ISSN 0023-1584, Kinetics and Catalysis, 2006, Vol. 47, No. 2, pp. 268–273. © MAIK "Nauka/Interperiodica" (Russia), 2006.

Seven- and Eight-Membered Saturated Fused Rings Zirconium and Titanium Metallocenes: A Route for the Synthesis of Elastomeric Polypropylene[1]

M. C. Sacchi[a], I. Tritto[a], F. Bertini[a], S. Losio[b], G. Zecchi[b], and E. Polo[c]
[a] *ISMAC-C.N.R., via Bassini 15, 20133 Milano, Italy*
e-mail: sacchi@ismac.cnr.it
[b] *Università dell'Insubria, Dipartimento di Scienze Chimiche e Ambientali, via Valleggio 11, 22100 Como, Italy*
[c] *ISOF-C.N.R. Sezione di Ferrara, via L. Borsari 46, 44100 Ferrara, Italy*
e-mail: tr3@unife.it
Received August 8, 2005

Abstract—Unbridged zirconium and titanium catalysts, where a seven- or eight-membered ring fused to a cyclopentadiene is associated with a phenyl substituent in position 2, were tested in propylene polymerization in order to investigate the possibility of observing a "fluxional behavior" and to obtain stereoblock polypropylene, even in the absence of the aromatic ring, usually present in this kind of catalysts, by introducing the conformational flexibility of the saturated ring as a new parameter. The microstructure, molecular properties, and thermal behavior of the polymers obtained showed that it is possible to observe a "fluxional behavior" even by replacing the basic indenyl structure with a slightly flexible saturated ring. Furthermore, this structural feature sensibly increases the stability of the complexes, thus making it possible to observe for the first time the oscillating behavior in titanocenes.

DOI: 10.1134/S0023158406020170

INTRODUCTION

Metallocene complexes are well-established highly active single-site catalysts for the homo- and copolymerization of α-olefins [1–7]. The scientific interest arises primarily from their single-center nature and from the availability of a large variety of π-ligand structures that allow the preparation of polymers with a wide range of microstructures and properties. The discovery by Coates and Waymouth [8] that a single catalytic species (i.e., $(IndPh)_2ZrCl_2$ activated by methylaluminoxane (MAO)) is able to produce elastomeric polypropylene has aroused an increasing interest in unbridged substituted indenyl systems. The source of the oscillating behavior in this type of metallocenes has been attributed mainly to the free rotation around the ligand–metal bond and the consequent possibility of interconversion between chiral and achiral rotational isomers on the time scale of the polymerization reactions. It was soon clear that it was possible to influence these conformational dynamics and to obtain a polymer consisting of alternating sequences of isotactic/atactic stereoblocks by a careful selection of the structure of the catalyst and of the polymerization conditions [9–22]. When the isotactic blocks are of the appropriate length, the resulting polymer will display interesting elastomeric properties. Despite the number of papers appearing in recent years, a complete understanding of the behavior of this type of catalysts is still controversial and prevents a precise prediction of the stereoselectivity for a specific metallocene. The early mechanism based on the interconversion of *rac/meso* isomers was later questioned by several authors [23–25] and reformulated by Waymouth himself [16]. What seems quite established is that the steric hindrance and position of the ligands and the type of cocatalyst [13, 25–28] are the main factors that can increase the life of the catalytic species capable of producing long isotactic blocks. Although there are some exceptions, the replacement of the basic indenyl ligand usually leads to a significant loss of capacity of the catalyst to give isotactic blocks.

A few years ago, we decided to enter this field by studying a new family of unbridged catalysts based on a bicyclic ligand with a saturated ring of different sizes (six, seven, and eight carbon atoms) fused to a cyclopentadiene and bearing different substituents in position 2. Our target was to explore the possibility of observing a "fluxional behavior" even in the absence of the aromatic ring, by introducing the conformational flexibility of the saturated ring as a new parameter. We synthesized and studied several sets of complexes, focusing our attention not only on the indenyl substituents but also on the role played by the saturated ring condensed to the cyclopentadienyl moiety [29]. After a systematic investigation on several 2-substituted bicy-

---

[1] The text was submitted by the authors in English.

