



Polymerization of 1,3-dienes with iron complexes based catalysts Influence of the ligand on catalyst activity and stereospecificity

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

Abstract

Various iron dichloride complexes with aliphatic and aromatic bidentate amine ligands have been synthesized and used, in combination with aluminium-compounds (AlR₃ or methylaluminumoxane (MAO)), for the polymerization of 1,3-dienes. Catalyst activity, chemo- and stereoselectivity are strongly influenced by the type of ligand; systems based on iron complexes with aromatic bidentate amines (e.g. bipyridine or phenanthroline), in particular, exhibit an extremely high activity, giving from butadiene a 1,2-syndiotactic polymer. These systems are also able to polymerize substituted butadienes (e.g. isoprene, (*E*)-1,3-pentadiene, 2,3-dimethyl-1,3-butadiene) giving polymers with different structure from the different monomers; these results have permitted to confirm some aspects of the polymerization mechanism previously proposed.

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1. Introduction

Iron catalysts have not been extensively studied in the field of conjugated diolefin polymerization: only a few papers are reported in the literature concerning the homo- and copolymerization of butadiene and isoprene with the catalytic system obtained by mixing Fe(acac)₃, Al(*i*-Bu)₃ and 1,10-phenanthroline (phen) [1–3]. This system is reported to have a low activity and a poor stereoselectivity: it gives a polybutadiene

with a mixed *cis*-1,4/1,2 structure and a polyisoprene with an essentially 3,4 structure. The active species in this catalytic system, as suggested by the authors, is probably an iron(II) complex, originating from the reduction of Fe(acac)₃ by the aluminium-alkyl, containing one phenanthroline ligand. More recently, papers have been reported in the patent literature concerning the polymerization of butadiene with catalyst systems obtained by combining an iron-containing compound (e.g. carboxylates), an organomagnesium compound and a dihydrocarbyl hydrogen phosphite [4]. These systems are reported to have a good activity and give equibinary *cis*-1,4/1,2-polybutadienes or essentially 1,2-syndiotactic polybutadienes having various melting temperatures and

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syndiotacticity degree, depending on the catalyst formulation.

Now we have synthesized and characterized several Fe(II) complexes by reacting FeCl₂ with various bidentate ligands (e.g. 1,10-phenanthroline and bipyridine), as already described in the literature [5–11]; all these complexes have then been used in combination with aluminium-alkyls (Al(*i*-Bu)₃, Al(Et)₃, methylaluminoxane (MAO)) for the polymerization of various 1,3-dienes (butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, (*E*)-1,3-pentadiene), giving catalysts much more active and stereospecific than the previous ones. The most significant results of this work are reported in this paper.

2. Experimental

2.1. Materials

FeCl₂ anhydrous and FeCl₂·4H₂O (Aldrich, 99.9% pure), Al(*i*-Bu)₃ (Aldrich), Al(Et)₃ (Aldrich, 93% pure), MAO (Crompton, 10 wt% solution in toluene), *N,N,N',N'*-tetramethylethylenediamine (tmeda) (Fluka, ≥99% pure), *N,N'*-dimethylethylenediamine (dmeda) (Fluka, ≥98% pure), 2,2'-bipyridine (bipy) (Fluka, ≥98% pure), 1,10-phenanthroline (Fluka, ≥99.5% pure), 5-methyl-1,10-phenanthroline (5-methyl-phen) (Aldrich, ≥99% pure), 4-methyl-1,10-phenanthroline (4-methyl-phen) (Aldrich, 99% pure), 5,6-dimethyl-1,10-phenanthroline (5,6-dimethyl-phen) (Aldrich, 99% pure), 4,7-dimethyl-1,10-phenanthroline (4,7-dimethyl-phen) (Aldrich, 98% pure), 4,7-diphenyl-1,10-phenanthroline (4,7-diphenyl-phen) (Aldrich, 97% pure), 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8-tetramethyl-phen) (Aldrich, ≥99% pure), 2,9-dimethyl-1,10-phenanthroline (2,9-dimethyl-phen) (Aldrich, 99%), 1,2-bis(dimethylphosphino)ethane (dmpe) (Aldrich, >97% pure), were used as received. 1,3-Butadiene (Air Liquide, >99.5% pure) was evaporated from the container prior to each run, dried by passing through a column packed with molecular sieves, and condensed into the reactor which had been precooled to -20 °C. Isoprene (Aldrich, 99% pure), (*E*)-1,3-pentadiene (Aldrich, 98% pure) and 2,3-dimethyl-1,3-butadiene (Aldrich, 98% pure) were refluxed over CaH₂ for ca. 2 h, then distilled trap-to-trap and stored under dry nitrogen.

