Microstructure of Isotactic Polypropylene Prepared with Homogeneous Catalysis: Stereoregularity, Regioregularity, and 1,3-Insertion

Alfonso Grassi and Adolfo Zambelli*

Dipartimento di Fisica, Università di Salerno, 84100 Salerno, Italy

Luigi Resconi, Enrico Albizzati, and Romano Mazzocchi

Istituto G. Donegani, 28100 Novara, Italy. *Received July 2, 1987*

ABSTRACT: Regioirregularly arranged units have been observed by ^{13}C NMR analysis of isotactic polypropylene prepared in the presence of either racemic ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dichlorozirconium or racemic ethylenebis(indenyl)dichlorozirconium and methylalumoxane. However, the stereochemical placement of the regioirregular units is controlled by the catalyst so that one can speak of more or less stereoregular placement of regioirregular units. The η^5 ligands of zirconium affect the stereochemical and regiochemical structure of the polymer. 1,3-Propene insertion has also been observed at a relatively high polymerization temperature.

1. Introduction

As reported in the literature, isotactic polymerization of propene can be achieved in the presence of both heterogeneous[1,2] and homogeneous catalytic systems.[3,4] However, it is worth pointing out that the details of the microstructure of the resulting polymers depend on the particular catalytic system used for promoting polymerization as well as on the reaction conditions. In every case the insertion of the monomer on the metal-carbon bond of the active site is exclusively or predominantly primary.[5-7] In this paper we are reporting the results of a comparative investigation, by ^{13}C NMR analysis, of the stereochemical structure of a number of samples of isotactic polypropylene prepared with homogeneous catalytic systems under different reaction conditions. For comparison we also discuss the spectra of highly isotactic polypropylene prepared with a heterogeneous catalytic system and of syndiotactic polypropylene.[8]

2. Experimental Section

All the operations and manipulations were carried out under dry nitrogen atmosphere.

Toluene (Carlo Erba) was purified by refluxing over $Al(i\text{-}C_4H_9)_3$ and subsequent distillation under nitrogen. Propene was polymerization grade, used without further purification. Racemic ethylenebis(indenyl)dichlorozirconium, racemic ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dichlorozirconium, and methylalumoxane were prepared according to the literature.[9,10] The purity of the zirconocenes was checked by ^1H NMR before using.

GPC data were obtained from a Waters 150C ALC-GPC in ODCB at 135 °C. Melting points were measured on a Perkin-Elmer DSC 7 calorimeter with a temperature rate of 20 °C/min on previously melted and recrystallized samples.

The NMR samples were prepared by dissolving ca. 100 mg of polymer in 0.8 mL of tetrachloro-1,2-dideuterioethane in a 5-mm-o.d. tube. Hexamethyldisiloxane (HMDS) was used as an internal chemical shift reference. All the spectra were obtained by using a Bruker AM-250 spectrometer operating at 62.89 MHz in FT mode at a temperature of 393 K; pulse width = 65°, acquisition time = 2.7 s without relaxation delay, and BB decoupling were used.

Polymerization experiments were run in a 300-mL glass autoclave equipped with thermocouple and mechanical stirrer. Samples A-C were prepared according to ref 2, 3, and 8. Samples D-F were prepared as follows. For sample D, methylalumoxane (350 mg) and *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dichlorozirconium (5 mg) were dissolved in toluene (150 mL). The solution was charged into the autoclave thermostated at 0 °C, freed from N_2, and charged with 4 atm of propene. The polymerization was run at 0 °C for 5 h. The polymer was coagulated with CH_3OH/HCl, washed with CH_3OH, and dried, yield 30.5 g. The raw polymer was then extracted in Kumagawa extractor with boiling *n*-heptane for 24 h, the insoluble residue was 70.2%. Sample E was prepared in the same manner as sample D, except that 300 mg of methylalumoxane, 1.6 mg of *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dichlorozirconium, and 250 mL of toluene were used. The polymerization was run at 25 °C for 2 h, monomer pressure 1 atm, yield 6 g. Sample F was prepared in the same manner as sample D, except that 150 mg of methylalumoxane, 0.6 mg of *rac*-ethylenebis(indenyl)dichlorozirconium, and 150 mL of toluene were used. The polymerization was run at 0 °C for 4 h, monomer pressure 4 atm, yield 2.5 g.

The most important data concerning the heptane-insoluble fractions of samples A and D and the raw polymers of samples E and F are summarized in Table II.

