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Microstructure of Elastomeric Polypropylenes Obtained with Nonsymmetric *ansa*-Titanocene Catalysts[1]

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Ziegler–Natta (ZN) catalysis is in a state of renaissance with new scientific and technological advances in both heterogeneous and homogeneous systems. One discovery of immense significance to the catalytic, organometallic, and polymer sciences is the stereoselective polymerization of propylene by racemic ethylenebis(tetrahydroindenyl)dichlorotitanium[4] and -zirconium.[5] Studies made on such a metallocene compound, the structure of which can be determined by X-ray diffraction, had increased our understanding of the molecular mechanism of stereochemical control in α-olefin polymerization.

The polymerizations of propylene by *rac*-Et[Ind]$_2$ZrCl$_2$/MAO[6] (=methylaluminoxane) and *rac*-Et[IndH$_4$]$_2$ZrCl$_2$/MAO[7] are characterized by pronounced dependence of stereoselectivity on temperature (T_p).[8] The specific tritium radioactivities in polypropylene fractions[7d] indicate the existence of two dominant active states differing in polymerization rate constants,[7d,9] stereoselectivities,[7d] and stereoelectivities.[10] These differences were magnified for the nonsymmetric *rac*-[*anti*-ethylidene(1-η^5-tetramethylcyclopentadienyl)(1-η^5-indenyl)titanium dichloride (**1**)[11] and the dimethyl derivative (**2**).[12]

The X-ray molecular structure of **2**[12] showed that the two Ti–Me groups are nonequivalent, differing in nonbonded interactions. Thus it is reasonable to postulate that the catalytic species can exist in two isomeric states A and C in equilibrium. Monomer insertion in A is less stereoselective than in C and isomerization A $\rightleftarrows$ C (site switching) occurs many times during the growth of TPE–PP chains. In this mechanism, a catalyst site is conceptualized to switch back and forth between the two states as propagation proceeds. The resulting polymer is, in effect, a copolymer consisting of alternating blocks of stereoirregular/amorphous and stereoregular/crystallizable PP segments which conform to the propagation statistics corresponding to the two states. The structure of such a TPE–PP may be represented by $[(am\text{-PP})_\alpha(crys\text{-PP})_\beta]_n$. In this work ^{13}C-NMR is used to determine the structures and to test the two-state propagation hypothesis.

Compounds **1**,[11] **2**,[12] and MAO[13] were synthesized by published methods. Procedures for the purification of monomer and solvent and for propylene polymerization have been described previously.[14] A total of 27 μM of a metallocene compound and [MAO] at [Al]/[Ti] = 2000 was used for the polymerization. Polypropylene was precipitated from the reaction mixture by a large volume of acidic methanol. The filtrate was evaporated to dryness, washed with methanol, and combined with the precipitated polymer. ^{13}C-NMR spectra were measured at 101 MHz.[15] Table I summarizes the observed methyl and tacticity distributions for all the TPE–PP samples, which are the averages of three data sets. The intensities of the methyl pentads for the corresponding TPE–PP's produced by the two catalysts at the same T_p are in good agreement.[16] Thus, the two catalysts produce essentially the same polymers, indicating they have very similar or probably the same active species. This is to be expected because the facile alkylation of **1** by MAO produces the compound **2**.

The NMR spectra of polymers are often fitted with enantiomorphic-site[17] (E) or Bernoullian (B) statistics to elucidate the propagation mechanism.[18] Ewen[4] reported that the methyl pentad distributions of the polypropylenes made with Et[Ind]$_2$TiCl$_2$/MAO can be approximately fitted with a simple E stereochemical control model. The observed distributions for our TPE–PP were fitted with simple E and B statistics. The B model was obviously inadequate, as can be seen by the large mean deviations shown for the B rows in Table I. The fitting to the E model is reasonably satisfactory (compare the O and E rows in Table I).

Until recently, there has been no known analysis for consecutive (CS) two-state enantiomorphic-site stereochemical control models (E$_1$/E$_2$).[19] We have derived the reaction probability expressions[24] for the consecutive (CS) two-state models of E$_1$/E$_2$, E/B, and B$_1$/B$_2$. We have also obtained[25] the equations for the concurrent (CC) two-state models of E$_1$–E$_2$, E–B, and B$_1$–B$_2$. Computer programs have been written to automate the NMR analysis by both models.[24,25] The observed spectra were tested assuming that one of the switching states produces random monomer placements, i.e., $P_\mathrm{r} = P_\mathrm{m} = 0.5$. The probabilities for the E and the B states are the same in this special case. When this random state is coupled with an isotactic E-state to form the two-state models, they have approximately the same probabilities for both the concurrent and consecutive cases. The mean deviation values are virtually the same (CC and CS rows in Table I); they are all better than the mean deviations for the one-state E model, except for sample 1 (−20 °C), which seems to have larger errors. The parameters obtained from the analysis are summarized in Table II.

