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Effect of 1-allyl-3,4-dimethoxybenzene on propene polymerization with the $TiCl_4$/DBP(dibutylphthalate)/$MgCl_2$ catalyst

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Summary

Propene polymerization was carried out using the $TiCl_4$/DBP(dibutylphthalate)/$MgCl_2$-$Al(C_2H_5)_3$ catalyst combined with various kinds of aromatic ether compounds as external donor. Addition of o-dimethoxybenzene derivatives, especially, 1-allyl-3,4-dimethoxybenzene(ADMB), caused a marked increase in both yield and molecular weight of atactic polypropylene.

Introduction

Highly active $MgCl_2$-supported Ti catalysts have played an important role in the production of polyolefins. Enormous efforts have been made mainly to increase the catalyst activity and stereospecificity. On the other hand, the demand of atactic polypropylene has been increased in the recent years, too. Homogeneous catalyst system developed by Kaminsky and Sinn using methylalumoxane as cocatalyst are known to produce atactic polypropylene in high yield[1]. The structure of this polymer is, however, completely random, which differs markedly from that of "atactic" polypropylene obtained with common heterogeneous catalysts containing blocks of isotactic and atactic sequences[2]. Such a block type atactic polypropylene may be more useful, e.g.,to produce elastomers etc[3-5]. It is of great importance, therefore, to develop highly active heterogeneous catalysts which selectively produce block type atactic polypropylene.

We have recently found that the $TiCl_4$/DBP/$MgCl_2$-$Al(C_2H_5)_3$ catalyst combined with a suitable aromatic ether as external donor predominantly gives high molecular weight atactic polypropylene in a very high yield.

In this communication, we report the preliminary results on the polymerization.

Experimental

Materials

Commercial, extra pure grade heptane was dried by passing through a molecular sieve 3A column in argon atomosphere. Dibutylphthalate(from Tokyo Kasei Co, Ltd.) was dried over molecular sieve 3A. Propene(from Takachiho Chemical Co.Ltd., research grade), $MgCl_2$(from Toho Titanium Co. Ltd.) and other chemicals were commercially obtained and used without further purification.

Preparation of catalysts

The mixture of 28 g of $MgCl_2$ and 16,9 mmol of dibutylphthlate(DBP) was

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ground in a 0,82 dm^3 stainless steel ball mill pot with 40 balls of 22 mm in diameter and 55 balls of 13 mm in diameter under argon for 60 h at room temperature. The product was brought into contact with 0,2 dm^3 of $TiCl_4$ at 120 ℃ for 2 h with a vigorous stirring. The solid part was separated by filtration and adequately washed with plenty of heptane under argon atomosphere. The content of Ti and DBP in the catalyst were 0,33 and 0,40 mmol/g-cat.,respectively. The ester-free catalyst was prepared by co-grinding the mixture of 28 g of $MgCl_2$ and 26 mmol of $TiCl_4$ by the same procedure as described above. The content of Ti in the catalyst was 0,60 mmol/g-cat.

Polymerization of propene

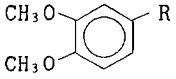
Polymerization was carried out in a 1 dm^3 stainless steel autoclave at 70 ℃. Into the autoclave, which was filled with argon, were put 0,4 dm^3 of heptane, 1 mmol of $Al(C_2H_5)_3$, 8 mg of solid catalyst and a given amount of aromatic ether. Propene was continuously fed at constant pressure (8 bar). Polymers obtained were adequately washed with methanol, filtered and dried i.vac. at 65 ℃.

Analysis

The isotactic index (I.I.) of polymer produced was determined by fractionation with boiling heptane. The ^{13}C-NMR spectra of polymers were recorded on a JEOL FX-200 spectrometer at 50,10 MHz under proton decoupling in Fourier Transform (FT) mode. Instrument conditions were ; $\pi/4$ pulse of 8,0 μs, 5,0 s repetition rate and 8000 Hz sweep width. The number transients accumulated were 1000-2000. Solutions were made up in o-dichlorobenzene to 15 w/v-%. The intrinsic viscosity of polymers was measured at 135 ℃ in decalin containing 0,1% 2,6-tert-butyl-4-methylphenol (BHT). The molecular weights of polymers were measured by gel permeation chromatography (Waters Associate,Model 150) with 5 polystyrene gel columns at 135℃ using o-dichlorobenzene as solvent. The MW calibration curve was obtained on the basis of universal calibration with 10 standard samples of monodisperse polystylene of MW between 3600 and 820000.

