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Polymerization of Propylene to Syndiotactic Polymer. VIII. Steric Control Forces

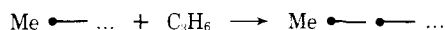
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ABSTRACT: The syndiotactic specific polymerization of propylene in the presence of homogeneous vanadium-based catalyst systems has been studied by ¹³C nmr as a four-step copolymerization between "head-to-tail" and "tail-to-head" propylene. The activation barriers responsible for the prevailing syndiotactic reaction pattern have been evaluated.

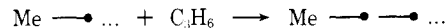
Propylene polymers obtained in the presence of vanadium-based syndiospecific catalyst systems contain a non-negligible proportion of monomer units arranged in head-to-head (—CH(CH₃)CH₂—CH₂—CH(CH₃)—) and tail-to-tail (—CH₂—CH(CH₃)CH(CH₃)—CH₂—) sequences.³ Preliminary data also seem to indicate that these polymer chains consist of long stereoblocks with a predominantly syndiotactic structure and of shorter stereoblocks with a sterically disordered structure.⁴

It has been suggested⁵ that syndiotactic stereoblocks are formed by addition of the monomer to a growing chain ending in a substituted carbon atom, i.e., by insertion of the monomer at a secondary metal-carbon bond.



(Here, Me, \bullet , — \bullet indicate respectively the metal atom of the catalytic complex and the monomer units in the orientation —CH(CH₃)CH₂— and —CH₂CH(CH₃)—.) Sterically

disordered stereoblocks should instead form by addition of the monomer to a growing chain ending in a methylene carbon, i.e., by insertion at a primary metal-carbon bond.



Consequently, the ends of each stereoblock should consist of one pair of head-to-head units (\bullet — \bullet) and of one pair of tail-to-tail (\bullet — \bullet) units.

On the basis of these hypotheses, we have attempted to measure the forces of steric and arrangement controls involved in the polymerization considered by comparing the structures of the polymers obtained at different temperatures.

Results

According to the previous hypotheses, propylene polymerization in the presence of vanadium-based syndiospecific catalysts may be represented as a particular type of co-

Table I
Syndiotactic Propylene Polymerizations with
 $\text{VCl}_4\text{--Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ Catalyst Systems^a

Run	Catalyst system	$T, ^\circ\text{K}$	$[\text{rrrr}]^b$	$[\text{rrmr}]^b$	$(\text{CH}_2)_2^c$ g/100 g polymer	I.S. ^d
a	$\text{VCl}_4\text{--Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	195	0.51	0.02	2.1	1.3
b	$\text{VCl}_4\text{--Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	215	0.44	0.04	2.4	0.4
c	$\text{VCl}_4\text{--Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	235	0.34	0.06	3.5	0.2
d	$\text{VCl}_4\text{--Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	254.5	0.33	0.06	3.9	0.3
e	$\text{VCl}_4\text{--Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ - anisole	215	0.40	0.25	2.8	0.9
f	$\text{VCl}_4\text{--Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ - anisole	235	0.34	0.04	3.3	1.6
g	$\text{VCl}_4\text{--Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ - anisole	254.5	0.24	0.08	4.4	0.1

^a Polymerizations were carried out in *n*-heptane (100 cm³) in the presence of C_3H_6 (14 g), VCl_4 (0.001 mol), $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (0.005 mol), and anisole (none or 0.003 mol). ^b Values are expressed in fractions. ^c $(\text{CH}_2)_2$ (g/100 g polymer) \times 1.5 = mole fraction of head-to-head units entering into the chain in step 2 or step 4 (Results). ^d I.S. = index of syndiotacticity, from infrared measurements.

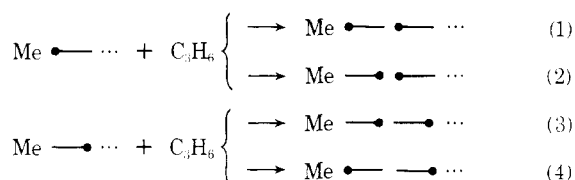
Table II
Comparison Among Activation Energies of
Possible Propagation Steps

i^a	j^a	$\Delta E_{(j-i)}^b$ kcal mol ⁻¹	A_i/A_j^c
1	1'	2.3	0.17
1	2	1.3	0.68
3	4	1.6	0.17

^a i, j = propagation steps numbered consistently with the copolymerization scheme shown in the Results section. ^b $\Delta E_{(j-i)}$ = difference in activation energies of steps j, i . ^c A_i/A_j = ratio of preexponential factors of steps i, j .

polymerization of head-to-tail oriented propylene (—●) with tail-to-head oriented propylene (●—).