If we assume that the polymer structure consists of (*am*-PP) and (*crys*-PP) blocks, then the analysis indicates that the consecutive and the concurrent models fit the NMR data equally well. Further discrimination between these two models can be made by employing a computer simulation approach (program TADIS).[28] Using the same model parameters for the two models as given in Table II, we can simulate the tacticity *distribution* curves for sample 2 (25 °C). These are given in Figure 1.

According to the concurrent model, the catalyst system comprises two active sites, each site generating polymer chains independent of the other.[25] As expected, the tacticity distribution curve corresponding to this model (Figure 1) indicates the presence of two components. Such a copolymer would be separated into at least two fractions by solvent fractionation. It has been shown earlier[11c] that the actual TPE–PP samples obtained at $T_p \geq 25$ °C are homogeneous in their steric microstructures and that they are soluble in a single solvent, diethyl ether. Similarly, such a polymer would be expected to have a broad or bimodal molecular weight distribution. The actual TPE–PP's have $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} < 2$.[11c] Thus, the concurrent model is not compatible with the polymer properties of TPE–PP.

In contrast, the consecutive E$_1$/E$_2$ model gives a tacticity distribution curve that indicates a single homogeneous component (Figure 1). This model is preferred. It may

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Table I
^{13}C-NMR Methyl Pentad Distribution of TPE-PP and Computer Fitting to Statistical Models

			pentads (%)										
sample	catal. with MAO	T_p (°C)	mmmm	mmmr	rmmr	mmrr	mmrm rmrr	mrmr	rrrr	rrrm	mrrm	model[a]	mean dev
1 (−20 °C)	**1**	−20	21.3	16.7	5.2	16.9	14.1	8.4	3.9	7.5	5.9	O	
			21.3	16.2	3.8	16.2	15.3	7.7	3.8	7.7	8.1	E, P_l = 0.733	0.77
			21.3	20.1	4.7	9.5	24.6	9.5	1.1	4.5	4.7	B, P_m = 0.679	3.32
			21.4	15.7	3.9	15.7	15.7	7.8	3.9	7.8	7.9	CC	0.89
			21.3	15.8	3.9	15.7	15.9	7.8	3.9	7.9	7.8	CS	0.89
1 (0 °C)	**1**	0	27.8	15.6	3.2	16.2	12.2	6.5	3.6	6.9	7.9	O	
			27.8	16.6	3.1	16.6	12.2	6.1	3.1	6.1	8.3	E, P_l = 0.774	0.43
			27.8	21.0	3.9	7.9	23.9	7.9	0.6	3.0	3.9	B, P_m = 0.726	4.27
			27.8	15.9	3.3	15.9	13.0	6.5	3.3	6.5	7.9	CC	0.25
			27.8	16.0	3.2	15.8	13.1	6.5	3.2	6.5	7.9	CS	0.29
1 (25 °C)	**1**	25	35.2	16.2	2.7	16.5	9.1	4.4	2.8	5.1	8.0	O	
			35.2	16.6	2.3	16.6	9.4	4.7	2.3	4.7	8.3	E, P_l = 0.811	0.29
			35.2	21.0	3.1	6.3	22.9	6.3	0.3	1.9	3.1	B, P_m = 0.770	4.65
			35.2	16.3	2.4	16.3	9.6	4.8	2.4	4.8	8.1	CC	0.27
			35.2	16.3	2.4	16.2	9.8	4.8	2.4	4.8	8.1	CS	0.28
2 (−20 °C)	**2**	−20	22.4	14.6	4.3	16.3	15.2	7.4	5.5	7.0	7.3	O	
			22.4	16.3	3.7	16.3	14.8	7.4	3.7	7.4	8.1	E, P_l = 0.740	0.65
			22.4	20.3	4.6	9.2	24.5	9.2	1.0	4.2	4.6	B, P_m = 0.688	3.80
			22.3	15.8	3.8	15.8	15.2	7.6	3.8	7.6	7.9	CC	0.60
			22.4	16.0	3.8	15.9	15.2	7.5	3.7	7.5	7.9	CS	0.62
2 (0 °C)	**2**	0	30.3	15.7	3.6	15.7	11.2	6.3	3.6	6.2	7.4	O	
			30.3	16.7	2.8	16.7	11.2	5.6	2.8	5.6	8.7	E, P_l = 0.787	0.65
			30.3	21.1	3.7	7.3	23.6	7.3	0.4	2.5	3.7	B, P_m = 0.742	4.22
			30.3	15.7	3.0	15.7	12.2	6.1	3.0	6.1	7.9	CC	0.33
			30.3	15.7	3.1	15.5	12.5	6.1	3.0	6.2	7.7	CS	0.36
2 (25 °C)	**2**	25	38.3	15.5	3.2	16.1	8.5	3.8	2.5	4.6	7.4	O	
			38.3	16.4	2.1	16.4	8.3	4.2	2.1	4.2	8.2	E, P_l = 0.825	0.49
			38.3	20.8	2.8	5.6	22.3	5.6	0.2	1.5	2.8	B, P_m = 0.787	4.64
			38.3	15.8	2.2	15.8	8.9	4.4	2.2	4.4	7.9	CC	0.40
			38.3	15.7	2.3	15.6	9.1	4.5	2.2	4.5	7.8	CS	0.42