Table 1. Results of propylene polymerizations with Zr and Ti catalysts

Catalyst	T_{pol}, °C	Activity, $kg_{PP}\ mol^{-1}_{Mt}\ h^{-1}$	$[mmmm]^a$	N^b_{iso}	T_m range^c, °C	ΔH^c_m, J/g	$M_w \times 10^{-3d}$	PDI^d
C_7Ph–Zr	0	96.2	14.0	5.6	90–110	<0.1	265	2.1
	–15	346.6	17.4	5.9	125–150	0.4	224	2.1
C_8Ph–Zr	0	372.7	13.6	5.5	100–140	0.2	125	1.8
	–15	251.9	16.3	5.7	110–150	0.3	157	2.5
w–Zr	0	469.9	15.9	6.2	120–150	0.3	297	4.1
	–15	193.9	11.9	5.6	90–105	<0.1	144	3.2
C_7Ph–Ti	0	141.5	5.5	5.8	120–155	0.5	290	5.8
	–15	145.5	7.9	6.2	120–155	1.2	234	6.5
C_8Ph–Ti	0	82.4	9.9	6.5	115–155	0.9	276	4.8
	–15	36.5	21.9	8.3	115–155	3.6	215	3.8
w–Ti	0	44.4	6.7	6.1	125–155	0.3	87	4.4
	–15	20.1	14.2	6.7	120–155	1.0	150	4.0

Note: Reaction conditions: toluene: 100 ml, [Mt] = 10 × 10^{-5} mol/l, [MAO]/[Mt] = 1000, P = 2.4 atm, t_{pol} = 1 h.

[a] Isotactic pentad content by ^{13}C NMR.

[b] Average length of isotactic blocks estimated by ^{13}C NMR [34].

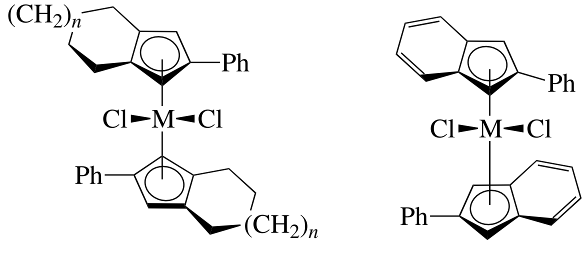
[c] By DSC on second heating scan.

[d] Molecular weight and polydispersity determined by SEC.

clic zirconocenes, we have successively investigated the effect of the change from zirconium to titanium on the most promising structures [30, 31]. Since the titanium center allows a closer interaction between the two bent cyclopentadienyl moieties, the effect of the substituents should favor the formation of longer isotactic blocks by exerting a stronger influence on the interconversion speed between aspecific and isospecific isomers. Up to now, indenyl titanocenes have been quite neglected as possible fluxional catalysts, because they tend to decompose rather easily during polymerization. The saturated ring imparted a higher stability to these complexes [32], allowing, for the first time, a full characterization of a polypropylene sample obtained through titanium-based catalysts. We report here a complete picture of the most interesting results obtained both with the zirconium (C_7Ph–Zr and C_8Ph–Zr) and the titanium catalysts (C_7Ph–Ti and C_8Ph–Ti) synthesized (Fig. 1). The corresponding indenyl complexes (w–Zr and w–Ti) have also been prepared, and their activity has been compared to one of the new metallocenes under the same polymerization conditions.

