Modeling Asymmetric and Symmetric Chains and the Structures of Stereo-Defects in Isotactic Polypropylenes

J. C. Randall

Baytown Polymers Center, Exxon Chemical Company, 5200 Bayway Drive, P.O. Box 5200, Baytown, Texas 77522-5200

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ABSTRACT: The microstructures of highly isotactic polypropylenes, prepared with magnesium chloride supported Ziegler−Natta catalyst systems, have been determined experimentally through ^{13}C NMR measurements and also predicted through Markovian statistical models. Polypropylene molecules are seldom 100% isotactic but possess long isotactic sequences interrupted by stereo- and regio-irregularities called chain defects that ultimately define the crystallinity of the polypropylene. The structures and numbers per 10 000 repeat units of the various interrupting stereo-irregularities, termed "stereo-defects", are determined in this study. It is shown that different families of stereo-defects in highly isotactic polypropylenes can be associated independently with symmetric and asymmetric chains. The single-parameter-zero order Markovian statistical approach typically utilized in the Doi two-state asymmetric and symmetric chain statistical models for characterizing polypropylene sequence distributions has been extended to first-order Markov for symmetric chains. First-order Markovian statistics for asymmetric chains naturally reduce to zero order for the isotactic polypropylenes examined in this study, whereas the symmetric chain components do not. Syndiotactic blocks of steadily increasing sequence lengths are predicted by first-order Markovian statistics for highly isotactic symmetric chains possessing a *meso* diad content of 0.99. The average sequence lengths of these syndiotactic blocks are predicted to become shorter as the polypropylenes become more isotactic. Finally, it was observed that the sequence distributions favored asymmetric chains with the addition of increasing amounts of an electron donor to the supported Ziegler−Natta catalyst system.

Introduction

It has long been recognized that heterogeneous titanium-based Ziegler−Natta catalysts are multisited.[1] Structurally unique polypropylene molecules are not produced during classical titanium-based Ziegler−Natta polymerizations; instead polypropylene molecules that differ in levels of stereo- and regio-irregularities and subsequently in crystallinities are produced simultaneously. The clearest example of this type of catalytic behavior is the presence of amorphous, so-called atactic, polypropylenes as a component within bulk, highly isotactic polypropylenes. The crystalline polypropylenes, which accompany the amorphous molecules, vary in levels of crystallinity and structure[1−3] and exhibit peak melting points and breadths of curves that reflect the level and distribution of stereo- and regio-irregularities.[3] It is the purpose of this study to identify as completely as possible the structures and generic types of stereo-defects that occur in crystalline polypropylenes. Toward this end, a series of polypropylenes with crystallizable components ranging from 60 to over 99% by weight was examined.

The presence of a polypropylene repeat unit with a configuration opposite to that of its immediate neighbors represents a stereo-defect in an otherwise identically recurring repeat unit structure. Highly isotactic polypropylenes have long runs of isotactic sequences with few stereo- or regio-irregularities. The resulting ^{13}C NMR pentad/heptad spectra are relatively free of interferences from resonances arising from sequences that connect closely spaced stereo-defects. Such circumstances improve the confidence of stereo-defect structural identifications. It has been reported previously that low to moderately isotactic polypropylenes contain syndiotactic blocks,[3] which are shown in this study to occur even in highly isotactic polypropylenes with a *meso* diad content of 0.99.

From a stereoregularity viewpoint, isotactic polypropylenes can be viewed as having either or both of two types of sequences:[4] asymmetric chains, where one configuration is dominant, and symmetric chains, where the two types of configurations have equal populations. Asymmetric chains are often referred to as "enantiomorphic-site control",[5] and symmetric chains are often called "chain-end", Bernoullian, or the Bovey model.[6,7] From a statistical standpoint, both symmetric and asymmetric chain sequence distributions have been treated successfully as zero-order Markov, which is often referred to as Bernoullian, with a single parameter describing the transition between Markovian states. In terms of the Price 0,1 nomenclature[4] symmetric chains require that $P_{00} = P_{11} = P_m$ and $P_{01} = P_{10} = P_r$, which is a special case of first-order asymmetric chain statistics.[8] An important objective of this study was to determine if various families of stereo-defects can be associated independently with either symmetric or asymmetric chains, which imply different modes of catalyst control.

Over 25 years ago, Price[4] noted, "Markovian mathematics does not necessarily demand particular reaction schemes for the production of the polymer. The mathematics is only a framework within which it is possible to describe polymer chains having particular sequential characteristics, regardless of how these chains, were produced." In studies of polypropylene structures produced by different types is catalyst systems, it should be noted whether symmetric chains, asymmetric chains or a mixture of the two types are produced. Isotactic polypropylenes, produced with classical Ziegler−Natta catalysts, offer examples where both symmetric and asymmetric chains can be produced simultaneously by the catalyst sites. Consequently, the sequences distributions are treated statistically as a combination of different levels of tacticity requiring at least two dif-

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Table 1. Experimental Variables and Characterization of Isotactic Polypropylenes Made with a Fourth Generation Supported Ziegler−Natta Catalyst

sample	amt of DCPMS (mmol)	H_2 pressure (psig)	catalyst efficiency (kg/g)	% cold xylene solubles	% cold xylene insolubles	[*meso*] insoluble fraction	T_m (°C)	ΔH (J/g)
PP-A	0.0	4	12.9	33.08	66.94	0.908	155.2	53.3
PP-B	0.0	80	22.7	27.93	72.12	0.941	159.2	65.1
PP-C	0.006	80	38.5	1.85	98.01	0.980	163.5	88.8
PP-D	0.050	80	38.2	0.99	98.94	0.990	164.4	105.0
PP-E	0.400	80	40.0	0.67	99.37	0.991	166.8	105.9
PP-F	1.000	80	41.6	0.56	99.46	0.991	166.3	105.0

ferent statistical models. Doi[9] and Hayashi et al.[10] used two-state, zero-order Markovian statistical models for both symmetric and asymmetric chains to mimic the distribution of polypropylene stereochemical structures obtained during Ziegler−Natta polymerizations. Coleman and Fox[11] used a two-state model to take into account reversible switches between different levels of catalyst behavior. Cheng[12] has discussed the various possible combinations of two-state models that can be used to simulate observed polypropylene sequence distributions. In a study analogous to this investigation, Chûjô et al.[13] used a two-state model to fit sequence distribution data from a series of polypropylenes created with different electron donors and suggested that some catalyst sites could fluctuate between producing asymmetric and symmetric chains. Recently, Busico et al.[14] introduced new parameters into a zero-order Markovian two-state model to account for syndiotactic blocks in highly isotactic polypropylenes. In the present study, it is shown that a two-state model using first-order Markovian symmetric chain statistics in place of zero-order Markovian symmetric chain statistics will lead to a prediction of short syndiotactic blocks in highly isotactic polypropylenes.

The crystallizable components from a highly isotactic polypropylene will generally have an isotactic pentad fraction [*mmmm*] of at least 0.97 and a *meso* diad content of at least 0.99. The zero-order Markovian symmetric and asymmetric chain statistical models, used successfully by Doi,[9] Bovey,[7] and Shelden et al.,[5] and others on polypropylenes with lower isotactic diad levels, should be re-examined where [*mmmm*] is >0.975 to show how the sequence distributions will respond to changing the Markovian order in the Doi two-state model. The Doi zero-order Markovian two-state model predicts large differences between the contents of asymmetric versus symmetric sequence distributions for highly isotactic polypropylenes.[13,14] The asymmetric chain transition probability, P_0 (called σ by Doi), is greater than 0.99 for asymmetric chains, while P_r is around 0.6 for symmetric chains. This leads to 99+% asymmetric chains (termed ω by Doi) in the final distribution. The results for the two-state model in this study are very close to those reported by Chûjô et al.[13] and Busico et al.[14] for corresponding highly isotactic polypropylenes.

Experimental Section

A series of polypropylenes, labeled PP-A through PP-F, were produced from the same fourth generation magnesium chloride supported Ziegler−Natta catalyst system, but with different amounts of an external electron donor, which led to polypropylenes with different levels of stereo-chemical irregularities. The donor was dicyclopentyldimethoxysilane, (DCPMS), which is known to produce highly isotactic polypropylenes.[15] The DCPMS concentrations were varied from zero to 1.00 mmol. Two different hydrogen levels were employed at the zero donor level for PP-A and PP-B because hydrogen was observed to affect the stereoregularity as shown in Table 1 and discussed in ref 15. Subsequent ^{13}C NMR spectra of PP-A through PP-F, which were made with different DCPMS levels, contained no detectable resonances from regio-irregularities. Consequently, the study could be restricted to a characterization of stereo-irregularities, detected at levels of ~0.0001 mole fraction and higher. It was necessary to remove amorphous polypropylenes from each of the samples so that it could be assured that the measured stereo-defects were from within crystalline polypropylene chains. This was accomplished by dissolving the samples in xylene at elevated temperatures and subsequently allowing the solutions to cool gradually to room temperature. The isotactic polymers crystallize, while the amorphous polymers remain in solution. A quantitative separation of amorphous polymers was accomplished by filtration. The crystalline polypropylene fractions are termed "cold xylene insolubles", and the amorphous fractions, "cold xylene solubles". The cold xylene insolubles fractions and the cold xylene solubles fractions, when sufficient amounts were available, were examined by ^{13}C NMR. Table 1 contains the xylene solubility information and DSC results, as well as DCPMS levels and other experimental variables associated with polymerization.

Carbon-13 NMR data were obtained at 100 MHz at 125 °C on a Varian VXR 400 NMR spectrometer. A 90° pulse, an acquisition time of 3.0 s, and a pulse delay of 20 s were employed. The spectra were broad band decoupled and were acquired without gated decoupling. Similar relaxation times and nuclear Overhauser effects are expected for the methyl resonances of polypropylene,[16] which were the only resonances used for quantitative purposes. A typical number of transients collected was 2500. Spectral integrations were obtained with scale settings between 5000 and 1 000 000, depending upon the strength of the signal being measured. At completion, all resonance areas were converted to a common scale factor. The samples were dissolved in tetrachloroethane-d_2 at concentrations between 10 and 15% by weight. Spectral frequencies were recorded with respect to 21.81 ppm for *mmmm*, which had been determined with respect to an internal tetramethylsilane standard and is close to the reported literature value of 21.855 ppm.[10] The pentad/heptad assignments used in this study are well established.[10,17,18]

Experimental pentad/heptad distributions for PP-A through PP-F, obtained from ^{13}C NMR methyl resonances observed from the cold xylene insoluble fractions, are given in Table 2. The corresponding data from amorphous fractions from PP-A, PP-B, and PP-C are also included in Table 2. Polypropylenes PP-D through PP-F had insufficient levels of amorphous polymers for ^{13}C NMR characterization. Particular care was given to the location of end group resonances that overlap with *mrmm* + *rmrr* (a broad resonance centered near 20.82 ppm) and the *mrrrmm* + *rmrrrr* resonance located near 20.14 ppm. Side chain methyl resonances from the *n*-propyl (20.82 ppm) and *n*-butyl (20.86 ppm) end groups overlap with *mrmm* + *rmrr*. The methylene resonance (20.14 ppm) from the 2-carbon of the *n*-propyl end group overlaps with *mrrrmm* + *rmrrrr*. The melt flow rates for this series of polypropylenes are consistently ≤1, which leads to the advantage that the end group resonances are hardly perceptible. At higher melt flow rates, end group corrections to the pentad/heptad intensities become necessary. Calculated pentad/heptad distributions are included in Table 2 to allow direct comparisons of calculated versus experimental distributions. Four significant figures were retained for the data in Table 2 to reflect the detection limits of the various pentads/heptads.

