Short Communication

# Asymmetric hydrodimerization of styrene by a chiral zirconium complex containing a tetradentate [OSSO]-type bis(phenolato) ligand

Nunzia Galdi, Orlando Santoro, Leone Oliva, Antonio Proto, Carmine Capacchione *

Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, via Ponte don Melillo, Fisciano I-84084, Salerno, Italy

## ABSTRACT

The chiral non racemic $(\Lambda,R,R)$-[OSSO]Zr(CH$_2$Ph)$_2$ (**1a**) activated by methylaluminoxane (MAO) and in presence of H$_2$ produces the chiral hydrodimer $(S)$-1,3-diphenylbutane with good selectivity respect to the achiral 1,4-diphenylbutane. The absolute configuration of the chiral dimer and the effect of the hydrogen pressure on the ratio between 1,3-diphenylbutane and 1,4-diphenylbutane give useful information about the regiochemistry and stereochemistry of insertion of the styrene into the Zr–H bond.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The synthesis of optically active molecules through the asymmetric formation of carbon–carbon bond by using reactions catalyzed by chiral non-racemic transition metal compounds is one of the most active tasks in chemistry [1–8].

In spite of the wide armory of reactions studied for this purpose, the catalytic oligomerization of olefins by using chiral metal complexes has received rather limited attention. As a matter of fact the possibility of obtaining optically active low molecular weight compounds through propene and higher olefins polyinsertion was first described by Pino et al. [9,10] that used a catalytic system based on a chiral C$_2$ symmetric ansa zirconocene. Beside the potential synthetic application, they used such chiral hydro-oligomer to infer useful information on the stereocontrol mechanism of such polymerization catalysts. More recently, some of us used the same approach not only to obtain some information about the regiochemistry and stereochemistry of the styrene polyinsertion [11] but also for the synthesis of the optically active 1,3-diphenylbutane (1,3-dpb) through styrene hydrodimerization in presence of an optically active zirconocene [12,13]. A severe limitation of this catalytic system is due to the concomitant production in larger amount of the achiral hydrodimer 1,4-diphenylbutane (1,4-dpb). Such occurrence has been explained considering that while into the initial Zr–H bond a primary (e.g. a methylene-Zr bond is formed) regiochemistry of insertion of styrene is favored, after the formation of the Zr–C bond

the secondary (e.g. a methine-Zr bond is formed) insertion becomes favored (Scheme 1).

Furthermore, by modification of the ligand framework, however, it was possible to increase the yield of the desired dimer 1,3-diphenylbutane but the development of the enantioselective version of this reaction remains unexplored due the not easy synthesis of the chiral non-racemic metallocene. More recently, a family of catalysts based on a tetradentate ligand having two phenolate units linked through a 1,ω-dithiaalkanediyl bridge S(CH$_2$)$_2$S has been shown to efficiently promote the isoselective polymerization of styrene [14–18]. In addition, the chiral version of this ligand was also developed and the corresponding titanium compounds were used for the synthesis of optically active oligostyrenes [19,20].

Here we report on the synthesis of the chiral zirconium OSSO complex **1a** and on the ability of this complex to give the optically active styrene hydrodimer when activated by methylaluminoxane.

## 2. Experimental

### 2.1. Materials

All air- and moisture-sensitive manipulations were performed under nitrogen atmosphere using standard Schlenk techniques and an MBraun dry-box. All reagents and solvents were purchased from Aldrich. Dry solvents were dried by standard methods and distilled before use.