EXPERIMENTAL

Manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques, or in a dry box under a nitrogen atmosphere (<10 ppm oxygen, <20 ppm water). Titanium (C_7Ph–Ti and C_8Ph–Ti) [32] and zirconium (C_7Ph–Zr and C_8Ph–Zr) [29, 33] complexes were synthesized as described previously. To prevent possible photodecomposition, solutions of titanium complexes were carefully protected from light during the preparative steps of the polymerization experiments. Toluene was dried by distillation from sodium under nitrogen. Methylaluminoxane (MAO) (Witco, 10 wt % solution in toluene) was used after drying in vacuum to remove the solvent and unreacted trimethylaluminium (TMA) and was stored under nitrogen. Nitrogen and propylene were purified by passage through columns of BASF RS-11 (Fluka) and Linde 4 Å molecular sieves. Polymerizations were performed in a 250-ml Büchi autoclave (reaction conditions: toluene: 100 ml, [Mt] = 10 × 10^{-5} mol/l, [MAO]/[Mt] = 1000, P = 2.4 atm, t_{pol} = 1 h). ^{13}C NMR spectra of the polymers were recorded in $C_2D_2Cl_4$ at 103°C on a Bruker AM-400 spectrometer operating at 100.58 MHz (internal chemical shift reference: 1% hexamethyldisiloxane). Conditions: 10-mm probe; 90° pulse angle; 64 K data points; acquisition



M = Zr n = 2 (C_7Ph–Zr); 3 (C_8Ph–Zr) M = Ti (w–Ti)
M = Ti n = 2 (C_7Ph–Ti); 3 (C_8Ph–Ti) M = Zr (w–Zr)

Fig. 1. Structures of synthesized zirconium and titanium catalysts.

