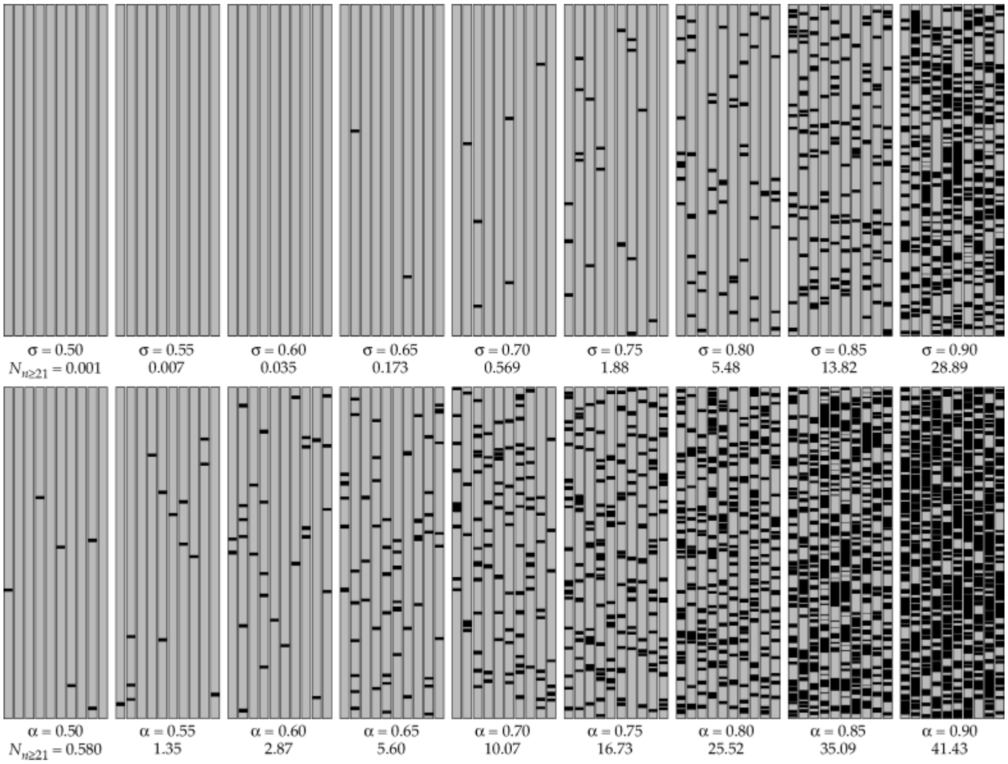


Figure 6. Simulated polymers with black regions depicting local isotacticity (isotactic blocks of length 21 or greater). For each value of σ (Bernoullian) or α (hemiisotactic), a randomly generated collection of 10 polymers with M_n = 100 000 is illustrated. Also provided is the average number of isotactic blocks ($n \geq 21$) per chain.

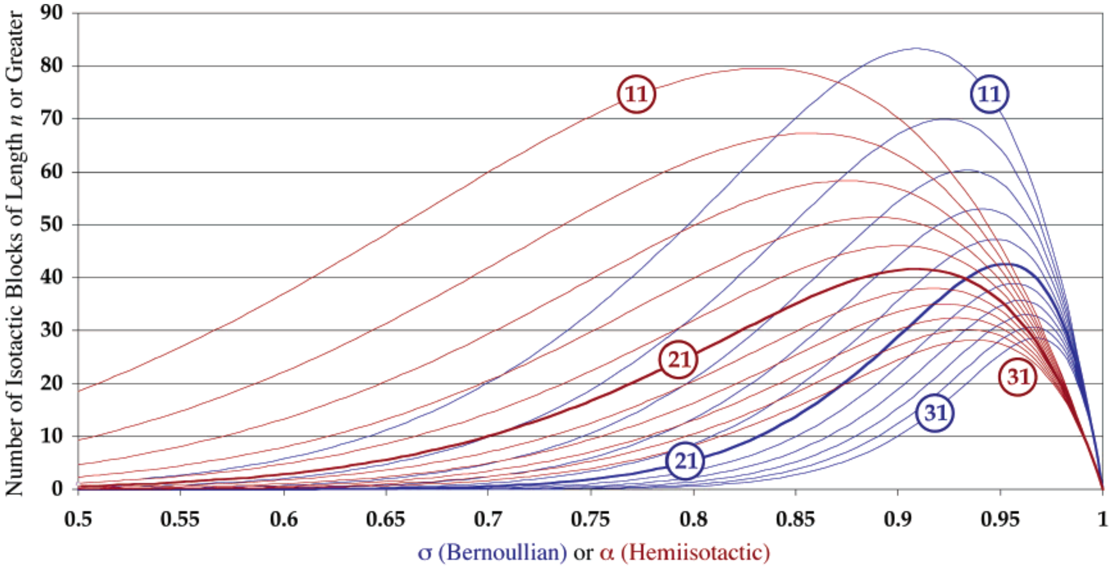


Figure 7. Variation of the total number of isotactic blocks present per polypropylene chain with molecular weight 100 000 as a function of the stereochemical parameter (σ or α), depending on the minimum threshold length for which isotactic blocks are capable of cocrystallization.

dominated by the crystalline phase (ca. 10%[19]). The latter condition ensures the ample presence of an amorphous component that allows for deformation, while the former condition provides the physical cross-links and restoring force necessary for hysteresis. For Bernoullian polypropylene, these conditions are met in the gray region of Figure 9. Note that the elastomeric range for σ is relatively small; for a polymer with M_n = 100 000—which is unusually high for most Bernoullian samples—σ must lie between 0.752 and 0.827. In contrast, the elastomeric range for hemiisotactic polypropylene is wider (Figure 10); for a polymer with M_n = 100 000, α must lie between 0.575 and 0.693.

Isotactic Block Length Distribution in High Molecular Weight Bernoullian Polypropylene. A limited number of reports have appeared describing the elastomeric properties of polypropylenes with Bernoullian stereochemistry.[5,20] Table 3 shows a representative (if not complete) list of such polymers. They are plotted in Figure 11 according to the reported σ and M_n values. As can be seen in Figure 11, only two of the 28 Bernoullian polymers fall into the gray area and are thus predicted to have two or more isotactic blocks ($n \geq 21$) per chain. The two polymers are calculated to contain 3.61 and 6.38 isotactic blocks per chain (entries 4 and 5, respectively). The remaining 26 polymers all

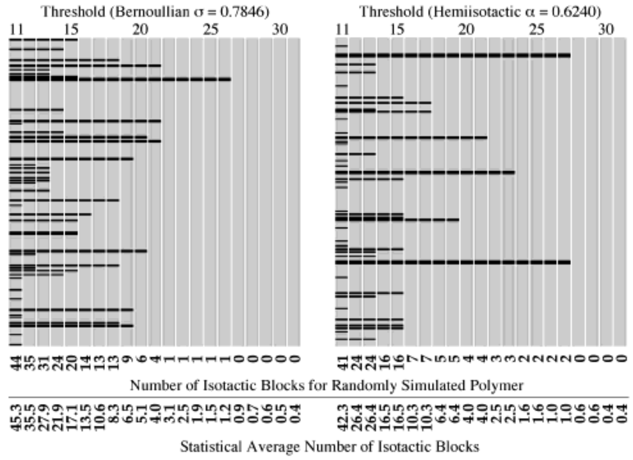


Figure 8. Ribbon plots showing the *exact* number and arrangement of isotactic blocks for a randomly simulated Bernoullian polymer ($\sigma = 0.7846$) and a randomly simulated hemiisotactic polymer ($\alpha = 0.6240$), each with a molecular weight of 100 000. The statistical *average* number of isotactic blocks for an ensemble of polymers with these stereochemical parameters is given at the bottom.