3. Results and Discussion

3.1. Isotactic Polypropylene Prepared in the Presence of Heterogeneous Catalytic Systems and Syndiotactic Polypropylene.

As mentioned in section 1, the ^{13}C NMR spectra of these polymers are reported just for comparison. In fact, their structures have already been investigated in a number of previous papers.[11-13] The spectrum of the isotactic sample A, reported in Figure 1a, is quite simple. The only observed resonances are those of methyl carbons (*mmmm* pentad[14] at 19.7_1 ppm, *mmmr* at 19.4_4 ppm, *mmrm* + *rmrr* at 18.7_1 ppm, *mmrr* at 18.9_1 ppm, *rrrr* at 18.1_5 ppm, *mrrm* at 17.7_1 ppm),[11,15] of methine carbons at 26.5 ppm, and of methylene carbons at 44.3 ppm. The relative intensities of the resonance of the *mmmr*, *mmrr*, and *mrrm* stereochemical pentads are roughly 2:2:1 (see also Figure 3a), as expected from the statistical model[16] of the "enantiomorphic sites" of the stereospecific propagation.[12] The spectrum of the syndiotactic sample B is reported in Figure 1b. The main resonances observed in the region of the methyl stereochemical pentads are *rrmr* at 18.7_1 ppm, *rrrr* at 18.1_7 ppm, and *rrrm* at 18.0_5 ppm.[11] In agreement with the Bernoullian model of the stereospecific propagation proposed by Bovey,[17] the intensity ratio *rrrm*:*rrmr* is equal to 1. The resonances of the methylene stereochemical hexads[18,19] are observed between 46 and 43 ppm (the main resonance due to the *rrrrr* hexad is centered at 45.0 ppm) and the main methine resonance at 26.2 ppm. The additional less intense and broad resonances observed in the spectrum have been assigned in previous papers[20,21] to the arrangements shown in Chart I. These resonances are due to the vicinal erythro and threo methyl carbons and to the vicinal me-

---

* Author to whom correspondence should be addressed.

0024-9297/88/2221-0617$01.50/0

Chart I
Fischer Projection of Vicinal Erythro and Threo Methyls (a and b) and Adjacent Methylenes (c) Bridging Primary and Secondary Blocks in Polypropylene

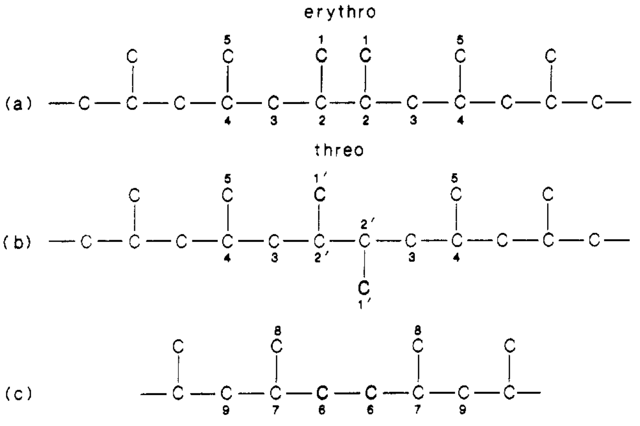


Table I
Chemical Shift of the Carbons Diagnostic of the Arrangement Shown in Chart I

carbon[a]	shift, ppm[b]	designation
1	15.6–14.4	P α,β erythro
1′	13.6–12.4	P α,β threo
2 + 6 + 2′	34.7–32.2	T α,β + S $\gamma,\alpha,\beta,\delta$
3	42.4–40.4	S $\gamma,\alpha,\alpha,\beta$
7	28.9	T β,γ
9	40.4–38.2	S $\gamma,\alpha,\alpha,\delta$

[a] C_4, C_5, and C_8 overlap with the main methylene and methyl resonances. [b] Downfield from HMDS = 0.

thylenes arising from regioirregularly arranged monomer units. The chemical shifts of the diagnostic carbons, labeled according to the Chart I, are reported in Table I (see also discussion in section 3.2). The assignments of Table I are in agreement with the intensities of the observed resonances. For instance, the number of vicinally methyl-substituted carbons ...$CH(CH_3)$–$CH(CH_3)$... and the number of methylene pairs ...$CH(CH_3)CH_2$–$CH_2CH(CH_3)$... must be equal to each other, and in fact, the area of the resonances due to C_1 and C_1', spread between 15.6 and 12.4 ppm, is approximately one-half of the area of the resonances spread between 35 and 32 ppm, which are due to both C_6 and C_2.

3.2. Isotactic Polypropylene Prepared with Homogeneous Catalytic Systems. Isotactic polypropylene can be obtained in the presence of several homogeneous catalytic systems consisting of group IV metallocenes and methylalumoxane.[3,4] The statistical model of the stereospecific polyinsertion may be either that of the "enantiomorphic sites" or Bernoullian depending on the metallocene.[3,6,7] In Figure 1c is reported the spectrum of polypropylene sample C obtained at −60 °C in the presence of dicyclopentadienyldiphenyltitanium and methylalumoxane. The resonances observed for the methyl, methylene, and methine carbons are those expected for an almost completely regioregular polymer, although with many stereoirregularities.

As reported in previous papers[3,6] the relative intensities of the stereochemical methyl pentads *mmmr* and *mmrm* (1:1) are those expected for the Bernoullian statistical model.[17] The main methylene and methine resonances occur at 44.2_7 ppm and at 26.6_0 ppm, respectively. Three more samples have been prepared in the presence of racemic ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dichlorozirconium and methylalumoxane at different reaction temperatures, i.e., 0 °C (sample D) and 25 °C (sample E), and in the presence of ethylenebis(indenyl)dichlorozirconium at 0 °C (sample F).