2.2. Synthesis of iron(II) complexes

Synthesis of Fe(tmeda)Cl₂ [5]: A suspension of FeCl₂·1,5-THF (2.632 g, 11.2 mmol) in toluene (50 ml) was treated with tmeda (*N,N,N',N'*-tetramethylethylenediamine) (11.2 mmol). The reaction was heated at ca. 80 °C for 4 h. The solid was isolated by filtration and dried in vacuum at room temperature obtaining a microcrystalline solid sensitive to oxygen and moisture (80% yield).

Synthesis of Fe(dmeda)Cl₂ [5]: A suspension of FeCl₂·1,5-THF (0.846 g, 3.6 mmol) in toluene (30 ml) was treated with dmeda (*N,N'*-dimethylethylenediamine) (0.38 ml, 3.6 mmol). The reaction was heated at ca. 60 °C for 2 h and the colorless solid was isolated by filtration and dried in vacuum at room temperature obtaining Fe(dmeda)Cl₂ (79% yield) as a microcrystalline solid sensitive to oxygen and moisture.

Synthesis of Fe(bipy)Cl₂ [6]: FeCl₂ (0.41 g, 3.24 mmol) was dissolved with mild heating (ca. 60 °C) and stirring in absolute ethanol (60 ml), which had been deoxygenated with nitrogen gas. Once the ferrous chloride powder was dissolved in ethanol a deoxygenated solution of 2,2'-bipyridine (0.51 g, 3.27 mmol) in absolute ethanol was added slowly. After all the bipy/ethanol solution has been added, heating and stirring were continued for another 3–5 min. The solid was then isolated by filtration and dried in vacuum obtaining Fe(bipy)Cl₂ (80% yield), orange powder. Fe(phen)Cl₂ was synthesized by the same procedure.

Synthesis of Fe(phen)₂Cl₂ [7]: A suspension of 1,10-phen (3.62 g, 19.5 mmol) in water (30 ml) was treated with FeCl₂·4H₂O (1.29 g, 6.5 mmol). The reaction was stirred for 1 h. The reaction mixture was dried in vacuum at 50 °C obtaining a purple solid which was heated at 160 °C in vacuum (10⁻² Torr) for 12 h in the presence of P₂O₅ with the formation of the blue Fe(phen)₂Cl₂ (85% yield).

Fe(5,6-dimethyl-phen)₂Cl₂, Fe(bipy)₂Cl₂, Fe(5-methyl-phen)₂Cl₂, Fe(4,7-dimethyl-phen)₂Cl₂, Fe(2,9-dimethyl-phen)₂Cl₂, Fe(4,7-diphenyl-phen)₂Cl₂, Fe(4-methyl-phen)₂Cl₂, Fe(3,4,7,8-tetramethyl-phen)₂Cl₂ compounds were synthesized by the same way [7].

Synthesis of Fe(phen)₃Cl₂ [8]: A suspension of 1,10-phen (3.62 g, 19.5 mmol) in water (30 ml) was treated with FeCl₂·4H₂O (1.29 g, 6.5 mmol). The

reaction was stirred for 1 h. The reaction mixture was dried in vacuum at 50 °C obtaining a purple solid.

$\text{FeCl}_2(\text{dmpe})_2$ was synthesized as described in the literature [9].

2.3. Polymerization of 1,3-dienes

A standard procedure is reported. 1,3-Butadiene was dried by passing through a column packed with molecular sieves and condensed (2 ml) in a 25 ml Schlenk tube kept at –20 °C; toluene and aluminium alkyl were then added. The reactor was brought to the polymerization temperature and the iron complex as toluene suspension was introduced at the end. The polymerization was terminated with methanol containing a small amount of hydrochloric acid; the polymer was coagulated and repeatedly washed with methanol and then dried in vacuum at room temperature.