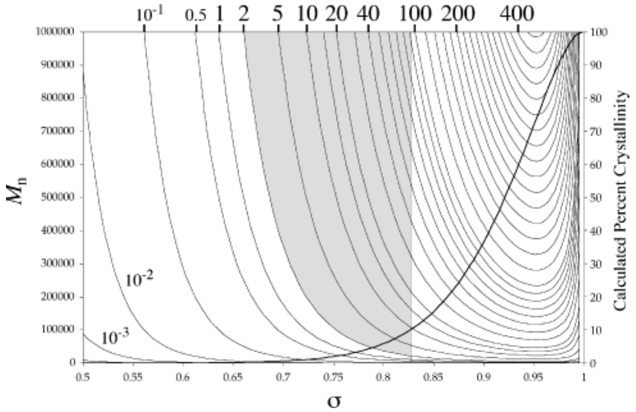


Figure 9. Contour plot depicting the average number of crystallizable isotactic stereoblocks ($n \geq 21$) present per chain in Bernoullian polypropylene as a function of the number-average molecular weight, M_n, and σ, the Bernoullian stereochemical parameter. Superimposed is the calculated percent crystallinity curve (threshold length of 21 repeat units), which is solely a function of σ. The gray region identifies the polymers that contain at least two crystallizable isotactic blocks but also have a calculated percent crystallinity of less than 10% ($\sigma = 0.827$).

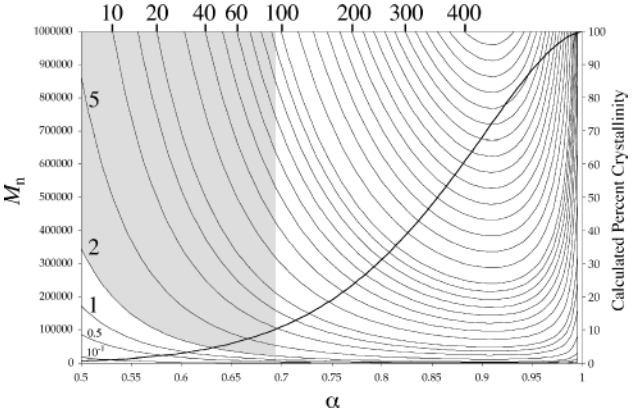


Figure 10. Contour plot depicting the average number of crystallizable isotactic stereoblocks ($n \geq 21$) present per chain in hemiisotactic polypropylene as a function of the number-average molecular weight, M_n, and α, the hemiisotactic stereochemical parameter. Superimposed is the calculated percent crystallinity curve (threshold length of 21 repeat units), which is solely a function of α. The gray region identifies the polymers that contain at least two crystallizable isotactic blocks but also have a calculated percent crystallinity of less than 10% ($\alpha = 0.693$).

contain significantly fewer isotactic blocks per chain (see Table 3 for values). For example, only one in every 47 chains ($1/(2.12 \times 10^{-2})$) is predicted to contain a crystallizable isotactic block for the polymer described by entry 16. For the polymer from entry 11, only one in every 29 900 chains ($1/(3.34 \times 10^{-5})$) will contain an isotactic block long enough to crystallize. For purely atactic polypropylene ($\sigma = 0.5$), an M_n value of 89 000 000 would be required to achieve an average of just one crystallizable block per chain ($n \geq 21$) and an M_n value of 177 000 000 would be required to have two such blocks. *Clearly Bernoullian polymers with σ near 0.5 will never have an elastomeric morphology dependent on the statistical presence of isotactic blocks since the required molecular weights are astronomical.* Even if a threshold value as low as 14 were considered, an average of two isotactic blocks per chain would not be found until M_n = 1 379 000 for atactic polypropylene. However, for Bernoullian polymers with significantly larger σ values, it is more plausible to invoke the statistical presence of isotactic blocks to explain an elastomeric morphology; entries 4 and 5 from Table 3 are examples ($\sigma = 0.671$ and 0.698). Therefore, the elastomeric properties of most reported Bernoullian polymers are likely dependent on other phenomena such as chain entanglements or the existence of non-Bernoullian chains abundant enough to alter the morphology.

Isotactic Block Length Distribution in Isotactic—Hemiisotactic Polypropylene. Just as the Bernoullian stereochemical parameter σ can deviate from $\sigma = 0.5$ (purely atactic), the hemiisotactic stereochemical parameter α can deviate from $\alpha = 0.5$ (purely hemiisotactic). Definitive control over the stereochemical parameter α in hemiisotactic polypropylene was first reported recently by Miller and Bercaw; α values covering the range of $\alpha = 0.103$ to $\alpha = 0.942$ (e.g., 0.103, 0.188, 0.434, 0.490. 0.553, 0.590, 0.616, 0.772, 0.889, 0.942) were readily accessible via a family of sterically altered zirconocene-based catalysts.[9a] For several samples with $\alpha > 0.5$, the term isotactic−hemiisotactic was applied since there existed a surplus of *m* dyads, but the hemiisotactic microstructure was not compromised since the stereochemical fidelity of every other stereocenter was maintained. Moreover, 10 polypropylene samples with $\alpha \approx 0.6$ were found to exhibit definitive elastomeric properties.[9b] These 10 samples are cataloged in Table 4. Entry 11 corresponds to an isotactic−hemiisotactic polymer ($\alpha = 0.753$) that is a nonelastomeric, rigid solid.

The polymers are plotted in Figure 12 according to the reported α and M_n values. As can be seen, most of the elastomeric polymers fall into the gray region where polymers are calculated: (1) to contain at least two isotactic blocks of crystallizable length per chain ($n \geq 21$); and (2) not to exceed the percent crystallinity threshold of 10%, above which the crystalline phase will dominate the physical properties. Indeed, such dominance is observed with entry 11. Despite having 6.62 crystallizable blocks per chain (a number consonant with an elastomeric morphology), this polymer displays no elasticity because approximately 20% of the polymer

