Synthesis of new Cr(II) complexes with bidentate phosphine ligands and their behavior in the polymerization of butadiene Influence of the phosphine bite angle on catalyst activity and stereoselectivity

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Abstract

Some new chromium(II) complexes were synthesized by reacting $CrCl_2(thf)$ with various bidentate phosphines [bis(diphenylphosphino)methane (dppm); 1,2-bis(diphenylphosphino)ethane (dppe); 1,3-bis(diphenylphosphino)propane (dppp); bis(diphenylphosphino)amine (dppa)] and a new family of catalysts for the polymerization of butadiene was prepared by reacting the above chromium complexes with methylaluminoxane (MAO). These systems were found to be in some cases extremely active and they gave predominantly 1,2-polybutadienes (1,2 content >85%) having different tacticity (syndiotactic or predominantly isotactic) depending on the phosphine ligand bonded to the chromium atom. The influence of the type of ligand on catalyst activity and selectivity is discussed.

1. Introduction

1,2-Polybutadiene is a polymer of industrial interest and industrially produced. It can exist in the amorphous atactic form and in two crystalline forms: isotactic and syndiotactic. At present, the two stereo-isomers that are commercially most used are the syndiotactic and atactic structures [1]. The interest for 1,2-polybutadiene is due to the fact that it is a thermoplastic resin showing the characteristics of both a thermoplastic and an elastomer [1,2]. Because of this peculiarity, it has a wide range of applications. 1,2 syndiotactic polybutadiene is used in films (packaging breathing items for fruits, vegetables and seafood), footwear soles, tubes, and hoses; atactic 1,2-polybutadiene is used in the rubber and tire industry [3].

1,2-Polybutadiene can be prepared with various catalyst systems [4] based on titanium [5] (e.g. $AlEt_3/Ti(OR)_4$), vanadium [6] (e.g. $AlEt_3/V(acac)_3$), molybdenum [7] (e.g. $AlR_3(Mo_2(OR)_2)$, cobalt [8] (e.g. $Co(acac)_3–AlEt_3/CS_2$;

$(C_4H_6)Co(\eta^5\text{-}C_8H_{13})$; $CoCl_2(PRPh_2)_2$–MAO, R = alkyl or cycloalkyl group), and chromium [9] (e.g. $Cr(acac)_3$–$AlEt_3$, $Cr(CNPh)_6/AlEt_3$).

The $AlEt_3$–$Ti(OR)_4$ system was the first catalyst used for the preparation of syndiotactic 1,2-polybutadiene, giving, however, a polymer of moderate crystallinity [5]. The $AlEt_3$–$V(acac)_3$ system gave a polymerization product consisting of about 85% 1,2 structure, from which a highly crystalline polymeric fraction having a syndiotactic structure was isolated by successive extractions with different solvents [6]. Catalysts based on molybdenum were characterized by a high stereospecificity, being the syndiotactic crystalline fraction (residue after extraction) about 80% [7]. All these systems based on Ti, V, and Mo were, however, characterized by a rather low activity and did not find an industrial application. 1,2-Syndiotactic polybutadiene is instead industrially produced with cobalt systems which exhibit without any doubt the highest activity and stereospecificity. The system AlR_3–$Co(acac)_3$–CS_2, for instance, is by far the most active and stereospecific catalyst for the preparation of 1,2-syndiotactic polybutadiene [8c–f].

Chromium catalysts, as cited above, were also used for the preparation of 1,2-syndiotactic polybutadiene. They were found

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to exhibit a very low activity [9] but, unlike the other systems based on Ti, V, Mo and Co, they were also able to give a 1,2-isotactic polymer from butadiene, and up to now 1,2-isotactic polybutadiene has been obtained only with chromium catalysts.

It has been recently reported, however, that more active and stereospecific chromium catalysts for the 1,2 polymerization of 1,3-butadiene can be prepared by using catalysts based on chromium(II) bidentate-phosphine complexes (e.g. $CrCl_2(dmpe)_2$–MAO; dmpe = 1,2-bis(dimethylphosphino)ethane) [10].

Bidentate phosphine ligands are well known in the field of homogeneous catalysis; in many homogeneous catalytic processes using transition metal complexes with bidentate phosphines as catalysts, the catalyst activity and stereoselectivity were found to be strongly dependent on the type of phosphorous ligand [11]. Many ligand parameters have been proposed in order to evaluate the relationship between ligand properties and catalytic performance; in particular in the case of bidentate phosphines the bite angle was used, which was reported to have both steric and electronic effect [11].