[a] O = observed; E = enantiomorphic-site model;[17,18] B = Bernoullian model;[17,18] CC = concurrent two-state E–E model;[24] CS = consecutive two-state E/e model.[24]

Table II
Results of Concurrent and Consecutive Two E State Model Fitting (Program EXCO Pentad[24])

	concurrent					consecutive				
sample	%	P_l[a]	%	P_l[b]	MD[d]	β	P_l[a]	α[c]	P_l[b]	MD[d]
1 (−20 °C)[e]	81	0.76	19	0.50	0.89	97	0.76	22	0.50	0.89
1 (0 °C)	81	0.80	19	0.50	0.25	120	0.80	27	0.50	0.29
1 (25 °C)	95	0.82	5	0.50	0.27	317	0.82	20	0.50	0.28
2 (−20 °C)	83	0.76	17	0.50	0.60	87	0.76	13	0.50	0.62
2 (0 °C)	80	0.82	20	0.50	0.33	107	0.82	30	0.50	0.36
2 (25 °C)	92	0.84	8	0.50	0.40	250	0.84	30	0.50	0.42

[a] First E state (more isotactic block). [b] Second E state (randon block, P_l set to 0.50). [c] Iteration of the random block size confined to values around 30. [d] Mean deviation. [e] Constraint imposed for a two-state model.

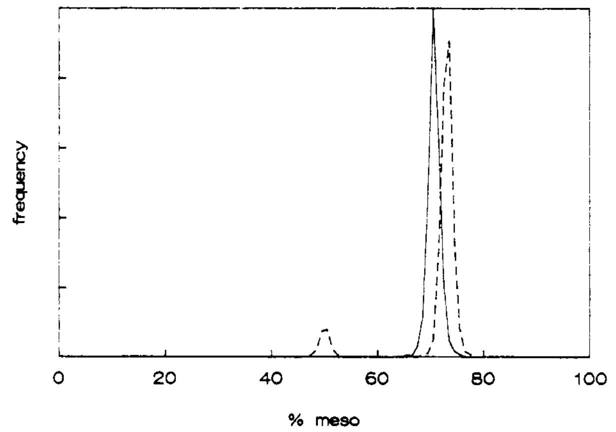

Figure 1. Calculated tacticity distribution curves for sample **2** (25 °C) in the case of consecutive E_1/E_2 (solid line) and concurrent E_1–E_2 models (dashed line).

be noted that in the model fitting procedure for the consecutive E_1/E_2 model the stereoregular and the stereoirregular block sizes (α and β in Table II) appear to be relatively insensitive. Large increases in the α and β values produce only minor changes in the mean deviation between calculated intensities. In all cases, however, $\beta > \alpha$. Furthermore, as α and β increase, the mean deviations decrease, albeit very slowly. The results given in Table II were obtained by adding the constraint $\alpha \leq 30$.

Earlier, using the equilibrium modulus, $\bar{M}_n$ by GPC, and the degree of crystallinity by X-ray,[11c] we had estimated the effective crystalline and amorphous block sizes (denoted by prime) to be $\alpha' \approx 50$, $\beta' \approx 20$, $n \approx 30$ for sample **1** (25 °C) and $\alpha' \approx 16$, $\beta' \approx 7$, $n \approx 100$ for sample **1** (0 °C). In other words, whereas the values of α in Table II are similar to α', $\beta \gg \beta'$. Previously, we have pointed out[11c] that the phase boundaries of the TPE consisting of a single monomer are diffuse. The *am*-PP segments render the immediate neighboring isotactic units not crystallizable. Even those isotactic units which were crystallized did so at very slow rates.[11] The fringe micelle model of Flory is probably a good description of the morphology of the TPE–PP. Furthermore, there are also present regioirregularities due to secondary and "1,3" misinsertions.[6b,26] Finally, for many of these polymer systems there are two kinds of stereochemical insertion errors, the rr and r types,[4] which conserve and invert the chain configurations, respectively. We have pointed out that the latter defect has a much greater depressing effect on crystallization, melting, morphological, mechanical, and chemical properties of polypropylene than the former.[6] Though several causes of the r diads had been suggested,[27] many more investigations are needed to identify the true origins.

In conclusion, the ^{13}C-NMR spectra of TPE–PP produced by the catalysts 1/MAO and 2/MAO have been analyzed by two-state stereochemical control models. If we assume that the polymer consists of amorphous and crystalline blocks, the tacticity and the tacticity distribution data favor the consecutive model. The NMR results indicate that only a fraction of the stereoregular segments were phase separated into the crystalline domains.

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(9) Polymerization quenched by tritiated methanol introduced radioactivities into polypropylene fractions, differing in stereoregularity and molecular weight. The active species, which produce the various fractions separated by solvent extraction, have very different rate constants of propagation and chain transfers as well as stereoselectivities.[7d]

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