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Effect of 1-allyl-3,4-dimethoxybenzene on the copolymerization of propene and small amount of ethylene with the $TiCl_4$/dibutylphthalate (DBP)/ $MgCl_2$ catalyst activated by $Al(i\text{-}C_4H_9)_3$

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Summary

Copolymerization of propene and small amount of ethylene was conducted with the $TiCl_4$/DBP/$MgCl_2$-$Al(i\text{-}C_4H_9)_3$ catalyst in the presence and absence of 1-allyl-3,4-dimethoxybenzene(ADMB). Addition of ADMB caused a decrease in the ethylene content in copolymer with an increase in the activity. From a detailed analysis of the copolymers fractionated with boiling diethylether, it was found that the ADMB-containing system gives ether-soluble polymers with higher molecular weight and narrower molecular weight distribution as well as less content of regioirregular sequences of propene. The microstructures of the ether-soluble parts suggested that ADMB might accelerate the propene polymerization at the aspecific sites formed.

Introduction

Highly active $MgCl_2$-supported Ti catalysts play an important role in the production of polyolefins. Much effort has been paid 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 methylaluminoxane 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 useful, e.g., to produce elastomers(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 suitable aromatic ether like ADMB as external donor predominantly gives atactic polypropylene with high molecular weight(6). When this type of catalyst is applied to the copolymerization of propene with ethylene, the copolymer produced is assumed to show higher elasticities even in the lower

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content of ethylene. Such copolymers might hardly contain the sticky polymers as by-product because of the enhanced molecular weight of atactic fraction produced. The catalytic system is , therefore, expected to develop a new class of propene-based copolymer as well as the elastomeric polypropylene(3-5) described above. Moreover, such a copolymerization may also be useful not only for the practical purpose but also for understanding the active sites in the catalytic system. From such a view point, we have conducted the copolymerization of propene and small amount of ethylene with the $TiCl_4/DBP/MgCl_2$-Al(i-C_4H_9)$_3$ catalyst in the presence and absence of ADMB and analyzed the microstructures of copolymers fractionated with boiling diethyleter in some detail. This paper reports on the effect of ADMB on the structures of copolymers formed on the non-stereospecific(aspecific) sites.

Experimental part

Materials

Commercial, extra pure grade heptane was dried by passing through a molecular sieve 3 Å column in argon atmosphere. Dibutylphthlate (from Tokyo Kasei Co.Ltd.) was dried over molecular sieve 3 Å. Propene, ethylene(both 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 the catalyst and polymerization procedure

The catalyst was prepared according to the same procedure as reported previously (6) except for changing the molar ratio of DBP to $MgCl_2$ in feed. The content of Ti was 0,22 mmol/g-cat. Polymerization was carried out in a 2 dm^3 stainless steel autoclave at 70 °C for 15 min. In case of copolymerization, the mixture of ethylene and propene was continuously supplied to keep both partial pressures unchanged during the copolymerization. Copolymerization was started by the addition of the catalyst suspension in 20 cm^3 of heptane to the autoclave filled with 1 dm^3 of heptane and 7,6 atm of monomers, and terminated by adding 30 cm^3 of methanol. Propene polymerization was conducted under similar conditions. The polymer obtained was precipitated in excess methanol, filtered off and dried i.vac. at 80°C; for 4 h.

Analysis

The ^{13}C NMR spectra of the polymers were recorded on a JEOL JNM-LA 500 spectrometer at 125,65 MHz under proton decoupling in Fourier Transform(FT) mode. Instrument conditions were: π /4 pulse of 9,0 μ s, 4,0 s repetition rate and 25000 Hz sweep width. The number of transients accumulated were 10000. Solutions were made up in 1,2,4-trichlorobenezene(TCB)/benzene-d6 (vol. ratio = 9/1) to 0, 15 g/ml. The molecular weight dependence of ethylene content in copolymer was measured by GPC(gel permeation chromatography)/FT-IR(fourier transform infrared spectrometer) method. The GPC/FT-IR system and data processing procedures used in this study were as reported previously(7). The polymer solutions were prepared by dissolving ca. 30 mg of polymer in 10 cm^3 of TCB at 135 °C. The molecular weights and molecular weight distributions were measured by GPC(Waters Associate, Model 150) with 5 polystyrene gel column at 145 °C using TCB as solvent.