Taking into account what above reported, we have synthesized several new chromium(II) complexes by reacting $CrCl_2(thf)$ with the following bidentate aromatic phosphines: bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) and bis(diphenylphosphino)amine (dppa). The behavior of these complexes, in association with MAO, in the polymerization of butadiene was examined and compared with that of other similar chromium systems previously reported [10]. They were found to give predominantly 1,2-polybutadienes having different type and degree of stereoregularity depending on the type of phosphine ligand bonded to the chromium atom. The catalytic activity too varied depending on the type of ligand, being for some complexes much higher with respect to the other chromium catalysts recently reported [10].

In the present paper we report on the synthesis of the various chromium complexes, on their use in combination with MAO in the polymerization of butadiene and on the characterization of the polymers obtained; the influence of the ligand on catalyst activity and stereoselectivity is also discussed.

2. Experimental

2.1. Materials and methods

Bis(diphenylphosphino)methane (dppm) (Strem, 97% pure), 1,2-bis(diphenylphosphino)ethane (dppe) (Strem, 99% pure), 1,3-bis(diphenylphosphino)propane (dppp) (Strem, 98% pure), bis(diphenylphosphino)amine (dppa) (Strem, 98% pure) and methylaluminoxane (MAO) (Crompton, 10 wt.% solution in toluene) were used as received. Toluene (Fluka, >99.5% pure) was refluxed over Na for ca. 8 h, then distilled and stored over molecular sieves under dry nitrogen; pentane (Prolabo, >99% pure) was refluxed over Na/K alloy for ca. 8 h, then distilled over molecular sieves under dry dinitrogen; diethylether(Lab-Scan, >99.8% pure) was refluxed over Na/K/benzophenone for ca. 8 h, then distilled; tetrahydrofurane (Baker, >99.8% pure)

was refluxed over K/benzophenone for ca. 8 h, then distilled; dichloromethane (Aldrich, 99.8% pure) was degassed under vacuum and then dried over molecular sieves. 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 $-20\,°C$. $CrCl_2$ (thf) [12] was prepared as reported in the literature, by reacting $CrCl_3$ with chromium powder in tetrahydrofurane; the bidentate phosphine chromium (II) complexes were prepared as reported below, following experimental procedures already reported in the literature for analogous complexes [10b,13]. The elemental analyses of the chromium complexes were performed by the analytical laboratories of Polimeri Europa-Centro Ricerche Novara-"Istituto Guido Donegani"; infrared spectra were recorded as KBr disks with a Bruker IFS 48 instrument.

2.2. Synthesis of $CrCl_2$ (dppm)

$CrCl_2(thf)$ (0.75 g, 3.8 mmol) and diethylether (25 ml) were introduced in a 100 ml schlenck tube. The suspension so obtained was kept under stirring at room temperature, then bis(diphenylphospino)methane (1.36 g, 3.5 mmol) was added. A green-blue precipitate was slowly formed; the suspension was kept under stirring at room temperature for 24 h, then filtered. The residue on the filter was dried under vacuum, transferred in a Soxhlet apparatus and then successively extracted in continuous for 24 h with boiling pentane in order to remove unreacted diphosphine and then with boiling dichloromethane for 24 h. The green dichloromethane solution was then concentrated and an excess of pentane was added. The green precipitate formed was filtered off and dried under vacuum. Yield: 0.87 g (45.1% based on $CrCl_2$). Anal. Calcd. for $C_{25}H_{22}CrCl_2P_2$: Cr, 10.25; Cl, 13.98; P, 12.21. Found: Cr, 10.5; Cl, 13.8; P, 12.5.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3059 (m), 1485 (m), 1438 (s), 1364 (m), 1138 (s), 1095 (s), 1046 (m), 1015 (m), 920 (w), 868 (s), 783 (s), 740 (s), 690 (s), 520 (s).