Table II
Most Relevant Data of Samples A, D, E, and F

sample	M_w[a]	M_w/M_n	T_m[b]	*mmmm*[c]	vicinal CH_3[d,e]
A[f]	218 000	5.4	163.9	95%	absent
D[f]	159 000	2.8	147.0	95%	1%
E[g]	6 300	1.8	125.0	75%	absent (h)
F[g]	33 900	4.7	136.8	83%	1%

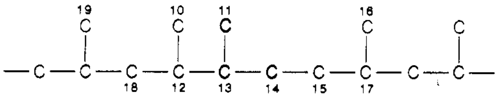
[a] Weight-average molecular weight. [b] Melting point, °C. [c] Area of the resonance of the methyl *mmmm* stereochemical pentad (percent with respect to the total area of the methyl resonance). [d] Area of the resonance of the vicinal methyls (percent with respect to the total area of the methyl resonances). [e] e = erythro, t = threo. [f] Heptane insoluble fraction. [g] Raw polymer. [h] See Table III.

Table III
Chemical Shifts of the Carbons Diagnostic of the 2,1 Units in Samples D and F,[a] of the Four Methylenes Sequences, and of the End Groups in Sample E[b]

				shift, ppm	
sample	carbon	design	mult[22]	measd	lit.[c]
D	10	P α,β	q	15.4_6	15.5_4
	11	P α,γ	q	15.1_2	15.0_8
	12	T α,β	d	33.6_8	33.7
	13	T α,γ	d	36.3_5	36.7
	14	S $\beta,\alpha,\beta,\delta$	t	28.3_8	29–29.9
	15	S $\gamma,\alpha,\beta,\gamma$	t	33.7_8	32.9–32.6
	16	P β,γ		not resolved	19.0_1
	17	T β,γ	d	29.3_3	29.2
	18	S $\beta,\alpha,\alpha,\gamma$	t	40.1_1	41.2–40.1
	19	P β,β		19.5_8	19.5_8
E	20	S β,γ	t	25.3_6	25.2
	21	S α,δ	t	35.1_6	35.4
	22	T $\beta,\gamma+$	d	28.7_3	28.8
	23	P $\beta,\gamma+$		18.7_7	18.8
	24		t	109.3_7	109.8
	25		s	142.6_5	142.6
	26			20.4_0	20.5_0[d]
	27			18.7_1	18.0_9
	28		d	28.3_3	28.7_5
	29		t	37.5_1	38.89
	30		t	17.9_9	18.4_5
	31		q	12.3_8	12.3_7

[a] Carbons labeled according to Charts II and V. [b] Carbons labeled according to Chart IV, part a, and Chart VI. [c] The experimental chemical shifts are compared with those reported in the literature[20,21,26–29] for the different carbons. [d] This chemical shift is tentatively assigned according to spectrum no. 482 of the Bruker ^{13}C data bank.

Chart II
Isolated 2,1 Unit with Erythro Adjacent Methyls (Bold Letters) in a Fischer Projection Inside the Polymer Chain



Sample D was fractionated by exhaustive extraction with boiling *n*-heptane. Both fractions were analyzed by ^{13}C NMR and are predominantly isotactic. The ^{13}C NMR spectrum of the heptane-insoluble fraction of sample D is reported in Figure 2b.

From the intensity of the resonance of the *mmmm* methyl pentads (see Table II) it can be observed that the fraction is highly isotactic. In this spectrum one can also distinctly observe a group of very sharp resonances having approximately the same intensity at the following chemical shifts downfield to hexamethyldisiloxane: 15.1_2 (q); 15.4_6 (q); 28.3_8 (t); 29.3_3 (d); 33.6_8 (d); 33.7_8 (t); 36.3_5 (d); 40.1_1 ppm (t).[22] These resonances are in agreement with the

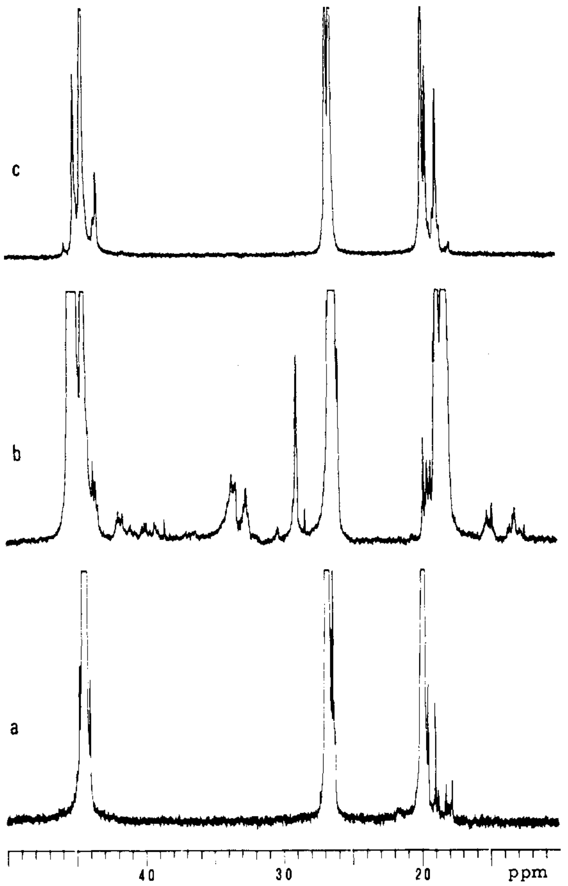


Figure 1. ^{13}C NMR spectra of samples A (a), B (b), and C (c). The main resonances are overexpanded in order to be able to observe the resonances of the regioirregularly arranged units; HMDS scale.

presence of isolated regioirregular monomer units.

