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Journal of Molecular Catalysis A: Chemical 236 (2005) 246–252

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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An examination of aluminum chain transfer reaction in *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind]_2ZrCl_2$/MAO-catalyzed propylene polymerization and synthesis of aluminum-terminated isotactic polypropylene with controlled molecular weight

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Received 10 January 2005; received in revised form 25 April 2005; accepted 26 April 2005

Abstract

Chain transfer to the aluminum cocatalyst was found to be the predominant chain transfer reaction in propylene polymerization mediated by the sterically hindered, highly isospecific *rac*-dimethylsilanediylbis(2-methyl-4-naphthyl)indenyl-zirconium dichloride (*rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind]_2ZrCl_2$)/methylaluminoxane (MAO) catalyst system. By finely tuning the polymerization conditions including the polymerization temperature and Al/Zr ratio, this predominant aluminum transfer reaction was directed to prepare aluminum-terminated isotactic polypropylene (*i*-PP) with high end-group selectivity and controlled and narrowly distributed molecular weight.

Keywords: Chain transfer; Aluminum cocatalyst; Metallocene; Isospecific; Propylene polymerization

1. Introduction

In the study of olefin coordination/insertion polymerization, an investigation of chain transfer reactions is very important because it relates to the control of molecular weights and end-group structures of resultant polyolefins. In a reaction of propylene polymerization over a metallocene catalyst/methylaluminoxane (MAO) cocatalyst system, where no external chain transfer agents are involved, β-hydride transfer (either after a primary propylene insertion or after a secondary propylene insertion and either unimolecular or bimolecular), β-methyl transfer and chain transfer to the aluminum cocatalyst (mainly to trimethyl aluminum ($AlMe_3$) contained in MAO) constitute the whole chain termination process. In general, β-hydride and β-methyl transfers are two major chain transfer reactions, whereas chain transfer to the aluminum cocatalyst is considered as a minor one, and therefore, lacks adequate attention [1].

However, recently some metallocenes including *rac*-$Et[2\text{-}{}^tBuMe_2SiO\text{-}(Ind)]_2ZrCl_2$, *rac*-$Et[2\text{-}{}^tBuMe_2SiO\text{-}(Ind)]_2HfCl_2$ and *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}{}^tBu\text{-}C_5H_2)_2ZrCl_2$ combined with MAO were found to possess a major aluminum chain transfer reaction in their respective propylene polymerisations [2,3]. Furthermore, when $AlEt_3$ was used in conjunction with $Ph_3CB(C_6F_5)_4$ as the cocatalyst, $AlEt_3$ was found to initiate significant chain transfer reaction even in propylene polymerization with some conventional metallocenes including *rac*-$Et(Ind)_2ZrCl_2$, *rac*-$Me_2Si(Ind)_2ZrCl_2$ and *i*-Pr(Cp)(Flu)$ZrCl_2$ [4].

rac-Dimethylsilanediylbis(2-methyl-4-naphthyl)indenylzirconium dichloride (*rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind)_2ZrCl_2$) and *rac*-dimethylsilanediylbis(2-methyl-4-phenyl)indenylzirconium dichloride (*rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$) as well as their methylated counterparts combined with MAO are so far among the best metallocene catalysts for

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doi:10.1016/j.molcata.2005.04.053

isospecific propylene polymerization in terms of activity, stereospecificity, and polymer molecular weight, due to their optimized ligand structures [5]. General knowledge that is known about the molecular weight and end-group control with these catalysts is that the rigid ligand frameworks of these catalysts are unfavorable to β-agostic interaction at zirconium centers during propylene polymerization, making β-hydride transfer (mainly occurs in a unimolecular fashion), the most frequent chain termination reaction in metallocene-catalyzed olefin polymerization, difficult to occur. Therefore, the molecular weights of PP produced by these catalysts are generally high. However, as far as chain transfer to the aluminum cocatalyst is concerned, little is known until recently Kokko and co-workers studied the kinetics of propylene polymerization with *rac*-Me_2Si(2-Me-4-Ph-Ind)$_2ZrMe_2$/MAO [6]. They found that chain transfer to the aluminum cocatalyst and β-methyl transfer reaction were the most important chain termination mechanisms with this catalyst. Weng et al. also observed significant β-methyl transfer reaction in propylene polymerization with *rac*-Me_2Si(2-Me-4-Ph-Ind)$_2ZrCl_2$/MAO [7].