2.3. Synthesis of $CrCl_2$ (dppe)

$CrCl_2(thf)$ (0.33 g, 1.69 mmol) was suspended in diethylether (25 ml) and 0.74 g of 1,2-bis(diphenylphosphino)ethane (1.86 mmol) in diethylether (25 ml) were added. The suspension so obtained was kept under stirring for about 24 h, after which the formation of a turquoise precipitate was observed. The solvent was removed under vacuum and the residue was extracted in continuous with boiling pentane for 24 h in order to separate unreacted phosphine. The residue on the filter was then extracted in continuous with boiling diethylether for ca. 72 h. The diethylether solution was then concentrated and the blue precipitate was separated by filtration and dried under vacuum. Yield: 0.264 g (30% based on $CrCl_2$). Anal. Calcd. For $C_{26}H_{24}CrCl_2P_2$: Cr, 9.97; Cl, 13.60; P, 11.88. Found: Cr, 9.9; Cl, 13.6; P, 11.5.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3052 (m), 1484 (m), 1435 (s), 1371 (w), 1159 (m), 1125 (m), 1099 (s), 1027 (w), 1000 (w), 861 (m), 741 (s), 693 (s), 550 (w), 517 (m), 488 (w).

2.4. Synthesis of CrCl₂ (dppp)

$CrCl_2$(thf) (0.86 g, 4.4 mmol) and the phosphine (2.25 g, 5.5 mmol) were introduced in a 100 ml flask together with diethylether (50 ml). A green suspension was rapidly formed; it was kept under stirring for one night, and then filtered. The residue on the filter was dried under vacuum, transferred in a Soxhlet, and extracted first with pentane for about 24 h in order to remove the excess of phosphine and then with dichloromethane for about 48 h. A green solution was formed which was concentrated under vacuum. A large amount of pentane was then added causing the formation of a green precipitate which was filtered off and dried in vacuum. Yield: 1.57 g (66.7% based on $CrCl_2$). Anal. Calcd. For $C_{24}H_{21}CrNCl_2P_2$: Cr, 10.23; Cl, 13.95; P, 12.19. Found: Cr, 10.1; Cl, 13.4; P, 11.9.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3054 (ms), 2934 (m), 1484 (m), 1437 (s), 1403 (mw), 1313 (w), 1245 (w), 1157 (s), 1121 (s), 1100 (s), 1072 (ms), 1028 (m), 998 (m), 972 (mw), 829 (mw), 744 (s), 721 (s), 695 (s), 551 (s), 510 (s).

2.5. Synthesis of CrCl₂ (dppa)

$CrCl_2$(thf) (2.58 g, 13.2 mmol) was suspended in diethylether (70 ml). Bis(diphenylphosphino)amine (5 g, 13 mmol) was then added and the reaction was kept under stirring at room temperature for ca. 24 h. The formation of a light green precipitate was observed while the supernatant solution was green. The green precipitate was separated by filtration, dried under vacuum, transferred in a Soxhlet and then extracted in continuous with boiling pentane for 48 h; in this way the unreacted phosphine could be separated in the pentane solution. The residue was then extracted in continuous with boiling dichlorometane for 48 h; at the end the dark green solution thus obtained was concentrated, a large amount of pentane was added causing the formation of a green precipitate which was separated by filtration and then dried under vacuum. Yield: 2.372 g (35.4% based on $CrCl_2$). Anal. Calcd. For $C_{24}H_{21}CrNCl_2P_2$: Cr, 10.23; Cl, 13.95; P, 12.19. Found: Cr, 10.4; Cl, 14.2; P, 12.3.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3227 (mw), 3148 (mw), 3053 (m), 1483 (m), 1436 (s), 1410 (w), 1184 (ms), 1126 (s), 1099 (s), 1026 (m), 999 (m), 944 (m), 741 (s), 693 (s), 618 (w), 592 (w), 540 (s), 515 (s).

2.6. Polymerization of butadiene

All operations were carried out under an atmosphere of dry dinitrogen. A standard procedure is reported. 1,3-Butadiene was condensed into a 25 mL dried glass reactor kept at −20 °C, then toluene was added and the solution so obtained was brought to the desired polymerization temperature. Methylaluminoxane (MAO) and the chromium compound were then added, as toluene solutions, in the order. The polymerization was terminated with methanol containing a small amount of hydrochloric acid; the polymer was coagulated and repeatedly washed with methanol, then dried in vacuum at room temperature.

