



Polymerisation with soluble metallocene chiral catalysts: a bridge between inorganic and macromolecular stereochemistry

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday.

Abstract

General criteria for a rational approach to the synthesis of metallocene complexes with chiral substituents and possessing a proper symmetry are presented. The symmetry of the complex is defined according to Farina's classification based on the local chirality of the catalytic site (the chirotopicity). Stereochemical results of propene polymerisation performed in the presence of bis(1-neomenthylindenyl)ZrCl₂ (I) and bis(1-neoisomenthylindenyl)ZrCl₂ (II) in different solvents and different temperatures are interpreted accordingly. Methylalumoxane (MAO) was used as activator. Elastomeric polypropene is obtained with catalyst I. A syndiotactic polypropene was obtained with the new rigid catalyst diphenylmethy(cyclopentadienyl)(1-neomenthylindenyl)ZrCl₂ (III).

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1. Introduction

The advent of Ziegler–Natta polymerisation made necessary a relationship between organic stereochemistry and the area of stereoregular polymers, the metallic component of the insoluble catalyst being only in part reactive. Farina's idea that a cyclic model can be used for a rational description of stereoregular polymers represented, at that time, a bridge between organic and macromolecular stereochemistry; as an

example, the *cis*- and *trans*-1,3-dimethylcyclobutane are, respectively, the model of isotactic and syndiotactic polypropene and can also be used for a first level study of polypropene NMR spectra.

In soluble metallocene catalysts, all the metal atoms are centres for the chain growth. The stereocontrol is exerted by each metal atom and can be modulated by a proper structure of the ligand. Therefore, a better control of the macromolecular structure is obtained [1,2].

In order to rationalise the stereochemical results of propene polymerisation in the presence of rigid ansa metallocene complexes, Farina and Di Silvestro proposed a classification according to the symmetry

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relationships existing between the two catalytic sites [3]. This idea comes observing that if symmetry exists between catalytic sites, the same relationship must be present between the energy levels accessible in the chain growth determining step and, as a consequence, in the microstructure of resulting polymer [4]. From a different point of view, the same idea is present in the conformational model presented by Corradini et al. [5]. When fluxional catalysts are used, classification must be applied to their instantaneous conformations [3].

The description of the chain growth process according to a chemical or stereochemical scheme is a common procedure in macromolecular science [6]; in the case of stereospecific polymerisation, the model proposed must be able to predict the microstructure of the resulting polymer. Farina and Di Silvestro [3] proposed a model for propene polymerisation in the presence of rigid metallocene soluble catalysts based on a stereochemical analysis of the catalyst used and according to the Cossee scheme (Fig. 1) [7]. A more detailed description was discussed in a recent review [7].

Out of clarity, we report here only the general criteria used for the stereochemical analysis of metallocene complexes.

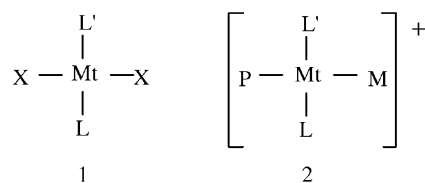
The general formula L_2MtX_2 can be used, where Mt is a 4th group transition metal (Ti, Zr, Hf), L_2 represents a bidentate or two monodentate cyclopentadienyl

ligands (η_5 (or η_3) bonded to the metal) and X represents halogen atoms or organic groups like methyl or phenyl. The two ligands may have either the same or different structures or they can constitute the two moieties of the bidentate ligand.

The substitutions in the part of the catalyst outside the reactive catalytic sites are considered unimportant for the stereochemical classification due to the distance from the reactive centre.

The activation reaction of the complex with methylalumoxane (MAO) or other electrophile reagents in the presence of the monomer produces the cationic species represented as $(L_2MtMP)^+$, where the monomer (M) is η_2 co-ordinated to the metal atom and the growing chain end (P) is σ -bonded. During the polymerisation, the original position of the halogen (X) represents each of the two polymerisation sites of the catalyst.

If we assume a tetrahedral coordination for the metal atom in the original complex and in the active centre, the corresponding Fisher projections (Formulas 1 and 2) can be drawn.