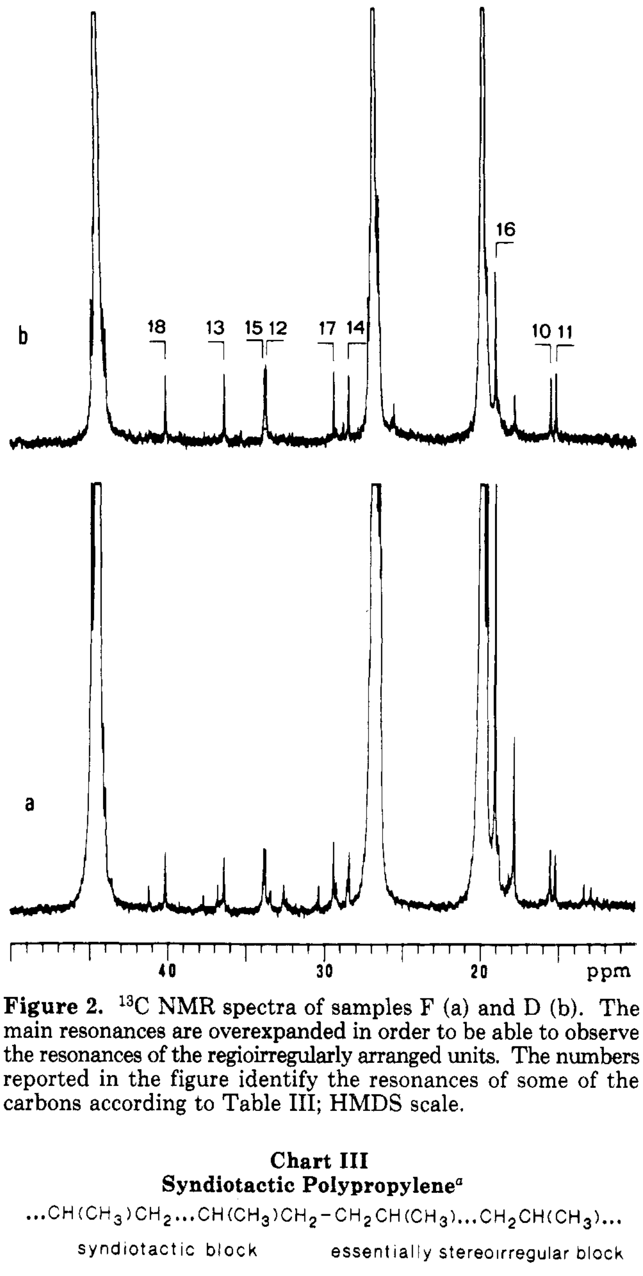


Figure 2. ^{13}C NMR spectra of samples F (a) and D (b). The main resonances are overexpanded in order to be able to observe the resonances of the regioirregularly arranged units. The numbers reported in the figure identify the resonances of some of the carbons according to Table III; HMDS scale.

Chart III
Syndiotactic Polypropylene[a]

$$...CH(CH_3)CH_2...CH(CH_3)CH_2-CH_2CH(CH_3)...CH_2CH(CH_3)...$$

syndiotactic block essentially stereoirregular block

[a] Blocks of different regioregularity also have different stereoregularity.

Table III compares the experimental chemical shifts with those observed in the spectra reported in the literature of suitable model compounds[20,21] for the corresponding carbons of the sequence reported in Chart II. Concerning the experimental chemical shifts, it is also worth observing that they not only agree with those anticipated by the rules of Grant and Paul[23] but for some carbons, i.e., C_{10}, C_{11}, C_{14}, C_{15}, C_{16}, C_{19}, they almost coincides with those measured on model compounds of known steric structure.[20,21] Since these chemical shifts are sensitive to the stereochemical environment, this fact suggests that the regioirregularly arranged units are located in a stereoregular environment, the one shown in Chart II by a Fisher projection. The chemical shift of C_{16} in the stereochemical arrangement shown in the Fischer projection in Chart II almost coincides with the chemical shift of the *mmrr* methyl stereochemical pentad. This fact explains the unusual features of the spectrum in the region 17.7–20.0 ppm (see Figure 3). In fact, previous investigations of the stereochemical structure of the end groups of polymers prepared with very similar catalytic systems[7] as well as the ^{13}C NMR spectrum of a copolymer of propene with a small amount of 1-^{13}C enriched ethylene, which we will report in a future paper, show that the stereospecific chain propagation is controlled by the chiral structure of the catalytic complexes. This type of steric control requires that the stereochemical sequence of the configurations of the substituted carbons must be in agreement with the statistical model of the "enantiomorphic sites" proposed by Shelden.[16] In particular, for highly stereoregular isotactic polymers, the ratio between the areas of the resonances of the *mmmr*, *mmrr*, and *mrrm* stereochemical pentads must be 2:2:1. On the other hand the ratio between the areas of the resonances observed at 19.0_1 and 17.7_5 ppm in the spectrum of sample D (Figure 3b) is roughly 4:1. In addition two sharp resonances of small intensity and not completely resolved are observed at 19.5 and 19.6 ppm. This apparent deviation can be easily explained by considering the overlap of the resonance of the *mmrr* pentad with that of C_{16} of Chart II. The stereoregular arrangement of the regioirregular monomer units can be indirectly confirmed by observing the spectrum of syndiotactic polypropylene, prepared with soluble vanadium catalysts (sample B), reported in Figure 1b. In fact, according to the literature,[21] this polymer consists of blocks of monomer units having different regiochemical arrangement (see Chart III). The longer blocks are syndiotactic and arise from secondary insertion of the monomer on the vanadium–secondary carbon bond of the active sites. The shorter blocks are essentially stereoirregular and arise from primary insertion of the monomer on the vanadium–primary carbon bonds of the active sites.[24] Pairs of methine carbons and pairs of methylene carbons alternately bridge the different blocks.