We recently investigated the aluminum chain transfer reaction in propylene polymerization with the MAO-activated *rac*-Me_2Si[2-Me-4-Naph-Ind]$_2ZrCl_2$ catalyst, by applying an oxidative workup approach [8] at the end of polymerization, and found that aluminum chain transfer reaction was predominant. Despite the structural similarity between *rac*-Me_2Si[2-Me-4-Naph-Ind]$_2ZrCl_2$ and *rac*-Me_2Si(2-Me-4-Ph-Ind)$_2ZrCl_2$, the difference in the degree of aluminum chain transfer reaction was attributed to the bulkier naphthyl substituent on the indenyl ligands possessed by the former catalyst, which actually has resulted in better propylene polymerization performance than the latter in terms of PP molecular weight and isotacticity [5]. The predominant aluminum chain transfer reaction in *rac*-Me_2Si[2-Me-4-Naph-Ind]$_2ZrCl_2$/MAO-catalyzed propylene polymerization was also utilized to prepare aluminum-terminated isotactic polypropylene (*i*-PP) with high end-group selectivity and controlled and narrowly distributed molecular weight, which has been known to be a valuable precursor of chain-end functionalized polypropylenes and polypropylene block copolymers [9,10].

2. Experimental

2.1. Materials and instruments

All O_2- and moisture-sensitive manipulations were carried out inside an argon-filled vacuum atmosphere dry-box equipped with a dry train. CP grade toluene was deoxygenated by argon purge before refluxing for 48 h and then distilled over sodium. MAO (10 wt.% in toluene) was purchased from Albermarle and used without further purification. Polymerization grade propylene was supplied by Yansan Petrochemical Co. of China. The catalyst, *rac*-Me_2Si[2-Me-4-Naph-Ind]$_2ZrCl_2$, was synthesized according to a published procedure [5].

All ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 instrument in *o*-dichlorobenzene-d_4 at 110 °C. The melting temperatures of the polymers were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 instrument controller operating from 30 to 180 °C with a heating rate of 20 °C/min. The data were collected on the second heating cycle. The molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) using a Waters Alliance GPC 2000 instrument equipped with a refractive index (RI) detector and a set of u-Styragel HT columns of 106, 105, 104, and 103 pore size in series. The measurement was operated at 150 °C with 1,2,4-trichlorobenzene as the eluent with a flow rate of 0.7 ml/min. Narrow molecular weight PS samples were used as standards for calibration.

2.2. Propylene polymerization with an oxidative workup process

In a typical reaction (run 3 in Table 1), a 300 ml three-necked round bottom flask was charged with 134 ml of toluene, 16 ml of MAO and 1 bar of propylene at 30 °C. About 0.75×10^{-6} mol (5.0×10^{-6} M) of *rac*-Me_2Si[2-Me-4-Naph(Ind)]$_2ZrCl_2$ catalyst was then added to initiate the polymerization. During the course of reaction, additional propylene was continuously fed into the flask to maintain a constant pressure (1 bar). After 30 min of reaction at 30 °C, the polymerization was terminated by stopping the monomer gas flow. The dry oxygen was bubbled into the polymer solution through a syringe needle for 2 h at the ambient temperature. Then, 29 ml of aqueous hydrogen peroxide solution (30 wt.%) and 10 g of sodium hydroxide (in 20 ml of aqueous solution) were added and the reaction mixture was heated to 50 °C. After stirring for 4 h, the reaction mixture was poured into excess acidic ethanol (10%) and filtered. The product was purified by repeatedly washing with water, acidic ethanol and water, and dried under vacuum at 60 °C for 8 h.

3. Results and discussion

Propylene polymerization was conducted with *rac*-Me_2Si[2-Me-4-Naph-Ind]$_2ZrCl_2$ catalyst and MAO cocatalyst containing 13.0 mol% of $AlMe_3$ [11]. Normally, at the end of polymerization, the reaction would then undergo quenching with acidic alcohol to terminate the polymerization. However, for a fast yet unambiguous understanding and possible quantification of the occurring frequency of the aluminum transfer reaction, the polymerization reactions were exempted from termination by acidic quenching but subjected to an oxidative workup using dry O_2 and H_2O_2/NaOH to transform the formed alkylaluminum-terminated polymer chains to hydroxyl-capped ones [8]. With this oxidative workup process, all

