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PII: S0032-3861(97)00311-X

Polymer Vol. 38 No. 26, pp. 6409–6411, 1997
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0032-3861/97/$17.00+0.00

polymer communications

Control of molecular weight distribution of isotactic polypropylene obtained by a $MgCl_2$-supported $TiCl_4$ catalyst

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(Received 16 January 1997; revised 3 March 1997; accepted 21 March 1997)

It is of great importance in propene polymerization to control molecular weight and molecular weight distribution as well as isotacticity. Propene polymerization was carried out with an isospecific $MgCl_2/TiCl_4$–Cp_2TiMe_2 catalyst in the presence of various kinds of external Lewis bases. It was found that the molecular weight distribution of the isotactic polymer could be controlled while retaining high activity, high isospecificity and high molecular weight only by changing the kind and/or amount of the Lewis bases. © 1997 Elsevier Science Ltd.

(Keywords: isotactic polypropylene; Lewis base; molecular weight distribution)

Introduction

In propene polymerization by $MgCl_2$-supported Ti-based catalysts, various kinds of Lewis bases are used as additives to the solid catalysts (called ‘internal donors’) and also to the polymerization system (called ‘external donors’) in order to improve isospecificity[1]. Control of the molecular weight and molecular weight distribution (MWD) is also very important in polymer synthesis. Usually, these $MgCl_2$-supported Ti-based catalysts giving isotactic polypropylene (PP) with a narrower MWD can be obtained by a conventional $TiCl_3$–$AlEt_2Cl$ catalyst. Isotactic PP with the narrowest MWD can be obtained in high yields with homogeneous metallocene catalysts. However, it is not easy to broaden the MWD of isotactic PP while keeping its high activity and high molecular weight, although this is strongly desired from the practical point of view.

We have previously reported that $MgCl_2$-supported $TiCl_4$ catalysts show high isospecificity even in the absence of any donor compound when Cp_2TiMe_2 is used as a cocatalyst[2,3]. We have investigated additive effects of ethyl benzoate (EB) and 2,2-diisobutyl-1,3-dimethoxypropane (DBDMP) as internal and external Lewis bases on propene polymerization with the isospecific $MgCl_2/TiCl_4$–Cp_2TiMe_2 catalyst and found that the Lewis bases affected not only the catalyst isospecificity and activity but the MWD of the produced polymer as well[4].

In this communication, we carried out propene polymerization with the $MgCl_2/TiCl_4$–Cp_2TiMe_2 catalyst in the presence of various kinds of external Lewis bases, and investigated the possibility of controlling the MWD of isotactic PP by external Lewis bases.

Experimental

Materials. Propene (from Mitsubishi Petrochemical Co., Yokkaichi), $MgCl_2$ ($97\,m^2\,g^{-1}$) and $TiCl_4$ (from Kanto Chemical Co., Tokyo) were used without further purification. Research grade heptane, commercially obtained from Kanto Chemicals Co., was purified according to the usual procedures. 2,2-di-tert-butyl-1,3-dimethoxypropane[5] and Cp_2TiMe_2[6] were synthesized according to the literatures. $MgCl_2$-supported $TiCl_4$ catalyst ($TiCl_4/MgCl_2$) was synthesized by adsorbing $TiCl_4$ on $MgCl_2$ in heptane at room temperature followed by washing with heptane. The Ti content in the catalyst determined by atomic absorption spectrophotometry (Shimadzu AA-6105) was 0.23 wt.%

Polymerization and analytical procedures. Polymerization of Propene was conducted at 40°C in a $0.2\,dm^3$ glass reactor equipped with a magnetic stirrer. After measured amounts of the catalyst and heptane were added to the reactor, the solvent was saturated with an atmospheric pressure of propene. Polymerization was started by introducing Cp_2TiMe_2 as a cocatalyst into the reactor. After about $1\,dm^3$ of propene was consumed, Lewis base was added if necessary. Polymerization was terminated by adding dilute hydrochloric acid solution in methanol. The polymer was fractionated by extraction with boiling heptane for 8 h to determine the isotactic index (i.i.).