Results and Discussion

Polymerization of propene was first carried out at 70 ℃ using the $TiCl_4/DBP/MgCl_2-Al(C_2H_5)_3$ catalyst system combined with various kinds of aromatic ether compounds. The results obtained are summarized in Table 1. A remarkable decrease in I.I. was observed when o-dimethoxybenzene derivatives given by structure [I] were used.



(R ; H, CH_3, $CH_2=CHCH_2$)

[I]

Polymerization of propene was then performed in some detail using 1-allyl-3,4-dimethoxybenzene (ADMB) which showed the highest activity.

In Table 2 are shown the number-average molecular weight (Mn) and steric pentad composition of boiling heptane soluble polymers (atactic) obtained with and without ADMB. Addition of ADMB not only caused a marked increase in Mn of atactic polymer, but also brought about a change in polymer structure.

Table 1 Results of propene polymerization with the $TiCl_4$/DBP/$MgCl_2$-$Al(C_2H_5)_3$ catalyst in the presence of various kinds of aromatic ethers[a].

Run	Additive	Polymer Yield [kg-PP/g-Ti]	I.I.	[η] [b]
1	none	276	57	2,01
2	methoxybenzene	284	49	1,91
3	p-dimethoxybenzene	296	52	1,82
4	m-dimethoxybenzene	289	41	1,69
5	o-dimethoxybenzene	352	19	1,98
6	1-allyl-3,4-dimethoxybenzene	410	19	1,91
7	3,4-dimethoxytoluene	327	17	1,75

a)Polymerization conditions : $TiCl_4$/DBP/$MgCl_2$ catalyst = 8 mg ; $Al(C_2H_5)_3$ = 1 mmol ; [Al]/[Ti] = 400 ; additive = 0,1 mmol ; heptane = 0,4 dm^3 ; polymerization temperature = 70 ℃ ; polymerization time = 2 h

b)Intrinsic viscosity for whole polymer,in decaline at 135 ℃

Table 2 Steric pentad compositions and molecular weights of atactic polypropylenes.

Addition of ADMB	mmmm	mmmr	rmmr	mmrr	mmrm rmrr	rmrm	rrrr	mrrr	mrrm	Mn [a] $\times 10^{-4}$
No	32	11	2	15	10	2	13	9	6	2,4
Yes	20	9	3	14	10	2	26	9	7	6,0

a)Measured by gel permation chromatography.

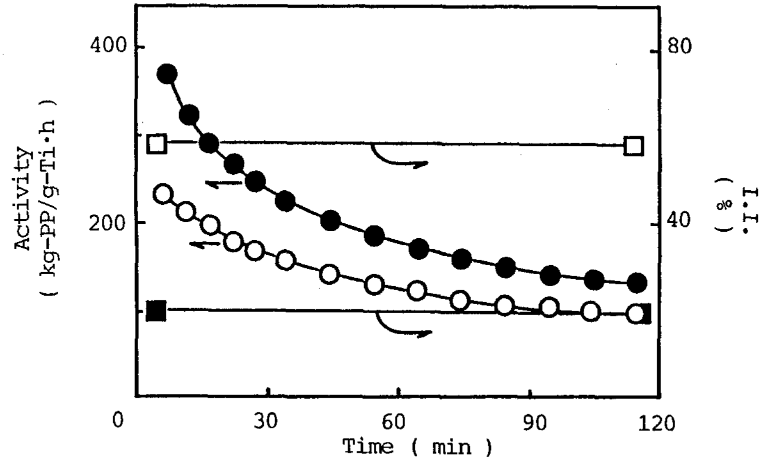


Figure 1 Plots of activity and I.I. against polymerization time. ●, ■ ; $TiCl_4$/DBP/$MgCl_2$-$Al(C_2H_5)_3$/ADMB catalyst system(ADMB/Ti= 40), ○, □ ; $TiCl_4$/DBP/$MgCl_2$-$Al(C_2H_5)_3$ catalyst system.

Atactic polypropylene obtained with ADMB showed the unique physical properties similar to those of elastomeric polypropylene(ELPP) reported by Collette et al.[3, 4).

The changes in polymerization rate and I.I. with polymerization time are illustrated in Figure 1, indicating that the kinetic profiles of the polymerizations hardly affected by the addition of ADMB.