The polymerizations of the other 1,3-dienes (isoprene, 2,3-dimethyl-1,3-butadiene, (*E*)-1,3-pentadiene) were carried out in a similar way.

2.4. Polymer characterization

^1H and ^{13}C NMR measurements were performed with a Bruker AM 270 instrument. The spectra were obtained in CD_2Cl_4 at 103 °C (hexamethyldisiloxane, HMDS, as internal standard) or in CDCl_3 at room temperature (tetramethylsilane, TMS, as internal standard). The concentration of polymer solutions was about 10 wt.%.

Differential scanning calorimetry (DSC) scans were carried out on Perkin-Elmer Pyris 1 instrument: typically, ca. 10 mg of polymer were analyzed in each run, while the scan speed was ca. 20 K/min under dinitrogen atmosphere.

The infrared spectra were performed with a Bruker IFS 48 instrument using polymer films on KBr disks. The films were obtained by deposition from solutions in benzene or hot (ca. 100 °C) solutions in 1,2,4-trichlorobenzene.

MW and MWD were determined by GPC analysis using the Universal Calibration method. The GPC system was composed by a Agilent 1100 pump, a detector IR Agilent 1100 and PL Mixed-A columns; tetrahydrofuran (1 ml/min) was used as solvent at 25 °C.

Polymer microstructure was determined as reported the literature [10–20].

3. Results and discussion

The results obtained by polymerizing butadiene with catalysts based on different iron complexes are reported in Table 1 and can be summarized as follows.

- (i) The systems FeCl_2/MAO is inactive in the polymerization of butadiene. The same can be said for the system $\text{FeCl}_2(\text{dmpe})_2\text{-MAO}$; most probably in this case the phosphine ligands are displaced by the monomer and the effective catalyst is FeCl_2/MAO .

Table 1

Polymerization of butadiene with iron catalysts: influence of the type of ligand on catalyst activity and stereospecificity

Fe-compound	Fe (mol) ($\times 10^6$)	Time (min)	Conversion (%)	Microstructure (%) ^a			MW ^b ($\times 10^{-3}$)	MWD ^b
				<i>cis</i>	<i>trans</i>	1,2		
FeCl_2	10	1110	–					
$\text{FeCl}_2(\text{dmpe})_2$	10	1110	–					
$\text{FeCl}_2(\text{tmeda})$	10	100	10	66.6	6.5	26.9	400	
$\text{FeCl}_2(\text{dmeda})$	10	1110	46.5	63.2	16.0	20.8	450	
$\text{FeCl}_2(\text{bipy})_2$	1	0.5	100	32.5		67.5	1400	1.3
$\text{FeCl}_2(\text{phen})_2$	1	0.5	100	30.0		70.0	1517	1.2

Polymerization conditions: butadiene, 2 ml; toluene, 16 ml; MAO/Fe = 1000; +20 °C. dmpe: 1,2-bis(dimethylphosphino)ethane; tmeda: *N,N,N',N'*-tetramethylethylenediamine; dmeda: *N,N'*-dimethylethylenediamine; bipy: 2,2'-bipyridine; phen: 1,10-phenanthroline.

^a Determined by NMR (^{13}C and ^1H) and IR analyses.

^b Determined by GPC analysis.

- (ii) FeCl_2 complexes with aliphatic nitrogen ligands (e.g. *tmeda* and *dmeda*) in combination with MAO exhibit very low activity and stereospecificity; polybutadienes with a mixed 1,4/1,2 structure are obtained.
- (iii) When aromatic diamine ligands (e.g. *bipy* and *phen*) are used instead of aliphatic ones, catalysts with an extremely high activity are obtained; the polymerization kinetic is extremely fast and complete conversions are obtained in a few seconds. The chemoselectivity too is different; polybutadienes with a predominantly 1,2 structure are obtained, indicating that insertion of the incoming monomer at C3 of the allylic unit is in this case much favored. The molecular weight (MW) of the polymers is very high and the molecular weight distribution (MWD) is very narrow; this fact seems to indicate a semiliving single site nature of these iron systems. This is only a working hypothesis and further work is necessary to support this conclusion.