Styrene (99% GC, Aldrich) was stirred for 1 h over calcium hydride before distillation under nitrogen at reduced pressure. The commercial methylaluminoxane (10% in toluene from Aldrich) was dried by removing *in vacuo* solvent and traces of trimethylaluminium and used
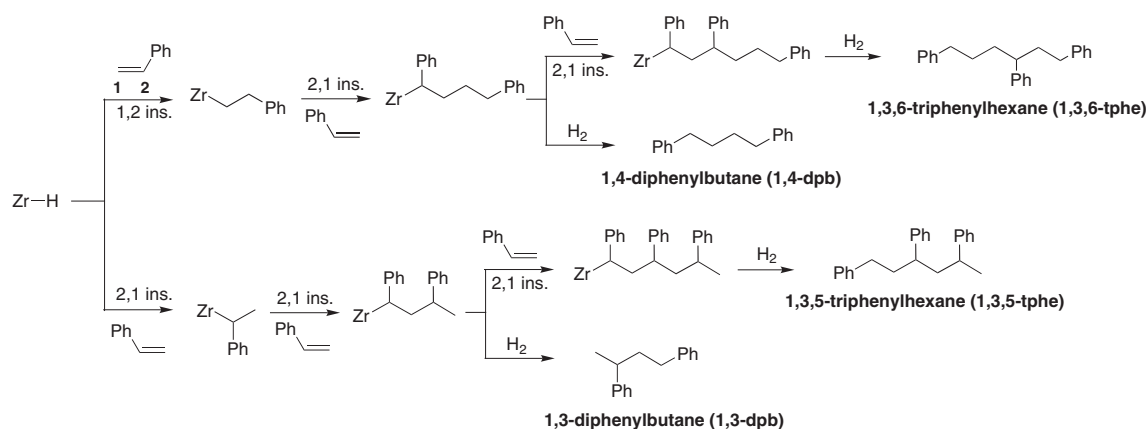
**Scheme 1.** Possible pathways for the production of styrene hydrodimers and hydrotrimers.

as powder. (R,R)-ligand **1** [19,20], tetrabenzylzirconium $Zr(CH_2Ph)_4$ [21] and the oxidation of 1,3-(dpb) to 2-methylglutaric acid [12] were prepared by using the procedures described in the literature.

## 2.2. Characterization

NMR spectra were recorded on Bruker Avance 400 or on Bruker Avance 300 spectrometers at 25 °C, unless otherwise stated. Chemical shifts ($\delta$) are listed as parts per million. $^1H$ NMR spectra are referenced using the residual solvent peak at $\delta$ 7.16 for $C_6D_6$ and $\delta$ 7.27 for $CDCl_3$. $^{13}C$ NMR spectra are referenced using the residual solvent peak at $\delta$ 128.39 for $C_6D_6$ and $\delta$ 77.23 for $CDCl_3$. $^{13}C$ NMR spectra of polymer was recorded on a Bruker Avance 600 spectrometer.

The assignment of resonance signals in the $^{13}C$ NMR spectra of the hydrooligomers has been carried out through the additivity rules and through comparison with the literature data [12].

Gas chromatographic measurements of the mixture of hydro-oligomers were performed on a GC Thermo Electron Corporation equipped with a flame ionization detector operated at 250 °C and with Famewax column (crossbond PEG, 30 m, 0.32 mm ID). Optical rotations were measured with a JASCO DIP-1000 polarimeter. Enantiomeric excess of 2-methylglutaric acid was determined by using a Jasco PU-2089 Plus and a Jasco MD-2010 Plus multi-wavelength detector HPLC System equipped with a Chiralpak R OD-H.

## 2.3. Synthesis of **1a**

To a stirred solution of (R,R)-ligand **1** (0.31 g, 0.56 mmol) in 20 mL of toluene was added a solution of tetrabenzylzirconium (0.255 g, 0.56 mmol) in 10 mL of toluene at 0 °C. A yellow solid is formed immediately and the mixture was stirred for 2 h. The solvent was removed under reduced pressure and the solid was washed twice with fresh hexane ($2\times1$ mL) to give (Λ,R,R)-[OSSO]Zr(CH₂Ph)₂ (**1a**) (0.29 g, 0.35 mmol, 62.5%) as a yellow powder. Elemental analysis (calc.): C: 69.15 (69.80); H: 7.56 (7.79); S 7.23 (7.74).