On the other hand, the effect of the ADMB/Ti ratio on propene polymerization is shown in Figure 2. With an increase in ADMB/Ti ratio, both the yield and molecular weight of the atactic polymer drastically increased to approach the stationary values, whereas the yield of the isotactic polymer decreased with a slight increase in molecular weight. For reference, similar experiments were performed using the $TiCl_4/MgCl_2$ catalyst in place of the $TiCl_4/DBP/MgCl_2$ catalyst. The results obtained are shown in Figure 3. Surprisingly, the yield of the atactic polymer decreased to a great extent with increasing ADMB/Ti ratio. The molecular weight of atactic polymer monotoniously increased with the increase in ADMB/Ti ratio, which was quite different from the result shown in Figure 2. Therefore, the combination of DBP and ADMB as internal and external donors might form new active species which selectively give atactic polypropylene with high molecular weight.

In conclusion, we have found that the $TiCl_4/DBP/MgCl_2$-$Al(C_2H_5)_3$/ADMB catalyst system is very effective for the production of atactic polypropylene with high molecular weight. The precise mechanism for the formation of such new active sites is, however, not clear at present. A more precise study is now being carried out and the results will be published in another paper.

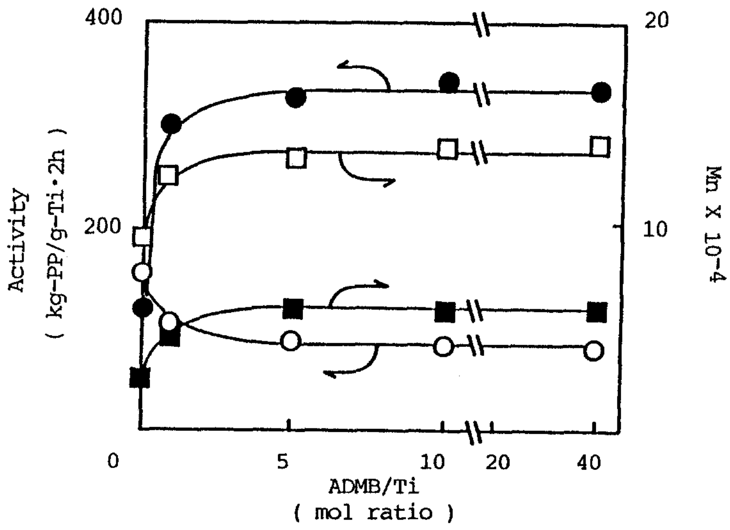


Figure 2 Changes in activity and molecular weight with ADMB/Ti ratio. Polymerization conditions : $TiCl_4/DBP/MgCl_2$ catalyst = 8 mg ; $Al(C_2H_5)_3$ = 1 mmol ; [Al]/[Ti] = 400 ; heptane = 0,4 dm^3 ; polymerization temperature = 70 ℃ ; polymerization time = 2 h

●, ■ ; for atactic polymer

○, □ ; for isotactic polymer

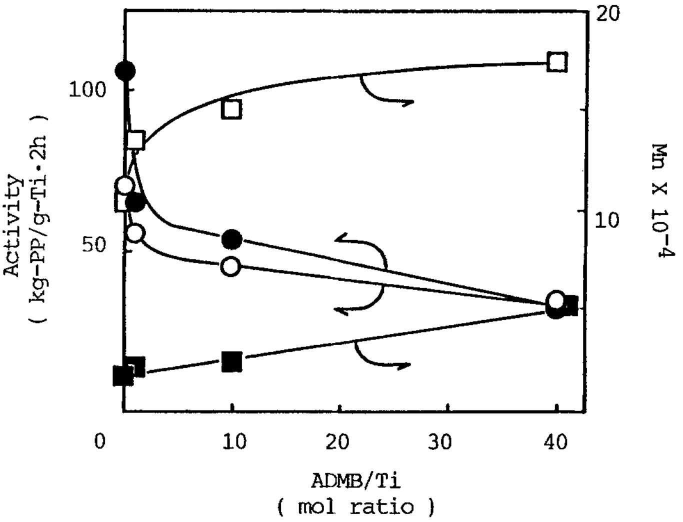


Figure 3 Changes in activity and molecular weight with ADMB/Ti ratio. Polymerization conditions : $TiCl_4/MgCl_2$ catalyst = 5 mg ; other conditions are the same as in Figure 2
● , ■ ; for atactic polymer
○ , □ ; for isotactic polymer

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