

Secondary syndiotactic-specific propene insertion in the presence of homogeneous V-based catalysts

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Dedicated to Prof. Gian Paolo Chiusoli on the occasion of his 75th birthday

Abstract

This paper shows, by terminating the polymerization through deuteration with $\text{CF}_3\text{CH}_2\text{OD}$, that the propyl end groups of syndiotactic polypropylene obtained in the presence of homogeneous catalysts, based on vanadium salts and alkylaluminum halides, such as $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ -Anysole, arise, at least mostly, from termination, thus confirming the Coleman–Fox type of the statistical model of the propagation already proposed in previous papers. Direct evidence is also provided that secondary insertion of propene is the only syndiotactic specific polymerization step. In view of this, the early hypotheses concerning the structure of the active species promoting syndiotactic specific polymerization are critically reconsidered. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Syndiotactic; Propene insertion; V-based catalysts

1. Introduction

Syndiotactic polypropylene was isolated for the first time by fractionating polypropylene produced in the presence of heterogeneous catalytic systems such as $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ [1].

Actually, the main product obtained by promoting propylene polymerization with many heterogeneous catalysts is isotactic but the polymer fractions soluble in boiling heptane also comprise some syndiotactic polymer stereoregular enough to crystallize.

Later, three classes of homogeneous catalytic systems, selectively promoting syndiotactic-specific polymerization of propene, have been developed.

(1) The reaction products resulting at low temperature from vanadium compounds soluble in hydrocarbons and alkylaluminum halides, e.g., $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ [2].

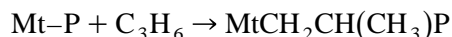
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(2) The organometallic cations resulting from reaction of group 4 bridged metallocenes of C_5 -symmetry with either methylalumoxane or $B(C_6F_5)_3$ or $C(C_6H_5)_3:B(C_6F_5)_4$, e.g., the 9-fluorenyl-1-cyclopentadienyl-isopropylidene-zirconium methyl cation [3,4].

(3) The homogeneous catalytic systems based on Ni(II) diimine derivative and methylalumoxane recently discovered by Johnson et al. [5], Du Pont [6], and Pellechia and Zambelli [7].

The reaction mechanism for these three classes of catalysts is quite different between each other.

In the presence of class 2 catalysts, the statistical model of the stereospecific propagation is basically, as proposed by Ewen et al. [4], that the polymerization is highly regiospecific (primary insertion).

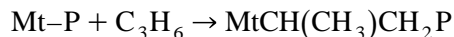


with Mt = metal centre and P = growing polymer chain.

The chiral metallic centre of the active species [4] controls the stereochemistry of the insertion.

Classes 1 and 3 share similar Bernoullian statistic models of the stereospecific propagation with $P_r > P_m = 1 - P_r$ [7–9] with P_r = probability of the r (= syndiotactic) stereochemical diad, $P_m = 1 - P_r$ probability of the m (= isotactic) stereochemical diad, and produce crystalline syndiotactic polypropylene only at low temperature (e.g., -78°C) [2,7].

The polymers are not very regioregular in both cases [7,9] but, according to the literature [10–12], the syndiotactic specific propagation is a secondary (= metal to C_2) polyinsertion in the presence of class 1 catalysts [10,11],



while it is a primary (= metal to C_1) insertion in the presence of class 3 catalysts [12].

Since the main goal of this paper is that of providing some additional evidence about the reaction mechanism in the presence of class 1 catalysts, it is also worth to mention that for these catalysts has been previously proposed a statistical model of the entire propagation [9] comprehending both secondary (stereospecific) and primary (non-stereospecific) steps. The model is Coleman–Fox type [13] and combines a first-order Markov model for the regiospecificity with the Bernoullian symmetrical model for stereospecificity proposed by Bovey [8]. The reader is referred to Ref. [9] for a detailed description of this model that, however, will be outlined in Section 2.