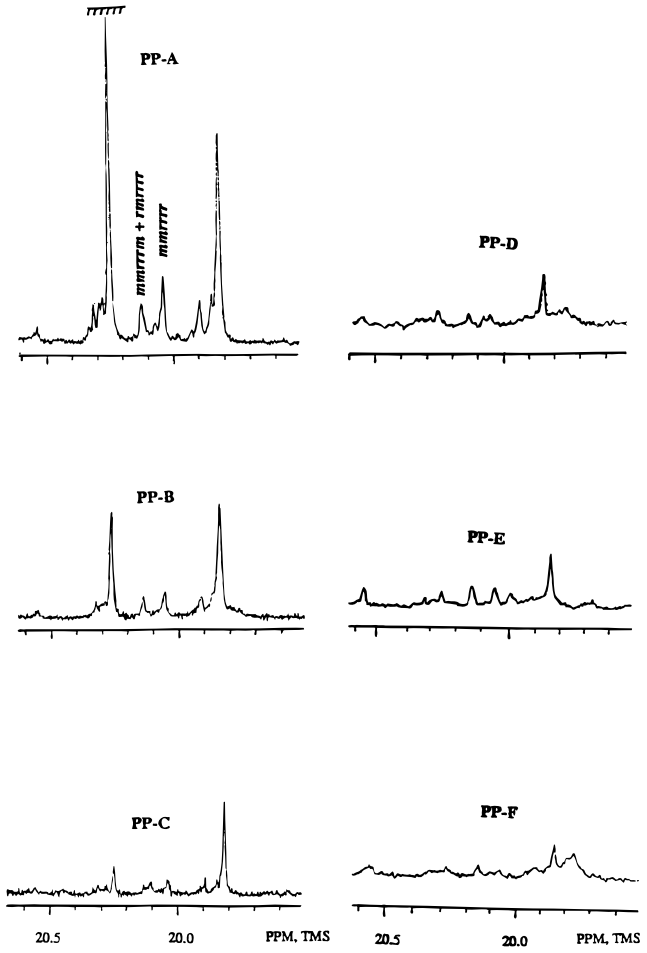

Figure 1. Syndiotactic-centered pentad/heptad regions from the ^{13}C NMR spectra at 100 MHz of polypropylene samples PP-A through PP-F.

The "solver routine" of Excel-4[19] was used to minimize standard deviations between Markovian and observed pentad/heptad sequence distributions. Limits of 0 and 1 were selected for each of the conditional transition probabilities and the fraction of asymmetric chains. All parameters were allowed to vary simultaneously between 0 and 1 using the solver routine, which located a minimum between calculated and observed results. The solver routine is particularly well suited for calculations of this type because it is easy to switch from zero- to first-order Markovian models when testing the behavior of the observed sequence distributions. Care must be taken to identify the optimum minimum between calculated and observed results because more than one minimum is typically found by the solver routine for any particular pentad/heptad distribution.

Characterization of Symmetric and Asymmetric Chains

In Table 2, the isotactic pentad fraction, *mmmm*, varies steadily from 0.822 to 0.982 for the crystalline fractions of PP-A through PP-F. The highest *meso* diad content, observed for PP-F, is 0.991. The pentad/heptad distributions contain sequences with consecutive *racemic* diads at the highest level of stereoregularity. Figure 1 shows the important *rrrr*-centered heptad resonances and the *mrrr*-centered heptad resonances and the progressive decreasing intensities with increasing *meso* content. In this series of polypropylenes, resonances are observed independently for *racemic* diad sequences of lengths three through six, as evidenced by the heptad resonances *mrrrmm*, *mrrrrm*, *mrrrrr*, and *rrrrrr*, as shown in Figure 1 for samples PP-A through PP-F. Of the three possible *mrrr*-centered heptad resonances,[18] only two are observed, *mrrrmm* + *rmrrrr* and *mmrrrr*. The decreasing intensity of the *rrrr*-centered and *mrrr*-centered heptad resonances, as the *meso* diad content increases, can be seen in Figure 1. It is clear that syndiotactic types of chain defects are still present in the highly isotactic PP-F because *racemic*-centered heptad and other pentad resonances are observed in addition to the expected 2:2:1 ratio for *mmmr:mmrr:mrrm* for a single, inverted configuration. The latter was the only chain defect observed by Paukkeri et al.[20] for a comparable isotactic polypropylene fraction with a content [*mmmm*] similar to that of PP-F but obtained from an overall lesser isotactic polypropylene. Paukkeri et al.[3] also reported syndiotactic blocks in crystalline polypropylenes at moderate isotactic levels, but again were unable to detect syndiotactic sequences in polypropylene fractions of exceptional isotacticity. The syndiotactic heptad resonance, *rrrrrr*, has also been reported by Busico et al.[14,18] in the spectra of other highly crystalline polypropylenes. The presence of syndiotactic blocks within long isotactic sequences has been explained by catalyst sites reversibly switching from "isotactoid" to "syndiotactoid" sequences in times less than the growth times of the polymer molecules.[14,18,20] This study shows that short syndiotactic blocks connecting longer isotactic blocks can be accurately predicted by employing first-order Markovian statistics to describe the sequence distributions. Because of the presence of syndiotactic sequences of at least three to seven units in length even in a polypropylene with a *meso* diad content >0.99, the sequence distributions from which stereo-defects arise and the existence of other possible stereo-defects in highly isotactic polypropylenes should be probed. One advantage in examining highly isotactic polypropylenes is that chain defects are well-spaced, which facilitates identification. A second advantage is that Markovian statistical models, which are used to identify symmetric versus asymmetric chain sequence distributions,[4] can be better tested for either zero or first-order behavior with respect to the number and types of predicted stereo-defects.

There have been precedents for examining higher order Markovian statistical models for polypropylene. Second-order Markovian statistics for symmetric chains have been suggested previously by Collette et al.[21] but were applied to whole polymers and ether soluble fractions with little success. Later, Chûjô applied first-order Markovian statistics to asymmetric chains for propylene polymers made with supported fourth generation Ziegler−Natta catalysts to show a preference for "00" over "11" diads with the addition of electron donors[22] (for 0,1 nomenclature, see Price[4,23]). One of the advantages of utilizing higher order Markovian statistics is that the systems will naturally reduce to lower orders if that should be the case, that is, $P_{01} = P_{11} = P_1$ and $P_{00} = P_{10} = P_0$. Secondly, first-order statistics for asymmetric chains will reduce to zero-order statistics for symmetric chains when $P_{00} = P_{11} = P_m$ and $P_{01} = P_{10} = P_r$. Consequently, first-order Markovian statistics were tested in the Doi two-state model to see if improvements could be obtained in predicting the sequence distributions observed in highly isotactic polypropylenes. First-order Markovian statistical descriptions have been given previously,[4,23] but it may be useful to review briefly the transition state definitions for both

Table 2. Experimental vs Two-State Markovian Model Results[a]

	A					B				
	Doi-0/0	Doi-1/1	Doi-0/1	I-1/1	obsd	Doi-0/0	Doi-1/1	Doi-0/1	I-1/1	obsd
mmmm	0.8220	0.8216	0.8216	0.8244	0.8215	0.8765	0.8763	0.8763	0.8784	0.8759
mmmr	0.0515	0.0521	0.0509	0.0578	0.0524	0.0389	0.0390	0.0387	0.0435	0.0393
rmmr	0.0012	0.0020	0.0022	0.0013	0.0019	0.0008	0.0013	0.0013	0.0007	0.0029
mmrr	0.0522	0.0521	0.0528	0.0467	0.0519	0.0395	0.0394	0.0398	0.0368	0.0382
mmrm + *rmrr*	0.0098	0.0086	0.0080	0.0155	0.0085	0.0058	0.0052	0.0050	0.0091	0.0045
rmrm	0.0024	0.0031	0.0021	0.0042	0.0019	0.0015	0.0018	0.0013	0.0035	0.0009
mrrrrm	0.0011	0.0011	0.0012	0.0020	0.0028	0.0007	0.0007	0.0007	0.0009	0.0018
mrrrrr	0.0051	0.0063	0.0066	0.0074	0.0045	0.0029	0.0035	0.0037	0.0025	0.0018
rrrrrr	0.0205	0.0202	0.0201	0.0085	0.0202	0.0088	0.0086	0.0085	0.0024	0.0084
rmrrrm	0.0007	0.0005	0.0006	0.0003	0.0000	0.0005	0.0004	0.0004	0.0001	0.0000
mmrrrm + *rrrrmr*	0.0052	0.0035	0.0040	0.0055	0.0047	0.0030	0.0022	0.0024	0.0025	0.0025
mmrrrr	0.0021	0.0057	0.0057	0.0103	0.0052	0.0013	0.0032	0.0033	0.0037	0.0031
rmrrmr	0.0003	0.0001	0.0001	0.0000	0.0012	0.0003	0.0001	0.0001	0.0000	0.0009
mmrrmr	0.0016	0.0016	0.0016	0.0011	0.0038	0.0009	0.0010	0.0010	0.0008	0.0028
mmrrmm	0.0242	0.0220	0.0224	0.0150	0.0197	0.0186	0.0174	0.0174	0.0150	0.0169
% asym	95.9	93.5	94.3	46.4		97.8	96.9	96.8	70.1	
std dev	0.0017	0.0012	0.0013	0.0048		0.0013	0.0010	0.0010	0.0028	