$^1H$ NMR (400 MHz, $\delta$, ppm, $C_6D_6$): 0.37 (m, 2H, CH, $C_6H_{10}$), 1.13 (m, 2H, CH, $C_6H_{10}$ overlapping with tBu signal), 1.27 (s, 18H, $C(CH_3)_3$), 1.36 (m, 2H, CH, $C_6H_{10}$), 1.58 (s, 18H, $C(CH_3)_3$), 1.84 (m, 2H, CH, $C_6H_{10}$), 1.98 (d, 2H, CH2Ph), 2.31 (m, 2H, CHS), 2.33 (d, 2H, $CH_2Ph$), 6.88 (t, 2H), 6.93 (d, 2H), 7.0 (d, 2H), 7.03–7.1 (m, 4H), and 7.49 (s, 4H).

$^{13}C$ NMR (400 MHz, $\delta$, ppm, $C_6D_6$): 26.06 ($CH_2$, $C_6H_{10}$), 30.43 ($C(CH_3)_3$), 31.71 ($C(CH_3)_3$), 32.47 ($CH_2$, $C_6H_{10}$), 34.88 ($C(CH_3)_3$), 36.23 ($C(CH_3)_3$), 53.86 (CHS), 60.94 ($CH_2Ph$), 117.74 (arom.), 123.54 (arom.), 127.0 (arom.), 129.87 (arom.), 130.85 (arom.), 131.67 (arom.), 137.85 (arom.), 141.24 (arom.), 143.95 (arom.), and 165.65 (arom.).
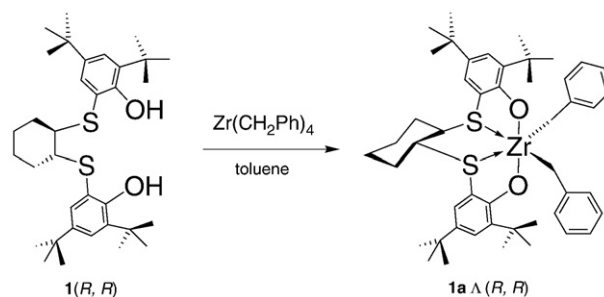
## 2.4. Styrene hydrooligomerization

A 100 mL steel autoclave thermostated at 50 °C was evacuated and then charged with a mixture of styrene, MAO and **1a** (Al/Zr in mol = 500) and, when necessary, toluene. The reactor was feed with hydrogen at constant pressure (11, 20 or 30 atm) and magnetically stirred.

The reactions were stopped after 48 h by venting off the hydrogen and the reaction mixture was poured into acidified ethanol. By shaking with water and n-pentane ($3\times$) the organic phase was separated and recovered. After drying of the solution with $Na_2SO_4$, the n-pentane was removed under reduced pressure and a yellow oily mixture of oligomers was recovered. The composition of the mixture, determined by GC analyses and $^{13}C$ NMR spectra, shows the complete consumption of the monomer in all cases.
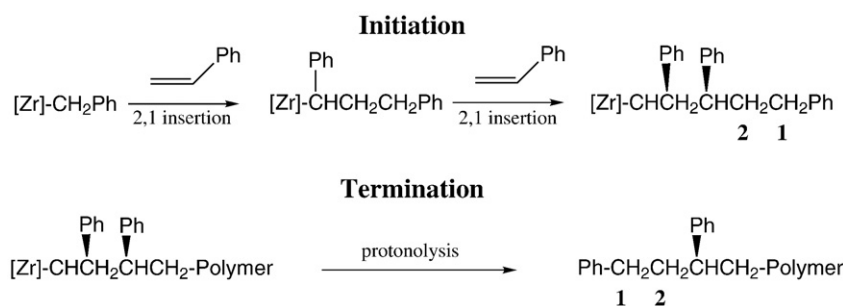
A further distillation under reduced pressure affords a fraction of hydrogenated monomer, the second fraction containing the mixture of hydrodimers, and the third one containing a mixture of hydro-trimers and hydrotetramers.