Table 3. Reported Elastomeric Polypropylenes with Bernoullian Stereochemistry

entry	σ	M_w	M_n	M_w/M_n	$N_{n\geq 21}$	% crystallinity^d	ref
1	0.411	395 600	197 800	*2.0*^{c}	5.24×10^{-5}	2.42×10^{-5}	5a
2	0.547	340 000	262 000	1.3	1.62×10^{-2}	5.79×10^{-3}	5b
3	0.577	560 000	295 000	1.9	4.96×10^{-2}	1.58×10^{-2}	5b
4	0.671	2 300 000	1 350 000	1.7	3.61	2.59×10^{-1}	5b
5	0.698	2 000 000	1 180 000	1.7	6.38	5.30×10^{-1}	5b
6	0.497	300 000	56 600	5.3	5.72×10^{-4}	9.35×10^{-4}	5b
7	0.443	400 000	108 000	3.7	1.21×10^{-4}	1.03×10^{-4}	5b
8	0.441	280 000	84 800	3.3	8.72×10^{-5}	9.43×10^{-5}	5b
9	0.485	260 000	50 000	5.2	3.17×10^{-4}	5.86×10^{-4}	5b
10	0.498	160 000	29 600	5.4	3.11×10^{-4}	9.72×10^{-4}	5b
11	0.424	270 000	69 200	3.9	3.34×10^{-5}	4.41×10^{-5}	5b
12	0.438	170 000	34 700	4.9	3.13×10^{-5}	8.27×10^{-5}	5b
13	0.713^a	120 000	29 900	4.02	2.35×10^{-1}	7.77×10^{-1}	5c
14	0.589^a	100 000	50 000	*2.0*^{c}	1.23×10^{-2}	2.33×10^{-2}	5c
15	0.573^a	132 000	55 200	2.39	8.15×10^{-1}	1.39×10^{-2}	5c
16	0.593^a	160 000	75 800	2.11	2.12×10^{-2}	2.64×10^{-2}	5c
17	0.615^a	150 000	49 300	3.04	2.70×10^{-2}	5.21×10^{-2}	5c
18	0.598^a	232 000	72 500	3.20	2.37×10^{-2}	3.09×10^{-2}	5c
19	0.592^a	157 000	78 100	2.01	2.12×10^{-2}	2.56×10^{-2}	5c
20	0.545^a	112 000	41 000	2.73	2.37×10^{-3}	5.40×10^{-3}	5c
21	0.600^a	105 000	42 900	2.45	1.49×10^{-2}	3.29×10^{-2}	5c
22	0.33^b	690 000	345 000	*2.0*^{c}	1.29×10^{-6}	3.38×10^{-7}	5e
23	0.33^b	565 000	282 500	*2.0*^{c}	1.06×10^{-6}	3.38×10^{-7}	5e
24	0.33^b	273 000	136 500	*2.0*^{c}	5.10×10^{-7}	3.38×10^{-7}	5e
25	0.33^b	80 000	40 000	*2.0*^{c}	1.49×10^{-7}	3.38×10^{-7}	5e
26	0.33^b	442 000	221 000	*2.0*^{c}	8.25×10^{-7}	3.38×10^{-7}	5e
27	0.33^b	345 000	172 500	*2.0*^{c}	6.44×10^{-7}	3.38×10^{-7}	5e
28	0.33^b	289 000	144 500	*2.0*^{c}	5.40×10^{-7}	3.38×10^{-7}	5e

[a] Polypropylene samples from entries 13−21 were described as "almost atactic" and were prepared with nonbridged group IV metallocenes in conjunction with methylaluminoxane. Since the full pentad distribution was not provided, the σ parameter has been extrapolated from the reported *mmmm* pentad value according to the Bernoullian model. [b] Although only one triad distribution was explicitly reported, the text of this reference suggests all polymers have $\sigma = 0.33$. [c] Italicized values are calculated based on an assumed M_w/M_n value of 2.0. [d] The calculated percent crystallinity is the weight fraction of the monomers residing in isotactic stereoblocks with $n \geq 21$.

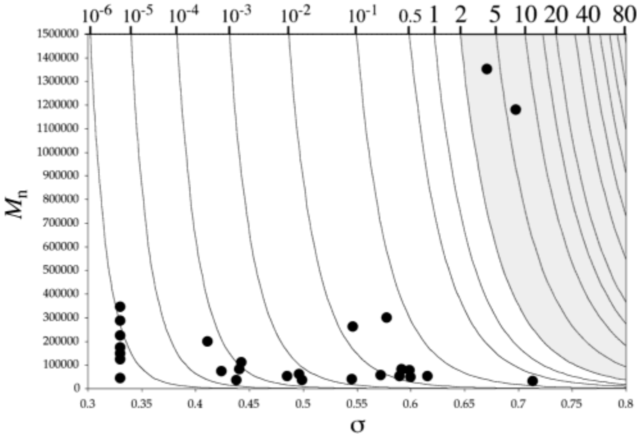


Figure 11. Contour plot of the 28 elastomeric Bernoullian polymers from Table 3 (entries 16 and 19 overlap), which shows the average number of crystallizable isotactic blocks ($n \geq 21$) present per chain.

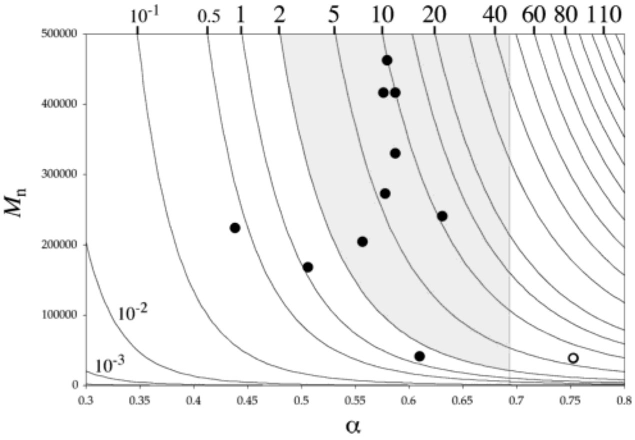


Figure 12. Contour plot of the 10 elastomeric isotactic−hemiisotactic polymers from Table 4, which shows the average number of crystallizable isotactic blocks ($n \geq 21$) present per chain. An additional data point (○) is included for an isotactic−hemiisotactic polymer with $\alpha = 0.753$ and $M_n = 38\,500$, which is a rigid, nonelastomeric solid (Table 4, entry 11).

resides in the crystalline phase. In contrast, the seven polymers that lie in the gray region of Figure 12 ($\alpha = 0.557-0.630$) have a calculated percent crystallinity of 1.50−4.45%; the average number of crystallizable blocks per chain is between 3.09 and 10.48. The remaining three polymers are reported to be elastomeric, yet they have fewer than two crystallizable blocks per chain (0.39, 1.09, and 1.42). These may be elastomeric for the same reasons that Bernoullian polymers with $\sigma \approx 0.5$ can be elastomeric (vide supra). However, one must consider that a *polydisperse* polypropylene sample with an average of 0.39 isotactic blocks per chain can still have a significant fraction of the polymer reside in chains with two or more crystallizable blocks. Figure 13 displays the GPC trace for entry 1 of Table 4. Notwithstanding the low α value of 0.438, 11% of the polymer chains (by weight) are calculated to contain two or more crystallizable isotactic blocks per chain (the gray region where molecular weight > 1 153 000). For comparison, Figures 14 and 15 show GPC traces for entries 4 and 10 of Table 4, respectively. These polymers contain a markedly larger weight fraction of chains with two or more crystallizable blocks per chain (95% and 97%, respectively). This is a consequence of the larger α values (0.576 and 0.630, respectively). For entries 4 and 10, chains are calculated to average two or more crystallizable blocks for molecular weights exceeding 98 800 and 46 200 respectively (Figures 14 and 15, shown in gray).

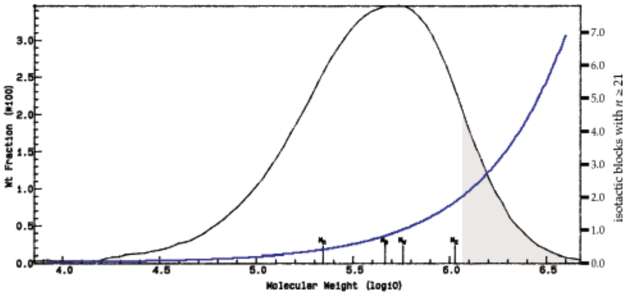


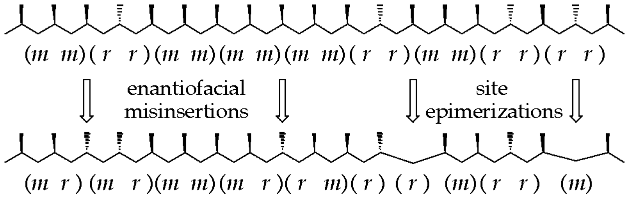
Figure 13. GPC trace corresponding to the polymer from Table 4, entry 1 (α = 0.438). Superimposed is a curve that indicates the number of crystallizable isotactic blocks per chain as a function of the molecular weight. Fully 11% of the polymer (the gray region) is estimated to have at least two crystallizable blocks per chain.