We have seen that the type of ligand strongly affects the catalyst activity; this fact is also evident from Table 2, in which data concerning the polymerization of butadiene with catalysts based on phenanthroline iron complexes are shown. It can be observed that the presence of substituents on phenanthroline ring highly influences the catalyst activity while the effect on polymer microstructure is not so evident. Catalyst activity decreases by increasing the steric hindrance around

the metal center; $\text{FeCl}_2(2,9\text{-dimethyl-phen})_2\text{-MAO}$ is much less active than $\text{FeCl}_2(\text{phen})_2\text{-MAO}$, due to the presence of the two methyl groups disfavoring the monomer coordination. The number of ligands coordinated to the metal (n) does not seem to have any influence on the catalyst; most probably, as previously reported, only one ligand remains attached to the metal in the active site, while the second and third ligands are easily removed from the metal by the monomer.

The influence of the Al/Fe molar ratio and of the type of aluminium-alkyl on catalyst activity and stereospecificity is shown in Table 3. In the polymers obtained with the system $\text{FeCl}_2(\text{bipy})_2\text{-MAO}$, the 1,2 content slightly increases with increasing the Al/Fe molar ratio. Catalysts based on MAO resulted to be more active than those based on AlR_3 , giving polybutadienes with a higher 1,2 content. As reported in the literature [21,22], one of the factors determining the formation of 1,2 or 1,4 units in the diene polymerization is the orientation of the incoming monomer with respect to the allylic group of the growing chain. This reciprocal orientation can be influenced by the catalyst geometry; the different chemoselectivity observed with the two systems $\text{FeCl}_2(\text{bipy})_2\text{-MAO}$ and $\text{FeCl}_2(\text{bipy})_2\text{-AlR}_3$ could be due indeed to the formation of different ion pairs in case of AlR_3 and MAO.

The catalytic systems $\text{Fe}(\text{N-N})_2\text{Cl}_2/\text{MAO}$ (N-N: *phen*, *bipy*) are also able to polymerize 1,3-dienes different from butadiene, such as isoprene, (*E*)-1,3-pentadiene and 2,3-dimethyl-1,3-butadiene; the results obtained, reported in Table 4, are very interesting

Table 2
Polymerization of butadiene with $\text{FeCl}_2(\text{phen})_n/\text{MAO}$: influence of the number and type of ligands

Ligand	Number of ligand (n)	Time (min)	Conversion (%)	Polymer microstructure (%) ^a	
				<i>cis</i> -1,4	1,2
Phen	1	0.5	100	28	72
Phen	2	0.5	100	30	70
Phen	3	0.5	100	27	73
5-Methyl-phen	2	1	43	27	73
5,6-Dimethyl-phen	2	1	32	30	70
4-Methyl-phen	2	1	22	33	67
4,7-Dimethyl-phen	2	3	90	25	75
4,7-Diphenyl-phen	2	3	61	29	71
3,4,7,8-Tetramethyl-phen	2	22	19	35	65
2,9-Dimethyl-phen	2	600	15	40	60

Polymerization conditions: butadiene, 2 ml; toluene, 16 ml; Fe, 1×10^{-6} mol; MAO/Fe = 1000; +20 °C. *phen*: 1,10 phenanthroline.

^a Determined by ¹H NMR and IR analyses.

Table 3

Polymerization of 1,3-butadiene with Fe(bipy)₂Cl₂ based catalysts: influence of Al-compound and Al/Fe molar ratio on catalyst activity and stereospecificity

Cocatalyst	Fe (mol) ($\times 10^6$)	Al/Fe (molar ratio)	Time (min)	Conversion (%)	Polymer microstructure (%) ^a	
					<i>cis</i> -1,4	1,2
MAO	0.1	10000	3	42	31	69
	1.0	1000	0.5	100	32.5	67.5
	1.0	100	1	100	35.5	64.5
	5.0	50	2	100	39	61
Al(<i>i</i> -Bu) ₃	5.0	30	5	90	55	45
Al(Et) ₃	5.0	30	10	91	54	46

Polymerization conditions: butadiene, 2 ml; toluene, 16 ml; +20 °C.