Table 1
A summary of conditions[a] and results of propylene polymerization with *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind]_2ZrCl_2$/MAO catalyst undergoing an oxidative workup process

Run no.	Polym. temp. (°C)	[MAO] (mol/l)	[Al]/[Zr]	Yield (g)	A[b]	M_n[c]	PDI[d]	T_m (°C)	M_n[g]	Chain-end unit to total propylene units (mol%)[f]			Estimated frequency of each chain transfer reaction (%)		
										$-C(CH_3)=CH_2$	$-CH=CH_2$	$-CH_2-OH$	β-H transfer	β-Me transfer	Al transfer
1	60	0.15	3000	6.79	18.1	0.81	2.10	147.7	0.87	0.031	0.022	0.425	≈7	≈5	≈88
2	40	0.15	3000	8.48	22.6	1.32	2.30	154.4	1.31	0.016	0.012	0.292	≈5	≈4	≈91
3	30	0.15	3000	7.69	20.5	1.55	2.58	157.5	1.61	0.008	0.007	0.246	≈3	≈3	≈94
4	10	0.15	3000	6.41	17.1	6.65	2.54	161.2	7.64	n.d.[e]	n.d	0.055	≈0	≈0	≈100
5	0	0.15	3000	1.40	3.73	12.42	2.89	161.9	15.0	n.d.	n.d	0.028	≈0	≈0	≈100
6	10	0.50	10000	11.7	31.2	2.46	2.10	158.2	3.50	n.d.	n.d.	0.120	≈0	≈0	≈100
7	10	0.25	5000	11.2	29.4	4.30	2.23	160.2	5.45	n.d.	n.d.	0.077	≈0	≈0	≈100
8	10	0.10	1500	7.42	19.8	8.61	2.94	160.5	11.05	n.d.	n.d.	0.038	≈0	≈0	≈100
9	10	0.025	500	5.81	15.5	17.90	2.49	160.7	23.33	n.d.	n.d.	0.018	≈0	≈0	≈100

[a] Other conditions: propylene = 1.0×10^5 Pa (1 bar), [Zr] = 5.0×10^{-6} M, time = 30 min, toluene as the solvent, solvent + MAO solution = 150 ml.

[b] Activity, $\times 0^6$ g of PP/mol Zr h bar.

[c] M_n, $\times 10^4$ g/mol, calculated from GPC measurement.

[d] PDI, polydispersity index.

[e] n.d., not detectable.

[f] mol% of functional groups to propene molecules incorporated in the main chain.

[g] M_n, $\times 10^4$ g/mol, calculated from ^1H NMR by the comparison of mol% of chain-end units to total propylene units.

possible chain ends that might result from β-hydride transfer, β-methyl transfer (unsaturated groups), and chain transfer to the aluminum cocatalyst (Chart 1) would exhibit their distinctive characteristic resonances in a ^1H NMR spectrum.

3.1. *Predominant aluminum chain transfer reaction*

Propylene polymerization was first run under the conditions of Al/Zr ratio of 3000 and polymerization temperature of 60 °C (run 1 in Table 1). This reaction afforded, with a catalyst activity of 18.14×10^6 g PP/mol Zr h bar, polypropylene polymer having a number-average molecular weight (M_n) of 8150 g/mol, a molecular weight distribution (PDI) of 2.1 and a melting temperature (T_m) of 147.7 °C. In Fig. 1(a) is shown its ^1H NMR spectrum measured at 110 °C in *ortho*-dichlorobenzene-d_4. In addition to the three major peaks at 0.95–1.65 ppm corresponding to CH_3, CH_2 and CH protons in propylene repeating units, several minor peaks are observed at 3.0–6.0 ppm when the spectrum is adequately enlarged. These peaks are the fingerprints of polymer chain ends due to different chain transfer mechanisms. At the first glance, it has been clear that hydroxyl methyl ($-CH(CH_3)-CH_2-OH$), the chain-end group formed by chain transfer to aluminum followed by hydroxylation with O_2 and H_2O_2/NaOH in the oxidative workup process, represents the uppermost chain-end structure of the obtained polypropylene, as the peak at 3.3–3.5 ppm corresponding to $-CH_2-OH$ protons exhibits an overwhelmingly strong intensity compared with the others. The peaks at 4.5–6.0 ppm assignable to protons on unsaturated groups formed by β-hydride and β-methyl transfer reactions all show very weak intensities. However, it is still necessary to confirm that the hydroxyl methyl groups come exclusively from the aluminum–carbon bonds at the aluminum transfer-generated polymer chain ends. For such a purpose, we run a comparative polymerization under identical reaction conditions but terminating it by direct quenching with acidic alcohol to avoid the use of O_2 and H_2O_2/NaOH. ^1H NMR spectrum of thus-obtained polymer (Fig. 1(b)) was compared with that of its hydroxylated counterpart. Except for no signals observed at 3.3–3.5 ppm, the former spectrum is almost identical to