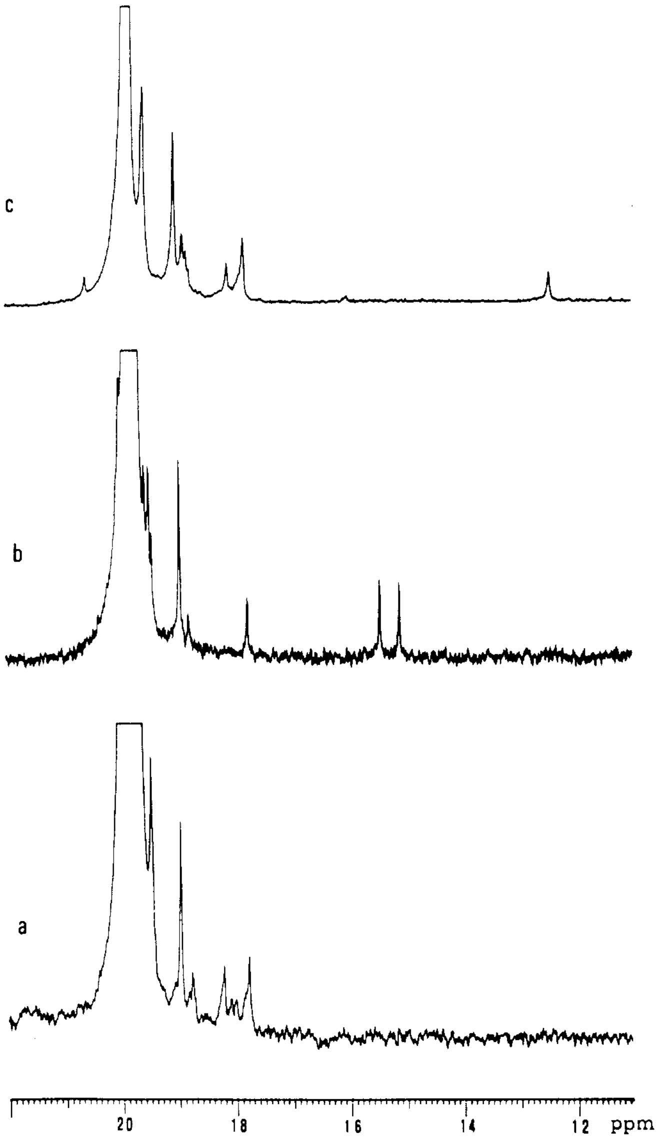


Figure 3. ^{13}C NMR spectra of the methyl region of samples A (a), D (b), and E (c); HMDS scale.

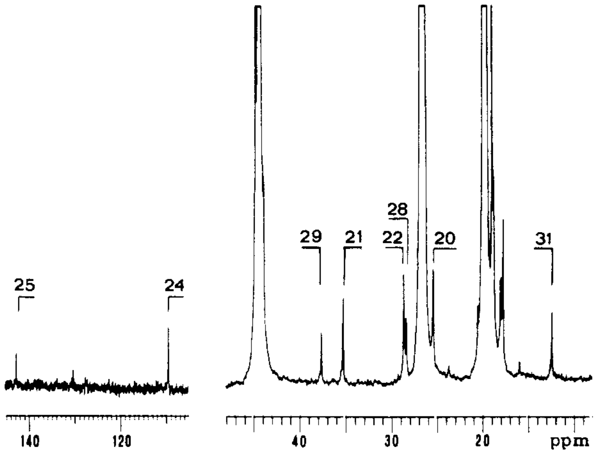
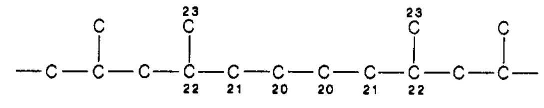
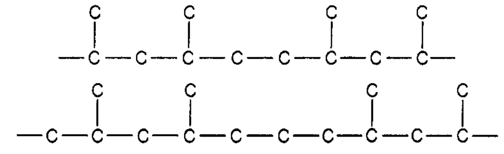


Figure 4. ^{13}C NMR spectrum of sample E. The main resonances are overexpanded in order to be able to observe the resonances diagnostic of the regioirregularly arranged units and end groups. The numbers reported in the figure identify the resonances of some of the carbons according to Table III; HMDS scale.