Table 4. Reported Elastomeric Polypropylenes with Isotactic−Hemiisotactic Stereochemistry[a]

entry	α = [m]	M_w	M_n	M_w/M_n	$N_{n \geq 21}$	% crystallinity[b]
1	0.438	572 000	224 000	2.55	0.39	0.16
2	0.506	390 000	168 000	2.32	1.09	0.63
3	0.557	435 000	204 000	2.14	3.09	1.50
4	0.576	806 000	417 000	1.93	8.45	2.02
5	0.578	638 000	273 000	2.33	5.70	2.08
6	0.579	1 081 000	463 000	2.33	9.81	2.12
7	0.587	1 006 000	416 000	2.42	9.92	2.39
8	0.588	802 000	330 000	2.43	7.98	2.43
9	0.610	134 000[c]	43 000[c]	3.15[c]	1.42	3.36
10	0.630	535 000	242 000	2.21	10.48	4.45
11[d]	0.753	77 400	38 500	2.01	6.62	19.61

[a] Entry 1 has α < 0.5 and thus is termed syndiotactic−hemiisotactic. [b] This value reflects the calculated percentage of monomers which reside in isotactic stereoblocks of length $n \geq 21$. [c] These values were estimated based on a polymerization performed with the same catalyst at the same temperature. [d] Entry 11 is a nonelastomeric, rigid solid with a normal DSC trace and a melting temperature of 98 °C.

Effects of Stereoerrors in the Isotactic Block Length Distribution for Hemiisotactic and Isotactic—Hemiisotactic Polypropylene. In metal-mediated hemiisoselective polymerizations, at least two key stereoerror events may impact the isotactic block length distribution: enantiofacial misinsertions at the more stereoselective site and site epimerizations. Each of these events will alter the normal succession of *mm* and *rr* triads otherwise present in an ideal hemiisotactic polymer. In particular, the enantiofacial misinsertion stereoerror will introduce *mr* and *rm* triads and the site epimerization stereoerror will introduce *m* and *r* dyads.



To a first approximation, hemiisoselective metallocene catalysts will not provide the *r* dyad as a result of site epimerization since such an epimerization requires the unimolecular migration of the growing polymer chain *toward* a large substituent on the cyclopentadienyl ring. In contrast, the related migration of the growing polymer chain *away* from the cyclopentadienyl substituent can be prevalent and will afford an isolated *m* dyad through two sequential insertions at the more stereoselective site (assuming no concomitant enantiofacial misinsertions).[21] Thus, in the present estimation of the contribution of stereoerrors, only sequential units of the following type will be considered: *mm*, *rr*, *mr*, *rm*, and *m*.

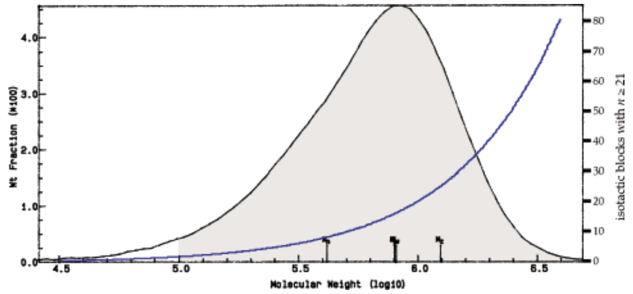


Figure 14. GPC trace corresponding to the polymer from Table 4, entry 4 (α = 0.576). Superimposed is a curve that indicates the number of crystallizable isotactic blocks per chain as a function of the molecular weight. Fully 95% of the polymer (the gray region) is estimated to have at least two crystallizable blocks per chain.

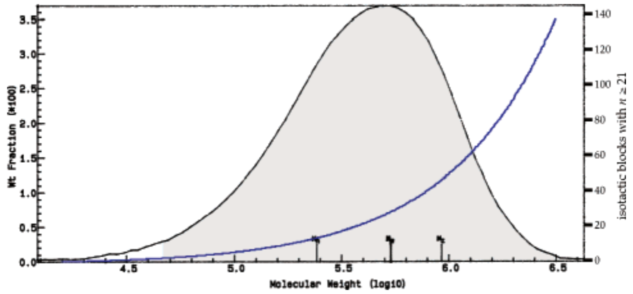


Figure 15. GPC trace corresponding to the polymer from Table 4, entry 10 (α = 0.630). Superimposed is a curve that indicates the number of crystallizable isotactic blocks per chain as a function of the molecular weight. Fully 97% of the polymer (the gray region) is estimated to have at least two crystallizable blocks per chain.

In the absence of stereoerrors, isotactic blocks consist of sequential *mm* triads that are initiated and terminated by *rr* triads. With stereoerrors, however, an isotactic block consists of sequential *mm* triads and/or *m* dyads while initiation and termination occur with *rr*, *mr*, or *rm* triads. The nine possible modes of initiation and termination are shown in Table 5 for an isotactic block of length 9. The corresponding probabilities are included. The factor η is close to 0.5, and represents the likelihood that a randomly selected repeat unit begins a triad; the factor η will increase with increasing site epimerization since it equals the fraction of monomers that inserts at the more stereoselective site (vide infra). Additionally, one must account for the fact that the *mr* and *rm* triads can each be formed in two distinct ways: $P_{mr} = (P_{\uparrow\uparrow\downarrow}) + (P_{\downarrow\downarrow\uparrow})$ and $P_{rm} = (P_{\uparrow\downarrow\downarrow}) + (P_{\downarrow\uparrow\uparrow})$. While $P_{\mathrm{rr}} = (P_{\uparrow\downarrow\uparrow})+(P_{\downarrow\uparrow\downarrow})$, exclusion of the component $(P_{\downarrow\uparrow\downarrow})$ is justified since this term requires two enantiofacial misinsertions and thus is practically negligible. Considering all this, one can write a general equation for $N_n = P_n(\mathrm{DP})$ as follows:

$$\begin{aligned} N_n = (DP)(\eta)[&(P_{\uparrow\downarrow\uparrow})(P_{(n-1)m})(P_{\uparrow\downarrow\uparrow}) + (P_{\uparrow\downarrow\uparrow})(P_{(n-2)m})(P_{\uparrow\uparrow\downarrow}) + \\ &(P_{\uparrow\downarrow\uparrow})(P_{(n-1)m})(P_{\uparrow\downarrow\downarrow}) + (P_{\downarrow\downarrow\uparrow})(P_{(n-1)m})(P_{\uparrow\downarrow\uparrow}) + \\ &(P_{\downarrow\downarrow\uparrow})(P_{(n-2)m})(P_{\uparrow\uparrow\downarrow}) + (P_{\downarrow\downarrow\uparrow})(P_{(n-1)m})(P_{\uparrow\downarrow\downarrow}) + \\ &(P_{\downarrow\uparrow\uparrow})(P_{(n-2)m})(P_{\uparrow\downarrow\uparrow}) + (P_{\downarrow\uparrow\uparrow})(P_{(n-3)m})(P_{\uparrow\uparrow\downarrow}) + \\ &(P_{\downarrow\uparrow\uparrow})(P_{(n-2)m})(P_{\uparrow\downarrow\downarrow})] \end{aligned} \quad (8)$$

Table 5. The Nine Possible Sequences and Corresponding Probabilities that Generate an Isotactic Block of Length Nine (Using the *rr*, *mr*, and *rm* Triads To Initiate and Terminate)