Formulas 1 and 2

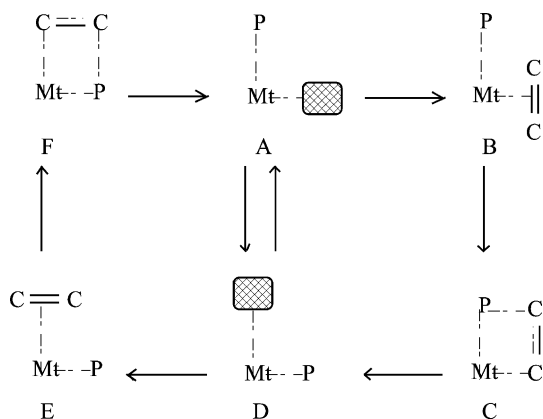


Fig. 1. Cossee scheme valid for the Ziegler–Natta polymerisation with soluble metallocene catalysts. Successive steps of chain growth are represented by A–F. The equilibrium $A \rightleftharpoons D$ results in a skipped insertion.

According to Farina's analysis, catalysts can be divided in five classes (and no more than five). This number was obtained by considering all the possible chirotopicitities (the local chiralities) of the catalytic sites X. If they are not chirotopic (e.g. they are bisected by a mirror plane) the two sites are *equal* or *different*. If, on the contrary, they are *chirotopic*, three possible chirotopicitities exist: the *two catalytic sites* are *homotopic* (equal), *enantiotopic* (mirror image of each other) or *diastereotopic* (different).

The symmetry relationships between the X atoms and the local symmetry of the metal atom can be deduced from the actual structure of the catalyst or from the naive representation given in Fig. 2 where the shaded areas represent the shape requirement of the ligand respect to the L_1 –Mt– L_2 plane.

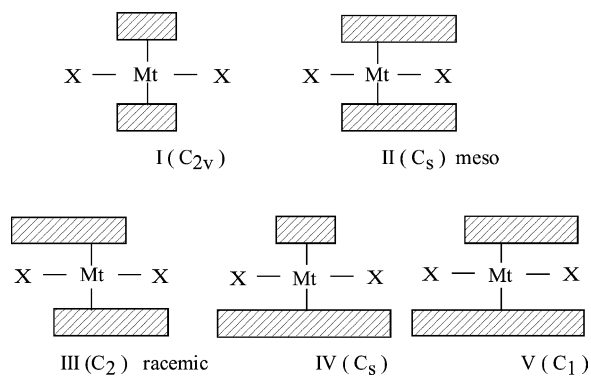


Fig. 2. Symmetry elements of the five classes of metallocene catalysts.

The five symmetry classes for all stereorigid catalysts and the corresponding symmetry relationships are reported in Table 1. The last line of the table shows the expected tacticity of the polymer according to the Cossee scheme and under the hypothesis that the stereocontrol is due only to the catalytic site and not to the chain-end chirality [3].

In the first two classes the X atoms are achirotopic: in class I, they are related by two orthogonal symmetry planes and the two sites are identical. In class II, the X atoms lie on the plane of symmetry and the two sites are different. The difference between classes I and II can be better understood if we use the asymmetric submolecular unit concept [9]: in class I, the X groups occupy a generic position and are related by a symmetry operation while in class II they are in a special position since they lie on the symmetry operator. No stereocontrol is predicted for the polymerisation process and atactic polymers are expected and obtained.

In classes III, IV and V the two sites are chirotopic: in class III, a two-fold rotation axis relates the two sites so that they are homotopic. In class IV, the two X atoms occupy the two specular positions respect to the vertical mirror plane of symmetry so that they are enantiotopic. In class V, no elements of symmetry exist, the two sites are diastereotopic.

As reported in Table 1, stereoregular polymers are obtained only in the presence of chirotopicity in the X atoms.

Two important observations derive from the comparison of cyclic models for stereoregular polymers and of the relationships between X atoms in metallocene complexes.

Polymer microstructure does not reproduce the local chirality of each site, as in an equivalent organic reaction, but reproduces relationships between the two sites. As a matter of fact, the same isotactic and achiral polypropene is obtained by using one or both enantiomers of the racemic mixture of a class III complex. In the catalyst, in the isotactic polymer and in its cyclic model the two methyls are in a homotopic relationship.

The same principle holds for the syndiotactic polymer. The local chirality inverts in the two adjacent tertiary atoms of the polymer as well as in the complex: chirotopicities of the two sites are in an enantiotopic situation like those of methyls in the *trans*-dimethylcyclobutane.