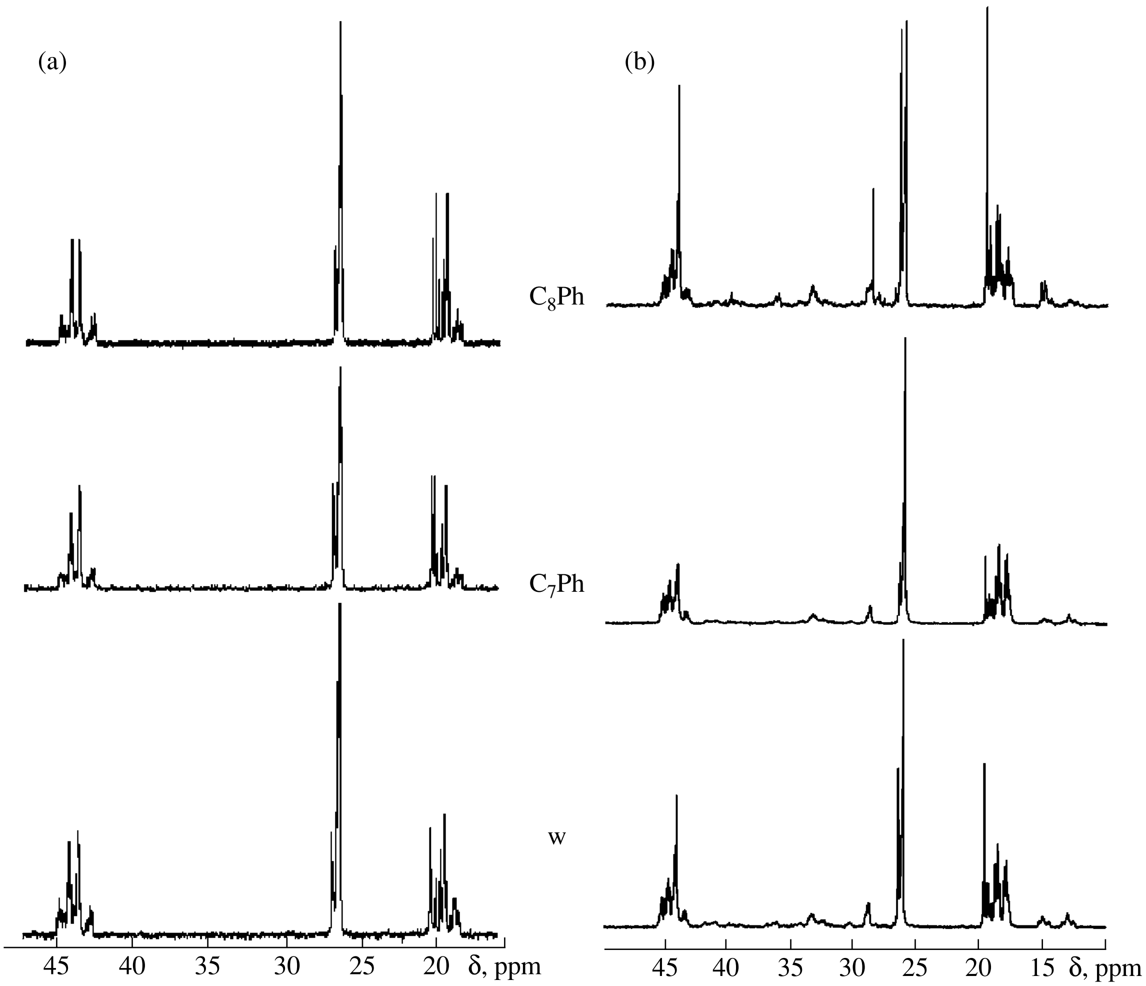


Fig. 2. ^{13}C NMR spectra of the polypropylenes from zirconium and titanium catalysts at –15°C.

time 5.56 s; relaxation delay 20 s; 3–4 K transients. Proton broadband decoupling was achieved with a 1D sequence using bi_waltz16_32 power-gated decoupling. Molecular mass distributions were determined by using a GPCV2000 size-exclusion chromatography (SEC) system from Waters, equipped with a differential refractometer. The column set was composed of three mixed TSK-Gel GMH$_{XL}$-XT columns from Tosohaas (mobile phase *o*-dichlorobenzene; temperature 145°C; flow rate 0.8 ml/min; injection volume 300 μl). Differential scanning calorimetry (DSC) scans were carried out on a Perkin-Elmer Pyris 1 instrument equipped with a liquid nitrogen device, at a scanning rate of 20 K/min.

RESULTS AND DISCUSSION

In Table 1 are reported the polymerization, microstructural, and molecular data along with the thermal behavior of the samples obtained with zirconium and titanium catalysts at the constant propylene pressure of 2.4 atm and at 0 and –15°C. Because the oscillating behavior is extremely sensitive to the polymerization conditions, we have taken as reference the classical Waymouth catalyst (w–Zr) and the corresponding titanium homologue (w–Ti), both synthesized in our labs.

As to the activities, the acceptable polymer yields (although lower than from the zirconium homologues) obtained with C$_7$Ph–Ti and C$_8$Ph–Ti at 0°C, despite the well-known low stability of titanium-based metallocenes, are a quite remarkable result. On the contrary, w–Ti, likely owing to the unsaturated ring, is a less effective catalyst. Only with the sample from C$_8$Ph–Ti at low temperature can we appreciate the expected increase in isotacticity (from 16.3% with C$_8$Ph–Zr to 21.9% with C$_8$Ph–Ti). With the other catalysts, in particular, in the more productive experiments, the isotacticity is lower than that obtained with the corresponding zirconocenes. Surprisingly enough, even when the isotactic pentad content is lower (see samples from titanium derivatives at 0°C), the average length of the isotactic blocks ($N_{iso} = 4 + 2\,[mmmm]/[mmmr]$) is almost equal or even slightly higher if compared with the zirconium homologues. This feature is appreciable in the methyl region of the spectra of the samples prepared