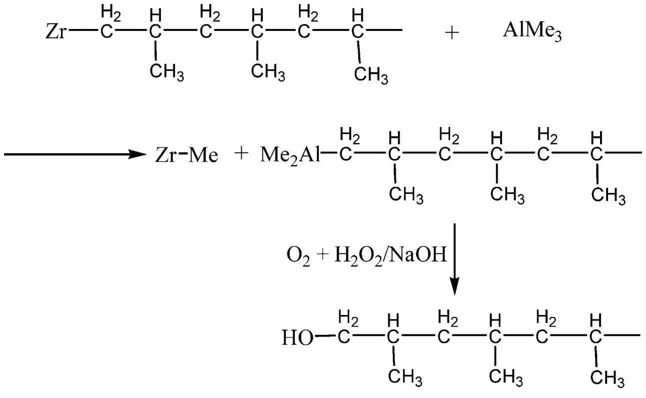

Chart 1. Chain transfer to aluminum and subsequent oxidative workup.

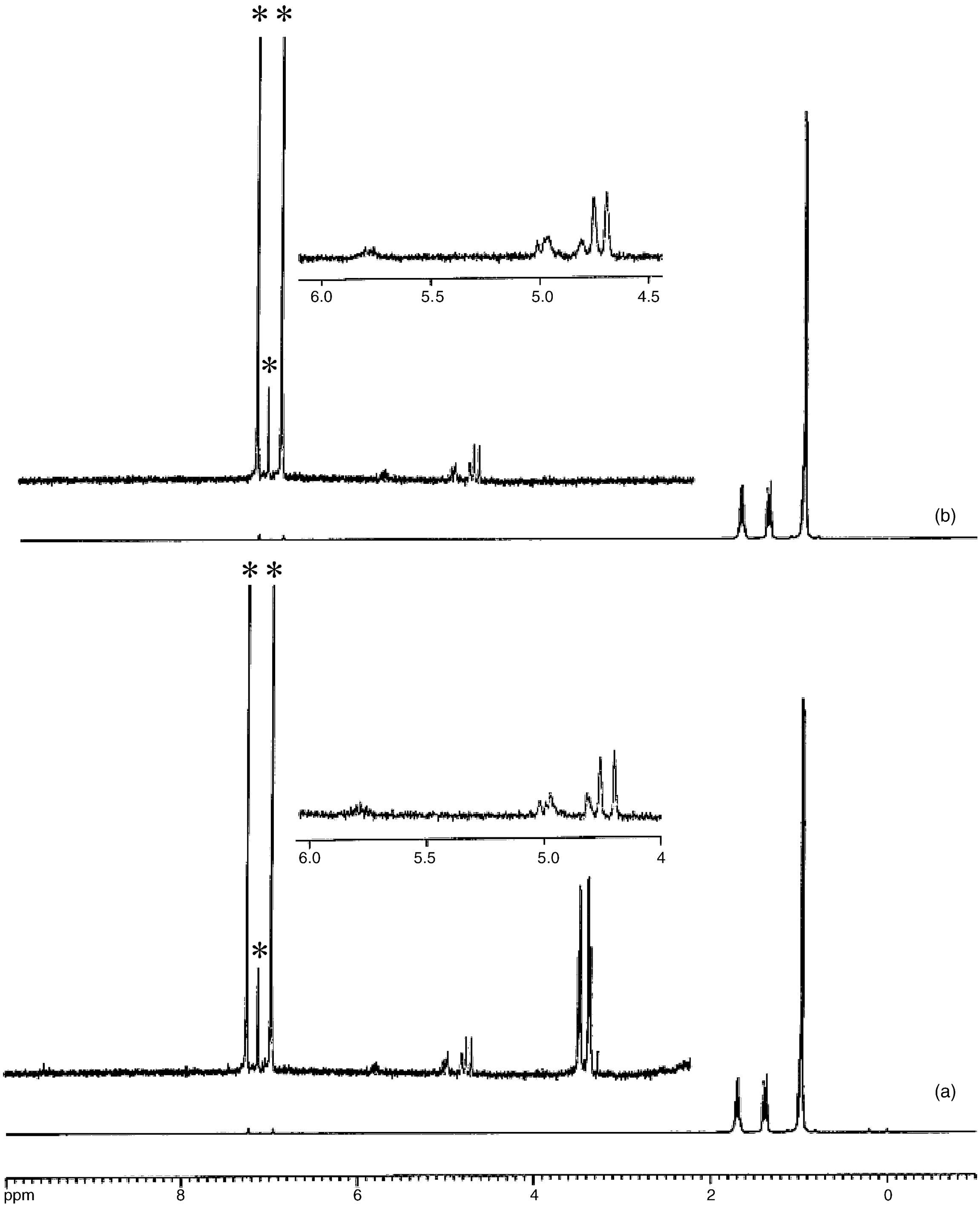

Fig. 1. ^1H NMR spectra of polypropylenes obtained (a) with an oxidative workup process and (b) without an oxidative workup process (polymerization conditions: temperature = 60 °C, Al/Zr = 3000) (*solvent: *o*-dichlorobenzene-d_4, temperature: 110 °C).

the latter one. Both of them show the characteristic peaks of three types of unsaturated groups at 4.65–4.75 ppm (terminal vinylidene, $-C(CH_3)=CH_2$), 4.9–5.0 ppm (terminal allyl, $-CH=CH_2$) and 5.7–5.8 ppm (terminal allyl, $-CH=CH_2$), and 4.81–4.82 ppm (internal vinylidene, $-CH_2C(=CH_2)CH_2-$) [12]. The integrated intensity ratios between each of these peaks and the main chain proton peaks at 0.95–1.65 ppm are of good consistency for these two spectra, indicating that, during the oxidative workup process in the presence of O_2 and H_2O_2/NaOH, no side reactions occurred with the unsaturated groups. These results strongly support the deduction that the hydroxyl methyl end groups are solely formed from the terminal aluminum–carbon bonds. On the basis of these experimental results, with the assumption of a nearly quantitative conversion of aluminum–carbon bonds to hydroxyl methyl groups [8], we may be able to roughly quantify the occurring frequency of the predominant aluminum transfer reaction in the overall chain termination reactions including β-hydride transfer, β-methyl transfer and chain transfer to the aluminum cocatalyst, provided that we identify and quantify all the corresponding chain-end structures. In fact, as mentioned above, terminal vinylidene and allyl represent the only two detected chain ends resulting from chain termination via β-hydride and β-methyl transfer reactions, respectively. The formation of internal vinylidene, although also occurring