^a Determined by ¹H NMR and IR analyses.

from the mechanistic point of view. Two in particular have to be pointed out:

(1) FeCl₂(bipy)₂-MAO gives an essentially 1,2-syndiotactic polymer from butadiene (Fig. 1a) and a *cis*-1,4-polymer from 2,3-dimethyl-1,3-butadiene (Fig. 2). Such a behavior has already been observed in the polymerization of 1,3-dienes with other transition metal catalysts, e.g. CpTiCl₃-MAO [23], and had been interpreted on the basis of the polymerization mechanism by Porri and co-workers [21,22,24–27], proposing that from an allylic unit both 1,4- and 1,2-monomer units can originate and that one of the main factors de-

termining the formation of a 1,4 unit rather than a 1,2 unit is the presence of substituents on the allylic unit. The same interpretation can be valid in this case, confirming indeed the validity of the mechanistic hypothesis.

(2) The system FeCl₂(bipy)₂-MAO gives at room temperature, as mentioned above, an essentially 1,2-syndiotactic polymer from butadiene and a predominantly 3,4-polymer from isoprene (Fig. 1). Further NMR studies are in progress in order to completely determine the polyisoprene microstructure, but the ¹³C NMR spectrum (Fig. 1b) seems to indicate that both *rr* triads (peaks around 110 ppm) and *mr* triads (peaks around 109.5 ppm)

Table 4

Polymerization of 1,3-dienes with Fe(bipy)₂Cl₂/MAO at different temperature

Monomer	<i>T</i> (°C)	Time (min)	Conversion (%)	Polymer microstructure (%) ^a			[<i>rrrr</i>] ^b (%)	mp ^c (°C)
				<i>cis</i>	1,2	3,4		
Butadiene	+20	0.5	100	32.5	67.5		36.9	93
	-40	10	20	16.8	83.2		42.5	110
	-78	4200	17	9.0	91.0		52.5	142
Isoprene	+20	0.5	100	33		67		
	-40	18	14	22.5		77.5		
	-78	4200	15	7.0		93		163
(<i>E</i>)-1,3-Pentadiene	+20	5	100	30	70			
2,3-Dimethyl-1,3-butadiene	+20	0.5	100	~99				200
	-40	60	25	~99				203

Polymerization conditions: monomer, 2 ml; toluene, 16 ml; Fe, 3·10⁻⁶ mol; MAO/Fe = 1000.

^a Determined by NMR (¹³C and ¹H) and IR analyses.

^b Syndiotactic index (percentage of syndiotactic pentads); determined by ¹³C NMR.

^c Determined by DSC analysis.

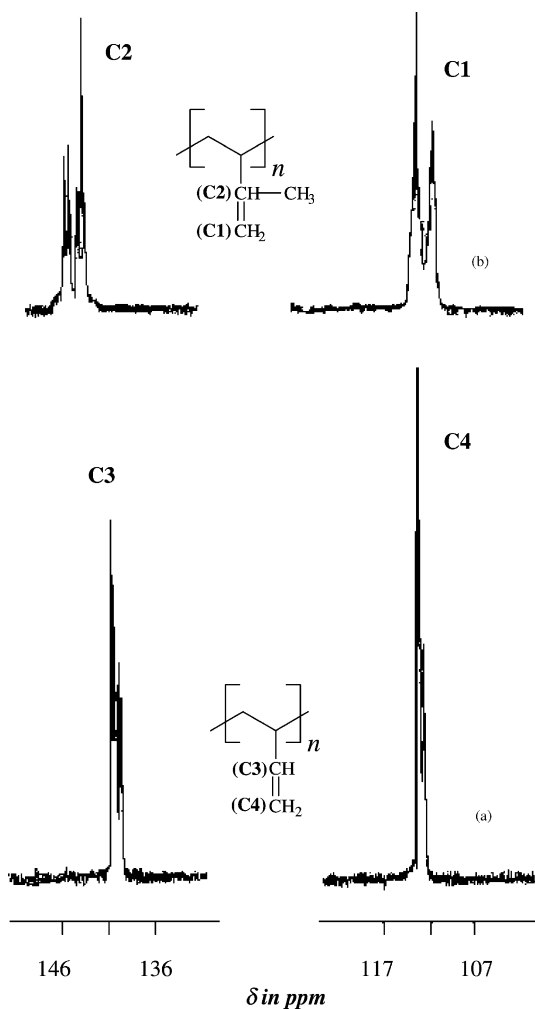


Fig. 1. ^{13}C NMR spectra ($\text{C}_2\text{D}_2\text{Cl}_4$, 103°C , HMDS as internal standard; olefinic region) of (a) 1,2-polybutadiene and (b) 3,4-polyisoprene obtained with the system $\text{FeCl}_2(\text{bipy})_2\text{-MAO}$ at room temperature.

are present in comparable amount, confirming a lower stereoregularity of 3,4-polyisoprene with respect to 1,2-polybutadiene.