To clear up the concept, we can observe the Cossee scheme (Fig. 1). If we start from A, we see that the growing chain experiences the local chirality of the two sites during insertion processes (C and F) by moving through B–F. We also note that the equilibrium between A and D points is equivalent to an epimerisation of the catalyst and a skipped insertion in the chain growth results [10].

Table 1
Symmetry relations in achiral rigid metallocene catalysts

	Catalyst				
	I	II	III	IV	V
Symmetry of the L_2MtX_2 complex	C_{2v}	C_s	C_2	C_s	C_1
Chirotopicity of atoms X in L_2MtX_2	No	No	Yes	Yes	Yes
Relationship between atoms X in L_2MtX_2	Equal	Different	Homotopic	Enantiotopic	Diastereotopic
Chirotopicity of atom Mt in $(L_2MtMP)^+$	No	No	Yes	Yes	Yes
Stereogenicity of atom Mt in $(L_2MtMP)^+$	No	Yes	No	Yes	Yes
Polymer structure predicted for catalyst control and alternating mechanism	Atactic	Atactic	Isotactic	Syndiotactic	Not determined

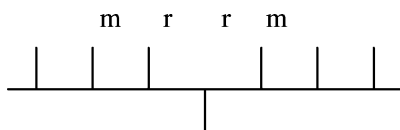


Fig. 3. Examples of pentad representation as m (meso) and r (racemic) successions.

Using the concept that the macromolecular chain is a static representation of relationships between successive reaction acts is very common in macromolecular science and, for example, NMR spectra interpretation is based on it. As a further example, in propene polymerisation, ^{13}C NMR spectra are interpreted at pentad level as a succession of five reaction steps represented as a succession of four relationships (m or r symbols) (Fig. 3); however heptads, nonads, undecads and some tridecads were recognised in the methyl portion of ^{13}C NMR spectrum of a polypropene [11]. The most used kinetic or statistic models of stereochemical chain growth use pentad concentration as experimental data.

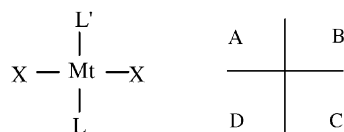
Also the γ -ray induced radical polymerisation of diene monomers included in the crystalline adducts of perhydrotriphenylene (PHTP) can be interpreted by using the same concept. In this case, the stereochemical control is exerted at each reaction step and the channel looks like a mono-dimensional space possessing an elicoidal symmetry where all reaction points are homotopic. Pure 1,4-*trans*-isotactic polypentadiene is obtained by inclusion polymerisation in PHTP adducts and it reflects the homotopicity of all points of the elicoidal symmetry of the channel [12]. In a different field, also the duplication process of DNA can be interpreted in the same way as a succession of base sequences.

In this paper, we present a rational approach to the synthesis of metallocene catalysts containing chiral substituents and possessing a defined symmetry together with some polymerisation results using catalysts like the one synthesised by Erker [13]. Some aspects of this work were reported in a recent review [8].

2. Synthesis of metallocene complexes with chiral ligands and defined symmetry

When ligands with chiral groups are used, the catalytic sites of the complex can be either represented

with their Fisher projection or as a plane with four sectors (A–D). The axes of this last representation are centred on the metal atom and are perpendicular to each other. In this case, the symmetry relationships between the sectors determine the class of symmetry of the catalyst.



Using the sector representation, the symmetries of catalysts having 1–4 substituents R (where (+) and (–) will represent the absolute configuration of stereocentres) will be presented. As explained before and from literature experimental data, only symmetrically substituted catalysts possess C_1 symmetry (class V according to Farina's classification) and it is impossible to predict the final stereochemistry of the polymer.

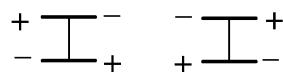
The stereochemical analysis presented here can be used for the synthesis of 3,4-cyclopentadienyl, indenyl or 5,6-fluorenyl derivatives. It is evident that non symmetric substitution produces only C_1 symmetry molecules (class V). The classification is more general and can be applied to other kinds of molecular structures; the possible ways to obtain catalysts with chiral ligands and the same group chirality reported in scheme 2 for achiral ligand will be now discussed.