	C					D				
	Doi-0/0	Doi-1/1	Doi-0/1	I-1/1	obsd	Doi-0/0	Doi-1/1	Doi-0/1	I-1/1	obsd
mmmm	0.9581	0.9580	0.9580	0.9591	0.9579	0.9776	0.9776	0.9776	0.9781	0.9775
mmmr	0.0130	0.0130	0.0130	0.0152	0.0119	0.0066	0.0069	0.0069	0.0081	0.0069
rmmr	0.0005	0.0006	0.0006	0.0001	0.0011	0.0006	0.0005	0.0005	0.0001	0.0010
mmrr	0.0135	0.0136	0.0135	0.0129	0.0145	0.0067	0.0065	0.0065	0.0058	0.0064
mmrm + *rmrr*	0.0026	0.0024	0.0024	0.0027	0.0019	0.0022	0.0023	0.0022	0.0025	0.0021
rmrm	0.0010	0.0007	0.0007	0.0012	0.0007	0.0011	0.0006	0.0006	0.0009	0.0005
mrrrrm	0.0003	0.0003	0.0003	0.0002	0.0007	0.0002	0.0002	0.0002	0.0001	0.0003
mrrrrr	0.0010	0.0012	0.0012	0.0006	0.0005	0.0003	0.0005	0.0005	0.0005	0.0004
rrrrrr	0.0012	0.0014	0.0015	0.0006	0.0014	0.0002	0.0004	0.0004	0.0004	0.0004
rmrrrm	0.0004	0.0003	0.0003	0.0000	0.0000	0.0003	0.0002	0.0002	0.0000	0.0000
mmrrrm + *rrrrmr*	0.0012	0.0012	0.0012	0.0006	0.0012	0.0006	0.0008	0.0007	0.0005	0.0005
mmrrrr	0.0005	0.0009	0.0009	0.0010	0.0011	0.0003	0.0006	0.0006	0.0007	0.0006
rmrrmr	0.0002	0.0001	0.0001	0.0000	0.0001	0.0001	0.0001	0.0001	0.0000	0.0002
mmrrmr	0.0003	0.0003	0.0003	0.0001	0.0011	0.0003	0.0003	0.0003	0.0000	0.0006
mmrrmm	0.0063	0.0060	0.0060	0.0056	0.0058	0.0029	0.0026	0.0026	0.0023	0.0024
% asym	99.0	98.8	98.8	76.2		99.1	98.7	98.7	61.9	
std dev	0.0006	0.0006	0.0005	0.0012		0.0003	0.0002	0.0002	0.0005	

	E					F				
	Doi-0/0	Doi-1/1	Doi-0/1	I-1/1	obsd	Doi-0/0	Doi-1/1	Doi-0/1	I-1/1	obsd
mmmm	0.9809	0.9809	0.9809	0.9814	0.9809	0.9820	0.9820	0.9820	0.9826	0.9819
mmmr	0.0054	0.0056	0.0056	0.0069	0.0055	0.0045	0.0047	0.0047	0.0063	0.0046
rmmr	0.0005	0.0005	0.0005	0.0001	0.0004	0.0006	0.0006	0.0006	0.0001	0.0010
mmrr	0.0056	0.0055	0.0055	0.0050	0.0056	0.0047	0.0046	0.0046	0.0041	0.0043
mmrm + *rmrr*	0.0019	0.0020	0.0020	0.0021	0.0019	0.0024	0.0025	0.0025	0.0024	0.0023
rmrm	0.0009	0.0007	0.0007	0.0008	0.0006	0.0012	0.0009	0.0009	0.0007	0.0007
mrrrrm	0.0002	0.0002	0.0002	0.0001	0.0002	0.0002	0.0002	0.0002	0.0001	0.0003
mrrrrr	0.0004	0.0005	0.0005	0.0004	0.0003	0.0004	0.0005	0.0005	0.0005	0.0003
rrrrrr	0.0003	0.0003	0.0003	0.0003	0.0004	0.0002	0.0003	0.0003	0.0004	0.0005
rmrrrm	0.0003	0.0002	0.0002	0.0000	0.0000	0.0003	0.0003	0.0003	0.0000	0.0000
mmrrrm + *rrrrmr*	0.0006	0.0007	0.0007	0.0003	0.0006	0.0007	0.0008	0.0008	0.0004	0.0005
mmrrrr	0.0003	0.0005	0.0005	0.0006	0.0006	0.0004	0.0005	0.0005	0.0007	0.0005
rmrrmr	0.0001	0.0001	0.0001	0.0000	0.0003	0.0002	0.0001	0.0001	0.0000	0.0003
mmrrmr	0.0002	0.0002	0.0002	0.0000	0.0006	0.0003	0.0003	0.0003	0.0000	0.0009
mmrrmm	0.0024	0.0022	0.0022	0.0020	0.0022	0.0019	0.0017	0.0017	0.0015	0.0019
% asym	99.2	99.0	99.0	65.3		99.0	98.8	98.8	51.9	
std dev	0.0002	0.0001	0.0001	0.0005		0.0003	0.0003	0.0003	0.0006	

	A-am.					B-am.				
	Doi-0/0	Doi-1/1	Doi-0/1	I-1/1	obsd	Doi-0/0	Doi-1/1	Doi-0/1	I-1/1	obsd
mmmm	0.2006	0.1924	0.1955	0.1515	0.1928	0.2516	0.2439	0.2458	0.2225	0.2449
mmmr	0.1326	0.1341	0.1317	0.1346	0.1176	0.1315	0.1252	0.1312	0.1480	0.1224
rmmr	0.0284	0.0284	0.0305	0.0332	0.0327	0.0238	0.0231	0.0272	0.0265	0.0276
mmrr	0.1350	0.1579	0.1430	0.1658	0.1503	0.1370	0.1516	0.1470	0.1585	0.1537
mmrm + *rmrr*	0.1353	0.1089	0.1236	0.1221	0.1241	0.1225	0.0895	0.1072	0.1012	0.1080
rmrm	0.0568	0.0402	0.0501	0.0466	0.0359	0.0477	0.0245	0.0374	0.0312	0.0264
mrrrrm	0.0132	0.0165	0.0132	0.0203	0.0196	0.0130	0.0140	0.0132	0.0157	0.0180
mrrrrr	0.0320	0.0356	0.0425	0.0370	0.0261	0.0354	0.0463	0.0481	0.0526	0.0408
rrrrrr	0.1177	0.1260	0.1155	0.1127	0.1144	0.0889	0.1273	0.0866	0.0798	0.0864
rmrrrm	0.0121	0.0096	0.0115	0.0124	0.0163	0.0115	0.0076	0.0108	0.0094	0.0108
mmrrrm + *rrrrmr*	0.0422	0.0350	0.0405	0.0357	0.0392	0.0428	0.0389	0.0420	0.0392	0.0384
mmrrrr	0.0265	0.0413	0.0396	0.0517	0.0458	0.0259	0.0413	0.0440	0.0625	0.0456
rmrrmr	0.0061	0.0056	0.0051	0.0081	0.0196	0.0057	0.0039	0.0040	0.0038	0.0120
mmrrmr	0.0245	0.0278	0.0230	0.0323	0.0261	0.0219	0.0213	0.0193	0.0201	0.0324
mmrrmm	0.0369	0.0405	0.0347	0.0360	0.0392	0.0408	0.0416	0.0361	0.0292	0.0324
% asym	80.3	78.1	71.5	20.7		78.3	66.9	61.2	20.0	
std dev	0.0113	0.0089	0.0088	0.0144		0.0112	0.0131	0.0065	0.0113	

Table 2. (Continued)

	C-am.				
	Doi-0/0	Doi-1/1	Doi-0/1	I-1/1	obsd
mmmm	0.1786	0.1563	0.1550	0.1134	0.1486
mmmr	0.1236	0.1336	0.1240	0.1244	0.1121
rmmr	0.0299	0.0346	0.0351	0.0369	0.0378
mmrr	0.1300	0.1682	0.1419	0.1591	0.1389
mmrm + *rmrr*	0.1514	0.1303	0.1418	0.1398	0.1340
rmrm	0.0598	0.0439	0.0532	0.0436	0.0414
mrrrrm	0.0142	0.0205	0.0149	0.0213	0.0219
mrrrrr	0.0434	0.0473	0.0560	0.0648	0.0438
rrrrrr	0.1061	0.0768	0.1046	0.0965	0.1011
rmrrrm	0.0154	0.0137	0.0153	0.0159	0.0183
mmrrrm + *rrrrmr*	0.0541	0.0471	0.0536	0.0571	0.0487
mmrrrr	0.0285	0.0523	0.0469	0.0674	0.0512
rmrrmr	0.0077	0.0076	0.0063	0.0087	0.0195
mmrrmr	0.0238	0.0308	0.0227	0.0273	0.0410
mmrrmm	0.0335	0.0369	0.0288	0.0237	0.0414
% asym	74.5	73.3	60.0	23.3	
std dev	0.0146	0.0128	0.0098	0.0152	

[a] Doi-0: zero-order Markov for both asymmetric and symmetric chains. Doi-1: first-order Markov for both asymmetric and symmetric chains. Doi-0/1: zero-order Markov for asymmetric chain, first-order Markov for symmetric chain. Calcd-1/1: first-order Markov for both symmetric and asymmetric chains, fit independently and then blended.

symmetric and asymmetric chains below:

Symmetric Chains

$00 \xrightarrow{+0} 00$
$11 \xrightarrow{+1} 11$ P_{mm} probability of a *meso* diad following another *meso* diad

$00 \xrightarrow{+1} 01$
$11 \xrightarrow{+0} 10$ P_{mr} probability of a *racemic* diad following another *meso* diad

$01 \xrightarrow{+1} 11$
$10 \xrightarrow{+0} 00$ P_{rm} probability of a *meso* diad following a *racemic* diad

$01 \xrightarrow{+0} 10$
$10 \xrightarrow{+1} 01$ P_{rr} probability of *racemic* diad following another *racemic* diad

where

$$P_{mm} + P_{mr} = 1 \quad (1)$$

$$P_{rm} + P_{rr} = 1 \quad (2)$$

Asymmetric Chains

$\sim 0 \xrightarrow{+0} \sim 0$ P_{00} probability of a "0" configuration following another "0" configuration

$\sim 0 \xrightarrow{+1} \sim 1$ P_{01} probability of a "1" configuration following a "0" configuration

$\sim 1 \xrightarrow{+0} \sim 0$ P_{10} probability of a "0" configuration following a "1" configuration

$\sim 1 \xrightarrow{+1} \sim 1$ P_{11} probability of a "1" configuration following another "1" configuration

where

$$P_{00} + P_{01} = 1 \quad (3)$$

and

$$P_{10} + P_{11} = 1 \quad (4)$$

The Doi two-state zero-order Markovian predictions[9] for both symmetric and asymmetric chains were obtained to determine if the calculated sequence distributions at the high levels of tacticity for PP-C through PP-F ([*m*] = 0.980−0.991) reasonably simulate the observed sequence distributions. At lower levels of isotacticity, two-state zero-order statistical models have been successfully employed to simulate observed sequence distributions in polypropylenes.[5,7,9,18,20] Results, labeled Doi-0/0, are given in Table 2 for PP-A through PP-F. The resulting transition probabilities for Doi-0/0 are given in Table 3. Excellent agreements between calculated and observed pentad/heptad sequence distributions were obtained for the lesser isotactic polypropylenes PP-A and PP-B. The calculated Doi-0/0 sequence distributions for PP-C through PP-F also showed generally good overall agreement with the observed sequence distributions with the exceptions that the predicted syndiotactic sequence fractions were generally less than observed in the highly crystalline fractions, as also noted by Busico, et al.[14]

The next step was to repeat the Doi two-state asymmetric and symmetric chain models with first-order Markovian statistics in place of zero-order Markovian statistics. Once again, good overall agreements between calculated and observed sequence distributions were obtained for the first-order Markovian Doi two-state model, as shown by Doi-1/1 in Table 2. The use of first-order Markovian statistics in the Doi two-state model led to one significant improvement by yielding concentrations for the syndiotactic sequences closer to observed than obtained for Doi-0/0. The use of first-order Markovian statistics led to another important observation as well. As can be seen in Table 3, the conditional transition parameters, P_{00} and P_{10}, are nearly equal in all cases for asymmetric chains, which indicates that the zero-order Markovian statistical approach is better suited for asymmetric chain statistics. The corresponding observation did not hold true for symmetric chain statistics. The conditional transition parameters, P_{mm} and P_{rm}, are sufficiently different to indicate that the symmetric chain statistical model does not reduce from first to zero order. This result led to a Doi two-state model with zero-order Markovian statistics for asymmetric chains and first-order Markovian statistics for symmetric chains, termed Doi-0/1 in Table 2. The