A similar result was recently observed in the polymerization of 1,3-dienes with $\text{CrCl}_2(\text{dmpe})_2\text{-MAO}$ [28]. The interpretation given at that time [28] can also be used to explain the results obtained with the iron catalysts of this work, confirming again the validity of the diene polymerization mechanism previously proposed [21,22,24–27].

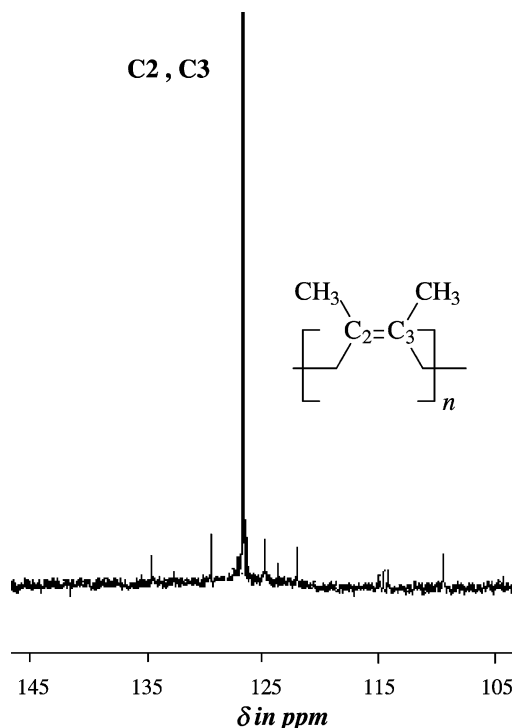


Fig. 2. ^{13}C NMR spectrum ($\text{C}_2\text{D}_2\text{Cl}_4$, 103°C , HMDS as internal standard; olefinic region) of *cis*-1,4-poly(2,3-dimethyl-1,2-butadiene) obtained with $\text{FeCl}_2(\text{bipy})_2\text{-MAO}$ at room temperature.

Finally, the data reported in Table 4 indicate that the polymer stereoregularity increases with decreasing the polymerization temperature. Polybutadienes obtained at room temperature have lower 1,2 content (67.5%), syndiotactic index (36.9%) and melting point (93°C) with respect to those obtained at -78°C (1,2 content, 91.0%; [*rrrr*], 52.5%; mp, 142°C); polyisoprene obtained at low temperature (-78°C) is a crystalline polymer with a melting point of 159°C and peaks around 110 ppm, likely corresponding to syndiotactic sequences, are largely predominant in its ^{13}C NMR spectrum.

4. Conclusions

The iron catalysts reported in this work, obtained by combining $\text{FeCl}_2\cdot\text{L}_2$ (L: phen or bipy) with methylaluminoxane (MAO), are able to give 1,2-syndiotactic

polybutadiene, a polymer of industrial interest, with an extremely high activity. These systems are easily prepared, at low cost using shelf ligands and of environmental friendly impact. For all these reasons they could represent an effective alternative to the cobalt catalysts actually used for the industrial production of 1,2-syndiotactic polybutadiene [13,29–31]. The cobalt–polybutadiene has a higher melting point ($\geq 200^\circ\text{C}$) and a higher stereoregularity but for industrial application a 1,2-syndiotactic polybutadiene of lower stereoregularity is also useful.

Moreover, the results obtained have also some interest from the mechanistic point of view since they have permitted to confirm the validity of the polymerization mechanism previously proposed.

