Stereoregulation Energies in Propene Polymerization

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ABSTRACT: The stereoregulation energies for isotactic and syndiotactic polymerization of propene have been evaluated from the stereochemical dyad composition of the polymers. Comparison of the calculated energies suggests that the coordination of the monomer may be the stereospecific step in isotactic polymerization and the insertion of the monomer at the reactive metal–carbon bond may be the stereospecific step in syndiotactic polymerization.

Ideal propagation models for stereospecific polymerization of propene have been proposed in previous papers.[3-8] Isotactic polymerization seems to occur according to the "enantiomorphous sites" propagation model proposed by Shelden and co-workers[9] and is completely regiospecific (no head-to-head and tail-to-tail arranged units are detectable in the polymers) at least when heterogeneous, highly stereospecific catalyst systems are employed.[10] The structure of the polymers may deviate somewhat from that contemplated by the "enantiomorphic sites" propagation model because heterogeneous catalyst systems may include, in addition to the typical isotactic-specific catalytic centers, some nonisotactic-specific centers which give rise to a concurrent nonisotactic propagation process.[11] However, the importance of these deviations can be minimized by properly choosing the catalyst system.

Syndiotactic polymerization occurs essentially via secondary insertion of the monomer[12,13] at the reactive metal–carbon bond, but it is not wholly regiospecific. Both the monomer insertion (primary or secondary) and the monomeric unit configuration should be controlled by related first-order Markov propagation models.[8,14]

The difference $E_{DL} - E_{DD}$ between the activation energies for the formation of L and D placements at the D preferring sites in the "enantiomorphic sites" propagation process is the driving force for isotactic control. Let P_{DD} be the probability of formation of a D placement at a D preferring site and let P_{DL} be the probability of formation of an L placement at a D preferring site.[9] We then have:

$$\ln \frac{P_{DD}}{P_{DL}} = \ln \frac{a_{DD}}{a_{DL}} + \frac{E_{DL} - E_{DD}}{RT} \tag{1}$$

where T is the polymerization temperature and a_{DD} and a_{DL} are the Arrhenius preexponential coefficients. The ratio P_{DD}/P_{DL} can be related to the stereochemical structure of polymers obtained with a given isotactic-specific catalyst system once the stereospecific propagation model is known. For the formation of one syndiotactic dyad at a D preferring site one requires either one D placement followed by one L placement or one L placement followed by one D placement. Therefore the concentration of r dyads will be proportional to $P_{DD}P_{DL} + P_{DL}P_{DD}$ or $2P_{DL}P_{DD}$. The concentration of m dyads will be the sum of P_{DD}^2 (representing two successive D placements at D preferring sites) and P_{DL}^2 (representing two successive L replacements at D preferring sites). Therefore:

$$\frac{[m]}{[r]} = \frac{P_{DD}^2 + P_{DL}^2}{2P_{DL}P_{DD}} \simeq \frac{P_{DD}}{2P_{DL}}$$

since L placements at D preferring sites have a very low probability. We accordingly have

$$P_{DD}/P_{DL} \simeq 2[m]/[r] \tag{2}$$

Here, $[m]$ and $[r]$ are the mole fractions of isotactic and syndiotactic dyads, respectively. The relationship

$$\ln \frac{2[m]}{[r]} \simeq \frac{a_{DD}}{a_{DL}} + \frac{\Delta E_{(DL-DD)}}{RT} \tag{3}$$

allows one to evaluate the minimum value of $E_{DL} - E_{DD}$. Actually, $\Delta E_{(DL-DD)}$ equals $E_{DL} - E_{DD}$ for ideal isotactic-specific catalysts which have only isotactic-specific centers, while in general[16]

$$\Delta E_{DL-DD} \leq (E_{DL} - E_{DD})$$

With regard to syndiotactic polymerization it is known[8,13,17] that: (1) only propagation occurring via secondary insertion of the monomer is syndiotactic-specific; and (2) regiospecificity decreases with increase of the polymerization temperature.[14]

It may be shown that for polymers obtained with homogeneous, syndiotactic-specific catalyst systems:

$$\ln \frac{P_m}{P_r} \simeq \ln \frac{[m]}{[r]} \simeq \ln \frac{a_m}{a_r} + \frac{\Delta E_{r-m}}{RT} \tag{4}$$

where P_m is the probability of isotactic placement[18] (here <0.5), P_r is the probability of syndiotactic placement, a_m and a_r are the Arrhenius preexponential coefficients, and

$$\Delta E_{r-m} \leq (E_r - E_m)$$

where E_r and E_m are the activation energies for the formation of syndiotactic and isotactic dyads in the secondary insertion propagation process. $E_r - E_m$ is the driving force for the syndiotactic control. We should have $\Delta E_{r-m} = E_r - E_m$ for an ideal catalyst system which is completely regiospecific and strictly follows the symmetric Bernoullian chain propagation model suggested by Bovey and Tiers.[19] In that case

$$\frac{[m]}{[r]} = \frac{P_m}{P_r}; \qquad \ln \frac{[m]}{[r]} = \ln \frac{a_m}{a_r} + \frac{E_r - E_m}{RT}$$