through β-hydride transfer, does not necessarily lead to chain transfer, and so internal vinylidene is not taken into account as a result of β-hydride transfer-initiated chain termination reaction. For these three chain-end structures including hydroxyl methyl, terminal vinylidene and allyl, their respective amounts are calculated from comparison of the relative intensities of the characteristic peaks (3.3–3.5 ppm for hydroxyl methyl, 4.65–4.75 ppm for vinylidene, and 4.9–5.0 ppm for allyl) with that of the main chain proton peaks at 0.95–1.65 ppm together with a consideration of the number of protons each peak represents. Values of 0.43, 0.031 and 0.022 mol% are obtained for hydroxyl methyl, vinylidene and allyl groups, respectively. Comparing the amount of each chain-end group with the total chain-end amount gives the occurring frequency of the corresponding chain transfer reaction in the overall chain termination reactions. Values of 88, 7 and 5% are obtained for chain transfer to aluminum, β-hydride and β-methyl transfer reactions, respectively, implying that a great majority of chain termination reactions occurred in the polymerization via chain transfer to the aluminum cocatalyst.

3.2. Synthesis of aluminum-terminated polypropylene

β-Methyl transfer is known to be a unimolecular process [13,14]. It has been experimentally revealed that β-hydride transfer also occurs in *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind]_2ZrCl_2$/MAO-catalyzed propylene polymerization without monomer involvement [5]. Thus, further enhancement of the selectivity of the bimolecular aluminum transfer reaction might be expected by reducing the polymerization temperature. Propylene polymerization reactions were then conducted at some lower temperatures, i.e., 40, 30, 10 and 0 °C. The results are summarized in Table 1. In Fig. 2 are compared ^1H NMR spectra of the resultant polymers.