The gel permeation chromatograms (g.p.c.) of the polymers were recorded on Waters 150C (Millipore Co., MA) equipped with a Shodex GPC UT-806L column (Showa Denko K.K., Tokyo) at 135°C using o-dichlorobenzene as solvent at a flow rate of $1.0\,cm^3\,min^{-1}$. The molecular weights of polymers were determined by the universal calibration technique.

Differential scanning calorimetry (d.s.c.) measurements were made on a Seiko DSC-220 (Seiko Instruments Inc., Tokyo). Polymer samples (ca. 4 mg) were encapsulated in aluminium pans and scanned at $10°C\,min^{-1}$.

Results and discussion

Polymerization was performed at 40°C under an atmospheric pressure of propene by a $MgCl_2$-supported $TiCl_4$ catalyst using Cp_2TiMe_2 as a cocatalyst. The catalyst system gave polypropylene containing more than 90% of a boiling heptane-insoluble fraction with considerable activity (run no. 2 in *Table 1*). We had already investigated the additive effect of ethyl benzoate (EB) on this system and

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Table 1 Results of propene polymerization with the $TiCl_4/MgCl_2$–Cp_2TiMe_2 catalyst system [a,b]

Run	External donor [c]	[D]/[Ti] [d]	Activity (kg PP/g Ti·h)		i.i. (%) [e]	Mn (× 10^{-4}) [f,g]	M_w/M_n [f,g]	T_m (°C) [f,h]	ΔH (mJ mg^{-1}) [f,h]
			Isotactic	Atactic					
1	None [i]	0	7.34	26.16	21.9	7.4	2.9	154.9	78.3
2	None	0	3.05	0.25	92.5	12.7	8.3	160.3	87.5
3	EB	0.2	4.36	0.21	95.4	15.1	7.2	161.4	89.7
4		1.0	3.36	0.12	96.7	14.5	6.1	161.6	87.9
5	TMP	0.2	4.45	0.23	95.0	14.1	7.5	160.6	88.3
6		1.0	3.49	0.18	95.2	– [j]	–	161.1	87.3
7	BHT	0.2	4.11	0.26	94.0	13.1	10.5	160.3	87.0
8		1.0	3.19	0.18	94.8	–	–	160.5	85.3
9	TBME	0.2	3.60	0.21	94.4	14.2	13.1	160.6	88.2
10		1.0	3.13	0.18	94.6	–	–	160.6	86.7
11	THF	1.0	1.60	0.13	92.5	–	–	–	–
12	Pyridine	1.0	2.10	0.16	93.1	–	–	–	–
13	2-BuOH	1.0	1.83	0.17	91.6	–	–	–	–
14	DBDMP	0.2	2.91	0.22	93.1	15.0	14.1	160.3	88.2
15		1.0	2.51	0.15	94.5	15.6	11.4	160.8	86.7
16	DIBP	0.2	3.14	0.19	94.4	17.4	7.4	160.9	85.6
17		1.0	2.00	0.11	94.6	13.2	8.0	160.9	86.1
18	DMDPS	0.2	2.80	0.16	94.6	14.4	9.3	160.9	85.6
19		1.0	2.94	0.13	95.7	–	–	161.1	87.5

[a] Ti content in the solid catalyst = 0.23 wt.%

[b] Polymerization conditions; propene = 1 atm, heptane vol. = 0.1 dm^3, [Cp_2TiMe_2] = 5.60 mM, [Ti] = 0.28 mM, 40°C, 0.5 h

[c] EB, ethyl benzoate; TMP, 2,2,6,6-tetramethylpiperidine; BHT, 2,6-di-tert-butyl-4-methylphenol; TBME, tert-butyl methylether; DBDMP, 2,2-diisobutyl-1-3-dimethoxypropane; DIBP, diisobutyl phtharate; DMDPS, dimethoxydiphenylsilane

[d] Molar ratio of external donor per Ti

[e] Isotactic index (weight fraction of boiling heptane-insoluble part)

[f] Boiling heptane-insoluble part

[g] Number average molecular weight (M_n) and polydispersity (M_w/M_n) determined by GPC

[h] Melting point (T_m) and heat of fusion (ΔH) determined by d.s.c.