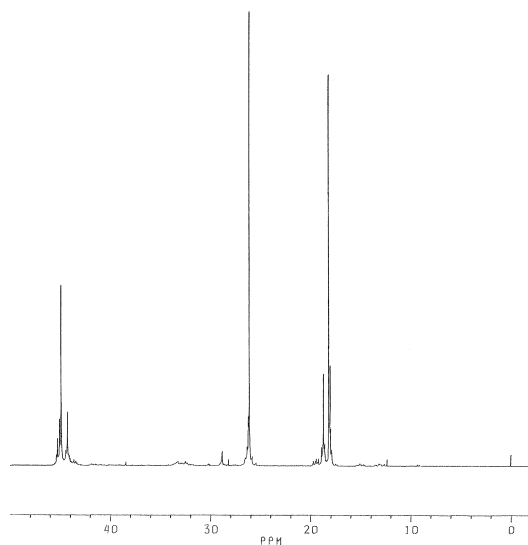
2. Results and discussion

The ^{13}C -NMR spectrum (0–50 ppm from HMDS) of a low molecular weight sample of polypropylene prepared in the presence of the catalytic system VCl_4 –Anisole– $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (sample 1) as described in the experimental part at -78°C , is reported in Fig. 1.

The stereochemical methyl pentad composition can be evaluated, at least in first approximation, from the areas of the methyl resonances ranging from 17.65 to 19.70 ppm, according to the literature [14] and is reported in Table 1.

The agreement with the composition anticipated according to Bovey's Bernoullian statistical model (Table 1) is quite reasonable although, in the evaluation, have been neglected the methyl regioirregular pentad sequences that overlap with the methyl regioregular pentad stereosequences.

The amount of regioirregular arrangements can be evaluated either from the methylene resonances between 28.5 and 34.2 ppm (head to head arranged units) [15] or from the methyl resonances between 12.69 and 15.30 ppm (tail to tail arrangements) [16] and are respectively about 5%.

Fig. 1. ^{13}C -NMR spectrum of sample 1.

The splitting of the considered methyl and methylene resonances comes from the highly stereoirregular environment [15,16].

In Fig. 2a is observed a sharp methyl resonance, at 12.37 ppm, diagnostic of propyl end groups [17,18]... $\text{CH}(\text{CH}_3)^3\text{CH}_2^2\text{CH}_2^1\text{CH}_3$ and a split methyl resonance centred at 9.20 ppm (actually at 9.32, 9.14, 9.10 ppm) diagnostic of ethyl end groups [17]... $\text{CH}(\text{CH}_3)^2\text{CH}_2^1\text{CH}_3$.

The resonance centered at 9.20 ppm is only observed when $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ is used as cocatalyst [17]; therefore, the ethyl end groups come from “primary” insertion of propene on reactive metal–ethyl bonds



The splitting of this resonance shows that the stereochemical arrangement of the first few monomers is irregular. A similar behaviour was previously observed for polymerization in the presence of $\text{VCl}_4-\text{Al}(\text{CH}_3)_2\text{Cl}$ [17].

Table 1
Stereochemical structure of sample 1

| Pentad | Chemical shift | Mole fraction | |
|-----------------|----------------|---------------------------|------------------------|
| | | Experimental ^a | Calculate ^b |
| m m m m | 19.70 | 0.01 | 0.0016 |
| m m m r | 19.40 | 0.03 | 0.01 |
| r m m r | 19.16 | 0.02 | 0.03 |
| m m r r | 18.86 | 0.03 | 0.05 |
| m r m m+r m r r | 18.66 | 0.20 | 0.21 |
| m r m r | 18.52 | 0.05 | 0.05 |
| r r r r | 18.12 | 0.43 | 0.41 |
| m r r r | 17.99 | 0.17 | 0.20 |
| m r r m | 17.85 | 0.04 | 0.03 |

^aFrom the areas of the methyl resonances.

^bAccording to Bovey's model with $P_r = 0.8$.