As expected, lowering the polymerization temperature effectively promotes the selectivity of aluminum transfer

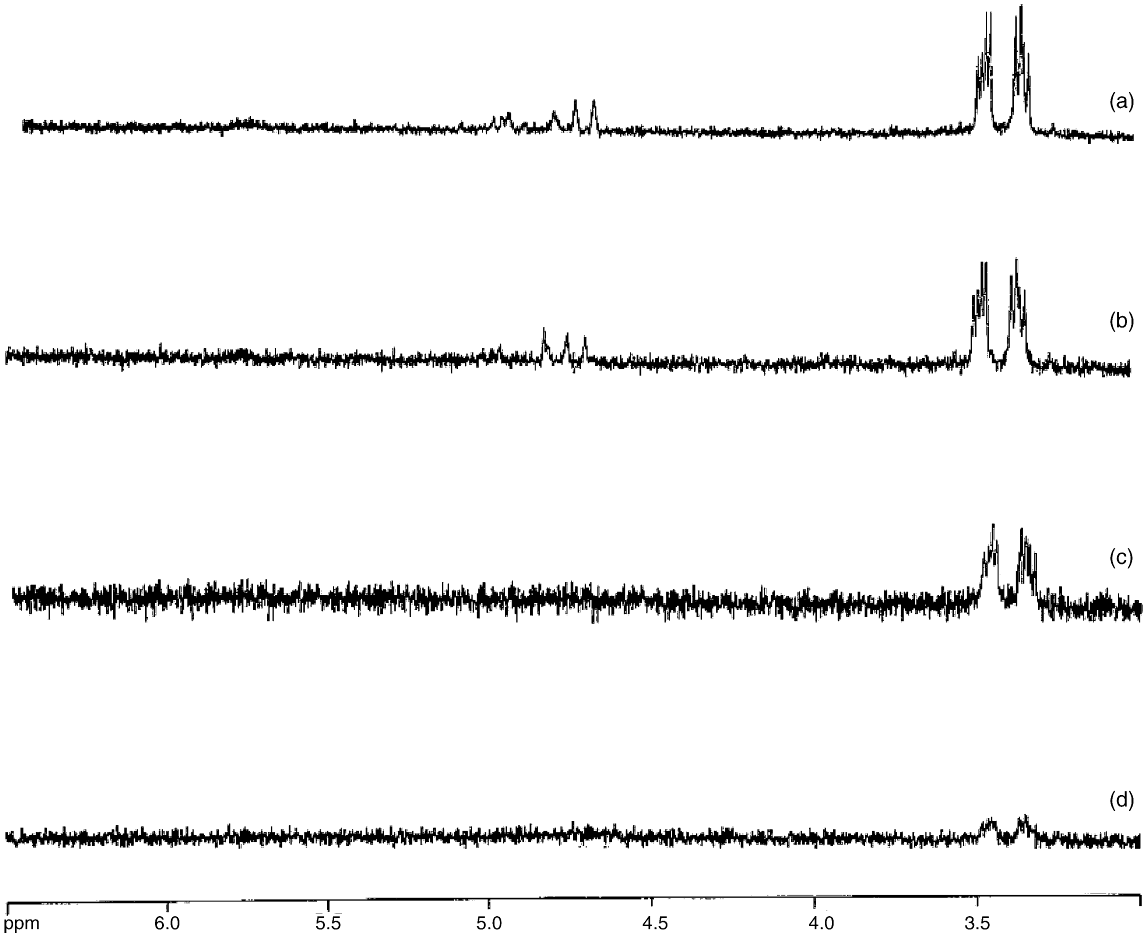

Fig. 2. Intercepted ^1H NMR spectra of polypropylenes prepared at (a) 40 °C, (b) 30 °C, (c) 10 °C and (d) 0 °C with a constant Al/Zr ratio of 3000 (solvent: *o*-dichlorobenzene-d_4, temperature: 110 °C).