Sequence	Probability
 r r m m m m m m m m r r	$(\eta)(P_{\uparrow\downarrow\uparrow})(P_{8m})(P_{\uparrow\downarrow\uparrow})$
 r r m m m m m m m m r	$(\eta)(P_{\uparrow\downarrow\uparrow})(P_{7m})(P_{\uparrow\uparrow\downarrow})$
 r r m m m m m m m m r m	$(\eta)(P_{\uparrow\downarrow\uparrow})(P_{8m})(P_{\uparrow\downarrow\downarrow})$
 m r m m m m m m m m r r	$(\eta)(P_{\downarrow\downarrow\uparrow})(P_{8m})(P_{\uparrow\downarrow\uparrow})$
 m r m m m m m m m m r	$(\eta)(P_{\downarrow\downarrow\uparrow})(P_{7m})(P_{\uparrow\uparrow\downarrow})$
 m r m m m m m m m m r m	$(\eta)(P_{\downarrow\downarrow\uparrow})(P_{8m})(P_{\uparrow\downarrow\downarrow})$
 r m m m m m m m m r r	$(\eta)(P_{\downarrow\uparrow\uparrow})(P_{7m})(P_{\uparrow\downarrow\uparrow})$
 r m m m m m m m m r	$(\eta)(P_{\downarrow\uparrow\uparrow})(P_{6m})(P_{\uparrow\uparrow\downarrow})$
 r m m m m m m m m r m	$(\eta)(P_{\downarrow\uparrow\uparrow})(P_{7m})(P_{\uparrow\downarrow\downarrow})$

Table 6 illustrates how one arrives at P_{xm} for $x = 1$ to 8. In general, P_{xm} is a polynomial with $(x + 1)/2$ terms for odd values of x and $(x + 2)/2$ terms for even values of x. To avoid a large number of small terms, the polynomial has been truncated to two terms in the present analysis. This means that terms containing $(P_m)^x$ with $x \geq 4$ are excluded. This is equivalent to the assumption that, during the formation of a single isotactic block, no more than three site epimerizations occur. It can be shown that this assumption is valid for small values of P_m.[22] The sequences embedded in Table 6 can be identified, and a general solution can be extracted for P_{xm} with odd values of x (eq 9) and for P_{xm} with even values of x (eq 10).[23]

$$P_{xm\ (\mathrm{odd}\ x)} = ((x + 1)/2)(P_{mm})^{((x-1)/2)}(P_m) + [((x - 1)/2)(((x - 1)/2) + 1)(((x - 1)/2) + 2)/6](P_{mm})^{((x-3)/2)}(P_m)^3 \quad (9)$$

$$P_{xm\ (\mathrm{even}\ x)} = (P_{mm})^{(x/2)} + [(x/2)((x/2) + 1)/2](P_{mm})^{((x-2)/2)}(P_m)^2 \quad (10)$$

Table 6. Possible Sequences and Collective Probability for *x* Sequential *m* Relationships (Terms Containing $(P_m)^x$ with $x \geq 4$ Excluded)

x	Possible Sequences	Collective Probability (P_{xm})
1	(m)	$1\,(P_{mm})^0(P_m)^1 + 0\,(P_{mm})^{-1}(P_m)^3$
2	$(m\ m)$ $(m)(m)$	$1\,(P_{mm})^1(P_m)^0 + 1\,(P_{mm})^0(P_m)^2$
3	$(m\ m)(m)$ $(m)(m\ m)$ $(m)(m)(m)$	$2\,(P_{mm})^1(P_m)^1 + 1\,(P_{mm})^0(P_m)^3$
4	$(m\ m)(m\ m)$ $(m\ m)(m)(m)$ $(m)(m\ m)(m)$ $(m)(m)(m\ m)$	$1\,(P_{mm})^2(P_m)^0 + 3\,(P_{mm})^1(P_m)^2$
5	$(m\ m)(m\ m)(m)$ $(m\ m)(m)(m\ m)$ $(m)(m\ m)(m\ m)$ $(m\ m)(m)(m)(m)$ $(m)(m\ m)(m)(m)$ $(m)(m)(m\ m)(m)$ $(m)(m)(m)(m\ m)$	$3\,(P_{mm})^2(P_m)^1 + 4\,(P_{mm})^1(P_m)^3$
6	$(m\ m)(m\ m)(m\ m)$ $(m\ m)(m\ m)(m)(m)$ $(m\ m)(m)(m)(m\ m)$ $(m)(m)(m\ m)(m\ m)$ $(m\ m)(m)(m\ m)(m)$ $(m)(m\ m)(m\ m)(m)$ $(m)(m\ m)(m)(m\ m)$	$1\,(P_{mm})^3(P_m)^0 + 6\,(P_{mm})^2(P_m)^2$
7	$(m\ m)(m\ m)(m\ m)(m)$ $(m\ m)(m\ m)(m)(m\ m)$ $(m\ m)(m)(m\ m)(m\ m)$ $(m)(m\ m)(m\ m)(m\ m)$ $(m\ m)(m\ m)(m)(m)(m)$ $(m\ m)(m)(m)(m)(m\ m)$ $(m)(m)(m)(m\ m)(m\ m)$ $(m\ m)(m)(m\ m)(m)(m)$ $(m\ m)(m)(m)(m\ m)(m)$ $(m)(m\ m)(m\ m)(m)(m)$ $(m)(m\ m)(m)(m\ m)(m)$ $(m)(m\ m)(m)(m)(m\ m)$ $(m)(m)(m\ m)(m\ m)(m)$ $(m)(m)(m\ m)(m)(m\ m)$	$4\,(P_{mm})^3(P_m)^1 + 10\,(P_{mm})^2(P_m)^3$
8	$(m\ m)(m\ m)(m\ m)(m\ m)$ $(m\ m)(m\ m)(m\ m)(m)(m)$ $(m\ m)(m\ m)(m)(m)(m\ m)$ $(m\ m)(m)(m)(m\ m)(m\ m)$ $(m)(m)(m\ m)(m\ m)(m\ m)$ $(m\ m)(m)(m\ m)(m)(m\ m)$ $(m\ m)(m)(m\ m)(m\ m)(m)$ $(m\ m)(m\ m)(m)(m\ m)(m)$ $(m)(m\ m)(m)(m\ m)(m\ m)$ $(m)(m\ m)(m\ m)(m)(m\ m)$ $(m)(m\ m)(m\ m)(m\ m)(m)$	$1\,(P_{mm})^4(P_m)^0 + 10\,(P_{mm})^3(P_m)^2$

In the derivation that ignored stereoerrors, only two independent parameters were needed: α and DP. However, with stereoerrors arising from enantiofacial misinsertions and site epimerizations, it is necessary to have a total of four independent parameters. Two additional parameters must be defined: ϵ, the probability of an enantiofacial misinsertion at the more stereoselective site; and δ, the probability that a site epimerization will skip an insertion at the less stereoselective site and lead to an m dyad. Table 7 defines the dependent stereochemical parameters in terms of α, ϵ, and δ. To render the model statistically complete, the probabilities of several short isotactic blocks must be accounted for. For example, an isotactic block of length 1 is formed with every rr triad and whenever $(P_{\uparrow\uparrow\downarrow})$ is followed by $(P_{\downarrow\uparrow\uparrow})$. Additionally, an isotactic block