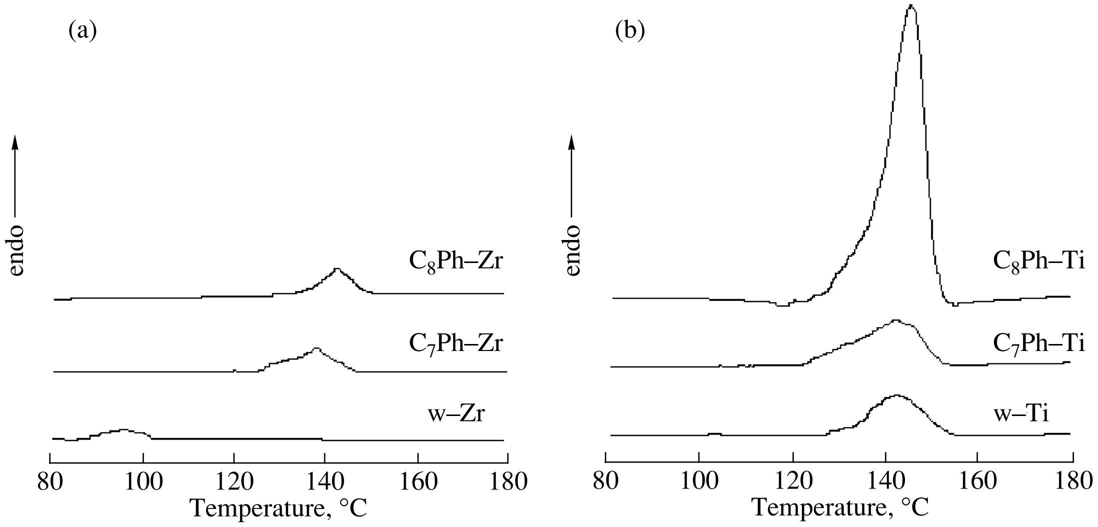


Fig. 3. DSC curves of the polypropylenes prepared with zirconium and titanium catalysts at –15°C.

with the titanium catalysts (Fig. 2b), which are characterized by the presence of the narrow signal of the [*mmmmmm*] heptad at 19.67 ppm. The pattern of the ^{13}C NMR spectra reported in Fig. 2 is evidence of the remarkable increase in the [*rr*] centered pentads (17.8–18.2 ppm) along with the presence of a considerable amount of regioirregularities (12.2–15.5 ppm) in the polymers obtained with titanium catalysts (Fig. 2b).

The appearance of broad melting transitions spanning from 90 to 150°C in the moderately isotactic samples from C_7Ph–Zr and C_8Ph–Zr (Fig. 3a), the same phenomenon observed in the sample prepared with w-Zr, allows us to hypothesize that C_7Ph–Zr and C_8Ph–Zr can also produce isotactic blocks. Independently of the isotactic pentad content [*mmmm*], in accordance with the N_{iso} values, the melting peaks observed in the DSC curves of polypropylenes generated with titanium catalysts are more evident than with the zirconium homologues (Fig. 3). The enthalpies of fusion are sensibly increased and the melting peaks are shifted toward higher temperatures (115–155°C). But despite the remarkable amount of the syndiotactic [*rr*] centered pentads, only isotactic crystallinity is observed.

The molecular weights of polypropylenes obtained with the zirconium catalysts, C_7Ph–Zr and C_8Ph–Zr, are of the same order of magnitude of those obtained with w–Zr, but the polydispersity is about 2 (typical of single-site catalysts), while it is higher for the reference catalyst. The samples obtained with titanium catalysts show molecular weight values similar to those of the polymers obtained with the zirconium homologues, while the molecular weight distributions are much

Table 2. Polymer fractionation data

Sample	wt %	[*mmmm*][a]	$N_{\text{iso}}^{\text{b}}$	T_m range[c], °C	$\Delta H_{\text{m}}^{\text{c}}$, J/g	$M_{\text{w}} \times 10^{-3\text{d}}$	PDI[d]
w–Ti	100	14.2	6.7	120–155	1.0	150	4.0
ESw–Ti	73	3.7	5.1	–	Amorphous	114	2.8
EIw–Ti	27	44.8	10.0	125–155	3.2	198	3.2
C_7Ph–Ti	100	7.9	6.2	120–155	1.2	234	6.5
ESC_7Ph–Ti	48	3.4	5.0	–	Amorphous	130	2.4
EIC_7Ph–Ti	52	18.4	8.1	120–155	2.1	293	3.3
C_8Ph–Ti	100	21.9	8.3	115–155	3.6	215	3.8
ESC_8Ph–Ti	60	14.5	6.3	–	Amorphous	178	2.5
EIC_8Ph–Ti	40	54.8	11.7	115–155	9.3	260	3.1

[a] Isotactic pentad content by ^{13}C NMR.
[b] Average length of isotactic blocks by ^{13}C NMR.
[c] By DSC on second endotherm scan.
[d] Molecular weight and polydispersity determined by SEC.