reaction. As shown in Table 1 and illustrated in Fig. 2, the relative frequencies of chain terminations via both β-hydride and β-methyl transfer reactions gradually decrease with the decrease of polymerization temperature. Propylene polymerization at 10 °C yields, with a still high catalyst activity, a completely saturated polymer free of any terminal and internal vinylidene or allyl groups, implying the effective inhibition of β-hydride and β-methyl transfer reactions during the polymerization. ^{1}H NMR spectrum of the polymer (Fig. 2(c)) reveals a strong hydroxyl methyl signal at 3.3–3.5 ppm, suggesting a still intense aluminum transfer reaction. These results indicate that chain transfer to aluminum has become dominant in the overall chain termination process under these conditions. Under these circumstances, further decreasing the polymerization temperature is of little significance. As a matter of fact, due to a significant suppression of aluminum transfer reaction, propylene polymerization at 0 °C yields a polymer exhibiting a much weaker hydroxyl methyl signal in ^{1}H NMR spectrum as compared with that polymerized at 10 °C. The catalyst activity is also greatly reduced.

The domination of chain termination by chain transfer to aluminum results in an aluminum concentration dependence of polymer molecular weights. Table 1 includes the results of propylene polymerization at 10 °C with varied Al/Zr ratios from 500 through 10,000. ^{1}H NMR spectra (shown in Fig. 3) prove the absence of chain terminations via β-hydride and β-methyl transfer reactions in these polymerization reactions, as no polymer is shown to have evident vinylidene and allyl terminal groups. Only a very weak resonance representing the internal vinylidene group is detected at 4.81–4.82 ppm when a very low Al/Zr ratio (500) was adopted in the polymerization. The polymer number-average molecular weights (M_n) estimated from GPC examination exhibit a linearly decreasing trend with the increase of aluminum concentrations in the polymerization reactions (runs 9, 8, 4, 7 and 6).

Besides GPC estimation, M_n values of the polymers can also be calculated from ^{1}H NMR by the comparison of mol% of chain-end units to total propylene units. The results are listed in Table 1 (column 10). In general, the calculated M_n values are in fairly good accordance with those estimated