Table 3. Transition Probabilities for Two-State Models for Isotactic Polypropylene for Crystalline Fractions PP-A through PP-F[a]

sample	P_0	P_m	P_{mm}	P_{rm}	P_{00}	P_{10}	% asym chain
PP-A-1 (Doi-0/0)	0.9607	0.1096					95.9
PP-B-1 (Doi-0/0)	0.9783	0.1420					97.8
PP-C-1 (Doi-0/0)	0.9935	0.2964					99.0
PP-D-1 (Doi-0/0)	0.9971	0.4787					99.1
PP-E-1 (Doi-0/0)	0.9976	0.4299					99.2
PP-F-1 (Doi-0/0)	0.9982	0.4604					99.0
PP-A-2 (Doi-1/1)			0.6266	0.1339	0.9719	0.9479	94.4
PP-B-2 (Doi-1/1)			0.6069	0.1679	0.9797	0.9652	96.9
PP-C-2 (Doi-1/1)			0.4877	0.2889	0.9938	1.0	98.8
PP-D-2 (Doi-1/1)			0.6868	0.4216	0.9976	1.0	98.7
PP-E-2 (Doi-1/1)			0.5978	0.4173	0.9979	1.0	99.0
PP-F-2 (Doi-1/1)			0.5826	0.4379	0.9985	1.0	98.8
PP-A-3 (Doi-0/1)	0.9722		0.5806	0.1407			94.3
PP-B-3 (Doi-0/1)	0.9799		0.5887	0.1764			96.8
PP-C-3 (Doi-0/1)	0.9938		0.4927	0.2852			98.8
PP-D-3 (Doi-0/1)	0.9976		0.6868	0.4216			98.7
PP-E-3 (Doi-0/1)	0.9979		0.5976	0.4162			99.0
PP-F-3 (Doi-0/1)	0.9985		0.5826	0.4379			98.8
PP-A-4 (I-1/1)			0.9684	0.3007	0.9637	0.8612	46.4
PP-B-4 (I-1/1)			0.9776	0.3352	0.9751	0.8881	70.1
PP-C-4 (I-1/1)			0.9928	0.3405	0.9919	0.8896	76.2
PP-D-4 (I-1/1)			0.9960	0.3754	0.9958	0.7781	61.9
PP-E-4 (I-1/1)			0.9967	0.3714	0.9965	0.7728	65.3
PP-F-4 (I-1/1)			0.9969	0.3736	0.9968	0.6933	51.9
PP-A-am-1 (D-0/0)	0.7580	0.0892					80.3
PP-B-am-1 (D-0/0)	0.7968	0.1436					78.3
PP-C-am-1 (D-0/0)	0.7393	0.1427					74.5
PP-A-am-2 (D-1/1)			0.2079	0.1093	0.7496	0.8450	78.1
PP-B-am-2 (D-1/1)			0.3839	0.1991	0.8108	0.9006	66.9
PP-C-am-2 (D-1/1)			0.2419	0.1577	0.7199	0.8563	73.3
PP-A-am-3 (D-0/1)	0.7666		0.4641	0.1335			71.5
PP-B-am-3 (D-0/1)	0.8214		0.5230	0.2072			61.2
PP-C-am-3 (D-0/1)	0.7508		0.4790	0.1930			60.0
PP-A-am-4 (I-1/1)			0.7197	0.2884	0.6919	0.8728	20.7
PP-B-am-4 (I-1/1)			0.7601	0.2994	0.7417	0.8601	20.0
PP-C-am-4 (I-1/1)			0.6697	0.3024	0.6314	0.8967	23.3

[a] Nomenclature: PP-A-1, PP-A-2, PP-A-3, etc. = Doi two-state models with different orders of statistical parameters; PP-A-4, etc. = symmetric and asymmetric first-order Markov chains fit separately and then blended; PP-am-1, etc. = amorphous fraction from PP-A, etc.

standard deviations given in Table 2 between calculated and observed pentad/heptad distributions for Doi-0/1 were improved over Doi-0/0 and similar to Doi-1/1, even with one less variable than Doi-1/1, as shown in Table 3. The Excel-4[19] solver routine also found similar sets of P_0 and P_{mm}, P_{rm} transition probabilities for Doi-0/1 as observed independently in Doi-0/0 and Doi-1/1, respectively.

In addition to the overall improved qualities of the PP-A through PP-F fits for Doi-0/1, there are other reasons to consider Doi-0/1 for highly isotactic polypropylenes. Although the overall Doi-0/0 two-state model fits for the crystalline fractions are overall gratifying in spite of the predicted low syndiotactic fractions, a close inspection of the conditional transition probabilities for symmetric chains reveals that the sequences predicted for symmetric chains would hardly be crystalline. Doi-0/0 gave P_m values that increased from 0.3 to 0.5 for PP-C through PP-F with steadily increasing donor concentrations. In a related study, Busico et al.[14] obtained P_m's of 0.2−0.3. It would be surprising if a detached polypropylene with such a low level of isotacticity would be found among the crystalline species in the cold xylene insolubles fractions. Doi-0/1 gave an improved result but with the corresponding P_{mm} values around 0.6 and essentially invariant to increasing donor concentrations. If the symmetric chain sequences were part of an overall more highly crystalline sequence distribution as a consequence of a catalyst mechanism that switched reversibly from symmetric to asymmetric sequences,[13,14,18,20] then these much lesser isotactic sequences would exist in the crystalline fractions.

A set of polypropylenes that were created by only increasing hydrogen and the external donor concentrations during polymerization affords an opportunity to examine trends in the conditional transition probabilities with increases in stereoregularity. The only experimental variable responsible for the structural differences between PP-A and PP-B was a higher hydrogen concentration for PP-B. Neither sample was prepared with an electron donor. Polypropylenes PP-A and PP-B, which contained 33 and 28% amorphous polypropylenes, respectively, yielded crystalline components with P_0's of 0.972 and 0.980 and with asymmetric fractions of 0.94 and 0.97, respectively, for Doi-0/1. These conditional transition probabilities seem to reasonably reflect the observed behavioral differences of PP-A and PP-B, which melted at 155.2 and 159.2 °C and had *meso* diad contents of 0.908 and 0.941, respectively. As seen in Table 3, the symmetric chain transition probabilities are essentially in the same regime of $P_{mm} = 0.5-0.6$ and $P_{rm} = 0.1-0.3$ for both the amorphous and crystalline fractions of PP-A and PP-B with P_{mm} being only slightly higher for the crystalline fractions.

Donor is first added in PP-C and increased steadily from PP-C to PP-F. The melting points, as shown in Table 1, change from 159.2 to 163.5 °C from PP-B to PP-C and from 163.5 to 166.3 °C from PP-C to PP-F. The *meso* diad content of the crystalline fractions changed from 0.941 for PP-B to 0.980 for PP-C and from

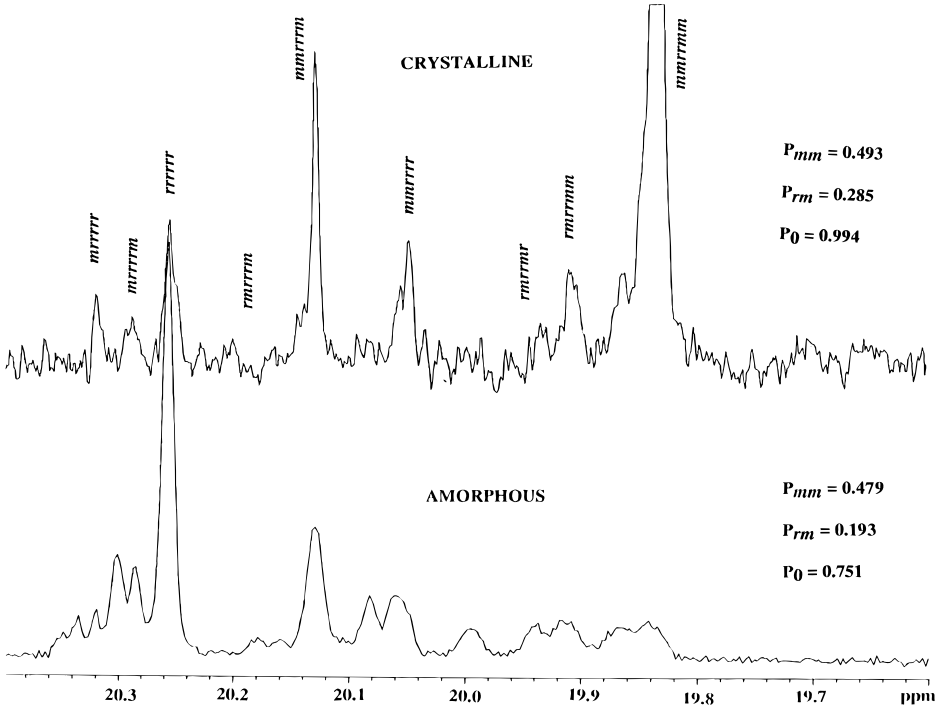

Figure 2. Comparison of corresponding ^{13}C NMR spectral regions displaying the *rrrr*-, *mrrr*-, and *mrrm*-centered heptads for an amorphous versus crystalline polypropylene fraction. (Doi-0/1 parameters are shown.)

0.980 to 0.991 from PP-C through PP-F. The average *meso* run length, which is the average isotactic run length between defects and which will be discussed in more detail later, increases systematically from 40 for PP-A to 430 for PP-F. There are large differences in the amounts of amorphous polypropylenes before and after the initial addition of donor (28% for PP-B versus 1.9% for PP-C) that reduces finally to 0.56% for PP-F. Increasing the amounts of donor have led to steady and dramatic improvements in the isotacticity of the resulting polypropylenes.

The changes in isotacticity with the initial addition of donor are not strongly reflected in the changes observed for the conditional transition probabilities for both symmetric and asymmetric chains between PP-B and PP-C for Doi-0/1. The transition probability for asymmetric chains, P_0, changes from 0.980 to 0.994 between the crystalline fractions of PP-B and PP-C. The amorphous fractions from PP-B and PP-C give consistent but lower values for P_0 around 0.8 (see Table 3). P_{mm} ranges from 0.5 to 0.6 for both the amorphous and crystalline fractions and P_{rm} also does not show any substantial differences between the amorphous and crystalline fractions. From PP-C to PP-F, increasing amounts of donor are added sequentially and lead to substantial improvements in isotacticity. These observed structural changes are, once again, only modestly reflected by changes in the asymmetric and symmetric chain transition probabilities for PP-C through PP-F for the Doi-0/1 two-state model. A similar observation has been made by Chûjô et al.[13] The asymmetric transition probability, P_0, increases from 0.994 to 0.999 for PP-C through PP-F. There are also no distinctive trends in P_{mm} and P_{rm} for the symmetric chain components for Doi-0/1 with increasing donor concentrations. In fact, the P_{mm}'s and P_{rm}'s are similar between the amorphous and crystalline fractions for PP-C. The fraction of asymmetric chains in the crystalline fractions for Doi-0/1 was invariant at essentially 99% for PP-C through PP-F. The Doi-0/0 behavior is similar.