## 2.5. Styrene polymerization

A 100 mL glass flask equipped with a magnetic stirrer was charged, under a nitrogen atmosphere, with Al–Oct₃ (1 mL, 7.6 mmol) as scavenger, styrene (5 mL, 43.5 mmol) and toluene (20 mL). The mixture was thermostated at the 50 °C and then a solution of toluene (1 mL), **1a** (5 mg, 6.03 μmol) and $B(C_6F_5)_3$ (3.09 mg, 6.03 μmol) was injected. The reaction was stopped after 15 min in order to obtain low molecular weight and the raw polymer was coagulated in methanol acidified with aqueous HCl and recovered by filtration. Then the



**Scheme 2.** Synthesis of the zirconium complex 1a.

## Initiation

[Zr]-CH₂Ph → (2,1 insertion) → [Zr]-CHCH₂CH₂Ph → (2,1 insertion) → [Zr]-CHCH₂CHCH₂CH₂Ph

**Scheme 3.** Initiation and termination reactions in styrene polymerization with secondary regiochemistry.

polymer was twice dissolved in chloroform, coagulated in ethanol, recovered by filtration and finally dried *in vacuo*.

Yields: 80 mg.

## 3. Results and discussion

The catalyst **1a** was synthesized by reacting the ligand **1** with an equimolar amount of tetrabenzylzirconium in toluene at room temperature (Scheme 2).

The resulting product is very soluble in all common organic solvents (hexane, pentane, $CH_2Cl_2$, and THF). The zirconium complex was preferred with respect to the corresponding titanium complex for the tendency shown in the zirconium complexes bearing the related ligand with 1,4 dithiabutanediyl bridge $S(CH_2)_2S$ to produce lower molecular weight isotactic polystyrene compared to the corresponding titanium complex [14].

The complex **1a** activated by $B(C_6F_5)_3$ was used in the polymerization of styrene in order to obtain some information about the regiochemistry of insertion of styrene during the polymerization process. As a matter of fact the polymer obtained in presence of the catalyst **1a** shows, in addition to the peaks of the isotactic sequences, relevant signals at 33.7 ppm and 37.5 ppm in the $^{13}C$ NMR spectrum that can both arise from the secondary insertion of styrene into the Zr–CH₂Ph and from protonolysis of the Zr-methine bond of the growing polymeric chain produced by consecutive secondary styrene insertions (see Fig. 1 and Scheme 3). It is important to point out that such chain-end is the only one detectable in the carbon spectrum revealing that the polymerization is highly regioselective both in the initiation and in the termination steps. It is worth reminding that a similar 2,1 insertion of the first monomer unit into the Ti–CH₃ bond was observed in the case of the dichloro{1,4-dithiabutanediyl-2,2′-bis (4,6-di-*tert*-butyl-phenoxy)}titanium activated by methylaluminoxane isotopically enriched with $^{13}CH_3$ groups [14].

The precatalyst **1a** activated by MAO was then used for the hydrodimerization of styrene in the presence of $H_2$. Under these reaction conditions one can assume that the catalytic active species is

solely a cationic Zr–H compound arising from the simultaneous presence of MAO and $H_2$. The results are summarized in Table 1.

It is worth noting that the selectivity of the catalysts **1a** with respect to the production of 1,3-dpb is remarkably higher compared to the zirconocene systems {e.g. (*R,R*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, **2**} giving, under the same reaction conditions, preferentially the 1,4-dpb and higher oligomers (see Fig. 2).

The potential interest of this reaction, in our opinion, lies in the possibility to obtain a chiral molecule starting form a large available, low-cost commodity such as styrene and in the fact that the main product of the reaction, ethylbenzene can be easily dehydrogenated regenerating the starting monomer. Assuming that the catalytic species is a cationic Zr–H, 1,3-dpb can arise by two consecutive insertion of the styrene monomer into the Zr–H bond with the same regiochemistry (primary or secondary) followed by the cut by $H_2$, while 1,4-dpb can only arise by a primary insertion into the Zr–H bond followed by a secondary insertion and then by the cut by $H_2$ (see Scheme 1).

In accordance with what was observed in the above described styrene polymerization, we can assume that the regiochemistry of insertion into the Zr–C bond is prevalently secondary, so the present results can be explained considering that the 1,3-dpb is arising by two consecutive secondary insertions while the 1,4-dpb is produced by the occasional misinsertion into the Zr–H bond followed by a secondary insertion into the Zr–C bond. This scenario is quite different from that observed in the case of zirconocenes: in this last case the primary insertion of the styrene unit into the Zr–H is favored followed by 2,1 insertion into the new Zr–C bond giving the 1,4-diphenylbutane as major product [12].