In the further discussion, we present the possible ways to obtain the catalyst with chiral ligands with the same group of symmetry as reported in scheme 2 for the correct achiral ligands.

2.1. Class I

Catalysts with this symmetry (C_{2v}) can be obtained by introducing four equal substituents.

In A and C sectors, R must have the same configuration; the same holds true for B and D, but R configurations are opposite to A and C, respectively. Only two structures possessing the high symmetry of this class are possible:



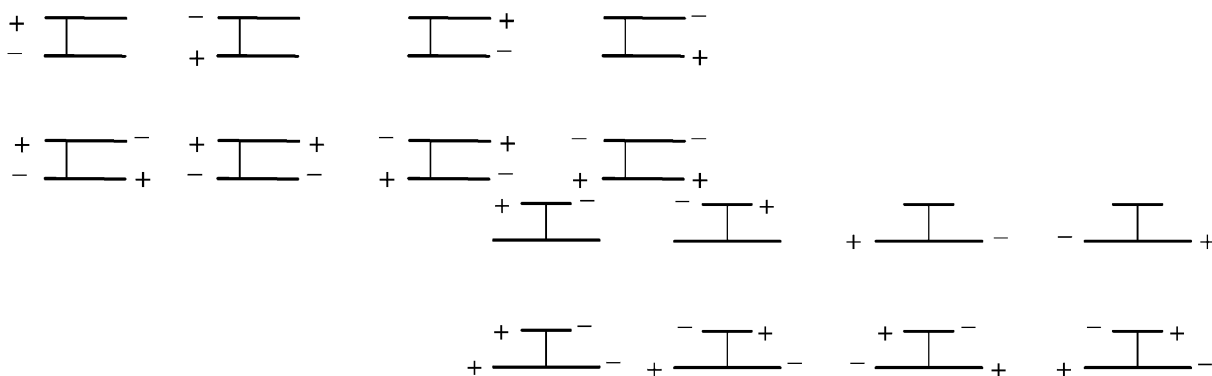
Different substitutions generate products with lower symmetry. Three structures of class II, three structures

of class III, three structures of class IV and 15 structures of class V can be obtained.

No stereocontrol can be expected in the presence of this kind of catalysts.

2.2. Class II

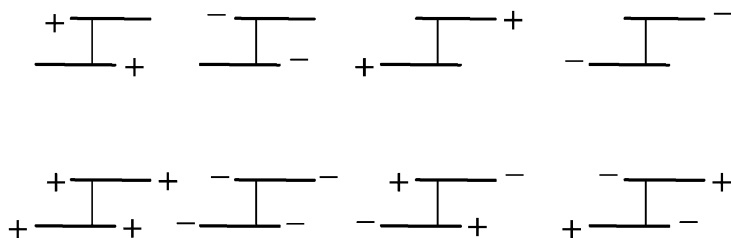
In this case either two or four substituents can be used: with opposite configuration in the A and D sectors and/or with opposite configuration in B and C sectors. The eight possible structures with C_s symmetry are depicted:



Also in this case, different substitutions produce 36 structures all belonging to class V and no stereocontrol can be predicted in the presence of class II catalysts.

2.3. Class III

Either two or four equal substituents can be used: configurations in A and C sectors are the same and/or configurations in B and D sectors are equal. This kind of catalysts is used in the synthesis of isotactic polymers. In this case, eight chiral structures with C_2 symmetry are possible. Only one enantiomer for each structure is shown:



Different substitutions generate 36 structures belonging to class V.

2.4. Class IV

Syndiotactic polymers are expected in propene polymerisation with class IV catalysts. In the case of achiral ligands, class IV catalysts represented an excellent test for the validity of the alternating scheme of the chain growth process. The control related to the catalyst's chirotopicity and to the chain end was easily recognised and measured.

The eight possible structures with C_s symmetry belonging to this class are reported in the figure.

Different substitutions give 36 structures of class V symmetry.

2.5. Class V

No symmetry operators are present in this case.

As shown in the previous discussion, catalysts belonging to this class are very common and no prediction on the stereocontrol of the resulting polymer can be done.

The symmetry of this class cannot be modified by different substitutions.