There is one notable change in the character of the sequence distributions that occurs with the addition of donor. The steady state population of asymmetric chains in the whole PP-B is 87% for Doi-0/1. This result for Doi-0/1 changes to 98% with the initial addition of donor for the whole PP-C and continues to improve modestly until it reaches nearly 99% for the whole PP-F, which was produced with the highest DCPMS concentration. There are only slight progressive changes in the character of the asymmetric sequence distributions for the crystalline components with additions of donor, while the population of asymmetric sequences in the whole polymer increases substantially with the initial addition of donor. The initially broad sequence distributions become progressively more narrow and more isotactic as the total steady state fraction of catalyst sites producing highly isotactic asymmetric chains increases. Collectively, the Doi-0/1 results suggest that the effect of adding donor is primarily to convert symmetric chain sites to asymmetric chain sites that produce highly isotactic polypropylenes.[13,24] The Doi-0/1 model also indicates that the supported Ziegler–Natta catalyst produces virtually all asymmetric chains at high DCPMS levels.

A final observation concerning the quality of the two-state model fits is that the P_m and P_{mm}, P_{rm} values from Doi-0/0 and Doi-0/1, which progress only mildly for the crystalline fractions, are also in a range typically observed for moderately syndiotactic to atactic polypropylenes. Consequently, the symmetric chain sequence distributions are expected to be similar between the amorphous and crystalline fractions. The weak *rrrr*-, *mrrr*-, and *mrrm*-centered heptad resonances found in the ^{13}C NMR spectra of the amorphous fractions differ from the corresponding resonances observed in the crystalline fractions as shown in Figure 2. No splitting among the *mrrrrm*, *mrrrrr*, and *mmrrrr* resonances, which leads to a much cleaner spectral pattern in Figure 2, is observed for any of the crystalline fractions. In addition, the *rmrrrm* resonance is consistently missing

in the ^{13}C NMR spectra of the crystalline fractions. It is predicted by Doi-0/0 and Doi-0/1 and observed in the ^{13}C NMR spectra of the amorphous fractions. See Table 2 and Figure 2.

The Doi two-state model was explored further for other possible solutions. The final solutions for Doi-0/0, Doi-1/1, and Doi-0/1 were obtained by iterating over each variable until a minimum was found in the standard deviation between calculated and observed pentad/heptad distributions. More than one minima, which depended upon the initial values chosen for the conditional probabilities and fraction of asymmetric chains, is typically found. The minima were reproducible and simply depended upon the directions taken in the iteration process. The final solutions were obtained by seeking the lowest possible minima between calculated and observed sequence distributions. At the high levels of observed isotacticity, it is possible that experimental errors during the measurements of weak resonances influence the final results.

The only source of the required syndiotactic sequences in the final distribution is from the symmetric chain distribution.[18,20] The solver routine of Excel-4 located the lowest standard deviation between observed and calculated sequence distributions through combining small amounts of highly syndiotactic symmetric chains with considerably larger quantities of highly isotactic asymmetric chains. This led to very high P_0's, low P_m's and P_{mm}'s, and very high percentages of asymmetric chains. It was surprising that PP-A and PP-B, which were lowly isotactic, have such high percentages of asymmetric chains. This result would change if the symmetric chain components were to become more isotactic, which would force larger quantities of symmetric chains to achieve the proper levels of syndiotactic and other defect fractions in the final distributions. This is precisely the directional change for Doi-0/1 versus Doi-0/0. The freedom introduced into the model by first-order Markovian symmetric chain statistics led to higher P_{mm}'s than the P_m's obtained for the one-parameter Doi-0/0 model. The limit of such behavior can be found by fitting the symmetric and asymmetric chain models independently to the observed sequence distributions and blending the results to obtain final sequence distributions. This would force the tacticity of the symmetric and asymmetric chain sequences to be nearly the same, but different stereo-defects would be found within the two types of sequence distributions. The success or failure of such an approach will be dictated by how well the overall sequence distributions match in addition to being able to predict short syndiotactic blocks at very high isotactic levels.

First-order Markovian statistics for both symmetric and asymmetric chains were employed in independent fits of the observed sequence distributions by iterating over those pentad/heptad sequence fractions that were specifically from the sequence distribution being tested. Those observed pentad/heptad fractions that were predicted to have measurable concentrations by asymmetric chain statistics, but were predicted to be negligible by symmetric chain statistics, were omitted from the symmetric chain fit. The pentad/heptad fractions used for the best symmetric chain statistical fit were *mmmm*, *mmmr*, *mmrr*, *mmrm* + *rrmr*, *mrrrm*, *mrrrr*, *rrrrr*, *mmrrrm* + *rrrrmr*, *mmrrrr*, and *mmrrmm*. This procedure was repeated for the corresponding first-order Markovian statistics for asymmetric chains. The first-order Markovian fits for asymmetric chains for PP-A through PP-F were obtained by optimizing the asymmetric chain transition probabilities to the following specific components of the pentad/heptad distribution, which were *mmmm*, *mmmr*, *rmmr*, *mmrr*, *mmrm* + *rrmr*, *rmrm*, and *mmrrmm*. It will become apparent later why these particular sets of pentads/heptads were used for symmetric and asymmetric chains, respectively. Finally, the independently obtained best fits from the asymmetric and symmetric chain statistical analyses were blended by iterating over the fraction of asymmetric chains for values that led to a minimum in the standard deviation between calculated and observed sequence distributions. The blended results would correspond to upper limits for the solutions to the Doi two-state model with the results from Doi-0/1 representing a lower limit. The final blends gave standard deviations between calculated and observed pentad/heptad distributions that were substantially improved over those for the individual fits. The final results, labeled I-1/1 are given in Table 2. Transition probabilities along with the percent asymmetric chain for PP-A through PP-F, which differ only by the donor and hydrogen levels used during polymerization, are given under PP-A-4, PP-B-4, etc. in Table 3. Overall, the I-1/1 fits are too close to the experimental distributions to be disregarded entirely. One of the surprising results from this approach was the high level of syndiotactic sequences predicted for PP-C through PP-F. As expected, the fractions of asymmetric chains required in the final blend was considerably lower than obtained for Doi-0/0, Doi-1/1, and Doi-0/1. The standard deviations for the independent fits are not so good as Doi-0/1, as expected, because the solution was forced by fitting the distributions separately. It is possible to find a similar result with Doi-1/1 by carefully selecting the starting points in the iterative process. What this exercise means is that there are likely other satisfactory and possibly valid fits somewhere between the P_{mm} levels of 0.4 and 0.99 for symmetric chains in this series of polypropylenes. For example, two minima were located when the transition probabilities, P_{mm}, P_{rm}, and P_{10}, and the fractions of asymmetric chains were allowed to iterate while holding the P_{00} asymmetric chain parameters constant during the blending operations in the I-1/1 schemes. One corresponded to the Doi-0/1 fits, and the other was a small correction to the I-1/1 blended results (with an improved standard deviation).

Other satisfactory fits likely exist between the two extremes obtained with Doi-0/1 and I-1/1. The fractionation results of Paukerri et al.[3,20,25] showed only asymmetric chains for the highly crystalline fractions. The appearance of symmetric chains occurred at lower crystallinities. This result clearly indicates that P_{00} cannot be the same as P_{mm}. The difficult point to establish is the exact difference between P_{00} (or P_0) and P_{mm} for a given isotactic polypropylene. It appears that the Doi-0/0 and Doi-0/1 results exaggerate this difference, which is possibly caused by experimental errors in the measurements of the pentad/heptad sequence distributions. The I-1/1 result takes the Doi two-state model to unreasonable similarities in P_{00} with P_{mm}. The I-1/1 fits were close enough to experimental observations to indicate that lower values of P_{mm} will give equally good or better fits, but it may not be necessary to have P_{mm} or P_m values as low as obtained with Doi-0/1 and Doi-0/0, respectively.

Applications of Markovian statistics to the observed pentad/heptad distributions from carefully fractionated

Table 4. Concentrations of Polypropylene Nonads above 0.0001 As Determined from a First-Order Markovian Symmetric Chain Model for PP-F[a]

$P_{mm} = 0.9969, \quad P_{mr} = 0.0031$

$P_{rm} = 0.3736, \quad P_{rr} = 0.6264$

nonad	concn
mmmmmmmm	0.9702
mmmmmmmr	0.0061
mmmmmmrm	0.0023
mmmmmrmm	0.0023
mmmmrmmm	0.0023*
mmmmmmrr	0.0038
mmmmmrrm	0.0014
mmmmrrmm	0.0014
mmmrrmmm	0.0007*
mmmmmrrr	0.0024
mmmmrrrm	0.0009
mmmrrrmm	0.0009*
mmmmrrrr	0.0015
mmmrrrrm	0.0006
mmrrrrmm	0.0003*
mmmrrrrr	0.0009
mmrrrrrm	0.0004*
mmrrrrrr	0.0006
mrrrrrrm	0.0001*
rrrrrrrm	0.0004*
rrrrrrrr	0.0003*
sum	0.9998

[a] The most important nonads are identified by an asterisk.

polypropylenes can offer a possible route to a unique solution of the Doi two-state model. It is clearly established that first order symmetric chain Markovian statistics can lead to appropriate syndiotactic levels in highly isotactic polypropylenes over a broad range of P_{mm} values.