[i] $AlEt_3$ was used in place of Cp_2TiMe_2: polymerization conditions; propene = 1 atm, heptane vol. = 0.1 dm^3, [$AlEt_3$] = 10.0 mM, [Ti] = 0.10 mM, 40°C, 0.5 h

[j] Not determined

found that both an internal and an external EB equivalent to the supported Ti decreased the activity very effectively[3]. When EB was added after the polymerization had started, however, the activity for isotactic PP increased accompanied with an decrease in that for atactic PP[4].

Therefore, the additive effect of several bulky monodentate Lewis bases were investigated by adding them shortly after the polymerization was started. The monodentate Lewis bases employed were EB, 2,2,6,6-tetramethylpiperidine (TMP), 2-6-di-tert-butyl-4-methylphenol (BHT) and tert-butyl methyl ether (TBME). The results are summarized in *Table 1*.

Less than an equimolar amount of the Lewis base to the supported Ti slightly decreased the activity for atactic PP and increased that for isotactic PP very effectively. As a consequence, catalyst isospecificity effectively increased to reach as high as 95%. Among the employed monodentate Lewis bases EB seems to be the best, although the difference between the Lewis bases is not so significant. The result suggests that the bulkiness of the base is more important than the electronic feature. The reason is maybe the interaction between the bases and cocatalyst (Cp_2TiMe_2) is neglected and the bulky bases effectively interact with less hindered non-stereospecific sites in the present polymerization system. In the usual catalyst systems where alkylaluminiums are used as cocatalysts, the Lewis bases competitively interact with both active Ti species and alkylaluminiums, hence the choice of Lewis base is more difficult.

When Lewis bases with less bulkiness, like tetrahydrofuran (THF), pyridine and butan-2-ol, were used as additives, the activities for both isotactic PP and atactic PP drastically decreased as expected (run nos. 11–13 in *Table 1*).

For comparison, typical bidentate Lewis bases were used as an external donor. The bidentate Lewis bases employed were 2,2-diisobutyl-1,3-dimethoxypropane (DBDMP), diisobutyl phthalate (DIBP) and dimethoxydiphenylsilane (DMDPS). Contrary to the bulky monodenate Lewis bases, these bidentate bases did not increase the activity for isotactic PP but decreased that for atactic PP to improve catalyst isospecificity. DBDMP and DIBP at a high donor/Ti ratio resulted in the reduction of isotactic PP.

The properties of isotactic PP were investigated by d.s.c. and g.p.c., the results of which are summarized in *Table 1*. The melting point of isotactic polymer obtained by Cp_2TiMe_2 without an external donor (160.3°C) is much higher than that obtained with $AlEt_3$ (154.9°C), which indicates that highly isospecific sites are present even in the absence of any donor in the former system. All the Lewis bases improved the melting point, although EB was also most effective in this case.

The number of average molecular weights (M_n) were also increased by addition of the Lewis bases. Polydispersity (M_w/M_n) of an isotactic polymer obtained by Cp_2TiMe_2 (8.3) is larger than that obtained by $AlEt_3$ (2.9), which suggests that several kinds of isospecific species are present in the $TiCl_4/MgCl_2$–Cp_2TiMe_2 catalyst as proposed previously[3]. It should be noted that the polydispersity of isotactic PP obtained by the $TiCl_4/MgCl_2$–Cp_2TiMe_2 catalyst depended upon the kind of Lewis bases. It seems that ester and amine compounds make the MWD narrower, while ethers make it broader. As a consequence, it was proved that polydispersity of highly isotactic PP could be controlled from about 6 to 14 only by adding a small amount of suitable Lewis bases in the present system.

The above results were probably obtained due to the lower Lewis acidity of Cp_2TiMe_2 than that of $AlEt_3$, which makes Lewis bases interact with active Ti species and/or $MgCl_2$ very effectively. The results obtained in this paper show the possibility of controlling the MWD of isotactic PP by Lewis bases in $TiCl_4/MgCl_2$ catalysts, although a precise mechanism is not clear at present.

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