Tables I and II show the stereochemical dyad composition of polymers prepared at different temperatures with typical isotactic and syndiotactic specific catalyst systems. For the highly isotactic-specific catalyst δ-$TiCl_3$–$Al(C_2H_5)_2I$[20] we calculate that

$$\Delta E_{DL-DD} = 4.8 \pm 0.5 \text{ kcal/mol}$$

For the syndiotactic-specific catalyst systems given in Table II[21] we find that

$$\Delta E_{r-m} = -2 \pm 0.4 \text{ kcal/mol}$$

The sign of ΔE shows the type of stereoregulation (+ for isotactic, − for syndiotactic) and the absolute values give an estimation of the driving forces of the steric control. The marked difference between the steric control energies for the two polymerizations is assumed to be a consequence of the fact that the syndiotactic propagation is essentially

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Table I
Stereochemical Composition of Isotactic Polypropylene Prepared at Different Temperatures[a,b]

run	T, K	time, h	polymer yield, g	boiling n-heptane insoluble fraction, %	r dyad composition[c]
1	288	24	8.57	98.5	0.005
2	329.5	7.2	7.63	98	0.007
3	349	5.7	13.49	94	0.021
4	358	4.5	5.44	92.5	0.019
5	372	3	24.51	76	0.060
6	388	2	5.51	75.5	0.045
7	403	1	2.51	64.5	0.044

[a] Polymerizations were carried out in 200 mL of solvent. Toluene (runs 1, 2, 3, 5) or n-octane (runs 4, 6, 7) was used. The propene mole fraction in solution was the same in all the runs (0.05) and was kept constant during the runs. [b] Catalytic system: 3.2×10^{-3} mol δ-$TiCl_3$ (12×10^{-3} mol in run 1), 7×10^{-3} mol $Al(C_2H_5)_2I$ (28×10^{-3} mol in run 1). [c] Values are expressed in mole fractions.

Table II
Stereochemical Dyad Composition of Syndiotactic Polypropylene Prepared at Different Temperatures[a,d]

run	V:anisole:Al molar ratio[b]	T, K	time, h	polymer yield, g	m dyad composition[c]
1	1:1:5	195	16	1.38	0.130
2	1:1:5	215	2	3.64	0.193
3	1:1:5	235	1.5	4.52	0.215
4	1:1:5	254.5	0.25	3.14	0.300
5	1:0:5	195	3	1.72	0.090
6	1:0:5	215	2	6.06	0.110
7	1:0:5	235	1	6.88	0.235
8	1:0:5	254.5	0.25	3.65	0.255

[a] Polymerizations were carried out in 100 mL of n-heptane in the presence of 14 g of C_3H_6 (24 g in run 5). [b] Catalytic systems: runs 1-4, 10^{-3} mol VCl_4, anisole, $Al(C_2H_5)_2Cl$; runs 5-8, 10^{-3} mol VCl_4, $Al(C_2H_5)_2Cl$. [c] Values are expressed in fractions. [d] The polymers contain 1-4% of $(CH_2)_2$ units expressed as g of $(CH_2)_2$/100 g of polymer.[26]

ruled by the asymmetric carbon of the last unit of the growing chain end, while the isotactic propagation is ruled by the asymmetric spatial arrangement of the ligands of the transition metal atoms of the isospecific-catalytic centers.[8,22]

The homogeneous syndiotactic-specific catalytic complexes may be less severely hindered than the isotactic-specific complexes. Therefore, in syndiotactic propagation coordination of the monomer should be stereospecific to a very limited extent if at all, and secondary insertion of the monomer should be possible. The secondary insertion step should be the stereospecific (syndiotactic-specific) step, as proposed previously.[12,17] On the more severely hindered heterogeneous isotactic-specific catalytic centers the coordination of the monomer on the transition metal atom should be the stereospecific step and only primary insertion should be possible.

It seems rather obvious that primary insertion entails smaller nonbonded interactions between the monomer methyl group and the transition metal ligands than secondary insertion does. It also seems reasonable to assume that interatomic distances between the methyl group of propene and the ligands of the transition metal of the catalytic center are smaller in coordination than in the primary insertion step and that, consequently, the difference in the nonbonded interaction for the presentation of either (chiral) face of the monomer to the (chiral) catalytic center reaches its maximum in the coordination step.

Experimental Section

Polymerization runs and purification of the reagents and of the polymers were performed as described in previous papers.[20,21] Reaction conditions and yields are given in the tables. Stereochemical triad analysis of the polymers was performed by ^{13}C NMR on polymers dissolved in 1,2,4-trichlorobenzene at 413 K;[23,24] the dyad ratio was derived from the triad analysis. A Bruker HX-90 spectrometer operating at 22.63 MHz in the FT mode was used.

In order to increase the sensitivity of the NMR analysis, isotactic polymers were subjected to exhaustive extraction with boiling n-heptane. The soluble and the insoluble fractions of each polymer were analyzed separately and the stereochemical analyses weight averaged. Only barely observable trace amounts of heterotactic triads where detected in all the insoluble fractions, which therefore were considered completely isotactic at all polymerization temperatures. This approximation leads one to underestimate $\Delta E_{(\mathrm{DL-DD})}$.

The presence of irregularly arranged units in syndiotactic polymers[8,25] was ignored in interpreting the ^{13}C NMR methyl spectra. The present paper includes the revision of ΔE_{r-m} found in ref 14.

References and Notes

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