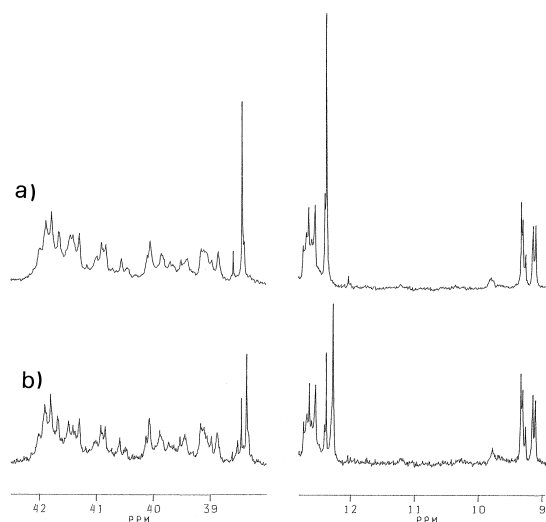
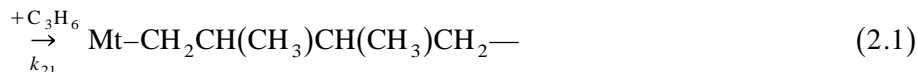
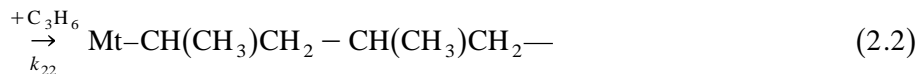
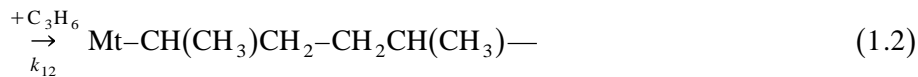
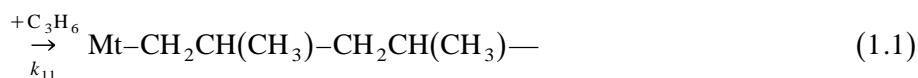


Fig. 2. Expansions of the ^{13}C -NMR spectra of (a) sample 1, (b) sample 2.

The methylene carbon of the ethyl end groups is not detected, because the chemical shift [17] is even more sensitive to the (closer) stereochemical environment, and further splitting is lost in the noise. The resonances of the methylene carbon labelled [2] in the formula of the propylene end group are also undetected because they overlap with the resonances of the methyl carbons of the chain.

Instead, a sharp resonance is observed at 38.45 ppm for the carbon labelled [3] one. The intensity of this resonance is somewhat less than that at 12.37 ppm probably because methylene 3 is sensitive to the stereochemical arrangement of the neighbouring monomer units that consequently should be prevailing, but not completely, regular, so that the minor resonances diagnostic of the non-stereoregular arrangements are lost in the noise.

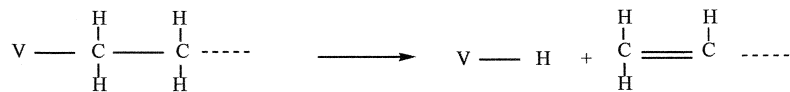
These data agree with the Coleman–Fox type mechanism mentioned in the introduction that considered four insertion steps with reference the regiochemistry of the insertion (first-order Markow model)



and assumed that the step 2.2 was the only syndiotactic-specific one (according to the Bernoullian statistical model of the stereospecific propagation proposed by Bovey and Tiers [8]).

Of course the whole argument rests on the assumption that the observed *n*-propyl end groups mainly come from hydrolysis of polymer chains bonded to metal atoms, rather than from primary

insertion of propene on active vanadium–hydrogen bonds that in principle could appear in the system as a consequence of β -hydrogen abstraction of the growing chain.



The expansions of the ^{13}C NMR spectrum of a sample of syndiotactic polypropylene (sample 2), (Fig. 2b) produced, in identical reaction conditions, as sample 1, but terminating the polymerization by addition of a mixture of $\text{C}_2\text{H}_5\text{OD}$ and $\text{CF}_3\text{CH}_2\text{OD}$ at -78°C compared with the same expansions of the spectrum of sample 1 (Fig. 2a) show that this is the case. In fact, the new resonances observed at 12.26 and 38.34 ppm are due to isotopic shift (0.1 ppm upfield) of the resonances of C-1 and C-3 of the *n*-propyl group when C-2 carries one deuterium [17], ... $\text{CH}(\text{CH}_3)\text{CH}_2\text{CHDCH}_3$.