Furthermore, Table 1 shows that the ratio between the two hydrodimers is not sensitive to the hydrogen pressure suggesting that the cut for both intermediates involves a Zr-methyne bond. As a matter of fact, for zirconocenes [12] as well as for hafnocenes [22] the ratio 1,3-dpb/1,4-dpb increases by increasing the hydrogen pressure due to the different Zr–C (metal-methylene and metal-methyne respectively) bonds existing when the hydrogen cuts the growing chain. The increase in the production of higher oligomers at higher
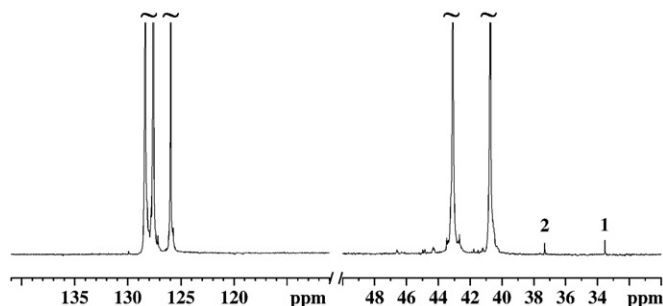


**Fig. 1.** $^{13}C$ NMR spectrum of the polystyrene obtained in the presence of **1a** activated by $B(C_6F_5)_3$ and Al–Oct₃.

**Table 1**
Relative amounts of hydrooligomers with different $H_2$ feed compositions[a].

| Entry | $P(H_2)$/[styrene] | 1,3-dpb[b] | 1,4-dpb[c] | Higher oligomers[d,e] | 1,3-dpb/1,4-dpb |
|-------|------------|--------|--------|---------------------|-----------------|
| 1 | 5.04 | 20 | 2.7 | 15.8 | 7.4 |
| 2 | 9.2 | 18.5 | 2.4 | 9.9 | 7.7 |
| 3 | 13.8 | 9.5 | 1.25 | 11.23 | 7.6 |

[a] Reaction conditions: $T = 50\,°C$, MAO/catalyst = 500, [styrene] = 2.18 M, $P(H_2)$ = 11, 20 or 30 atm.
[b] Percentage of styrene converted into 1,3-diphenylbutane.
[c] Percentage of styrene converted into 1,4-diphenylbutane.
[d] Percentage of styrene converted into higher oligomers.
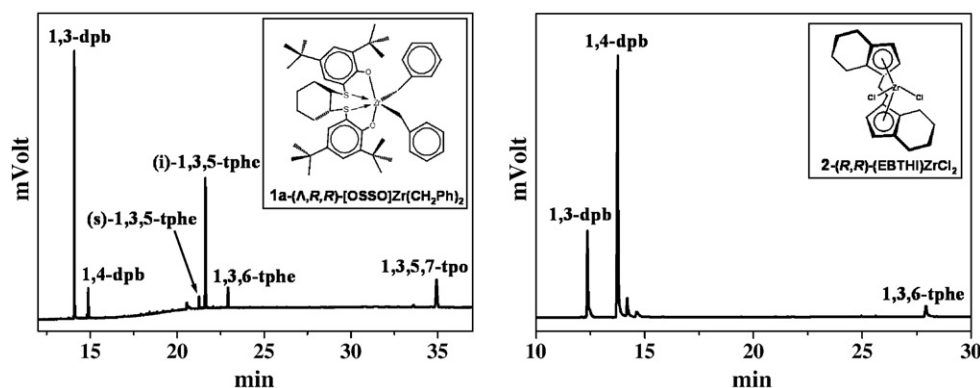[e] The complement to 100% is formed by ethylbenzene.

**Fig. 2.** Gas-chromatograms of the mixture of hydrooligomers obtained in the presence of the chiral (Λ,R,R)-[OSSO]Zr(CH$_2$Ph)$_2$ (**1a**) and of chiral (R,R)-(EBTHI)ZrCl$_2$ (**2**).

hydrogen pressure observed (run 3, Table 1) can be explained considering that at such hydrogen pressure a decomposition of the catalyst due to the cleavage of the sulfur–carbon bond is not unlikely.