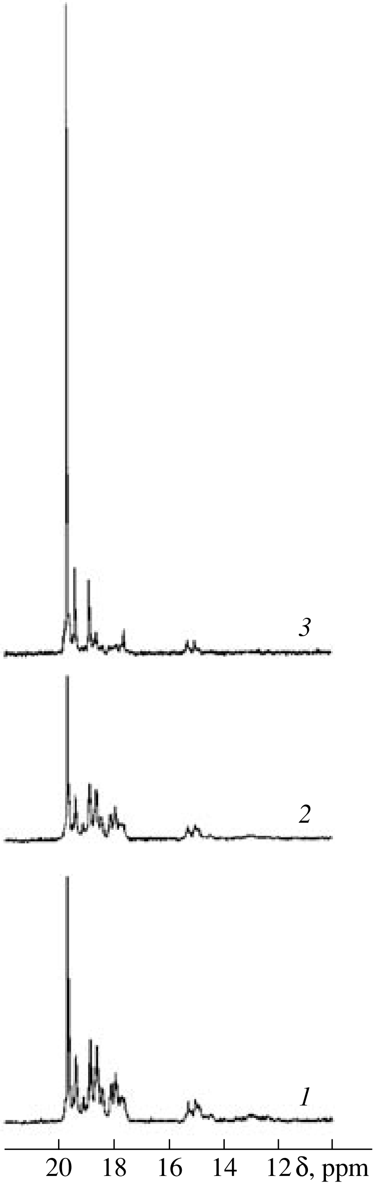


Fig. 4. Expansion of the ^{13}C NMR methyl region of raw polymer (*1*), ether-soluble (*2*), and ether-insoluble (*3*) fractions of the sample prepared with C_8Ph–Ti at –15°C.

wider, thus indicating a more heterogeneous material. Such heterogeneity is also evidenced by the fractionation data.

In the case of the zirconium catalysts, the molecular weight of the polymers obtained certainly plays a significant role in the sample solubility, because, even with w–Zr, the samples were either almost completely soluble in diethyl ether or separable in two fractions (one soluble and one insoluble in this solvent) of almost identical tacticity. This behavior, which differs from most published data [9], is supposedly due to the fact that, under our polymerization conditions, it is not possible to obtain isotactic segments long enough to give ether insoluble fractions. On the contrary, all samples from titanium could be separated into an ether-soluble (ES) fraction with low tacticity and an ether-insoluble (EI) fraction with higher tacticity, where the average length of isotactic sequences spans from 8.1 to 11.7 (Table 2).

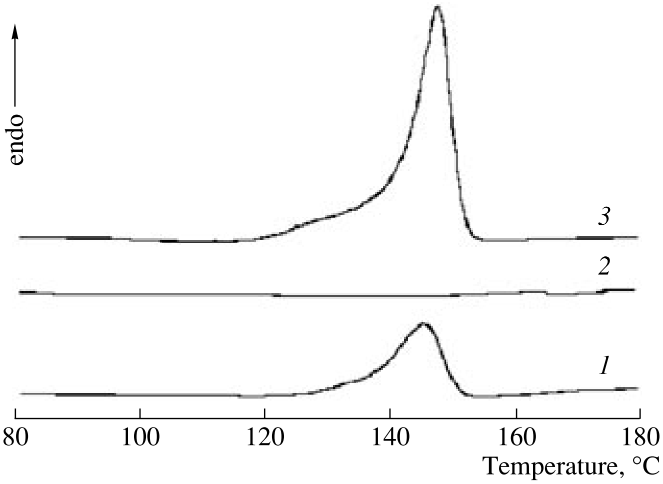


Fig. 5. DSC curves of raw polymer (*1*), ether-soluble (*2*), and ether-insoluble (*3*) fractions of the sample prepared with C_8Ph–Ti at –15°C.