Characterization of Stereo-Defect Structures

Another purpose in examining calculated pentad/heptad symmetric and asymmetric chain sequence distributions in highly isotactic polypropylenes was to afford an opportunity to identify the predicted stereo-defects connecting long runs of isotactic sequences that were associated independently with symmetric and asymmetric chains at high levels of isotacticity. The transition probabilities from the best independent fits for both symmetric and asymmetric chains can be used to calculate a concentration for any sequence of any particular length. Nonad distributions were calculated using the transition probabilities from the I-1/1 two state model for both asymmetric and symmetric chain sequence distributions. The I-1/1 model was selected because the stereo-defects will be well-spaced at high levels of isotacticity for both symmetric and asymmetric chains. This procedure does not work well for the Doi-0/1 model because the symmetric chains have P_{mm} values of 0.4−0.6 that do not lead to long isotactic sequences interrupted by stereo-defects. Shown in Table 4 are the 0.0001 and above nonad concentrations calculated from the symmetric chain transition probabilities for PP-F from the I-1/1 fit. In Table 5 are the 0.0001 and above nonad concentrations for PP-F from the independent first-order Markovian asymmetric chain fit. The sum of these nonad fractions, in each case, is close to unity, which means that the omitted nonads are inconsequential as a result of the stereo-defects being well spaced at this high level of stereo-regularity. In the Doi-0/1 model, these same sequences sum to nearly 1 for asymmetric chains but sum to less

Table 5. Concentrations of Polypropylene Nonads above 0.0001 As Determined from a First-Order Markovian Asymmetric Chain Model for PP-F[a]

$P_{00} = 0.9968, P_{01} = 0.0032$

$P_{10} = 0.6934, P_{11} = 0.3066$

	nonad	concn
mmmmmmmm	000000000 + 111111111	0.9701
mmmmmmmr	000000001 + 111111110	0.0063
mmmmmmrr	000000010 + 111111101	0.0043
mmmmmrrm	000000100 + 111111011	0.0043
mmmmrrmm	000001000 + 111110111	0.0043
mmmrrmmm	000010000 + 111101111	0.0021*
mmmmmmrm	000000011 + 111111100	0.0019
mmmmmrmr	000000110 + 111111001	0.0013
mmmmrmrm	000001100 + 111110011	0.0013
mmmrmrmm	000011000 + 111100111	0.0013*
mmmmmrmm	000000111 + 111111000	0.0006
mmmmrmmr	000001110 + 111110001	0.0004
mmmrmmrm	000011100 + 111100011	0.0004
mmrmmrmm	000111000 + 111000111	0.0002*
sum		0.9994

[a] The reverse nonads are not shown.

than 0.5 for symmetric chains. (The data in Tables 4 and 5 also clarify why only specific pentads/heptads were used in the first-order independent Markovian fits for both symmetric and asymmetric chains, respectively.) It becomes a relatively easy task to pick out the predicted stereo-defects from the calculated data in Tables 4 and 5. For symmetric chains, they are

S1 ∼*mmmmmmmmmrmmmmmmmmm*∼

S2 ∼*mmmmmmmmmrrmmmmmmmmm*∼

S3 ∼*mmmmmmmmmrrrmmmmmmmmm*∼

S4 ∼*mmmmmmmmmrrrrmmmmmmmm*∼

S5 ∼*mmmmmmmmmrrrrrmmmmmmmm*∼

S6 ∼*mmmmmmmmm*$(r)_x$*mmmmmmmm*∼

etc.

where "*x*" is 6 and larger. First-order Markovian statistics for symmetric chains, where there is equivalency of configuration, do no more than predict *racemic* diad stereo-defects of steadily increasing sequence lengths. Just the opposite is true for symmetric chain statistics of syndiotactic polypropylenes where *meso* defects of steadily increasing sequence lengths are predicted.

For asymmetric chains with a preference for a specific configuration, the major stereo-defects are

A1 ∼00000000000010000000000000∼

A2 ∼00000000000011000000000000∼

A3 ∼00000000000011100000000000∼ etc.

Analogous to the symmetric chain result, the first-order Markovian asymmetric chain model leads to chain defects of opposite configuration of steadily increasing sequence lengths. Sequences longer than those for A3 are insignificant in the fit for sample PP-F, which is a polypropylene that is exceptionally isotactic and, consequently, highly crystalline. Stereo-defects with much longer sequence lengths are predicted at the same level

Table 6. Determinant for Linear Regression Analyses To Determine Stereo-Defect Concentrations for PP-F ($x = 7.2$)

pentad/ heptad	fraction	defect								
		0	A1/S2	A2	A3	S1	S3	S4	S5	S6+
[*mmmm*]	0.9820	1	0	0	0	0	0	0	0	0
[*mmmr*]	0.0043	0	2	2	2	2	2	2	2	2
[*rmmr*]	0.0010	0	0	0	1	0	0	0	0	0
[*mmrr*]	0.0044	0	2	0	0	0	2	2	2	2
[*mmrm*]	0.0024	0	0	2	4	2	0	0	0	0
[*rmrm*]	0.0007	0	0	2	0	0	0	0	0	0
[*mrrrrm*]	0.0003	0	0	0	0	0	0	1	0	0
[*mrrrrr*]	0.0003	0	0	0	0	0	0	0	2	2
[*rrrrrr*]	0.0005	0	0	0	0	0	0	0	0	$x - 5$
[*mrrrmm*]	0.0006	0	0	0	0	0	2	0	0	0
[*mmrrrr*]	0.0006	0	0	0	0	0	0	2	2	2
[*mmrrmm*]	0.0017	0	1	0	0	0	0	0	0	0

of tacticity for symmetric chains. In PP-F, the fraction of the symmetric chain sequence, *rrrrrr*, is predicted at 0.0004, while the fraction for the asymmetric chain sequence, ~01110~, is predicted to have a concentration of only 0.0002. The only common stereo-defect predicted for both symmetric and asymmetric chains is A1(S2).

The experimental evidence supports the various stereo-defects predicted from the first-order Markovian models for both symmetric and asymmetric chains. The A1(S2) stereo-defect is the most significant, as judged by the relatively strong intensities of the *mmrr* and *mmrrmm* resonances. The *rmrm* and *rmmr* pentad resonances offer direct and independent evidence for stereo-defects A2 and A3, respectively, although the *rmmr* resonance, which fingerprints A3, is stronger than expected. Evidence for syndiotactic stereo-defects of differing block lengths can be found by the existence of the observed *mmrrrm* (S3), *mrrrrm* (S4), *mmrrrr* (S4 through S6+), *mrrrrr* (S5 through S6+), and *rrrrrr* (S6+) resonances. Evidence for S1 can be found in the presence of the *mmrm* (+*rrmr*) resonance, but defects A2 and A3 also contribute to this resonance.

With the predicted sets of stereo-defect structures available from both symmetric and asymmetric chains, the next step is to determine which of the defect concentrations can be measured directly from the ^{13}C NMR pentad/heptad distribution. Each type of stereo-defect gives rise to a unique set of pentads/heptads, which can be used to relate the independent pentad/heptad fractions to the concentrations of the various stereo-defects. Since many of the pentads/heptads arise from more than one type of defect, solving for the stereo-defect concentrations can best be accomplished through a determinant, shown in Table 6, relating stereo-defect concentrations to the distribution of pentad/heptad fractions.

One of the difficulties in defining the pentad/heptad determinant is that the final number of *racemic* diads in the last significant syndiotactic defect is unknown. *Racemic* diads up to a sequence length of six can be uniquely accommodated in the determinant relating the stereo-defect concentrations to pentad/heptad concentrations. What is needed is the average sequence length for the syndiotactic defects having a sequence length of six and greater. This was accomplished by defining the last significant stereo-defect concentration as

$$[\sim mmmmm(r)_x mmmmm\sim]$$

where "*x*" is 6 and larger. This particular defect has the following coefficients:

$(x - 5)$ [*rrrrrr*]

2 [*rrrrrm*]

2 [*rrrrmm*]

2 [*rrmm*]

2 [*rmmm*]

The probability parameters obtained from the best symmetric chain fit of polypropylenes A through F can also be used to calculate complete heptad distributions, which give perfect fits in the linear regression analyses for the defect concentrations S1 through S6+, if the coefficient for S6+ is known. Using the calculated heptad distributions, one can iterate over the possible S6+ coefficients until perfect fits are obtained. To force a solution, it was necessary to add the calculated data for *mrrrrm*. The coefficients and values for "*x*", the average syndiotactic sequence lengths over *racemic* diads of sequence lengths six and longer, are shown in Table 7 for polypropylene samples PP-A through PP-F.

With the coefficients for S6+ available, an attempt was made to determine the concentrations of seven stereo-defects, A1(S2), A2, S1, and S3 through S6+, by linear regression analyses over twelve observed pentad/heptad concentrations. The heptads *rmrrmr* and *rmrrmm* were not used in the analyses because stereo-defects giving rise to these heptads are not included in structures A1 through A3 and S1 through S6+.

Given in Table 8 are the experimental stereo-defect concentrations after linear regression analyses over pentad/heptad data from the six crystalline fractions of PP-A through PP-F. The description defect "0" is used in Table 8 for the concentration of the all *meso* pentad, *mmmm*. Defect A3 was omitted from the direct analyses because it is predicted to be weak by first-order statistics for asymmetric chains and not predicted at all for zero-order asymmetric chains. With a limited number of dependent variables available for the linear regression analyses, steps must be taken to reduce the number of independent variables. Defect S5 consistently gave negative results for all samples after the initial linear regressions. Consequently, S5 was omitted and the linear regression analyses were performed over the remaining six independent variables for the defect concentrations. With the number of dependent variables fixed at twelve, this omission improved the degrees of freedom. The stereo-defects that persisted throughout the linear regression analyses are

A1(S2) ~0000000000000100000000000~

A2 ~0000000000001100000000000~

S1 ~0000000000001111111111111~

S3 ~0000000000000101111111111~

S4 ~0000000000001010000000000~

S6+ ~00000000000$(01)_x$000000000~ $x = 8-10$

With the exceptions of S1 and S5, each of the above detected defects had a unique pentad/heptad that served as a signature for that particular stereo-defect. Both S1 and S5 depended upon linear combinations of pentads/heptads that were all shared with other defects. At these low concentrations, either experimental error in the measurements of the resonance intensities or

Table 7. Predicted Average Sequence Lengths and [*rrrrrr*] Coefficients for the Syndiotactic Block Stereo-Defect for the Series of Isotactic Polypropylenes Varying in Stereoregularity[a]

polypropylene	coeff	av syndiotactic defect sequence length for "*x*" > 6
PP-A	3.4	8.4
PP-B	3.0	8.0
PP-C	3.0	8.0
PP-D	2.7	7.7
PP-E	2.7	7.7
PP-F	2.7	7.7

[a] See text for definition of "*x*".

fortuitous overlap could cause problems with the linear regression analyses and cause those defects not uniquely identified to be eliminated. The detection and measurement of the concentrations for defect A2 depend upon the resonance for *rmrm*, which is weaker than *rmmr* throughout the data set. There may be fortuitous overlap with the *rmmr* pentad that uniquely identifies A3, which should always be substantially less than A2 according to the first-order Markovian asymmetric chain analyses. Defect S3 is detected directly by the heptad *mrrrmm* which has an odd *racemic* diad sequence length and also offers direct evidence for an isotactic chain leading up to a defect with a handedness opposite to that of an isotactic chain leading away from the defect. Unfortunately, the *mrrrmm* resonance overlaps with the *rrrrmr* resonance.[18] Although the presence of the latter is largely precluded by these statistical considerations, it can be predicted by the two-state model,[14] which leads to some uncertainty in the absolute detection of *mrrrmm*.

The sum of the directly determined stereo-defect concentrations for PP-A through PP-F are of the same orders of magnitude as the values calculated directly from the *mmmr* resonance, as shown in Table 9 and will be discussed shortly. Meaningful predicted results for stereo-defect populations for the Doi-0/1 two-state symmetric and asymmetric chain Markovian analyses could not be obtained because of the low P_{mm} values, which lead to exceptionally high concentrations of stereo-defects, obtained for symmetric chains. The symmetric chain sequences at P_{mm} values of 0.4−0.6 cannot be viewed as recurring isotactic sequences connected by stereo-defects. The I-1/1 statistical analyses do predict long isotactic runs for both asymmetric and symmetric chains, and meaningful concentrations can be calculated for the stereo-defects. These results are included in Table 9 because of the closeness of the I-1/1 calculated total defects to experimental results, which suggests that the symmetric chain sequences are more isotactic than the Doi-0/1 results would indicate and the true solution may lie somewhere between Doi-0/1 and I-1/1.