2.7. Polymer characterization

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. ^{13}C NMR measurements were performed with a Bruker AM 270 instrument. The spectra were obtained in $C_2D_2Cl_4$ at 103 °C (hexamethyldisiloxane, HMDS, as internal standard). The concentration of polymer solutions was about 10 wt.%. Differential scanning calorimetry (DSC) scans were carried out on a Perkin Elmer Pyris 1 instrument. Typically, ca. 10 mg of polymer were analyzed in each run, while scan speed was ca. 20 K/min under a dinitrogen atmosphere. The molecular weight averages (MW) and the molecular weight distribution (MWD) were obtained by a high temperature GPCV 2000 system (from Waters) using two on-line detectors: a differential viscometer and a refractometer. The experimental conditions consisted of three Olefi columns from PSS, *o*-dichlorobenzene as mobile phase, 0.8 mL/min of flow rate and 145 °C of temperature. The calibration of the GPC system was constructed by 18 narrow MWD polystyrene standards with the molar mass ranging from 162 to 3.3×10^6 g/mol. The polybutadiene microstructure was determined according to what already reported in the literature [8e,14].

3. Results and discussion

The chromium complexes were prepared according to a general experimental procedure already reported in the literature [10b,12,13]. $CrCl_2$(thf) was reacted with the various bidentate phosphines using diethylether as solvent. A suspension is always formed; the precipitate was separated by filtration and then worked up as described in the experimental part. The complexes were found to have, by elemental analysis, the general formula $CrCl_2$(L) (L = dppm, dppe, dppp, dppa).

The results obtained in the polymerization of 1,3-butadiene with the systems obtained by combining the above complexes with MAO are reported in Table 1 and can be summarized as follows:

(i) The systems $CrCl_2(Ph_2P(CH_2)_nPPh_2)$–MAO ($n = 1, 2, 3$) give from butadiene polymers having an essentially 1,2 structure. The 1,2 content varies in the range 80–90%, slightly increasing with decreasing the length of the bridge (n) between the two phosphorous atoms. The type of ligand has, however, a much stronger influence on catalyst stereoselectivity. As a matter of fact, $CrCl_2$(dppm)–MAO gives 1,2-polybutadienes in which isotactic sequences are predominant (see Fig. 1c), while $CrCl_2$(dppe)–MAO and $CrCl_2$(dppp)–MAO give essentially syndiotactic 1,2-polybutadienes (see Fig. 1b). The catalyst activity too, is greatly affected by the type of ligand, being the system $CrCl_2$(dppm)–MAO much more active than the other systems $CrCl_2$(dppe)–MAO and $CrCl_2$(dppp)–MAO (see Table 1).

(ii) As reported by van Leeuwen [11], the effect of bite angle (β_n) in catalytic reactions can be separated in steric bite

Table 1
Polymerization of butadiene with catalysts based on different Cr(II) phosphine compounds[a]

Run	Cr-compound	β_n[b] (°)	Al/Cr (molar ratio)	Time (min)	Conv. (%)	N[c] (h^{-1})	1,2-Polybutadienes[d] (%)	rr/mr/mm[e] (molar ratio)	mp (°C)
1	CrCl$_2$ (dppm)	72	1000	20	55.7	4,330	89	18/48/34	–
2	CrCl$_2$ (dppm)	72	500	25	52.1	3,241	87	19/48/33	–
3	CrCl$_2$ (dppm)	72	100	24	38.4	2,463	88	20/48/32	–
4	CrCl$_2$ (dppm)	72	50	32	22.7	1,104	88	19/48/33	–
5	CrCl$_2$ (dppe)	85	1000	1020	15.3	23	88	61/34/5	95
6	CrCl$_2$ (dppe)	85	100	1440	10.5	11	87	59/33/8	89
7	CrCl$_2$ (dppp)	91	1000	1440	17.6	18	80	64/32/4	106
8	CrCl$_2$ (dppp)	91	100	1440	13.7	14	80	66/31/3	105
9	CrCl$_2$ (dppa)		1000	5	37.5	11,667	91	66/30/4	104
10	CrCl$_2$ (dppa)		500	10	42.7	6,642	89	64/32/4	100
11	CrCl$_2$ (dppa)		100	30	84.0	4,356	89	64/33/3	98
12	CrCl$_2$ (dppa)		50	30	35.0	1,815	88	63/32/5	99
13	CrCl$_2$ (dppa)		1000	180	9.2	80	90	73/27/0	137

[a] Polymerization conditions: butadiene, 2 ml; toluene, total volume 16 ml; MAO; Cr, 1×10^{-5} mol; +20 °C (−30 °C in run 13).
[b] Natural bite angles β_n are taken from Ref. [11].
[c] N = moles of butadiene polymerized per mol of Cr per hour.
[d] Determined by ^{1}H NMR.
[e] Determined by ^{13}C NMR. The molecular weights (MW) of the polymers obtained with the various chromium systems were in the range 250,000–300,000 with a MW/MN of about 2.