The coupling with D also causes some broadening of the new resonances in comparison with those at 12.36 and 38.45 ppm.

The last ones are still observed in the spectrum of sample 2, although with lower intensity in comparison with sample 1, either because deuterolysis at low temperature is incomplete, as might suggest a previous paper [19], and the residual metal–carbon bonds were hydrolysed later when the polymer was treated with plenty of methanol acidified with HCl, or because actually some *n*-propyls come from primary insertion of the monomer on V–H bonds, or for both reasons.

The last possibility seems less likely because the catalyst we used produces polymers with molecular weight proportional to the conversion [20] suggesting the lack of whatsoever chain transfer process. It is also worth noting the lack of resonances suggesting any other saturated end group and, in particular, the butyl one that might suggest a catalyst resting after secondary propylene insertion.

The many other resonances observed in the spectra are due to the low regioregularity and stereoregularity of the polymers, and since the assignments are reported in the literature [22] and are not relevant to the object of this paper, are not discussed at all.

The number average molecular weight ($\overline{\text{MW}}_N$) of the samples (about 4000) determined by GPC is comparable with that evaluated from the ratio of the areas of the resonances of the inner methyls of the chain and the areas of the end groups ($\overline{\text{MW}}_N = 6000$) ($\overline{\text{MW}}_w =$ weight average molecular weight).

In previous papers, it was observed that in the presence of the title catalytic system (VCl_4 –anisole– $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$) both the polymer molecular weight and the polymerization rate linearly increase while increasing the polymerization time, at low monomer conversion [21,22]. In view of this the observed ratio $\overline{\text{MW}}_w/\overline{\text{MW}}_N = 1.8$ could be justified, even without any chain transfer, by considering a single site catalyst where the formation of the active sites from the catalyst precursor is slow in comparison with the polymerization [4,21,22].

3. Conclusion

The structure of syndiotactic polypropylene obtained in the presence of class 2 catalysts (from C_s symmetry ansa-metallocenes [4]) appears so different from that of syndiotactic polypropylene obtained in the presence of class 1 catalysts (from vanadium compounds [2]) that it is almost obvious that syndiotactic arrangement is achieved through completely different mechanisms.

On the contrary, when comparing by ^{13}C NMR analysis, the structure of syndiotactic polypropylenes obtained in the presence of either class 1 or 3 catalysts, they appear quite similar to each other, suggesting almost identical stereochemical reaction mechanisms.

However, the data reported in this paper seem to unequivocally confirm that syndiotactic-specific polyinsertion of propene is secondary (metal to C-2) in the presence of class 1 catalysts in full agreement with previous evidence by Doi et al. [23]. On the other hand, a paper recently reported in the literature [7] convincingly shows primary insertion for syndiotactic-specific propagation when propylene is polymerized in the presence of nickel catalyst.

The areas of ^{13}C resonances of the methyl carbons of the propyl and the ethyl end groups are appreciably identical to each other, suggesting that almost every chain has one ethyl (initiation) and one propyl (termination) end group.

On the matter, it is also worth mentioning that syndiotactic polymerization of 1-butene was also achieved with a catalyst based on metallocenes of C_{2v} symmetry [24], and that the polymerization mechanism proposed in the literature is quite similar to that of the class 3 catalysts mentioned in this paper.

4. Experimental

Commercial VCl_4 (Aldrich, distilled), $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (Schering), C_3H_6 (Sapio) have been used for preparing samples 1 and 2.

Samples 1 and 2 have been prepared at -78°C by dissolving 3.7 g of C_3H_6 in 100 ml anhydrous toluene containing 1×10^{-3} mol of anisole and injecting 1×10^{-3} mol $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$.

The corresponding polymerizations were terminated by injecting after 21 h at -78°C , while stirring, a mixture of $\text{CF}_3\text{CH}_2\text{OH}$ (5 ml) and $\text{C}_2\text{H}_5\text{OH}$ (3 ml) for sample 1 and a similar mixture of $\text{CF}_3\text{CH}_2\text{OD}$ and $\text{C}_2\text{H}_5\text{OD}$ for sample 2.