In spite of some of the determined concentrations being close to the detection limit, it is clear that the types of defect structures, predicted through first-order Markovian statistics for both symmetric and asymmetric chains, have been identified. There can be little doubt that progressive lengths of syndiotactic sequences are present as stereo-defects in highly isotactic polypropylenes prepared with a fourth generation, supported Ziegler−Natta catalyst. Direct experimental evidence was obtained for the stereo-defects predicted for asymmetric chains. ^{13}C NMR data taken at higher frequencies and at subsequently higher sensitivities may later confirm the presence of isotactic blocks of opposite handedness and the presence of part or all of the indicated syndiotactic sequences of progressively longer sequence lengths. First-order Markovian statistics, by definition, predict a steady progression in defect structure sequence lengths. The catalyst sites do not necessarily have to follow this behavior. Since the statistical parameters are related to kinetic rate constants and reactivity ratios,[4,23,26,27] it should not be surprising that syndiotactic types of chain defects are present. An interesting point is the presence or absence of long isotactic blocks of opposite handedness, as predicted by the statistics of symmetric chains and indicated by the heptad, *mrrrmm*.

Finally, the *mmrrmr* heptad was also present at considerably higher concentrations than predicted through Markovian statistics. It could arise from either of the following structures:

$$\sim 000000010010000000 \sim$$

or

$$\sim 000000010011111111 \sim$$

The former could arise from closely spaced asymmetric chain defects. The latter is particularly interesting because it could represent direct evidence for a catalyst site fluctuating from an asymmetric to symmetric chain.[13,14,20]

Asymmetric and symmetric chain statistics, whether zero- or first-order Markov, provide a systematic scheme for the production of stereo-defects. The catalyst sites, while producing the generic types of stereo-defects predicted by both asymmetric and symmetric chain statistics, do not have to follow any particular scheme for the creation of errors during the production of long runs of isotactic sequences. Conceivable possibilities are that only isotactic blocks of the same handedness are produced for symmetric chains, that is, the *racemic* diads always have even sequence lengths,[25] or a catalyst site switches from producing symmetric to asymmetric chains or vice versa during the course of a polymerization.[13,14,20] More detailed ^{13}C NMR analyses at higher sensitivities will provide key insights into chain defect structural determinations.

Finally, the row of 2's obtained for $mmmr + rmmm$ for the stereo-defects other than "defect 0" in the determinant in Table 6 occurs because all stereo-defects begin and end with an "*r*" unit regardless of the stereo-defect structure. Therefore, the $mmmr + rmmm$ pentad concentration can be used to calculate the total stereo-defect concentration even if the structures are not known. The concentration of total stereo-defects is given by eq 5. The total stereo-defect concentrations

$$[\text{total stereo-defects/10 000 units}] = 5000[mmmr + rmmm] \quad (5)$$

determined from eq 5 versus those summed from the data in Table 8 are listed for comparative purposes in Table 9. The agreement between the directly determined total stereo-defect concentration and the sum of those calculated by linear regression is within ∼20%.

The fact that $[mmmr + rmmm]$ can be utilized to determine the total number of stereo-defects per 10 000 repeat units independently of the specific structures also permits an average *meso* run length between stereo-defects to be calculated.

$$\text{average } meso \text{ run length} = 2/[mmmr + rmmm] \quad (6)$$

Table 8. Stereo-Defect Concentrations in a Series of Crystalline Polypropylenes As Determined from Linear Regression Analyses over Observed Pentad/Heptad Distributions

	defect								
sample	0	A1/S2	A2	A3	S1	S3	S4	S5	S6+
PP-A	0.9675	0.0217	0.0011		0.0022	0.0024			0.0052
predicted	0.9654	0.0185	0.0021	0.0002	0.0051	0.0025	0.0017	0.0013	0.0016
PP-B	0.9773	0.0176	0.0005		0.0012	0.0011			0.0022
predicted	0.9755	0.0173	0.0018	0.0002	0.0023	0.0010	0.0007	0.0005	0.0004
PP-C	0.9930	0.0057	0.0002			0.0002	0.0004		0.0004
predicted	0.9921	0.0059	0.0006	0.0001	0.0006	0.0003	0.0002	0.0001	0.0001
PP-D	0.9962	0.0025	0.0003		0.0005	0.0002	0.0002		0.0002
predicted	0.9959	0.0024	0.0005	0.0001	0.0006	0.0002	0.0001	0.0001	0.0001
PP-E	0.9969	0.0020	0.0003		0.0003	0.0002	0.0001		0.0001
predicted	0.9965	0.0021	0.0004	0.0001	0.0004	0.0002	0.0001	0.0001	0.0001
PP-F	0.9973	0.0015	0.0004		0.0005	0.0002	0.0001		0.0002
predicted	0.9968	0.0015	0.0004	0.0001	0.0006	0.0002	0.0001	0.0001	0.0001

Table 9. Stereo-Defects per 10 0000 Units, Calculated and Observed

sample	predicted by MARKOVIAN statistics	from direct defect analysis (Table 8)	from eq 7
PP-A	331	325	262
PP-B	240	227	197
PP-C	78	69	59
PP-D	40	38	35
PP-E	34	31	27
PP-F	31	27	23

Table 10. Average *Meso* Run Lengths for Polypropylenes PP-A through PP-F

polypropylene	av *meso* run length	polypropylene	av *meso* run length
PP-A	40	PP-D	290
PP-B	50	PP-E	360
PP-C	170	PP-F	430

Equation 6 gives a result similar to the average length of isotactic blocks having three or more repeating *meso* diad units, suggested by Collette et al.[21] The average *meso* run lengths preclude contributions from short *meso* runs such as ~*mrmrm*~ and ~*mrmmrm*~, which are part of stereo-defects. Average *meso* run lengths are given in Table 10 for PP-A through PP-F. The experimentally measured average *meso* run lengths show an excellent correlation with melting points, as measured by differential scanning calorimetry. In addition, the average *meso* run lengths increase steadily with the addition of electron donor. The straightforward method presented for determining the total numbers of stereo-defects per 10 000 repeat units, independently of whatever their structures might be, is also useful for correlations with thermal and physical property data.

Characterization of Amorphous Polypropylenes

There were sufficient xylene soluble samples collected for PP-A, PP-B, and PP-C to perform ^{13}C NMR analyses on the accompanying amorphous polypropylenes. This allowed a comparison of structures and statistical results with the corresponding crystalline fractions of PP-A, PP-B, and PP-C. In each soluble component of PP-A, PP-B, and PP-C, the *mmmm* pentad dominates the observed pentad/heptad distribution and the *rrrrrr* heptad is a significant contributor. The four two-state models used for characterizing the crystalline fraction sequence distributions were also applied to the three amorphous fractions. Results are given in Tables 2 and 3. Once again, Doi-0/1 gave the lowest standard deviations between calculated and observed pentad/heptad sequence distributions. Independent first-order Markovian symmetric and asymmetric chain statistical fits were obtained for the amorphous polypropylenes following precisely the same procedure as for the crystalline fractions. In each case, improved fits were obtained after blending.

Table 11. Transitional Probabilities from the Doi-0/1 and I-1/1 Models for the Amorphous and Crystalline Fractions of PP-A, PP-B, and PP-C

Doi-0/1	P_0	P_{mm}	P_{rm}
PP-A (cryst)	0.9722	0.5806	0.1407
PP-A (amorp)	0.7666	0.4641	0.1335
PP-B (cryst)	0.9799	0.5887	0.1764
PP-B (amorp)	0.8214	0.5230	0.2072
PP-C (cryst)	0.9938	0.4927	0.2852
PP-C (amorp)	0.7508	0.4790	0.1930

I-1/1	P_{mm}	P_{rm}	P_{00}	P_{10}
PP-A (cryst)	0.9684	0.3007	0.9637	0.8612
PP-A (amorp)	0.7197	0.2884	0.6919	0.8728
PP-B (cryst)	0.9776	0.3352	0.9751	0.8881
PP-B (amorp)	0.7601	0.2994	0.7417	0.8601
PP-C (cryst)	0.9928	0.3406	0.9919	0.8896
PP-C (amorp)	0.6697	0.3024	0.6314	0.8967

It is interesting to compare the conditional transition probabilities for amorphous versus crystalline fractions from Doi-0/1 and I-1/1, for PP-A, PP-B, and PP-C, as shown in Table 11. Overall, the symmetric chain transition probability, P_{rm}, from each model is similar for the crystalline versus amorphous components, particularly for PP-A and PP-B. The primary differences between amorphous and crystalline fractions occur in P_0, P_{00}, and P_{mm} for Doi-0/1 and I-1/1 for PP-A, PP-B, and PP-C. In I-1/1, significant differences did not exist among P_{rm} and P_{10} for the crystalline and amorphous fractions of PP-A, PP-B, and PP-C. The internal consistencies in the pentad/heptad sequence distribution data persisted sufficiently to permit similar behaviors with both the Doi-0/1 and I-1/1 models.

In Figure 2 is a direct comparison of the *rr*-centered regions from the ^{13}C NMR methyl spectra of amorphous and crystalline polypropylene fractions. Although key symmetric chain transition probabilities between the amorphous and crystalline phases for the Doi-0/1 fits are similar, the corresponding spectral regions that result primarily from symmetric chains differ substantially. Similar sets of symmetric chain transition probabilities would be expected to yield similar symmetric chain sequence distributions. This is not the case, as illustrated in Figure 2 where the ^{13}C NMR spectrum of the amorphous fraction has considerably more resonances than observed for the crystalline component. This observation also suggests that the symmetric chain distributions for the crystalline fractions have higher P_{mm} conditional probabilities than the Doi-0/1 result would indicate, but probably less than predicted by I-1/1.

The probabilities for continuation of isotactic sequences, P_0, P_{00}, and P_{mm} are the major sources of differences among statistical results for the amorphous versus the crystalline fractions from the same polymers for both the Doi-0/1 and I-1/1 two-state models. This result suggests that a primary difference between the structures of the crystalline fractions and the corresponding amorphous fractions is the length of the isotactic runs, with the amorphous components having isotactic sequence lengths too short to crystallize. Although the differences shown in Figure 2 indicate that the symmetric chain sequences from the amorphous fractions are more complex than the corresponding symmetric sequences in the crystalline fractions, the amorphous fractions must also contain the low end of the isotactic sequence distribution.

There were considerable differences in the fractions of asymmetric chains for the amorphous fractions for Doi-0/1 versus I-1/1. The percent asymmetric chains required for the best fit of the amorphous fractions for I-1/1 was approximately 20%, while the corresponding crystalline fractions give nominally 45−75% asymmetric chain sequences, as shown in Table 3. The Doi-0/1 two-state model gave nominally 60−70% asymmetric chains for the amorphous fractions and 94−99% asymmetric chains for the crystalline fractions. Others have noted that atactic polypropylenes from supported Ziegler−Natta catalyst systems are not pure symmetric chains.[20] The differences in results from the two different versions of the two-state models used in this study arise from the fact that a greater percentage of symmetric chains is required to fit the syndiotactic sequences for I-1/1 than Doi-0/1, analogous to the behaviors of the crystalline fractions.