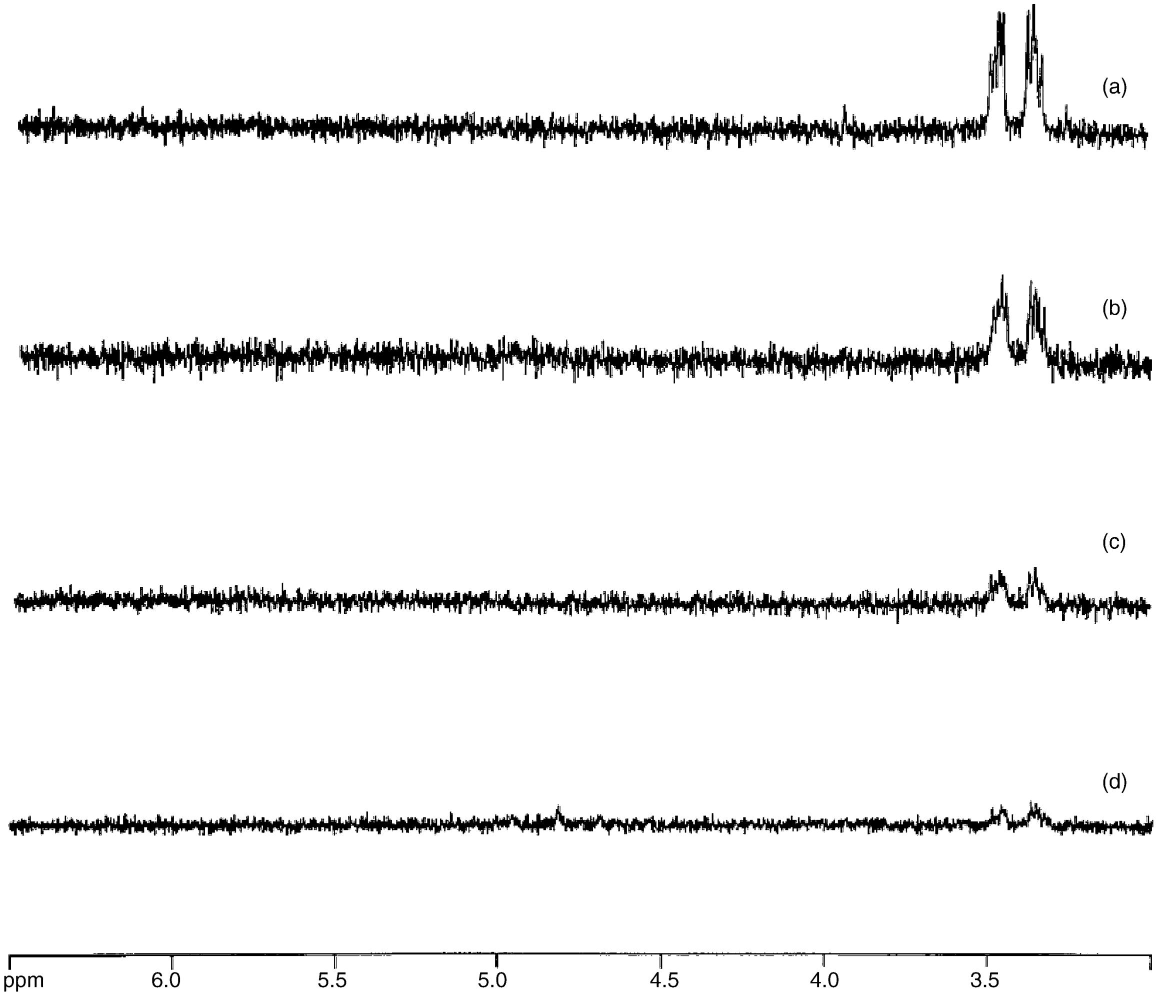

Fig. 3. Intercepted ^{1}H NMR spectra of polypropylenes prepared at 10 °C with varied Al/Zr ratios: (a) 10000, (b) 5000, (c) 1500 and (d) 500 (solvent: *o*-dichlorobenzene-d_4, temperature: 110 °C).

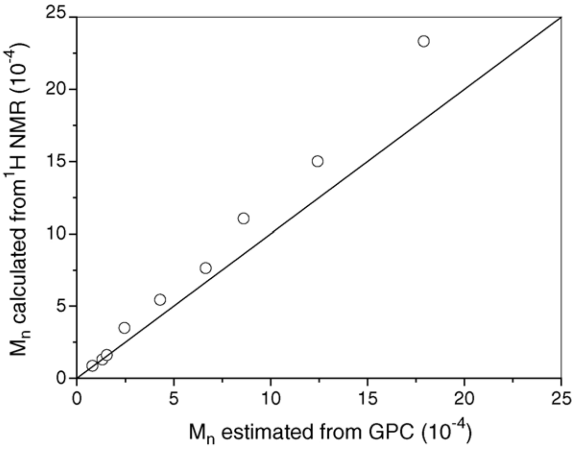

Fig. 4. Plot of M_n calculated from ^{1}H NMR vs. M_n estimated by GPC.

by GPC (column 7), especially for polymers with relatively lower molecular weight, indicating a high accuracy of the chain-end quantification. However, it is also noted that the calculated M_n values are somewhat higher than their GPC-estimated counterparts when the polymers possess relatively higher molecular weight. Fig. 4 shows the plot of M_n calculated from ^{1}H NMR versus M_n estimated by GPC. This inconsistency may be caused by the reduced quantification accuracy of the chain ends at high polymer molecular weight. In addition, it is also possible that the oxidation of the alkylaluminum terminal may be a little away from completion when the polymer has high molecular weight, which will also cause an overestimation of M_n.

4. Conclusions

In summary, this research clearly demonstrates that a predominant aluminum transfer reaction is achievable in metallocene-catalyzed isospecific polymerization of propylene by employing the highly hindered *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind]_2ZrCl_2$ in combination with MAO. Aluminum-terminated *i*-PP with high end-group selectivity as well as high melting points and controlled molecular weights are obtained with high yields. Currently, our research is focused on: (i) the continued and detailed study of the effects of different metallocene catalysts as well as different polymerization conditions on the selectivity of the aluminum transfer reaction and (ii) the application of the aluminum-terminated *i*-PP in the preparation of terminally functionalized *i*-PPs and *i*-PP-based block and graft copolymers. Those results will be reported elsewhere.

Acknowledgments

The authors are grateful to the Chinese Academy of Sciences, the Ministry of Science and Technology of China and the National Science Foundation of China for their financial supports through the “One Hundred Talents” program, the Major State Basic Research Development Program (G2003CB615600), and NSF funds Nos. 20304017, 50373048, and 20334030.

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