angle effect and electronic bite angle effect. The first one is related to the steric interactions (ligand–ligand or ligand–substrate) generated when the bite angle is modified by changing the backbone and keeping the substituents at the phosphorous donor atom the same. This likely means
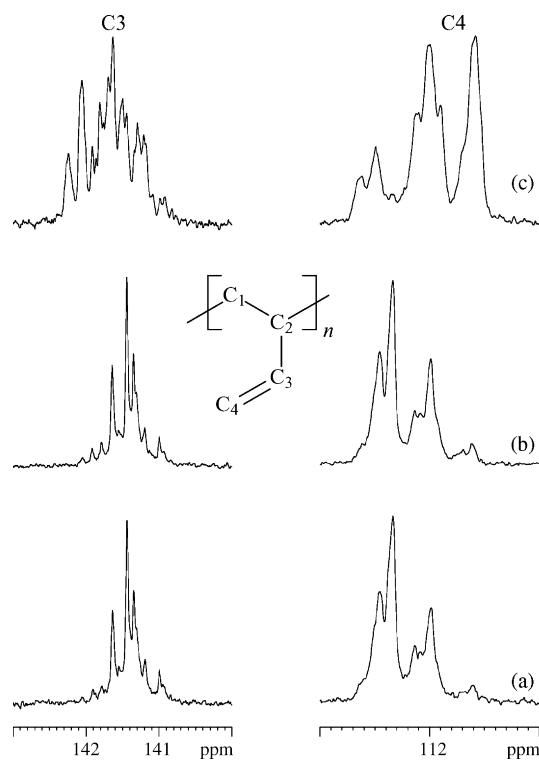

Fig. 1. ^{13}C NMR spectrum (olefinic region, C$_2$D$_2$Cl$_4$, HMDS as internal standard, 103 °C) of the 1,2-polybutadienes obtained with (a) CrCl$_2$(dppa)-MAO (Table 1, run 9); (b) CrCl$_2$(dppe)-MAO (Table 1, run 5); (c) CrCl$_2$(dppm)-MAO (Table 1, run 1).

that, at least in the series CrCl$_2$(Ph$_2$P(CH$_2$)$_n$PPh$_2$)–MAO (n = 1, 2, 3), the effect of the ligand on activity, chemoselectivity and stereoselectivity would be mainly due to steric factors; an increased hindrance of the ligand, from dppm to dppe and dppp, seems indeed to cause a decreasing in catalyst activity (the coordination of the monomer is likely more difficult when a hindered ligand is bonded to the metal) and a radical change in stereoselectivity, from isotactic to syndiotactic.

The fact that CrCl$_2$(dppm)–MAO gives 1,2-polybutadienes in which isotactic sequences are predominant, while CrCl$_2$(dppe)–MAO and CrCl$_2$(dppp)–MAO give predominantly syndiotactic 1,2-polybutadienes, can be interpreted according to the previously suggested diene polymerization mechanism [15]. The interpretation already given for the results obtained in the polymerization of butadiene with the two systems CrCl$_2$(dmpm)$_2$–MAO [10b] and CrCl$_2$(dmpe)$_2$–MAO [10a] and with the cobalt systems CoCl$_2$(PRPh$_2$)$_2$–MAO (R = methyl, ethyl, normal-propyl, iso-propyl and cyclohexyl) [8i] is still valid and applicable to the chromium systems of this work. The catalytic site in the polymerization of butadiene with the chromium systems of this work is most probably that shown in Fig. 2. The incoming monomer and the butadienyl unit can assume two different orientations (exo–exo and exo–endo). By insertion of the incoming monomer at C3 of the butadienyl group a 1,2 polymer is obtained in both cases, isotactic from an exo–endo situation (Fig. 2-right), syndiotactic from an exo–exo situation (Fig. 2-left). An orientation like that in Fig. 2-right is favored when no ligand or a low hindered ligand (low β_n value) is bonded to the metal while an orientation like that in Fig. 2-left is the favored one when an hindered ligand (higher β_n value) is present. This is the reason why predominantly isotactic
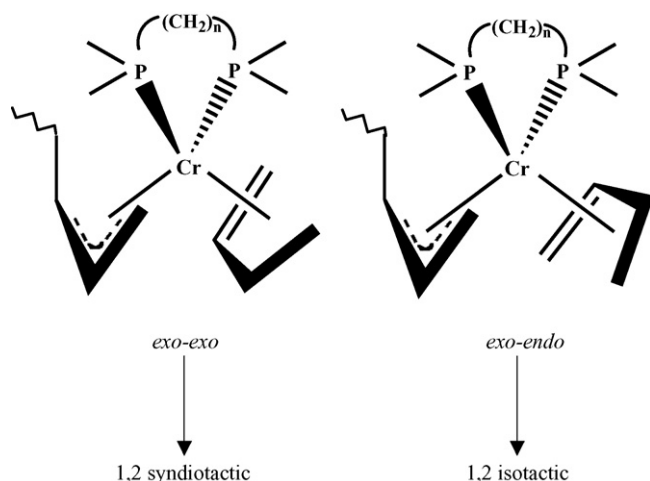
Fig. 2. Possible reciprocal orientation (*exo–exo* and *exo–endo*) of the butadiene entering monomer and the allylic unit of the polymer growing chain.