It is worth noting that the product 1,3-dpb holds a stereogenic center, therefore should be possible in principle, by using the chiral enantiopure catalyst **1a**, to obtain this molecule as pure enantiomer. From the stereochemical point of view, the analysis of the 1,3-dpb arising from the styrene hydrodimerization conducted in presence of the chiral non-racemic catalyst **1a** displays an $[\alpha]_D = +10.6$ with an estimated optical purity of 68% [23]. Due to the absence of functional groups into the 1,3-dpb molecule a direct separation by chiral HPLC in order to evaluate the enantiomeric purity was unsuccessful, therefore we transformed the 1,3-dpb into the 2-methylglutaric acid by oxidation promoted by ruthenium tetraoxide (see Scheme 4).

The analysis of the obtained 2-methylglutaric by chiral HPLC gives an enantiomeric excess of 71% very close to the value obtained from optical rotation.

In addition, from the sign of the optical rotation, we can safely attribute the absolute configuration of the carbon atom as S. This clearly indicates that the Λ,R,R complex **1a** prefers the coordination of styrene enantioface re with secondary regiochemistry of insertion. This result is in agreement with the molecular model based on a so-called octant scheme by Pino et al. which take into account the steric repulsion between the ligand sphere and the incoming monomer unit [20,24,25].

The high enantioselectivity is further supported by the analysis of the composition of the trimers 1,3,5-triphenylhexane (1,3,5-tphe) arising from three consecutive regioregular insertions. As a matter of fact Fig. 2 shows that the trimer arising by two consecutive insertions of the monomer with same enantioface (iso) (i)-1,3,5-tphe is largely prevailing with respect to the trimer produced by insertions with opposite enantioface (syndio) (s)-1,3,5-tphe (iso/syndio ≈ 12).

It is worth to note that in this polyinsertion process we observe the stereocontrol for the first monomer insertion, that is for the insertion into the Zr–H bond. On the contrary, the traditional Ziegler–Natta catalysts exhibit good enantioselectivity for the 1-alkenes only when the insertion occurs into a M–R bond with R greater than C$_2$H$_5$ while for the styrene a weak stereocontrol is reported when R is CH$_3$, for the insertion into the Ti-methyl bond [26].
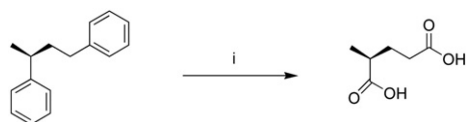
## 4. Conclusions

In this communication we have shown that the chiral non racemic (Λ,R,R)-[OSSO]Zr(CH$_2$Ph)$_2$ is able to catalyze the enantioselective formation of a C–C bond through styrene hydrodimerization affording the chiral (S)-1,3-diphenylbutane with good selectivity respect to the achiral dimer 1,4-diphenylbutane. In particular the regioselectivity toward this molecule is higher compared to the chiral ansa-zirconocene compounds. In spite of the overall low yield (20%) it is important to point out that styrene is a large available, low cost commodity and that the main product of the reaction ethylbenzene is the industrial precursor of the starting substrate. Furthermore the analysis of the composition of the oligomer mixture and of the configuration of the chiral carbon indicates the styrene secondary insertion into the Zr–H bond in the pathway affording 1,3-dpb. As a perspective, the nature of the coordinative framework of this complex gives wide possibility of improving both chemoselectivity and enantioselectivity towards the chiral hydrodimer, through the increase of size of the substituents of the aromatic ring. It is worth noting that with this system the stereocontrol works also without the assistance of a hindered alkyl group bound to the metal, at difference of what was observed with traditional as well homogeneous Ziegler–Natta catalysts.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.03.037.