After reaching room temperature (in about 20 min) the polymers were coagulated with plenty of $\text{CH}_3\text{OH}-\text{HCl}$ and purified by re-dissolving in CCl_4 washing with acidulated H_2O and then H_2O until neutral in separator funnel and coagulated again with CH_3OH . The polymers were subsequently dried in vacuum at 100°C (Yield sample 1: 1.465 g; sample 2: 1.325 g).

NMR spectra were recorded on a Bruker AMX 270 spectrometer operating at 270 MHz for ^1H and at 67.925 MHz for ^{13}C . Spectra were taken at 103°C using $\text{C}_2\text{D}_2\text{Cl}_4$ as solvent. The chemical shifts are reported in ppm vs. Hexamethyldisiloxane (HMDS).

Molecular weights have been determined by GPC analysis at 110°C with Waters 150C instrument using *o*-dichlorobenzene as solvent.

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References

- [1] G. Natta, I. Pasquon, P. Corradini, M. Peraldo, M. Pegoraro, A. Zambelli, *Rend. Acc. Naz. Lincei* 8 (28) (1961) 539.
- [2] G. Natta, I. Pasquon, A. Zambelli, *J. Am. Chem. Soc.* 84 (1962) 1488.
- [3] J.A. Ewen, *J. Am. Chem. Soc.* 106 (1984) 6355.

- [4] J.A. Ewen, R.L. Jones, A. Razavi, J.D. Ferrara, *J. Am. Chem. Soc.* 110 (1988) 6255.
- [5] L.K. Johnson, C.M. Killian, M. Brookhart, *J. Am. Chem. Soc.* 117 (1995) 6414.
- [6] WO-A/23010, E.I. Du Pont de Nemours.
- [7] C. Pellecchia, A. Zambelli, *Macromol. Rapid Commun.* 17 (1996) 333.
- [8] F.A. Bovey, G.V.D. Tiers, *J. Polym. Sci.* 44 (1960) 173.
- [9] P. Ammendola, X. Shijing, A. Grassi, A. Zambelli, *Gazz. Chim. Ital.* 118 (1988) 769.
- [10] A. Zambelli, C. Tosi, M.C. Sacchi, *Macromolecules* 5 (1972) 649.
- [11] A. Zambelli, C. Tosi, *Adv. Polym. Sci.* 15 (1974) 31.
- [12] C. Pellecchia, A. Zambelli, M. Mazzeo, D. Pappalardo, *J. Mol. Catal. A: Chem.* 128 (1998) 229.
- [13] B.D. Coleman, T.G. Fox, *J. Chem. Phys.* 38 (1963) 1065.
- [14] A. Zambelli, P. Locatelli, G. Bajo, F.A. Bovey, *Macromolecules* 8 (1975) 687.
- [15] A. Zambelli, M.C. Sacchi, P. Locatelli, *Macromolecules* 12 (1979) 783.
- [16] A. Zambelli, G. Gatti, *Macromolecules* 11 (1978) 435.
- [17] A. Zambelli, P. Locatelli, G. Bajo, *Macromolecules* 12 (1979) 154.
- [18] A. Zambelli, P. Locatelli, E. Rigamonti, *Macromolecules* 12 (1979) 156.
- [19] A. Zambelli, M.C. Sacchi, *Makromol. Chem.* 175 (1974) 2213.
- [20] A. Zambelli, I. Pasquon, R. Signorini, G. Natta, *Makromol. Chem.* 112 (1968) 160.
- [21] Y. Doi, S. Ueki, T. Keii, *Macromolecules* 12 (1979) 814.
- [22] H.N. Cheng, *Macromol. Symp.* 86 (1994) 77.
- [23] Y. Doi, T. Koyama, K. Soga, *Makromol. Chem.* 185 (1984) 1827.
- [24] L. Resconi, L. Abis, G. Franciscono, *Macromolecules* 25 (1992) 6814.