In Fig. 4, the ^{13}C NMR spectra of the ether-soluble and ether-insoluble fractions of the sample prepared with C_8Ph–Ti are compared with that of the raw polymer. The two fractions show different thermal behavior (Fig. 5): the ES fraction does not exhibit any thermal transition under these experimental conditions, while the EI fraction shows a melting transition centered at 148°C, with an enthalpy of fusion of 9.3 J/g. The degree of crystallinity, obtained by dividing the experimental heat of fusion by the enthalpy of fusion of 100% crystalline polypropylene (209 J/g), is found to be approximately 4.5%.

CONCLUSIONS

Unbridged zirconocene catalysts, where a seven- or eight-membered ring fused to a cyclopentadiene is associated with a phenyl substituent in position 2 (C_7Ph–Zr and C_8Ph–Zr), were tested to produce polypropylenes with microstructure, molecular properties, and thermal behavior similar to those prepared with $(IndPh)_2ZrCl_2$, the "classical" Waymouth catalyst.

The results obtained show that it is possible to observe a "fluxional behavior" and to obtain stereoblock polypropylene even by replacing the basic indenyl structure with a slightly flexible saturated ring. This structural feature sensibly increases the stability of the complexes, thus making it possible to investigate the effect of switching from zirconium to titanium as metal center on the oscillating catalyst behavior. The polymers obtained with the titanium catalysts (C_7Ph–Ti and C_8Ph–Ti) were rather different from those obtained with their zirconium homologues (C_7Ph–Zr and C_8Ph–Zr). Indeed, independently of the percent of total isotacticity (lower in several cases), longer isotactic blocks are undoubtedly formed with titanium catalysts, as clearly shown by more evident melting peaks. The fractionation data, along with the broad molecular weight distribution, are in favor of quite heterogeneous materials.

ACKNOWLEDGMENTS

We warmly thank Mr. G. Zannoni, who has carefully and expertly performed all the NMR spectra and Mr. A. Giacometti Schieroni for his helpful contribution to SEC measurements. Dr. P. Locatelli's intellectual and experimental contribution is also gratefully acknowledged.