Table 7. Definitions of Independent and Dependent Stereochemical Parameters

independent parameters	variable	range
stereoselectivity at the less stereoselective site	α	0 to 1
probability of enantiofacial misinsertion at the more stereoselective site	ϵ	0 to 1
probability of site epimerization, skipping the less stereoselective site	δ	0 to 1

dependent parameters	variable	relationship to α, ϵ, and δ
probability of an *mm* triad with α insertion	(P_{mm})	$\alpha[1 - (2\epsilon + \delta)]$
probability of an *rr* triad with $1 - \alpha$ insertion	$(P_{\uparrow\downarrow\uparrow})$	$(1 - \alpha)[1 - (2\epsilon + \delta)]$
probability of an *mr* triad with α insertion	$(P_{\uparrow\uparrow\downarrow})$	$\alpha\epsilon$
probability of an *mr* triad with $1 - \alpha$ insertion	$(P_{\downarrow\downarrow\uparrow})$	$(1 - \alpha)\epsilon$
probability of an *rm* triad with α insertion	$(P_{\downarrow\uparrow\uparrow})$	$\alpha\epsilon$
probability of an *rm* triad with $1 - \alpha$ insertion	$(P_{\uparrow\downarrow\downarrow})$	$(1 - \alpha)\epsilon$
probability of a sequential *m* dyad	(P_m)	δ
fraction of monomers inserted at the more stereoselective site	η	$1/(2 - \delta)$

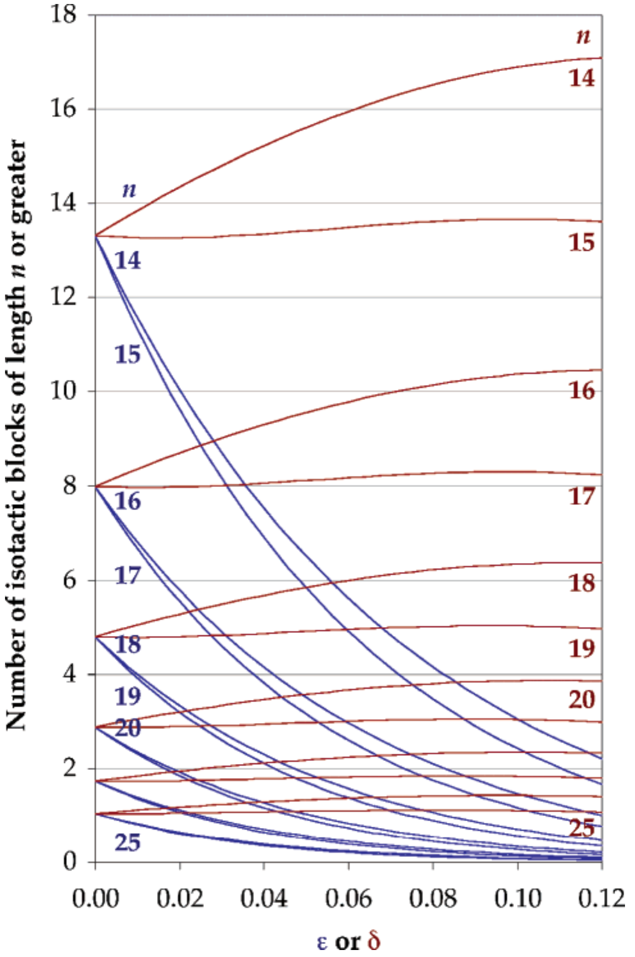


Figure 16. Number of isotactic blocks of length *n* or greater depending on the probability of enantiofacial misinsertion at the more stereoselective site (ϵ, blue) or site epimerization (δ, red) for a hemiisoselective catalyst. Here, $M_n = 100\,000$, and $\alpha = 0.6$.

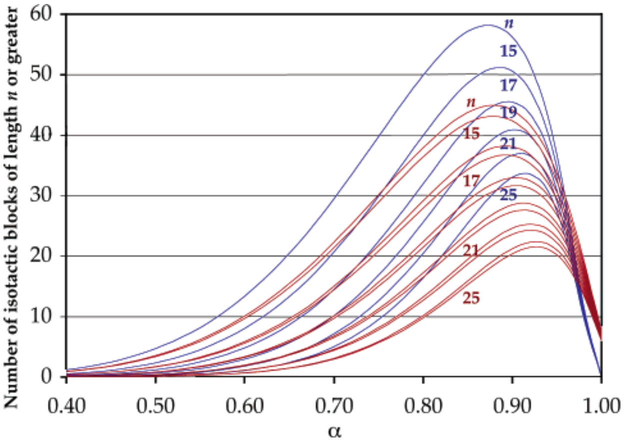


Figure 17. Isotactic block length distribution for varying values of α ($M_n = 100\,000$), which is sensitive to enantiofacial misinertions. Isotactic blocks are notably less abundant for $\epsilon = 0.02$ (red curves) than for $\epsilon = 0.00$ (blue curves).

of length two is formed whenever $(P_{\uparrow\uparrow\downarrow})$ is followed by $(P_{\downarrow\downarrow\uparrow})$ (see the Supporting Information for full details). These short blocks, however, are discounted in the analysis below, which considers longer isotactic blocks that are more likely to impact the polymeric properties.

Figure 16 reveals the effect that stereoerrors have on the number of isotactic blocks present in a hemiisotactic polymer with $\alpha = 0.6$ and $M_n = 100\,000$. Enantiofacial misinsertions (Figure 16, ϵ, blue curves) tend to diminish the number of isotactic blocks that exceed a given length. For example, an ϵ value of 0.02 will reduce the number of isotactic blocks of length 21 or greater from 2.87 to 1.84 blocks per chain. It is not surprising that enantiofacial misinsertions should attenuate the isotactic block length distribution since each enantiofacial misinsertion introduces an additional point of isotactic block initiation and termination. For varying values of α, enantiofacial misinsertions will have the effect illustrated in Figure 17. The notable difference between the blue ($\epsilon = 0.00$) and the red ($\epsilon = 0.02$) curves emphasizes the shorter distribution of isotactic blocks expected when enantiofacial misinsertions occur. The ϵ values previously reported for a series of 13 hemiisoselective catalysts were 0.014, 0.019, 0.031, 0.032, 0.015, 0.000, 0.013, 0.010, 0.007, 0.017, 0.002, 0.000, and 0.003 (liquid monomer, 0 °C).[9a] Thus, for most of these catalysts, enantiofacial misinsertions should be accounted for to obtain a more accurate isotactic block length distribution.

In contrast, site epimerization tends to augment the number of isotactic blocks that exceed a given length (Figure 16, δ, red curves). The increase is typically small; for example, a δ value of 0.05 will increase the number of isotactic blocks of length 21 or greater from 2.87 to 2.97 blocks per chain. Such lengthening is predicted since a site epimerization all but eliminates the possibility of isotactic block termination because insertion at the less stereoselective site is avoided. The lengthening is modest because site epimerization neither terminates nor elongates an isotactic block. For varying values of α, site epimerizations will have the effect illustrated in Figure 18. The parity between the blue ($\delta = 0.00$) and the red ($\delta = 0.05$) curves reveals the small effect that site epimerization has on the isotactic block length distribution. It is concluded that

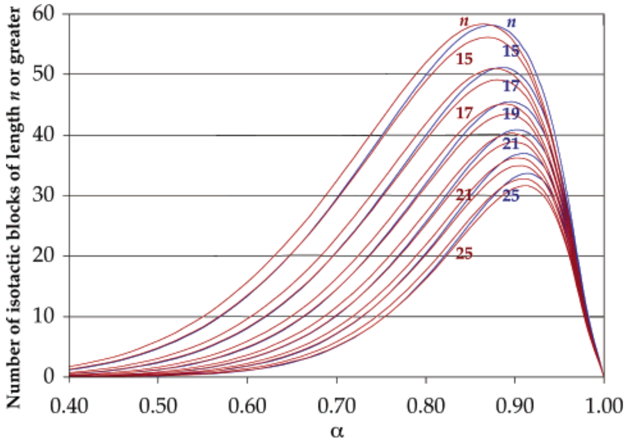


Figure 18. Isotactic block length distribution for varying values of α ($M_n = 100\,000$), which is largely insensitive to site epimerizations. Isotactic blocks are slightly less abundant for $\delta = 0.05$ (red curves) than for $\delta = 0.00$ (blue curves).

the site epimerization stereoerror has a comparatively minimal effect and, in many cases, accounting for it does not lead to a markedly more reliable isotactic block length distribution.