Chart IV



four-methylene sequence



two- and three-methylene sequences

Due to the fact that steric control arises from the asymmetric carbon of the monomer unit last inserted,[24] the environment of the regioirregularly arranged units is more or less stereoirregular. The spectrum reported in Figure 1b is in agreement with previous consideration. In fact, (i) in the spectrum of Figure 1b the resonances of the vicinal methyls, those of the bridge methylene pairs, and those of the bridge methine pairs are spread between 12–15 ppm and 32–35 ppm because of the stereoirregular environment;[21,25] (ii) one broad resonance is distinctly observed at 29 ppm for the methine linked by methylene pairs;[21] (iii) the other resonances detected in the spectrum of sample D (Figure 2b) around 28.5, 36.3, and 40.1 ppm are very weak in the spectrum of sample B; and (iv) other resonances that could be anticipated for the structure of the polymer by means of the rules of Grant and Paul[23] overlap with the resonances of the carbons of monomer units inside the regioregular blocks.

In Figure 4 is reported the spectrum of sample E prepared with *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dichlorozirconium and methylalumoxane at 25 °C. The main resonance of the methyl carbons is still that of the *mmmm* stereochemical pentad. Surprisingly the resonances observed in the spectrum of Figure 2b for the regioirregularly arranged units are not detectable. In addition, low-intensity resonances can be observed at 37.5_1 (t), 28.3_3 (d), 18.7_1, 17.9_9, and 12.3_8 ppm (q) in the region of the saturated carbons and at 142.6_5 (s) and 109.3_7 ppm (t)[22] in the region of the unsaturated carbons. The resonances at 37.5_1, 28.3_3, 18.7_1, 17.9_9, and 12.3_8 ppm can be attributed to the presence of *n*-propyl end groups, and those in the region of the unsaturated carbons, plus the resonance at 20.4_0 ppm, can be attributed to the presence of vinylidene end groups (as reported in Table III, carbons labeled according to Chart VI) simply by comparison with previous assignments reported in the literature.[26,27]

This fact is diagnostic of chain transfer via β-hydrido abstraction and of chain reinitiation on metal–hydrogen bond according to the reaction scheme

$$M{-}CH_2CH(CH_3)CH_2... \rightarrow M{-}H + CH_2{=}C(CH_3)CH_2...$$

$$M{-}H + CH_2{=}CHCH_3 \rightarrow M{-}CH_2CH_2CH_3$$

The presence of vinylidene end groups is confirmed by the fact that the resonances at 142.6_5, 109.3_7, and 20.4_0 ppm are no more observed in the spectrum of sample E after hydrogenation, being substituted by the resonances at 20.5_0 and 21.7_6 ppm diagnostic of isobutyl end groups. However, the most interesting feature of the spectrum is the presence of four resonances of equal intensity at 35.1_6 (t), 28.7_3 (d), 25.3_6 (t), and 18.7_7 ppm.[22,28] The multiplicity of these peaks in the off-resonance spectrum and comparison of the observed chemical shifts with the rules of Grant and Paul unequivocally suggest that they are due to sequences of four methylene carbons bridging methine carbons as shown in Chart IV, part a. It is important to stress that in the spectrum of sample E the resonances that could be expected for sequences of either two or three methylenes

Chart V
Isolated 2,1 Unit with Threo Adjacent Methyls (Bold Letters) in a Fischer Projection

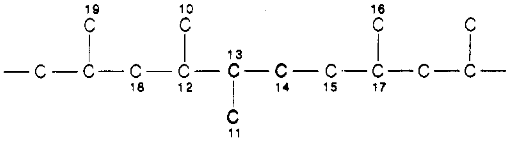
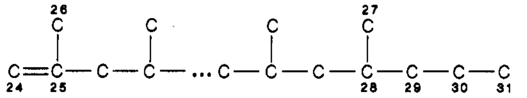


Chart VI
End Groups of Sample E



bridging methine carbons[21] (Chart IV, part b) are completely absent. For this reason one can easily convince himself that the sequences of four methylenes cannot arise from incorporation of two ethylene units between tail-to-tail propene units. In fact, in this case at least the sequence of two methylenes should be necessarily present. As a consequence the only explanation for the sequence of four methylenes is 1,3-propene insertion. 1,3-Propene insertion has been previously observed in the polymerization of propene with $Pd(CN)_2$.[29]

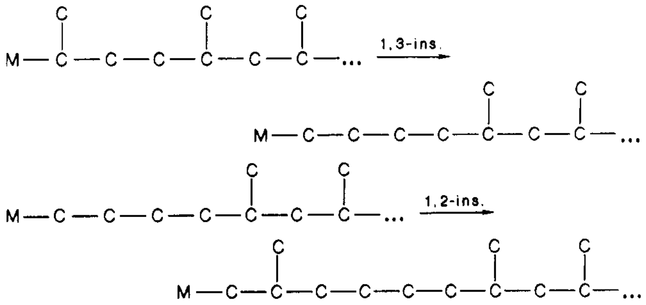
The spectrum of sample F reported in Figure 2a looks similar to that of sample D (Figure 2b). The polymer is highly isotactic and the resonances diagnostic of isolated regioirregular units are still observed. However, all the resonances diagnostic of the regioirregularly arranged units (see Chart II) are accompanied by resonances of lower intensity diagnostic of the threo arrangement between the vicinal methyls (see Chart V). This arrangement agrees with the data reported in the literature already quoted in this paper.[20]

This fact indicates that the bis(indenyl)ethane ligands are less effective than the bis(4,5,6,7-tetrahydro-1-indenyl)ethane lingands in controlling either the stereochemistry of the (secondary) insertion of a regioirregular monomer unit or the (primary) insertion of a regioregular unit occurring on a metal–secondary carbon bond.