The fundamental propagation steps should be



where (i) step 1 should be predominantly stereospecific in the syndiotactic sense, the addition of a new propylene unit almost always leading to the formation of syndiotactic dyads (*r*) and only now and then of isotactic dyads (*m*);⁶ (ii) step 3 should be nonstereospecific, yielding disordered sequences of *m* and *r* dyads in comparable amounts; (iii) steps 2 and 4 should be responsible for the switch from syndiotactic propagation to nonstereospecific propagation and for the opposite switch, respectively.

In order to determine the differences in activation energy barriers among the different steps, we prepared a series of polymers at varying temperatures in the presence of the catalyst systems $\text{VCl}_4\text{--}(\text{C}_2\text{H}_5)_2\text{Cl}$ and $\text{VCl}_4\text{--anisole--Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ in *n*-heptane. The content of *rrrr* and *rmrr* pentads was determined by ¹³C nmr and that of head-to-head units by infrared (Table I).

If, for the sake of simplicity, *rrrr* and *rmrr* pentads are assumed to form exclusively by step 1, and step 1 can give only *rrrr* or *rmrr* pentads (and of course *rrrm*, which we do

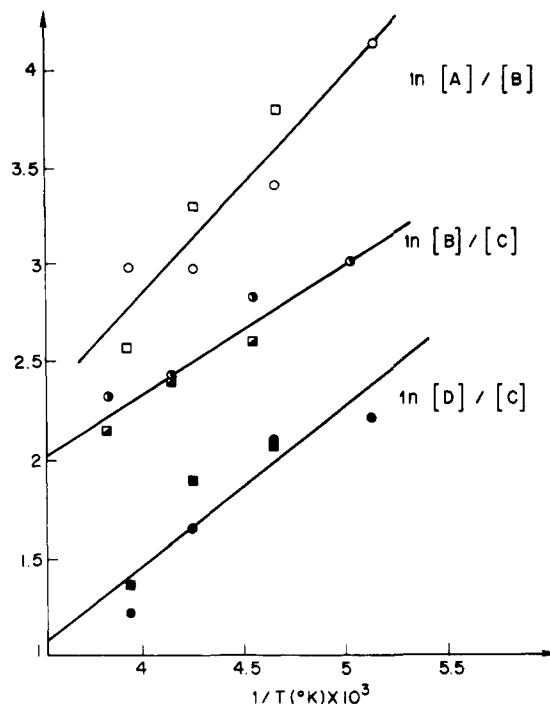


Figure 1. Arrhenius plots of $[\text{A}]/[\text{B}]$, \circ and \square ; $[\text{A}]/[\text{C}]$, \bullet and \blacksquare ; and $[\text{D}]/[\text{C}]$, \bullet and \blacksquare . The quantities are defined in the Results section. In each plot, the square marks represent the polymerizations with anisole and the round marks those without anisole.

not employ in this study), the fraction of units [A] that are added according to step 1, giving syndiotactic dyads, will be

$$[\text{A}] = [\text{rrrr}] + \frac{1}{2}[(\text{CH}_2)_2] + \frac{1}{2}[\text{rmrr}]$$

whereas the fraction of units [B] that are added according to step 1 to give isotactic dyads (step 1') will be

$$[\text{B}] = \frac{1}{2}[\text{rmrr}]$$

By taking into account the steady-state conditions⁷ of the concentrations of the different reactive chain ends, the fraction of units that are added by steps 2 and 4 is found to be

$$[\text{C}] = \frac{1}{2}[(\text{CH}_2)_2]$$

where $[(\text{CH}_2)_2]$ is the mole fraction of CH_2 lying in sequences of two methylenes and bound on both sides to $-\text{CHCH}_3-$ groups.

The fraction of units that are added in step 3 will be

$$[\text{D}] = 1 - [\text{rrrr}] - 2[\text{rmrr}] - \frac{1}{2}[(\text{CH}_2)_2]$$

Figure 1 shows Arrhenius plots giving the difference in activation barriers for the formation of *r* dyads (step 1) and *m* dyads (step 1') in step 1, for the difference in activation barriers between steps 1 and 2, and for the difference in activation barriers between steps 3 and 4. Table II shows the activation energy differences obtained and the ratios of preexponential factors.

Experimental Section

The samples were prepared as described previously.⁸ The reaction conditions and catalyst systems adopted are reported in Table I.