3. Application of classification to fluxional metallocene complexes with chiral substituents

In the previous paragraph, we analysed the case of chiral substituents connected to a rigid framework. When chiral substituents are used in the synthesis of fluxional metallocene catalysts, the previous classification must be applied to each instantaneous conformation. The final polymer microstructure will reflect the effect of the stereocontrol of each conformer and of its lifetime. The propagation rate of each conformer can be different and, under the hypothesis of a living polymerisation, a multiblock structure can be expected. It is worth to note that the multiblock structure of the polymer is not related to the chiral nature of the substituents but only to the presence, in the catalyst, of different reactive conformers; achiral substituents can give the same result.

4. Results and discussion

Polymerisations were carried out in different solvents and temperatures, in the presence of bis(1-neomenthylindenyl)ZrCl₂ (I), bis(1-neoisomenthylindenyl)ZrCl₂ (II) and diphenylmethyl(cyclopentadienyl)(1-neomenthylindenyl)ZrCl₂ (III) activated by MAO;

a Al/Zr ratio equal to 2000 was used. Catalyst III was used in toluene at room temperature.

Crystal structures, solution behaviour and some polymerisation data were published by Erker [13].

Catalyst I at room temperature is present as a single species possessing C₂ symmetry as a result of free rotation of different conformers. At lower temperature three different conformers are present; at least one of these possesses a C₁ symmetry.

Catalyst II presents C₁ symmetry in the crystal; in solution its symmetry is different and is due to a rapid disrotatory movements of the ligands. A C₂ symmetry was thus observed in the temperature range 190–300 K. Catalyst III is a new rigid ansa metallocene complex.

One example of ¹³C NMR spectrum of polypropene is reported in Fig. 4. The figure shows the methyl portion of the original spectrum and refers to the polymer obtained at –30 °C in liquid monomer in the presence of the catalyst I.

Tables 2, 4 and 3, 5 report experimental conditions and pentad concentrations as measured in ¹³C NMR spectra run at 105 °C in CD₂Cl₂. Standard procedure for quantitative ¹³C NMR spectra were used. The pentad concentrations reported in the tables show the lowest error respect to the stoichiometric relationships according to the procedure used in the review [7]. Literature data show a higher error (item 6 in Table 3).

Table 2
Experimental conditions used with catalyst

Item	Temperature (°C)	Solvent (g)	Monomer (g)	Polymerisation time (h)	Catalyst (mg)
1	–50	Toluene (105)	41.5	6	14
2	–50	CH ₂ Cl ₂ (151)	32	5	25.3
3	–30	–	Neat (81)	3	14.9
4	–30	Toluene (105)	35.9	3	12
5	–30	CH ₂ Cl ₂ (151)	32	5	34
6	–5	Toluene	Ref. 13	–	–

Table 3
Pentad concentration of polypropenes obtained with catalyst I

Item	mmmm	mmmr	rmmr	mmrr	xmrx	rmmr	rrrr	mrrr	mrrm
1	27.90	16.11	5.01	15.20	13.44	4.41	3.69	7.54	4.69
2	39.08	16.26	3.03	14.28	9.83	4.56	2.48	4.70	5.78
3	26.80	17.12	3.74	4.90	14.91	6.72	3.38	7.02	6.14
4	26.10	15.90	5.27	14.90	14.29	7.09	4.04	7.10	5.30
5	45.18	16.31	1.99	13.09	9.59	3.98	1.00	3.80	5.07
6	33	17	4	13	17	6	1	7	3