Conclusions

The isotactic block length distributions for both Bernoullian and hemiisotactic statistical polymerization models were derived. The resulting equations rely on only two independent variables: a stereochemical parameter and the number-average molecular weight. Although these equations can generally be applied to polymers of any α-olefin, herein they were utilized to compare and contrast elastomeric polypropylenes having either the Bernoullian or hemiisotactic tacticity.

It was evident that the elastomeric morphology—isotactic stereoblocks distributed among longer amorphous blocks—was possible with hemiisotactic polypropylene over a wider range of stereochemical values. For example, polypropylene with $M_n = 100\,000$ is calculated to have an elastomeric morphology for $\sigma = 0.752$ to 0.827 (Bernoullian) and for $\alpha = 0.575$ to 0.693 (hemiisotactic). The lower limit is the condition in which at least two crystallizable isotactic segments ($n \geq 21$) are present for cross-linking in an otherwise amorphous medium. The upper limit is the condition in which the polymeric properties are dominated by an abundance of crystallizable segments and the calculated percent crystallinity exceeds 10%.

The elastomeric properties of a series of hemiisotactic polypropylenes with $\alpha \approx 0.6$ were rationalized by the cocrystallization that presumably occurs among isotactic stereoblocks statistically present in a hemiisotactic microstructure (isotactic—hemiisotactic polypropylene). In contrast, it is concluded that the elasticity of most Bernoullian polymers (i.e., atactic with σ near 0.5) relies on chain entanglements rather than crystallization phenomena since the calculated distributions do not predict a sufficient number and arrangement of crystallizable isotactic blocks. In fact, purely atactic polypropylene ($\sigma = 0.5$) requires a molecular weight of 177 000 000 to obtain an average of two isotactic blocks per polymer chain. However, the calculations suggest that research directed toward Bernoullian polypropylenes with $\sigma \approx 0.79 \pm 0.04$ should reveal elastomeric morphologies very similar to those observed in isotactic—hemiisotactic polypropylenes with $\alpha \approx 0.64 \pm 0.06$.

Finally, the hemiisotactic model was elaborated to account for the two key stereoerrors committed by hemiisoselective metallocene catalysts. The effects of enantiofacial misinsertion and site epimerization on the isotactic block length distribution were quantified by including two additional independent parameters. Enantiofacial misinsertions noticeably attenuate the isotactic block length distribution; for a wide range of α values ($\alpha = 0.2-0.8$), the summation of $N_{n\geq 21}$ decreases to about 80%, 64%, or 51% of the original value when enantiofacial misinsertions occur 1%, 2%, or 3% of the time, respectively. In contrast, site epimerizations have a more subdued effect; for $\alpha = 0.6$, the summation of $N_{n\geq 21}$ deviates by no more than 6% as the likelihood of site epimerization increases from 0% to 16%.

Acknowledgment. This research is supported by grants from The Robert A. Welch Foundation (No. A-1537) and the Texas Advanced Technology Program (No. 010366-0196-2003). Dr. Andreas Ernst of BP Amoco is thanked for providing the gel permeation chromatography data.

Supporting Information Available: Text giving computational details and a description of the separate Excel spreadsheets employed for the generation of tabular and graphical data and the Excel spreadsheets themselves. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Fried, J. R. *Polymer Science and Technology*; Prentice Hall PTR: Englewood Cliffs, NJ, 1995; pp 314−327.

(2) (a) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223−1252. (b) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1345.

(3) (a) Bravakis, A. M.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000−1009. (b) Gauthier, W. J.; Collins, S. *Maromol. Symp.* **1995**, *98*, 223−231. (c) Gauthier, W. J.; Collins, S. *Macromolecules* **1995**, *28*, 3779−3786. (d) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, Y. G.; Winter, H. H.; Atwood, J. L.; Bott, S. G. *J. Polym. Sci., A: Polym. Chem.* **1992**, *30*, 2601−2617. (e) Llinas, G. H.; Dong, S. H.; Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1242−1253. (f) Chien, J. C. W.; Rausch, M. D. U.S. Patent 5,756,614, 1998.

(4) (a) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217−219. (b) Waymouth, R. M.; Coates, G. W.; Hauptman, E. M. U.S. Patent 5,594,080, 1997. (c) Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174−11182. (d) Carlson, E. D.; Krejchi, M. T.; Shah, C. D.; Terakawa, T.; Waymouth, R. M.; Fuller, G. G. *Macromolecules* **1998**, *31*, 5343−5351. (e) Kravchenko, R.; Masood, A.; Waymouth, R. M.; Myers, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 2039−2046. (f) Busico, V.; Cipullo, R.; Kretschmer, W. P.; Talarico, G. Vacatello, M.; Van Axel Castelli, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 505−508.

(5) (a) Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998−1005. (b) Ewart, S. W.; Sarsfield, M. J.; Jeremic, D.; Tremblay, T. L.; Williams, E. F.; Baird, M. C. *Organometallics* **1998**, *17*, 1502−1510. (c) Kimura, K.; Takaishi, K.; Matsukawa, T.; Yoshimura, T.; Yamazaki, H. *Chem. Lett.* **1998**, *7*, 571−572. (d) Xie, B. H.; Wu, Q.; Lin, S. G. *Acta Polym. Sinica* **1999** *1*, 15−19. (e) Xie, B. H.; Wu, Q.; Lin, S. G. *Macromol. Rapid Commun.* **1999**, *20*, 167−169.

(6) Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D.; Wedler, W.; Winter, H. H. *Macromolecules* **1997**, *30*, 3447−3458.

(7) (a) Ostoja Starzewski, K. A.; Kelly, W. M.; Stumpf, A.; Freitag, D. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2439−2443. (b) Ostoja Starzewski, K. A.; Kelly, W. M.; Stumpf, A. (Bayer AG), WO-A 98/01487, 1998. (c) Ostoja Starzewski, K. A.; Kelly, W. M.; Stumpf, A. (Bayer AG), WO-A 98/01486, 1998.

(8) (a) Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskelä, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348−4355. (b) Kukral, J.; Lehmus, P.; Feifel, T.; Troll, C.; Rieger, B.

Organometallics **2000**, *19*, 3767−3775. (c) Rieger, B.; Troll, C.; Preuschen, J. *Macromolecules* **2002**, *35*, 5742−5743.

(9) (a) Miller, S. A. Ph.D. Thesis, California Institute of Technology, 2000; Chapters 4 and 5. (b) Miller, S. A.; Bercaw, J. E. *Organometallics* **2002**, *21*, 934−945. (c) Miller, S. A.; Bercaw, J. E. U.S. Patent 6,469,188, 2002. (d) Miller, S. A.; Bercaw, J. E. U.S. Patent 6,693,153, 2004.