The index of syndiotacticity and the $(\text{CH}_2)_2$ content (sequences of two methylenes bound on both sides to CHCH_3 groups) were determined on each sample by ir analysis.^{3,8}

The contents of *rrrr* and *rmrr* pentads were determined by the ratios of the ¹³C methyl signals, assuming the assignments given in

a previous paper.⁴ Relative peak areas were determined using a Du Pont analog curve resolver. The samples were examined in 1,2,4-trichlorobenzene (10–15 wt %) at 130° using a Varian XL-100 spectrometer operating at 25 MHz in the F.T. mode. *d*₆-Dimethyl sulfoxide was used as external standard and lock.

Conclusion

The results of the comparison of activation barriers for the syndiotactic polymerization of propylene are shown in Table II and may be summarized as follows. (i) Syndiotactic propagation should be favored over isotactic propagation and over the formation of tail-to-tail units (—●●—) by differences in activation energy of 2.3 and 1.3 kcal/mol, respectively. Sterically disordered propagation should be favored over the formation of head-to-head units (●—●) by a difference in activation energy of 1.6 kcal/mol. (ii) Formation of tail-to-tail units should be the necessary step for the restoration of syndiotactic steric control. (iii) The activation energies of steric control and head-to-head *vs.* head-to-tail arrangement forces are comparable. Preexponential factors are likewise important for steric

control. (iv) The two catalyst systems employed, *i.e.*, with and without anisole, show essentially identical behavior. It may be noted that the interpretation of these experimental data is dependent on the hypotheses concerning chain growth outlined in the introductory section. These hypotheses are supported by previous studies^{3–5} and by paper IX of this series.⁹

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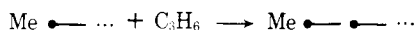
Polymerization of Propylene to Syndiotactic Polymer. IX. Ethylene Perturbation of Syndiotactic Propylene Polymerization

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ABSTRACT: The microstructure of ethylene-propylene copolymers, prepared in the presence of syndiospecific vanadium-based catalyst systems, has been examined by ¹³C nmr. The decrease in the fraction of *rrrr* methyl pentads when a propylene unit is replaced by an ethylene unit is interpreted with regard to the mechanism of steric and arrangement control previously proposed.

In a previous paper³ it was shown that the polymerization of propylene to syndiotactic polymer in the presence of homogeneous catalyst systems occurs mainly by *secondary* monomer insertion, that is, it gives rise to a growing chain ending in a substituted carbon



(Here —● and ●— mean —CH₂CH(CH₃)— and —CH(CH₃)CH₂— units, respectively; Me denotes the metal atom of the catalytic complex bonded to the growing chain end.) This conclusion was reached by consideration of the proportion of (CH₂)₂ sequences (*i.e.*, sequences of two methylenes bound on both sides to CHCH₃ groups³) in ethylene-propylene copolymers prepared with syndiotactic specific catalysts.

The aim of the present work is to determine whether such results are consistent with the perturbation of the steric pentads⁴ as detected by ¹³C nmr in such copolymers. The structure of a vinyl polymer chain can be described as a succession of steric *n*-ads⁴ provided that the monomer units are regularly arranged in head-to-tail fashion. Syndiotactic polypropylene, obtained in the presence of homogeneous vanadium-based catalysts, also contains head-to-head and tail-to-tail monomer units.³ A complete description of such chains, which probably consist of blocks of monomer units having different arrangements



is not possible in terms of steric *n*-ads only.

Clearly, the same considerations also apply to ethylene-propylene copolymers, making a detailed description of such chains rather complex. However, it is possible to compare the steric composition of such macromolecules by describing them in terms of blocks of equivalent, regularly arranged monomer units.

Results and Conclusions

We have determined the proportion of *rrrr* pentads⁵ by measurements in the methyl region of the ¹³C nmr spectra of a series of ethylene-propylene copolymers prepared using the syndiospecific catalyst VCl₄-Al(C₂H₅)₂Cl and ranging in composition between 0 and 12 mol % ethylene (Table I). These measurements are based on the assumption that the resonance at 172.5₉ ppm (from ¹³CS₂)⁶ is always exclusively due to the methyl groups of *rrrr* pentads. Table I also shows the proportion of (CH₂)₂ sequences as detected by infrared analysis.³ Such (CH₂)₂ sequences originate partly from ethylene units (—) in the arrangement —●—●— and partly from propylene units in a head-to-head arrangement (●—●). Part of the ethylene of such copolymers also gives rise to (CH₂)₃ sequences (●—●— or —●—●—), while longer sequences of methylenes are negligible due to the composition of the copolymers considered here. Table II gives the estimated proportion³ of ethylene in the structures we are considering.

Because of the stereoblock structure of the syndiotactic propylene homopolymers, one could in principle distinguish a syndiotactic propagation process and a stereoirreg-