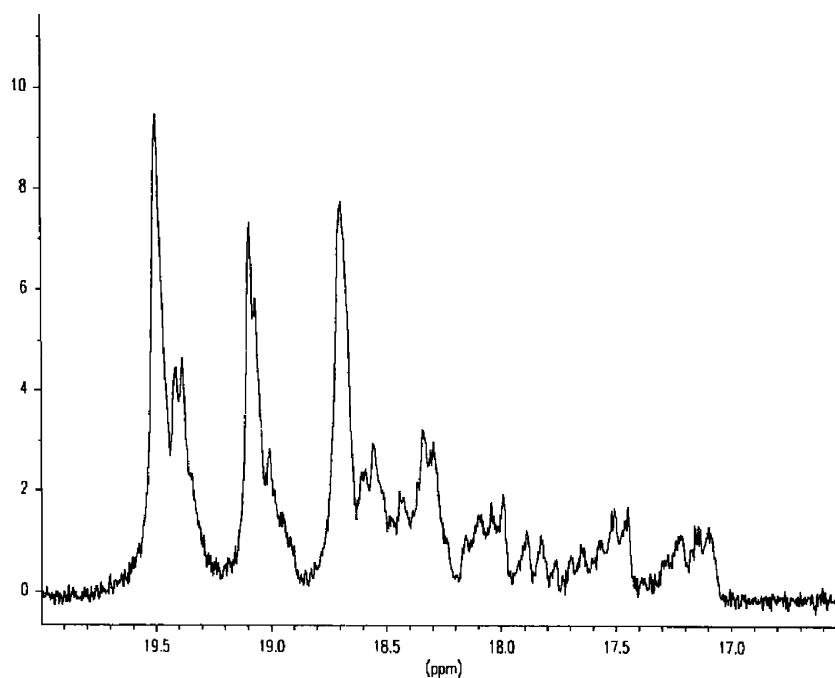


Fig. 4. NMR spectrum of sample number 3 in Table 3.

Table 4

Experimental conditions used in the synthesis with catalyst II

Item	Temperature (°C)	Solvent (ml)	Monomer (g or Pa* 10 ⁻⁵)	Polymerisation time (h)	Catalyst (mg)
1	-50	Toluene (125)	34	4	41.7
2	-50	CH ₂ Cl ₂ (155)	31.5	5	30.3
3	-30	–	Neat (92)	3	55.7
4	-30	Toluene (125)	34	4	31.6
5	-30	CH ₂ Cl ₂ (152)	31.6	5	33.7
6	-5	Toluene	Ref. 13	–	–
7	20	Toluene (100)	1.01	2	30
8	20	Toluene (100)	3.04	2	34
9	20	Toluene (135)	6.08	2	37.8

Table 5

Pentad concentration of polypropene obtained with catalyst II

Item	mmmm	mmmr	rmmr	mmrr	xmrx	rmrm	rrrr	mrrr	mrrm
1	85.80	6.46	0.00	5.52	0.00	0.00	0.00	0.00	2.21
2	77.87	8.58	0.12	7.11	2.25	0.37	0.21	0.42	3.07
3	60.38	14.19	1.00	11.82	4.42	2.00	0.00	1.01	5.17
4	75.26	10.04	1.11	6.48	3.07	1.35	0.00	0.00	2.69
5	65.88	10.21	2.57	9.20	4.98	2.88	0.43	0.94	2.91
6	77	10	0	7	3	0	0	0	2
7	63.22	15.41	0.34	13.00	2.53	1.02	0.00	0.00	5.48
8	55.74	15.06	1.28	11.86	6.13	2.38	0.52	0.92	6.07
9	53.48	14.54	2.81	13.03	6.03	3.16	0.40	11.43	5.11

By using pentad concentration, the probability parameters of the stereocontrol process during the chain growth can be estimated according to Farina's model. This model applied to a class V complex in the presence of stereocontrol due to the catalyst and to chain end and needs for eight independent probability parameters if the skipped insertion is also present [3]. The number of probability parameters is lower for complexes with higher symmetry. In the present case, an independent set of probability parameters should be used for each conformer; it is evident that the pentad data alone cannot support an estimation of such a high number of independent parameters. In these cases, simpler microstructure parameters can be evaluated; we will use one the average length of stereoregular block (the isotactic block) and will relate it to the melting temperature of the polymers.

As a general feature, polymers synthesised with the catalyst II are more isotactic (see the mmmm value) because of the presence, in solution, of conformers possessing C_2 symmetry. The effect of the presence of conformers with C_1 symmetry is higher in the catalyst I. The length of isotactic block (N_{iso}), is equal to 34 in the polymer with mmmm = 0.8577. In the corresponding polymer obtained with catalyst I, the N_{iso} value is 3.8. The higher length of the isotactic block is confirmed by DSC experiment ($T_{melting} = 130^\circ\text{C}$ and

a $\Delta H = 75\text{ J/g}$). No melting peak is observed in the more irregular polymer and its glass transition temperature is very near to the one observed in an atactic polypropene.