polymers when L = dppm ($\beta_n = 72°$) and essentially syndiotactic polymers when L = dppe or dppp ($\beta_n = 85°$ and 91°, respectively) are obtained.

(iii) We have also investigated the effect of Al/Cr molar ratio value on catalyst activity and selectivity. It was found to have practically no influence on catalyst chemo- and stereoselectivity, while catalyst activity was found to increase with increasing the Al/Cr molar ratio. A larger number of active sites is likely formed at higher Al/Cr ratio.

(iv) We have also examined the polymerization of butadiene with CrCl$_2$(dppa)–MAO. This system gave highly syndiotactic 1,2 polymer (percentage of syndiotactic triads, [rr], of about 65%) and exhibited a very high activity. If we compare this system with other syndiospecific chromium catalysts previously reported (e.g. CrCl$_2$(dmpe)$_2$–MAO) [10], we observe that the system CrCl$_2$(dppa) is less stereospecific (percentage of syndiotactic triads [rr] of 65% versus 85% for CrCl$_2$(dmpe)$_2$–MAO) but largely more active (N = moles of butadiene polymerized per mol of Cr per hour = 11667 h^{-1} versus 1024 h^{-1} for CrCl$_2$(dmpe)$_2$–MAO). The presence of a potential donor nitrogen atom in the backbone determining weak interactions with the metal center and, as reported by van Leeuwen [11a], leading to an enlargement of the bite angle, could in some way account for the high activity and syndiospecificity of the system CrCl$_2$(dppa)–MAO.

(v) The influence of the polymerization temperature on selectivity was also evaluated and, as already reported for other chromium systems [10], the polymer syndiotacticity was found to increase with decreasing the polymerization temperature. The system CrCl$_2$(dppa)–MAO gives a 1,2-polybutadiene with a melting point of 137 °C and a syndiotactic index [rr] of about 73% at −30 °C (Table 1, run 13), while the polymer obtained at room temperature has a melting point of 104 °C and a syndiotactic index of 66% (Table 1, run 9).

4. Conclusions

A new class of chromium catalysts, CrCl$_2$(Ph$_2$P–X–PPh$_2$)–MAO [X = (CH$_2$), (CH$_2$)$_2$, (CH$_2$)$_3$, NH] have been prepared and used in the polymerization of butadiene to essentially 1,2 polymers. Isotactic or syndiotactic polymers were obtained depending on the type of ligand. A relationship between stereoselectivity and ligand bite angle has been suggested.

The systems CrCl$_2$(dppa)–MAO and CrCl$_2$–(dppm)–MAO gave syndiotactic and predominantly isotactic 1,2-polybutadienes, respectively, and exhibited an activity much higher with respect to the other syndiospecific and isospecific chromium systems up to now known.

Moreover, these catalysts appear of interest from the industrial point of view, since their activities and stereospecificities are comparable with those of the cobalt catalysts actually used for the industrial production of 1,2-polybutadiene.

References

[1] A.F. Halasa, J.M. Massien, in: J.I. Kroschwitz (Ed.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 8, 4th ed., John Wiley and Sons, New York, 1989.

[2] D.P. Tate, T.W. Bethea, in: H.F. Mark, et al. (Eds.), Encyclopedia of Polymer Science and Engineering, vol. 2, 2nd ed., John Wiley and Sons, New York, 1989.

[3] J.E. Mark, Polymer Data Handbook, Oxford University, New York, 1999, p. 318.