(10) Farina, M. *Top. Stereochem.* **1987**, *17*, 1−111.

(11) The first examples if hemiisotactic polypropylene were prepared by the nonstereoselective hydrogenation of isotactic *trans*-1,4-poly(2-methylpentadiene). (a) Farina, M.; Di Silvestro, G.; Sozzani, P. *Macromolecules* **1982**, *15*, 1451−1452. (b) Farina, M.; Di Silvestro, G.; Sozzani, P.; Savaré, B. *Macromolecules* **1985**, *18*, 923−928. (c) Di Silvestro, G.; Sozzani, P.; Savaré, B.; Farina, M. *Macromolecules* **1985**, *18*, 928−932.

(12) Hemiisotactic polypropylene can be synthesized by the polymerization of propylene with well-defined organometallic catalysts. (a) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253−295. (b) Ewen, J. A. U.S. Patent 5,036,034, 1991. (c) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1995**, *497*, 105−111. (d) Herfert, N.; Fink, G. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 157−178.

(13) (a) Nele, M.; Mohammed, M.; Xin, S.; Collins, S.; Dias, M. L.; Pinto, J. C. *Macromolecules* **2001**, *34*, 3830−3841. (b) Nele, M.; Collins, S.; Pinto, J. C.; Dias, M.; Lin, S.; Waymouth, R. M. *Macromolecules* **2000**, *33*, 7249−7260. (c) Monaco, G. *Macromolecules* **2001**, *34*, 4406−4415. (d) vanderLeek, Y.; Angermund, K.; Reffke, M. Kleinschmidt, R.; Goretzki, R.; Fink, G. *Chem.*−*Eur. J.* **1997**, *3*, 585−591. (e) Bruce, M. D.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2707−2715.

(14) (a) The concept of *average* sequence length was developed by Randall: Randall, J. C. *J. Polym. Sci., Polym. Phys.* **1976**, *14*, 2083−2094. (b) An *explicit* equation for the block length distribution was derived for a concurrent model employing both enantiomorphic site control and Bernoullian control: Coates, G. W. Ph.D. Thesis, Stanford University, 1994; Chapter 5. The equation provided is: $P_i = Prm^{(n-1)}r = W_{\mathrm{E}}[(\alpha)^n(1-\alpha)^2 + (\alpha)^2(1-\alpha)^n] + W_{\mathrm{B}}[(P_m)^{n-1}(1-P_m)^2]$, which reduces to eq 1 when $W_{\mathrm{B}} = 1$ and $W_{\mathrm{E}} = 0$.

(15) (a) Busico, V.; Cipullo, R.; Corradini, P.; Landriani, L.; Vacatello, M.; Segre, A. L. *Macromolecules* **1995**, *28*, 1887−1892. (b) Busico, V.; Cipullo, R.; Monaco, G.; Vacatello, M. *Macromolecules* **1997**, *30*, 6251−6263.

(16) Collette, J. W.; Ovenall, D. W.; Buck, W. H.; Ferguson, R. C. *Macromolecules* **1989**, *22*, 3858−3866.

(17) Aggarwal, S. L. In *Polymer Handbook*, 2nd ed.; Bandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1975; p V-23.

(18) (a) Madkour, T. M.; Mark, J. E. *Polymer* **1998**, *39*, 6085−6091. (b) Madkour, T. M.; Mark, J. E. *Macromol. Theory Simul.* **1998**, *7*, 69−77. (c) Madkour, T. M.; Mark, J. E. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 2757−2764. (d) Madkour, T. M.; Mark, J. E. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 840−853.

(19) The estimation of 10% arises from the observation that hemiisotactic polymers with $\alpha = 0.630$ (4.45% calculated crystallinity) are elastomeric while hemiisotactic polymers with $\alpha = 0.750$ (19.01% calculated crystallinity) are rigid.[9] Hemiisotactic polymers with intermediate α parameters are currently unknown.

(20) Eisen and co-workers have reported a series of high molecular weight (M_n as high as 129 346) elastomeric polypropylene samples made with nonmetallocene group IV catalysts (methylaluminoxane cocatalyst). (a) Averbuj, C.; Tish, E.; Eisen, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 8640−8646. (b) Kühl, O.; Koch, T.; Somoza, F. B.; Junk, P. C.; Hey-Hawkins, E.; Plat, D.; Eisen, M. S. *J. Organomet. Chem.* **2000**, *604*, 116−125. (c) Shmulinson, M.; Galan-Fereres, M.; Lisovskii, A.; Nelkenbaum, E.; Semiat, R.; Eisen, M. S. *Organometallics* **2000**, *19*, 1208−1210. The sole pentad distribution reported in reference 20c does not conform to Bernoullian statistics and the authors argue that the high *mmmm* pentad content rules out the possibility that the material is simply high-molecular weight (Bernoullian) atactic polypropylene.

(21) (a) Farina, M.; Di Silvestro, G.; Sozzani, P. *Macromolecules* **1993**, *26*, 946−950. (b) Farina, M.; Terragni, A. *Makromol. Chem., Rapid Commun.* **1993** *14*, 791−798. (c) Di Silvestro, G.; Sozzani, P.; Terragni, A. *Macromol. Chem. Phys.* **1996** *197*, 3209−3228. (d) Ewen, J. A.; Elder, M. J. In *Ziegler Catalysts, Recent Scientific Innovations and Technological Improvements*; Fink, G., Mülhaupt, R., Brintzinger, H.-H., Eds.; Springer: Berlin, 1995; pp 99−109. (e) Razavi, A.; Vereecke, D.; Peters, L.; Den Dauw, K.; Nafpliotis, L.; Atwood, J. L. In *Ziegler Catalysts, Recent Scientific Innovations and Technological Improvements*; Fink, G., Mülhaupt, R., Brintzinger, H.-H., Eds.; Springer: Berlin, 1995; pp 111−147.

(22) For $\alpha = 0.5$, a 1% error in the calculated number of monomers is found when the probability of site epimerization (P_m) exceeds 0.135. That is, unimolecular site epimerization must compete with bimolecular propagation 13.5% of the time to effect a 1% error in the statistical model which excludes terms containing $(P_m)^x$ with $x \geq 4$. Recent work by S. A. Miller, J. E. Bercaw, and J. A. Ewen suggest that in liquid monomer, site epimerization occurs less than 2% of the time *even with* C_1*-symmetric, isoselective catalysts bearing large steric substituents such as* $Me_2C(3\text{-}t\text{-}BuC_5H_3)(C_{13}H_8)ZrCl_2/MAO$. See: (a) Miller, S. A. Ph.D. Thesis, Chapter 6, California Institute of Technology, 2000. (b) Ewen, J. A.; Jones, R. L.; Elder, M. J. In *Metalorganic Catalysts for Synthesis and Polymerization: Recent Results by Ziegler*−*Natta and Metallocene Investigations*; Kaminsky, W., Ed.; Springer-Verlag: Berlin, 1999; pp 150−169.

(23) Equation 9 (odd x): The mathematical form for the sequence 1, 4, 10, 20, 35, ... is $(n)(n+1)(n+2)/6$, where n is the nth term (sequence no. A000292). Here, $n = ((x-1)/2)$. Equation 10 (even x): The mathematical form for the sequence 1, 3, 6, 10, 15, ... is $n(n+1)/2$, where n is the nth term (sequence no. A000217). Here, $n = x/2$. The mathematical forms of the sequences were obtained from: Sloane, N. J. A., Ed. *The On-Line Encyclopedia of Integer Sequences* 2003, http://www.research.att.com/~njas/sequences/.

MA035206+