The N_{iso} value is affected also by the solvent and the polymerisation temperature. The more polar solvent reduces the N_{iso} value to 18.8 units when catalyst I is used in equivalent polymerisation conditions. A deeper analysis of NMR data shows the effect of the symmetry of the catalyst and of polymerisation conditions but this kind of analysis is out of the scope of this paper. We prefer, here, to discuss two examples of the use of symmetry criteria in propene polymerisation with metallocene complexes.

As reported in Table 1, when the two catalytic sites are diastereotopics no prediction can be made and the polymer microstructure is determined by the shape demanding property of each catalytic site in polymerisation conditions. In the presence of class V catalysts isotactic, hemiisotactic or, in the present case, syndiotactic polypropenes are obtained. According to the Cossee scheme, isotactic polymer is obtained if the catalyst possesses a very bulky substituent; in this case only one catalytic site works while the second site gives the skipped insertion. The hemiisotactic polymer was obtained in the presence of a small substituent and, as a consequence, one catalytic site gives a complete

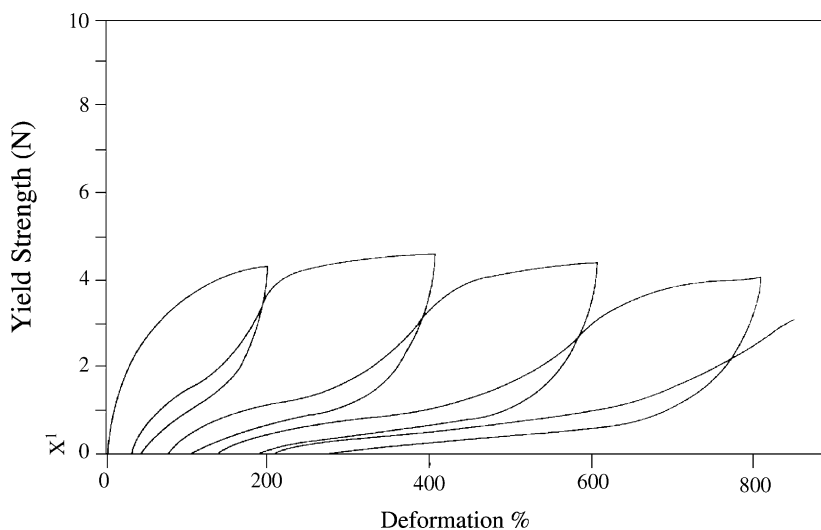
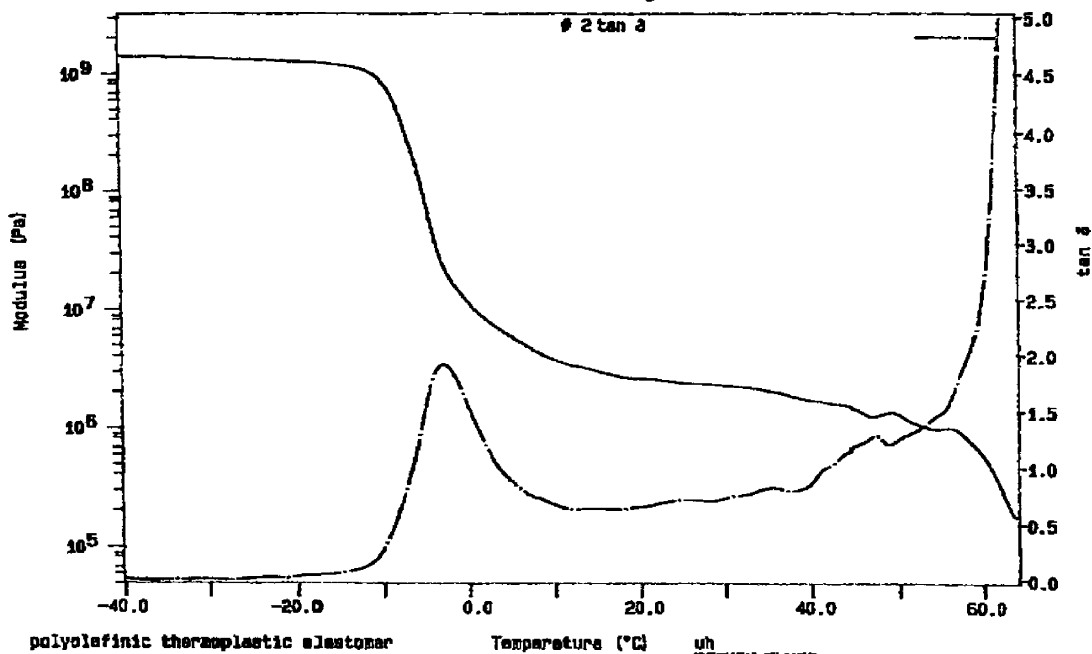


Fig. 5. Dynamo-mechanic curves of polypropene obtained with catalyst I at -30°C in pure monomer (sample 3 in Table 3).