Discussion and Summary

The present study extends earlier work[5,9,10,13,14,28−30] on the use of Markovian asymmetric and symmetric chain statistics for characterizing isotactic polypropylene sequence distributions by employing first-order symmetric chain statistics to predict short syndiotactic blocks in highly isotactic polypropylenes. The symmetric chain transition probabilities, P_{mm} and P_{rm}, are sufficiently different to indicate that a pure one-parameter, zero-order Markovian symmetric chain approach would not lead to as clear a delineation between symmetric and asymmetric chain sequence distributions in highly crystalline polypropylenes. In a related study, Busico et al.[14,30] introduced the probabilities for reversible switches from producing predominantly isotactic sequences to syndiotactic sequences in a zero-order Markovian two-state model to obtain improved results for predicting short syndiotactic blocks in highly isotactic polypropylenes. In this study, it is shown that first-order Markovian statistics for symmetric chains also lead to a prediction of short syndiotactic sequences in highly isotactic polypropylenes.

The methods presented in this study for determining the microstructures of highly crystalline, isotactic polypropylenes indicate that different pentad/heptad sequence distributions are obtained for symmetric versus asymmetric chains. The types of stereo-defect distributions predicted for symmetric and asymmetric chains were verified by independently identifying and quantitatively measuring members of the two different families of stereo-defects in crystalline polypropylenes. The two-parameter first-order Markovian statistical description for symmetric chains led to stereo-defect structures of increasing *racemic* diad lengths from one to six plus that diminish in concentration as the polypropylene becomes more isotactic. First-order Markovian statistics for asymmetric chains applied independently to the observed sequence distributions predict stereo-defects with opposite configurations of sequence lengths from one to three. Even though there was direct experimental evidence for all three of the expected stereo-defects for asymmetric chains, the third defect, A3 (∼0011100∼) was omitted from the direct analysis. The *rmmr* resonance, which uniquely identifies A3, was exceptionally strong experimentally, and fortuitous overlap could not be disregarded. Not all of the members of the symmetric chain distribution could be identified unequivocally, but sufficient numbers were found to state that the types of stereo-defects associated with symmetric chains could be identified generically.

In agreement with earlier literature studies on moderately crystalline polypropylenes,[9,10,13,14] the observed pentad/heptad sequence distributions for highly crystalline polypropylenes with [*mmmm*] fractions greater than 0.98 could be simulated using the Doi two-state model for symmetric and asymmetric chain statistical distributions. The Doi-0/1 model is shown to offer an improvement over the Doi-0/0 model for predicting short syndiotactic sequences in highly isotactic polypropylenes. There are questions concerning the solutions of the Doi two-state model that have not been completely answered by this study. More than one solution is possible for the Doi two-state models. Experimental differences among the *mrrr*-centered heptads between the amorphous and crystalline fractions from the same polypropylene suggest that the solution to the Doi two-state model may lie somewhere between the limits for P_{mm} of 0.6 and 0.99, established by Doi-0/1 and I-1/1, respectively, for PP-F in this study. The blending fractions are severely affected by the values obtained for P_{mm} for symmetric chains.

In an earlier study, Chûjô et al.[13] used the zero-order Markovian two-state models to suggest that increasing donor concentrations led to a corresponding increase in the fraction of the asymmetric sequence distribution. In this study, there was also a distinct increase in isotacticity with increasing donor levels and the fraction of asymmetric chains increased for the whole polymers with the addition of donor. The fractions of asymmetric chains within the crystalline fractions, however, were somewhat invariant to the level of donor, as also noted by Chûjô et al.[13] This observation was particularly true for the results from Doi-0/0, the zero-order Markovian two-state model. More precise conclusions concerning the distribution of asymmetric versus symmetric chains in highly crystalline polypropylenes will require experimental data that is well above the NMR detection limits. The results of this study do confirm that both asymmetric and symmetric chain sequences are present in highly isotactic polypropylenes, but the results do not indicate how the two types of behaviors and subsequent sequence distributions arise.

At the time of many of the very early studies,[5,9] ^{13}C NMR spectra were not sufficiently quantitative (at a level of only a few stereo-defects per 10 000 repeat units) to justify the use of higher order Markovian models. First-order Markovian statistics do predict families of both asymmetric and symmetric stereo-defects at [*mmmm*] levels of 0.98 and higher and has led to reasonable agreement between experimental and calculated pentad/heptad distributions. In addition, first-

order Markovian statistics have the innate capability to reduce to lower order statistics, if that should be the case. It is well established experimentally that syndiotactic stereo-defects of different sequence lengths are present in highly isotactic polypropylenes with *meso* diad contents >0.99 and polymerized with magnesium chloride supported fourth generation Ziegler−Natta catalysts.

An interesting result from the statistical components of this study is that the conditional transition probabilities for symmetric chains showed minimal changes with increasing isotacticity. It is possible that the symmetric chain producing sites are the least accessible to donor. The P_{rm}'s from both the Doi-0/1 and the I-1/1 analyses indicate that the syndiotactic blocks connecting long isotactic sequences become progressively shorter as the isotactic sequence lengths increase. A major difference between the two different results from the two-state models is that the Doi-0/1 connecting syndiotactic blocks are predicted to be longer than the I-1/1 connecting syndiotactic blocks. The amorphous fractions for PP-A, PP-B, and PP-C gave similar best fit values for the P_{rm} symmetric chain transition probabilities, as observed in the corresponding crystalline fractions in each of the two-state models. This latter result suggests that a considerable portion of the amorphous fraction arises from polypropylene chains with isotactic sequences too short to crystallize. The I-1/1 analyses indicate that the amorphous components are high in symmetric chain sequences, which was also observed by Hayashi et al.[10] and Paukkeri et al.[20] and leads to the suggestion that the catalyst sites that produce crystalline symmetric chains may also produce considerable quantities of amorphous polymers as a consequence of producing broad sequence distributions. The effect of adding an external electron donor to the catalyst is to increase the fraction of asymmetric chains in the whole polymer with only nominal increases in P_0, P_{00}, and P_{mm} (regardless of whether the model is Doi-0/1 or I-1/1). The net result of adding donor is a significant reduction in the amount of amorphous polymers, an increase in stereoregularity as noted by an increase in the average *meso* run length of the isotactic sequences and a substantial increase in catalyst activity (after the initial addition of electron donor). The latter was also noted by Paukkeri et al.[20] One possible explanation of the source of the continued presence of small amounts of amorphous polypropylenes is that it is produced from sites that never experience coordination with an electron donor. As the donor content increases, fewer and fewer sites remain unaffected. Support for this possibility is observed in the similarity of ^{13}C NMR spectra of amorphous polypropylenes produced from a variety of supported and unsupported Ziegler−Natta catalyst systems with different internal and external electron donors and also without any external electron donor whatsoever.

The Doi two-state model with a zero-order asymmetric chain and a first-order symmetric chain offers an improved technique for characterizing isotactic polypropylene sequence distributions. Considerable care must be given when obtaining solutions of the Doi two-state model because the results are sensitive to small differences among the observed sequence distributions. Independently applied first-order Markovian statistics are useful in establishing the range of possible Doi two-state solutions and in identifying the character of the observed sequence distributions. The use of Markovian statistics to identify both symmetric and asymmetric chain sequence distributions leads to the observation that the sites producing asymmetric chain sequences are dominating the sequence distributions as the stereoregularity increases with the addition of an electron donor. The amorphous polypropylenes that accompany the highly crystalline components are considerably higher in symmetric chain sequences and show little, if any, structural changes with the addition of electron donor.

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References and Notes

(1) Boor, J., Jr.; *Ziegler−Natta Catalysts and Polymerizations*; Academic Press: New York, 1979; Chapter 15.
(2) Wolfgruber, C.; Zannoni, G.; Rigamonti, E.; Zambelli, A. *Makromol. Chem.* **1975**, *176*, 2765.
(3) Paukkeri, R.; Vaananen, T.; Lehtinen, A. *Polymer* **1993**, *34*, 2488.
(4) Price, F. P. In *Markov Chains and Monte Carlo Calculations in Polymer Science*; Lowry, G. G., Ed.; Marcel Dekker: New York, 1970; Chapter 7.
(5) Shelden, R. A.; Fueno, T.; Tsunetsugu, T.; Furukawa, J. *J. Polym. Sci., Part B* **1965**, *3*, 23.
(6) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.
(7) Bovey, F. A. *High Resolution NMR of Macromolecules*; Academic Press: New York, 1972.
(8) Randall, J. C. *Polymer Sequence Determination: Carbon-13 NMR Method*; Academic Press: New York, 1977; Chapter 4.
(9) Doi, Y. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 635.
(10) Hayashi, T.; Inoue, Y.; Chujo, R.; Asakura, T. *Polymer* **1988**, *29*, 138.
(11) Coleman, B. D.; Fox, T. G. *J. Chem. Phys.* **1963**, *38*, 1065.
(12) Cheng, H. N.; Kasehagen, L. J. *Macromolecules* **1993**, *26*, 4774.
(13) Chûjô, R.; Kogure, Y.; Vaananen, T. *Polymer* **1994**, *35*, 339.
(14) Busico, V.; Cipullo, R.; Corradini, P.; De Biasio, R. *Macromol. Chem. Phys.* **1995**, *196*, 491.
(15) Chadwick, J. C.; van Kessel, G. M. M.; Sudmeijer, O. *Macromol. Chem. Phys.* **1995**, *196*, 1431.
(16) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1693.
(17) Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1980**, *13*, 270.
(18) Busico, V.; Corradini, P.; De Biasio, R.; Landriani, L.; Segre, A. L. *Macromolecules* **1994**, *27*, 4521.
(19) Person, R. *Using Excel-4 for Windows*; Que Corp.; Carmel, IN, 1992.
(20) Paukkeri, R.; Iiskola, E.; Lehtinen, A.; Salminen, H. *Polymer* **1994**, *35*, 2636.
(21) Collette, J. W.; Ovenall, D. W.; Buck, W. H.; Ferguson, R. C. *Macromolecules* **1989**, *22*, 3858.
(22) Chûjô, R. *Stepol '94 Abstracts*; International Symposium on Synthetic, Structural and Industrial Aspects of Stereospecific Polymerization, Milan, Italy, June 6−10, 1994; 1994; p II-13.
(23) Price, F. P. *J. Chem. Phys.* **1962**, *36*, 209.
(24) Soga, K.; Park, J. R.; Shiono, T.; Kashiwa, N. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 117.
(25) Paukkeri, R.; Lehtinen, A. *Polymer* **1994**, *35*, 1673.
(26) Cheng, H. N. *Macromolecules* **1991**, *24*, 2015.
(27) Cheng, H. N. *Macromolecules* **1992**, *25*, 2351.
(28) Cheng, H. N. *Makromol. Chem., Theory Simul.* **1993**, *2*, 901.
(29) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.
(30) Busico, V.; Cipullo, R.; Corradini, P.; Landriani, L.; Vacatello, M.; Segre, A. L. *Macromolecules* **1995**, *28*, 1887.

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