4. Conclusions

As reported in previous paper two different mechanism of isotactic steric control may occur during propene polymerization in the presence of homogeneous catalytic systems based on group IV metallocenes.[3,4] In the presence of achiral titanocenes the steric control can come from the asymmetric carbon of the last inserted unit of a growing chain.[3,6] In the presence of chiral zirconocenes or titanocenes the steric control arises from the chiral ligand environment of the metal atom of the catalytic complexes.[3,7] The same mechanism has been demonstrated for polymerization promoted by heterogeneous catalytic systems.[5] The stereospecificity of the homogeneous catalysts based on chiral zirconocenes is quite comparable with that of the best heterogeneous catalysts. However, the monomer insertion is less regiospecific. It is also worth noting that the isotactic specific catalysts based on achiral titanocenes are less stereospecific but more regiospecific than those based on chiral zirconocenes (see also ref 31). The regioirregular (secondary) insertions occur occasionally and may undergo steric control or not depending on the particular chiral metallocene catalyst.

Secondary insertion may be followed either by a primary insertion, which leads to vicinal methyls, or by isomerization of the secondary inserted unit, resulting into 1,3-insertion of the monomer, as shown in the scheme



Isomerization is favored by higher polymerization temperature.

Finally, the observation of vinylidene and n-propyl end groups in equal amount shows that the main chain transfer process involves β-hydrogen abstraction from a regioregular monomer unit followed by initiation of a new polymer chain on a metal hydrogen bond via primary insertion. Further work is in progress in order to confirm the anomalous 1,3-propene insertion.

Note. After this paper was finished, 1,3-insertion of propene in the presence of ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dichlorozirconium and methylalumoxane was reported in the literature.[32]

Acknowledgment. We thank Prof. U. Giannini for stimulating discussion and Dr. G. Giunchi for GPC and DSC measurements. Financial support by the Ministero della Pubblica Istruzione and Italian CNR is gratefully acknowledged.

Registry No. Isotactic polypropylene, 25085-53-4; ±-ethylenebis(tetrahydroindenyl)dichlorozirconium, 100163-29-9; (±)-ethylenediindenyldichlorozirconium, 100080-82-8; propene, 115-07-1.

References and Notes

(1) Natta, G.; Pino, P.; Mazzanti, G. Ital. Pat. 526 101, 1954, to Montecatini.
(2) Giannini, U.; Cassata, A.; Longi, P.; Mazzocchi, R. Belg. Pat. 785332, 1972, to Montedison.
(3) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.
(4) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507.
(5) Zambelli, A.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1982**, *15*, 211.
(6) Zambelli, A.; Ammendola, P.; Grassi, A.; Longo, P.; Proto, A. *Macromolecules* **1986**, *19*, 2703.
(7) Longo, P.; Grassi, A.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1987**, *20*, 1015.
(8) Natta, G.; Pasquon, I.; Zambelli, A. *J. Am. Chem. Soc.* **1962**, *84*, 1488.
(9) Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63.
(10) Kaminsky, W.; Hähnsen, H. U. S. Pat. 4 544 762, 1985.
(11) Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules* **1975**, *8*, 687.
(12) Wolfsgruber, C.; Zannoni, G.; Rigamonti, E.; Zambelli, A. *Makromol. Chem.* **1975**, *176*, 2765.
(13) Asakura, T.; Nishiyama, Y.; Doi, Y. *Macromolecules* **1987**, *20*, 616.
(14) The stereochemical sequences are named according to the *m* (meso) and *r* (racemic) system: Frisch, H. L.; Mallows, C. L.; Bovey, F. A. *J. Chem. Phys.* **1966**, *45*, 1565.
(15) The chemical shifts observed for the methyl carbons are somewhat different from those reported in the literature because of the different temperature and solvent.
(16) Shelden, R. A.; Fueno, T.; Tsunetsugu, T.; Furokawa, J. *J. Polym. Sci., Part B* **1965**, *3*, 23.
(17) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.
(18) Zambelli, A.; Locatelli, P.; Provasoli, A.; Ferro, D. R. *Macromolecules* **1980**, *13*, 267.
(19) Cheng, H. N.; Lee, G. H. *Macromolecules* **1987**, *20*, 436.
(20) Zambelli, A.; Gatti, G. *Macromolecules* **1978**, *11*, 1485.
(21) Zambelli, A.; Bajo, G.; Rigamonti, E. *Makromol. Chem.* **1978**, *179*, 1249.

(22) s, d, t, and q stand for singlet, doublet, triplet, and quarted denoting the multiplicity of the peaks in the off-resonance spectrum.
(23) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984.
(24) Zambelli, A.; Tosi. G. *Adv. Polym. Sci.* **1974**, *15*, 32.
(25) Zambelli, A.; Locatelli, P.; Rigamonti, E. *Macromolecules* **1979**, *12*, 156.
(26) Zambelli, A.; Locatelli, P.; Bajo, G. *Macromolecules* **1979**, *12*, 154.
(27) Cheng, H. N.; Smith, D. A. *Macromolecules* **1986**, *19*, 2065.
(28) Ammendola, P.; Zambelli, A.; Oliva, L.; Tancredi, T. *Makromol. Chem.* **1986**, *187*, 1175.
(29) Ketley, A. D.; Braatz, J. A. *Polym. Lett.* **1968**, *6*, 341.
(30) Doi, Y. *Macromolecules* **1979**, *2*, 218.
(31) Zambelli, A.; Longo, P.; Ammendola, P.; Grassi, A. *Gazz. Chim. Ital.* **1986**, *116*, 731.
(32) Soga, K.; Shiono, T.; Takemura, S.; Kaminsky, W. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 305.