Curve 1: DMA Temp/Time Scan in Extension
 File info: polef-1-bt Fri Oct 6 11:48:20 1995
 Frequency: 0.50 Hz Amplitude: 9.272u
 sample B Tension: 125.000%

1 sample B: polef-1-bt
 Storage Modulus (Pa) L



polyolefinic thermoplastic elastomer

Temperature (°C)

uh
 PERKIN-ELMER
 7 Series Thermal Analysis System
 Fri Oct 6 14:28:50 1995

Fig. 6. Dyna-mechanic curves of polypropene obtained with catalyst I at -30°C in pure monomer (sample 3 in Table 3).

stereocontrol while the second site allows the insertion but without stereocontrol. In the present case, an apparent plane of symmetry works in the activation energies of the two sites and the neomenthylindenyl portion of the catalyst is equivalent to the more symmetric fluorenyl group.

Figs. 5, 6 present the residual strain and dyna-mechanic curves of polypropene obtained with catalyst I at -30°C in pure monomer. Polymer behaves as an elastomeric material because of the presence of microcrystalline phase. This behaviour cannot be predicted from the ^{13}C NMR spectrum; as a matter of fact, in the spectrum we see only the average microstructure. In this case, the propagation rate/life-time ratio of conformers with C_2 symmetry generates microisotactic blocks while the C_1 symmetric conformer produces the atactic portion of the macromolecular chain; the elastomeric behaviour is due to the balance between the ordered and disordered segments.

5. Final remarks

We have discussed the classification of soluble metallocene complexes possessing chiral substituents. This classification allows a rational approach to the synthesis of rigid catalysts with well defined symmetry and a correct use of the effect of symmetry on the differences between the activation energies of chain growth steps both in rigid and in fluxional complexes.

Acknowledgements

The theoretical part of this work is the last contribution of Professor Mario Farina to the macromolecular stereochemistry; unfortunately Prof. Farina cannot see any experimental application. Authors are indebted to him. Many thanks to doctor Alberto Terragni who was the tutor of one of the authors.

References

- [1] J. Scheirs, W. Kaminsky (Eds.), AA.V.V., Mechanistic Aspects of Metallocene Catalysis, Part I, Wiley, Chichester, 2000.
- [2] J.A. Gladysz, Chem. Rev. 100 (4) (2000) 1167.
- [3] M. Farina, G. Di Silvestro, A. Terragni, Macromol. Chem. Phys. 196 (1995) 353.
- [4] M. Farina, Makromolekulare Chemie 122 (1969) 237.
- [5] P. Corradini, L. Cavallo, G. Guerra, Metallocene-Based Polyolefines, vol. II, Wiley, New York, p. 3.
- [6] J.A. Ewen, M.J. Elder, R.L. Jones, S. Curtis, H.N. Cheng, in: T. Keii, K. Soga (Eds.), Catalytic Olefin Polymerization, Elsevier, New York, 1980, p. 439.
- [7] P. Cossee, in: A.D. Ketley (Ed.), Stereochemistry of Macromolecules, vol. 1, Dekker, New York, 1967 (Chapter 3).
- [8] G. Di Silvestro, Metallocene-Based Polyolefines, vol. II, Wiley, New York, p. 37.
- [9] M. Farina, C. Morandi, Tetrahedron 30 (1974) 1819.
- [10] J.A. Ewen, J. Am. Chem. Soc. 106 (1984) 6355.
- [11] G. Di Silvestro, P. Sozzani, B. Savarè, M. Farina, Macromolecules 18 (1985) 928.
- [12] M. Farina, G. Di Silvestro, P. Sozzani, Macromol. Chem. Rapid Commun. 2 (1981) 51.
- [13] G. Erker, J. Am. Chem. Soc. 115 (1993) 4590.