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References

- [1] Y. Zhang, H.J. Zhang, H.M. Ma, Y. Wu, *J. Mol. Catal.* 17 (1982) 65.
- [2] W.L. Hsu, A.F. Halasa, US Patent 5,151,398 (1992).
- [3] W.L. Hsu, A.F. Halasa, US Patent 5,239,023 (1993).
- [4] S. Luo, US Patents 6,160,063 (2000); 6,180,734 B1 (2001); 6,211,313 B1 (2001); 6,277,779 B1 (2001); 6,284,702 B1 (2001); 6,388,030 B2 (2002).
- [5] F. Calderazzo, U. Englert, G. Pampaloni, E. Vanni, *C.R. Acad. Sci. Paris, Part 2, Ser. IIc* (1999) 311.
- [6] F. Charron, W. Reiff, *Inorg. Chem.* 25 (1986) 2786.
- [7] W. Brandt, F.P. Dwyer, E.C. Gyarfas, *Chem. Rev.* 54 (1954) 959.
- [8] E. Konig, *Coord. Chem. Rev.* 3 (1968) 471.
- [9] G.S. Girolami, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.* (1985) 1339.
- [10] D. Morero, A. Santambrogio, L. Porri, F. Ciampelli, *Chim. Ind. (Milan)* 41 (1959) 758.
- [11] V.D. Mochel, *J. Polym. Sci. A-1* 10 (1972) 1009.
- [12] K.F. Elgert, G. Quack, B. Stutzel, *Makromol. Chem.* 175 (1974) 1955.
- [13] H. Ashitaka, K. Inaishi, H. Ueno, *J. Polym. Sci.: Polym. Chem. Ed.* 21 (1983) 1973.
- [14] D. Kumar, M. Rama Rao, K.V. Rao, *J. Polym. Sci.: Polym. Chem. Ed.* 21 (1983) 365.
- [15] D.H. Beebe, C.E. Gordon, R.N. Thudium, M.C. Throckmorton, T.C. Hanlon, *J. Polym. Sci.: Polym. Chem. Ed.* 16 (1978) 2285.
- [16] P. Aubert, J. Sledz, F. Schuè, C. Brevard, *J. Polym. Sci.: Polym. Chem. Ed.* 19 (1981) 955.
- [17] B. Purevsuren, G. Allegra, S.V. Meille, A. Farina, L. Porri, G. Ricci, *Polym. J.* 30 (1998) 431.
- [18] D. Blondin, J. Regis, J. Prud'homme, *Macromolecules* 7 (1974) 187.
- [19] W. Ritter, K.F. Elgert, H.J. Cantow, *Makromol. Chem.* 178 (1977) 557.
- [20] S. Grossman, A. Yamada, O. Vogl, *J. Macromol. Sci. Chem.* A16 (1981) 897.
- [21] L. Porri, A. Giarrusso, in: G.C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt (Eds.), *Comprehensive Polymer Science*, vol. 4, Part II, Pergamon Press, Oxford, 1989, pp. 53–108.
- [22] L. Porri, A. Giarrusso, G. Ricci, *Prog. Polym. Sci.* 16 (1991) 405.
- [23] G. Ricci, S. Italia, A. Giarrusso, L. Porri, *J. Organomet. Chem.* 451 (1993) 67.
- [24] L. Porri, in: F. Ciardelli, P. Giusti (Eds.), *Structural Order in Polymers*, Pergamon Press, Oxford, 1981, pp. 51–62.
- [25] M.C. Gallazzi, A. Giarrusso, L. Porri, *Makromol. Chem., Rapid Commun.* 2 (1981) 59.
- [26] L. Porri, M.C. Gallazzi, S. Destri, A. Bolognesi, *Makromol. Chem., Rapid Commun.* 4 (1983) 485.
- [27] L. Porri, A. Giarrusso, G. Ricci, *Makromol. Chem., Macromol. Symp.* 48–49 (1991) 239.
- [28] G. Ricci, M. Battistella, L. Porri, *Macromolecules* 34 (2001) 5766.
- [29] H. Ashitaka, H. Ishikawa, H. Ueno, *J. Polym. Sci.: Polym. Chem. Ed.* 21 (1983) 1853.
- [30] H. Ashitaka, K. Jinda, H. Ueno, *J. Polym. Sci.: Polym. Chem. Ed.* 21 (1983) 1951.
- [31] H. Ashitaka, K. Jinda, H. Ueno, *J. Polym. Sci.: Polym. Chem. Ed.* 21 (1983) 1989.