Crystal Structure of Isotactic *trans*-1,4-Poly(1,3-pentadiene). An Analysis by Conformational and Packing Energy Calculations

Roberto Napolitano

Dipartimento di Chimica, Università di Napoli, via Mezzocannone, 4, I-80134 Napoli, Italy.
Received August 6, 1987

ABSTRACT: Conformational and packing energy calculations have been performed on isotactic *trans*-1,4-poly(1,3-pentadiene). Two different minimum energy conformations in agreement with the experimental chain axis have been found. One of them corresponds to a chain having the side methyl groups in a skew arrangement and the other to a chain having the side methyl groups in a cis arrangement with respect to adjacent double bonds. The two chains have been independently packed in the space group $P2_12_12_1$ and two corresponding packing energy minima have been found. The calculations show that the skew arrangement, corresponding to the lowest conformational and packing energies, is preferred as opposed to the cis arrangement, even if the latter should be partially present in the crystal structure of oriented samples of the polymer.

Introduction

Structural data on isotactic *trans*-1,4-poly(1,3-pentadiene) (ITPP) were first reported by Natta et al.[1] who performed X-ray and IR investigations showing that this polymer may exist in two different modifications, a crystalline and a paracrystalline one. The crystal structure of ITPP was determined by X-ray fiber patterns by Bassi et al.;[2] the proposed unit cell is orthorhombic, space group $P2_12_12_1$, with $a = 19.80 \pm 0.20$ Å, $b = 4.86 \pm 0.05$ Å, $c = 4.85 \pm 0.05$ Å, and $d_{RX} = 0.97$ g·cm^{-3}. Bassi et al. showed that the best agreement between calculated and observed intensities is obtained when the polymer chain is assumed to have the side methyl groups in a cis arrangement with respect to the adjacent double bonds (henceforth denoted the cis model) rather than in a skew arrangement (henceforth denoted the skew model). Later Neto et al.[3,4] performed a vibrational analysis on unstretched samples of ITPP and concluded that the comparison between observed and calculated spectra indicates better agreement in the case of the skew model, both for the crystalline and for the paracrystalline modification. Recently Brückner et al.[5] reported the results of a X-ray diffraction analysis on a powder sample of ITPP, showing that the skew model is in good agreement with their experimental data. They concluded that the disagreement between the conformational model proposed in ref 2 and that proposed in the succeeding papers is due to the different samples of ITPP studied (stretched sample in the first case, unstretched samples in the succeeding works[3-5]).

In this paper a study of the crystal structure of ITPP as dictated by conformational and packing energy calculations is reported. The effectiveness of energy calculations in the prediction of the chain conformations and crystal structures of various polymers,[6-9] and in particular of polydienes,[10-13] was tested in preceding papers. Therefore it seems interesting to extend this kind of analysis to ITPP with the purpose of contributing to the elucidation of the above-mentioned disagreement concerning the polymer chain conformation in the crystalline state.

Table I
Bond Lengths and Bond Angles Used in the Calculations of the Conformational Energy Maps of ITPP

bond lengths/Å		bond angles	
C—C	1.53	C—C—C	111°
C=C	1.34	C—Ĉ=C	127°
C—H	1.10	C—Ĉ—H	109.5°
		C=Ĉ—H	116.5°
		H—Ĉ—H	108.9°

Conformational Energy Calculations

The conformational energy calculations have been performed on the portion of the polymer chain represented in Figure 1. According to the equivalence postulate,[14] the geometrical equivalence of successive constitutional repeating units (CRUs) has been imposed with the aim of obtaining results representative of the polymer chain in the crystalline field. The method of calculation has been reported in preceding papers.[11,12] The methyl group has been taken as a single unit in the calculations of the nonbonded interactions. The potential functions used are those of Flory et al.[15-17] Threefold intrinsic torsional potential with barriers of 11.7 and 4.2 kJ·mol^{-1} have been used for the rotations around skeletal $—\mathrm{C}\circlearrowleft\mathrm{C}—$ and $—\mathrm{C}\circlearrowleft\mathrm{C}=$ torsion angles, respectively. However, the actual barriers to the rotations around these torsion angles depend on the different nonbonded interactions of the lateral substituents (hydrogen atoms or methyl groups). The force constants for the bending at the C_{sp^2} carbon atom are those reported by Zerbi and Gussoni.[18]

In order to find the low-energy regions in the multidimensional conformational energy surface, preliminary maps of the energy as a function of the torsion angles ϑ_1 and ϑ_2 have been calculated. In these calculations bond lengths and bond angles have been fixed at the values reported in Table I. The value of ϑ_3 has been fixed at 180° (trans conformation) as has also the double bond (trans

0024-9297/88/2221-0622$01.50/0