### References

[1]  A. de Meijere, F. Diederich, Metal-Catalyzed Cross-Coupling Reactions, 2nd Ed Wiley-VCH, Weinheim, Germany, 2004;
      B.A.H. Hoveyda, J.P. Morken, Angew. Chem. Int. Ed. Engl. 35 (1996).
[2]  A.H. Hoveyda, J.P. Morken, Angew. Chem. Int. Ed. Engl. 35 (1996) 1262–1284.
[3]  B.M. Trost, D.L. van Vranken, Chem. Rev. 96 (1996) 395–422.
[4]  M. Johannsen, K.A. Jorgensen, Chem. Rev. 98 (1998) 1689–1708.
[5]  G. Helmchen, A. Pfaltz, Acc. Chem. Res. 33 (2000) 336–345.
[6]  B.M. Trost, M.L. Crawley, Chem. Rev. 103 (2003) 2921–2943.
[7]  Z. Lu, S. Ma, Angew. Chem. Int. Ed. 47 (2008) 258–297.
[8]  M. Dieguez, O. Pamies, Acc. Chem. Res. 43 (2010) 3126–3322.
[9]  P. Pino, P. Cioni, J. Wei, J. Am. Chem. Soc. 109 (1987) 6189–6191.
[10] P. Pino, P. Cioni, M. Galimberti, J. Wei, N. Piccolrovazzi, in: W. Kaminsky, H. Sinn (Eds.), Transitions Metals and Organometallics as Catalysts for Olefin Polymerization, Springer-Verlag, Berlin Heidelberg, 1988, pp. 269–279.



**Scheme 4.** Reagents and conditions: i AcOEt, CH$_3$CN, H$_2$O, NaIO$_4$, RuCl$_3$, 17 h, rt.

[11] L. Izzo, M. Napoli, L. Oliva, Macromolecules 36 (2006) 9340–9345.
[12] N. Galdi, C. Della Monica, A. Spinella, L. Oliva, J. Mol, Cat. A: Chem. 243 (2006) 106–110.
[13] A. Correa, N. Galdi, L. Izzo, L. Cavallo, L. Oliva, Organometallics 27 (2008) 1028–1029.
[14] C. Capacchione, A. Proto, H. Ebeling, R. Mülhaupt, K.T.P. Spaniol, K. Möller, J. Okuda, J. Am. Chem. Soc. 125 (2003) 4964–4965.
[15] C. Capacchione, A. Proto, H. Ebeling, R. Mülhaupt, K.R. Mannivannan, K. Möller, T.P. Spaniol, J. Okuda, J. Mol. Cat. A: Chem. 213 (2004) 137–140.
[16] K. Beckerle, C. Capacchione, H. Ebeling, R. Manivannan, R. Mülhaupt, A. Proto, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 689 (2004) 4636–4641.
[17] C. Capacchione, R. Manivannan, M. Barone, K. Beckerle, R. Centore, L. Oliva, A. Proto, A. Tuzi, T.P. Spaniol, J. Okuda, Organometallics 24 (2005) 2971–2982.
[18] F. De Carlo, C. Capacchione, V. Schiavo, A. Proto, J. Polym. Sci. A: Polym. Chem. 44 (2006) 1486–1491.
[19] K. Beckerle, R. Manivannan, B. Lian, G.-J.M. Meppelder, G. Raabe, T.P. Spaniol, H. Ebeling, F. Pelascini, R. Mülhaupt, J. Okuda, Angew. Chem. Int. Ed. 46 (2007) 4790–4793.
[20] G.-J.M. Meppelder, K. Beckerle, R. Manivannan, B. Lian, G. Raabe, T.P. Spaniol, J. Okuda, Chem. Asian J. 3 (2008) 1312–1323.
[21] U. Zucchini, E. Albizzati, U. Giannini, J. Organomet. Chem. 26 (1971) 357–372.
[22] N. Galdi, L. Izzo, L. Oliva, Organometallics 29 (2010) 4434–4439.
[23] C. Fouquet, J. Jacques, Bull. Soc. Chim. Fr. (1973) 618–621.
[24] P. Pino, J. Am. Chem. Soc. 109 (1987) 6189–6191.
[25] P. Pino, M. Galimberti, P. Prada, G. Consiglio, Makromol. Chem. 191 (1990) 1677–1688.
[26] P. Ammendola, T. Tancredi, A. Zambelli, Macromolecules 19 (1986) 307–310.