[4] (a) L. Porri, A. Giarrusso, in: G.C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt (Eds.), Comprehensive Polymer Science, Vol. 4, Part II, Pergamon Press Ltd., Oxford, 1989, pp. 53–108;
(b) S.K.H. Thiele, D.R. Wilson, J. Polym. Sci. Polym. Rev. C43 (2003) 581.

[5] G. Natta, L. Porri (Montecatini SpA), Ital. Pat. 538453 (1956) [Chem. Abstr., 52 (1958) 5032].

[6] G. Natta, L. Porri, G. Zanini, L. Fiore, Chim. Ind. (Milan) 41 (1959) 526 [Chem. Abstr., 54 (1960) 1258].

[7] G. Natta, Chim. Ind. (Milan) 42 (1960) 1207.

[8] (a) E. Susa, J. Polym. Sci., Part C 4 (1963) 399;
(b) C. Longiave, R. Castelli, J. Polym. Sci., Part C 4 (1963) 387;
(c) H. Ashitaka, H. Ishikawa, H. Ueno, A. Nagasaka, J. Polym Sci., Polym. Chem. Ed. 21 (1983) 1853;
(d) H. Ashitaka, K. Jinda, H. Ueno, J. Polym Sci., Polym. Chem. Ed. 21 (1983) 1951;
(e) H. Ashitaka, K. Inaishi, H. Ueno, J. Polym Sci., Polym. Chem. Ed. 21 (1983) 1973;
(f) H. Ashitaka, K. Jinda, H. Ueno, J. Polym Sci., Polym. Chem. Ed. 21 (1983) 1989;
(g) G. Ricci, S. Italia, L. Porri, Polym. Commun. 29 (1988) 305;
(h) G. Ricci, A. Forni, A. Boglia, T. Motta, G. Zannoni, M. Canetti, F. Bertini, Macromolecules 38 (2005) 1064;
(i) G. Ricci, A. Forni, A. Boglia, A. Sommazzi, F. Masi, J. Organomet. Chem. 690 (2005) 1845.

[9] G. Natta, L. Porri, G. Zanini, A. Palvarini, Chim. Ind. (Milan) 41 (1959) 1163 [Chem. Abstr. 55 (1961) 20906].

[10] (a) G. Ricci, M. Battistella, L. Porri, Macromolecules 34 (2001) 5766;
(b) G. Ricci, A. Forni, A. Boglia, M. Sonzogni, Organometallics 23 (2004) 3727.

[11] (a) P. Dierkes, P.W.N.M. van Leeuwen, J. Chem. Soc., Dalton Trans. (1999) 1519;
(b) P.W.N.M. van Leeuwen, P.C.J. Kamer, J.N.H. Reek, P. Dierkes, Chem. Rev. 100 (2000) 2741;
(c) Z. Freixa, P.W.N.M. van Leeuwen, Dalton Trans. (2003) 1890.

[12] P. Betz, P.W. Jolly, C. Kruger, U. Zakrewski, Organometallics 10 (1991) 3520.

[13] (a) G.S. Girolami, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1985) 1339;
(b) A.R. Hermes, G.S. Girolami, Inorg. Chem. 27 (1988) 1775.

[14] (a) D. Morero, A. Santambrogio, L. Porri, F. Ciampelli, Chim. Ind. (Milan) 41 (1959) 758;
(b) V.D. Mochel, J. Polym. Sci. A-1 10 (1972) 1009;
(c) J. Zymonas, E.R. Santee, H.J. Harwood, Macromolecules 6 (1973) 129;
(d) K.F. Elgert, G. Quack, B. Stutzel, Makromol. Chem. 175 (1974) 1955;
(e) D. Kumar, M. Rama Rao, K.V. Rao, J. Polym. Sci.: Polym. Chem. Ed. 21 (1983) 365.

[15] (a) L. Porri, in: F. Ciardelli, P. Giusti (Eds.), Structural Order in Polymers, Pergamon Press Ltd., Oxford, 1981, p. 51;
(b) L. Porri, A. Giarrusso, G. Ricci, Prog. Polym. Sci. 16 (1991) 405;
(c) L. Porri, A. Giarrusso, G. Ricci, Makromol. Chem., Macromol. Symp. 48/49 (1991) 239;
(d) L. Porri, A. Giarrusso, G. Ricci, Macromol. Symp. 178 (2002) 55.