REFERENCES

1. Jordan, R.F., *Adv. Organomet. Chem.*, 1991, vol. 32, p. 325.
2. Möhring, P.C. and Coville, N.J., *J. Organomet. Chem.*, 1994, vol. 479, nos. 1–2, p. 1.
3. Brintzinger, H.-H., Fischer, D., Mülhaupt, R., Rieger, B., and Waymouth, R.M., *Angew. Chem., Int. Ed. Engl.*, 1995, vol. 34, no. 11, p. 1143.
4. Bochmann, M., *J. Chem. Soc., Dalton Trans.*, 1996, vol. 3, p. 225.
5. Kaminsky, W. and Arndt, M., *Adv. Polym. Sci.*, 1997, vol. 127, p. 143.
6. Resconi, L., Cavallo, L., Fait, A., and Piemontesi, F., *Chem. Rev.*, 2000, vol. 100, no. 4, p. 1253.
7. Kaminsky, W., *J. Polym. Sci., Part A: Polym. Chem.*, 2004, vol. 42, no. 16, p. 3911.
8. Coates, G. and Waymouth, R.M., *Science*, 1995, vol. 267, no. 5195, p. 217.
9. Lin, S. and Waymouth, R.M., *Acc. Chem. Res.*, 2002, vol. 135, no. 9, p. 765.
10. Reybuck, S.E., Meyer, A., and Waymouth, R.M., *Macromolecules*, 2002, vol. 35, no. 3, p. 637.
11. Dankova, M., Kravchenko, R.L., Cole, A.P., and Waymouth, R.M., *Macromolecules*, 2002, vol. 35, no. 8, p. 2882.
12. Wilmes, G.M., Lin, S., and Waymouth, R.M., *Macromolecules*, 2002, vol. 35, no. 14, p. 5382.
13. Wilmes, G.M., Polse, J.L., and Waymouth, R.M., *Macromolecules*, 2002, vol. 35, no. 18, p. 6766.
14. Dankova, M. and Waymouth, R.M., *Macromolecules*, 2003, vol. 36, no. 11, p. 3815.
15. Reybuck, S.E. and Waymouth, R.M., *Macromolecules*, 2004, vol. 37, no. 7, p. 2342.
16. Wilmes, G.M., France, M.B., Lynch, S.R., and Waymouth, R.M., *Organometallics*, 2004, vol. 23, no. 10, p. 2405.
17. Schneider, N., Schaper, F., Schmidt, K., Kirsten, R., Geyer, A., and Brintzinger, H.-H., *Organometallics*, 2000, vol. 19, no. 18, p. 3597.
18. Schmidt, R. and Alt, H.G., *J. Organomet. Chem.*, 2001, vol. 62, nos. 1–2, p. 304.
19. Dreier, T., Erker, G., Fröhlich, R., and Wibbeling, B., *Organometallics*, 2000, vol. 19, no. 20, p. 4095.
20. Dreier, T., Bergander, K., Wegelius, E., Fröhlich, R., and Erker, G., *Organometallics*, 2001, vol. 20, no. 24, p. 5067.
21. Grimmer, N.E., Coville, N.J., de Koning, C.B., Smith, J.M., and Cook, L.M., *J. Organomet. Chem.*, 2000, vol. 616, nos. 1–2, p. 112.
22. Schmidt, R., Deppner, M., and Alt, H.G., *J Mol. Catal. A: Chem.*, 2001, vol. 172, nos. 1–2, p. 43.
23. Busico, V., Cipullo, R., Kretschmer, W.P., Talarico, G., Vacatello, M., and Castelli, V.V.A., *Angew. Chem., Int. Ed. Engl.*, 2002, vol. 41, no. 3, p. 505.
24. Busico, V., Cipullo, R., Segre, A.L., Talarico, G., Vacatello, M., and Castelli, V.V.A., *Macromolecules*, 2001, vol. 34, no. 24, p. 8412.
25. Rodriguez-Delgado, A., Hannant, M.D., Lancaster, S.J., and Bochmann, M., *Macromol. Chem. Phys.*, 2004, vol. 205, no. 3, p. 334.
26. Maciejewski Petoff, J.L., Myers, C.L., and Waymouth, R.M., *Macromolecules*, 1999, vol. 32, no. 24, p. 7984.
27. Song, F., Hannant, M.D., Cannon, R.D., and Bochmann, M., *Macromol. Symp.*, 2004, vol. 213, p. 173.
28. Fujita, M., Seki, Y., and Miyatake, T., *Macromolecules*, 2004, vol. 207, no. 26, p. 9676.
29. Polo, E., Losio, S., Forlini, F., Locatelli, P., Provasoli, A., and Sacchi, M.C., *Macromol. Chem. Phys.*, 2002, vol. 203, no. 12, p. 1859.
30. Polo, E., Losio, S., Forlini, F., Locatelli, P., and Sacchi, M.C., *Macromol. Symp.*, 2004, vol. 213, p. 89.
31. Polo, E., Losio, S., Zecchi, G., Bertini, F., and Sacchi, M.C., *Macromol. Rapid. Commun.*, 2004, vol. 25, no. 21, p. 1845.
32. Polo, E., Barbieri, A., and Traverso, O., *New J. Chem.*, 2004, vol. 28, no. 5, p. 652.
33. Polo, E., Barbieri, A., and Traverso, O., *Eur. J. Inorg. Chem.*, 2003, vol. 9, no. 2, p. 324.
34. Mansel, S., Pérez, E., Benavente, R.J., Pereña, M., Bello, A., Roll, W., Kirsten, R., Beck, S., and Brintzinger, H.-H., *Macromol. Chem. Phys.*, 1999, vol. 200, no. 6, p. 1292.