Results and discussion

Copolymerization of propene and small amount of ethylene was carried out at 70°C by using the $TiCl_4/DBP/MgCl_2$ catalyst combined with $Al(i\text{-}C_4H_9)_3$ or the mixture of $Al(i\text{-}C_4H_9)_3$ and ADMB. The results are shown in Tab. 1, where those of propene polymerization are also shown for reference. The weight percent of atactic polypropylene determined by fractionation with boiling heptane were 45 and 75 wt.-% in sample 1 and 3, respectively. If the same method was applied to the fractionation of the present copolymer samples, the heptane-soluble fractions might be partly contaminated with the polymers formed on the highly stereospecific sites. Then, the polymers produced were all extracted with boiling diethylether for 16 h to get the ether-soluble polymers, which were expected to produce mainly at the non-stereospecific sites, i.e., the aspecific ones. In Tab.1 are also shown the weight fraction of ether-soluble polymer : Esol.. The Esol. values were certainly lower than the weight percent of atactic polypropylene in each catalytic system, implying that no polymer produced at the highly stereospecific sites existed in the ether-soluble fraction. The results may suggest that the ether-insoluble fractions were formed not only on the highly stereospecific sites but also on the lower stereospecific ones. It is evident from Tab.1 that the addition of ADMB caused a marked increase in both activity and Esol. in the present copolymerization as well as in propene polymerization. Whereas, the ethylene content in the crude copolymer somewhat decreased by adding ADMB. It should be noticed here that the addition of small amount of ethylene to the propene polymerization caused a remarkable enhancement in the activity. The precise reason for which is, however, not clear at the present stage.

Tab.1 Results of ethylene-propene copolymerization with the $TiCl_4/DBP/MgCl_2\text{-}Al(i\text{-}C_4H_9)_3$ catalyst in the presence and absence of ADMB [a)]

Sample No	Addition of ADMB	$\frac{P_E}{P_E + P_P}$ [b)]	Activity in kg/g-Ti	C_2H_4content [c)] in mol-%	Esol. [d)] in wt.-%
1	No	0	33	0	15
2	〃	0,01	65	5,4	25
3	Yes	0	57	0	30
4	〃	0,01	125	4,0	45

a)Polymerization was conducted at 70℃ for 15 min by using 23 mg of $TiCl_4/DBP/MgCl_2$ catalyst and 5 mmol of $Al(i\text{-}C_4H_9)_3$. In Sample 2 and 4, 0,005 mmol of ADMB was added as an external donor.

b)P_E and P_P denote the ethylene and prepene pressure, respectively.

c)Determined by ^{13}C NMR spectra.

d)Determined by extraction with boiling diethylether.

The microstructures of ether-insoluble fraction in copolymer was first analyzed by ^{13}C NMR spectroscopy and the results are shown in Tab.2. The monomer sequence distributions reveals that ADMB leads to a decrease in the ethylene content in copolymer even in the fraction. In case of propene-based copolymers containing a very small amount of ethylene, the peaks in methyl carbon region (δ : 19,5- 22,5 ppm, c.f. Fig. 1) are said to be principally split by the stereoregularities in propene sequences. Accordingly, the steric triad compositions: [mm], [mr] and [rr], could be roughly evaluated from the peak areas in these signals. The steric triad compositions thus estimated strongly indicate that the fraction might result from the active sites potentially having the stereospecificities. The discrepancies in these values between two samples may be attributed to the differences in the weight percent of highly stereoregular polymers in the fraction.

Tab.2 Analytical data of the ether-insoluble fractions in copolymers obtained with and without ADMB a)

Sample No	Addition of ADMB	[EE] b)	[EP] b)	[PP] b)	[E] c)	[mm]	[mr]	[rr]
		in mol %				in mol %		
2	No	0,6	3,7	95,7	2,5	77	15	8
4	Yes	0	2,8	97,2	1,4	63	19	18

a)Polymerization conditions are described in Tab.1.
b)[EE], [EP] and [PP] denote the dyad sequence distributions, where E and P represents ethylene and propene, respectively.
c) [E] : ethylene content in copolymer

The ether-soluble fraction was then analyzed by GPC/FT-IR and GPC as well as ^{13}C NMR to obtain useful information on the aspecific sites formed. The ^{13}C NMR spectra of the ether-soluble fractions in sample 2 and 4 are shown in Fig. 1, where S, T and P denote secondary(methylene), tertiary(methine) and primary(methyl) carbons and the Greek subscripts refer to the distance of given carbon from neighboring methine carbon bearing methyl group(8). As shown in Fig. 1, the stereoregularities in both samples were remarkably lower than those in the corresponding ether-insoluble samples shown in Tab.2. Moreover, the values in Fig, 1 suggested that the fraction was mainly given by the aspecific sites having no stereospecificity. The ethylene content of the samples shown in Fig. 1-a and Fig, 1-b were determined to be 9,8 and 5,2 mol %, respectively , which indicates that the aspecific sites were much more reactive toward ethylene than the stereospecific ones (see Tab.2) in both systems and the addition of ADMB caused a decrease in the ethylene content of the ether-soluble copolymer.

There is a big difference in around δ =35 ppm between the two spectra. The signals could be assigned to S $\alpha\beta$ carbons originated from the following propagation reactions including the 2,1-insertion of propene at the active titanium-carbon bonds, where the methylene carbons marked by the asterisk and the broken line represents S $\alpha\beta$ carbon and the polymer chains, respectively.

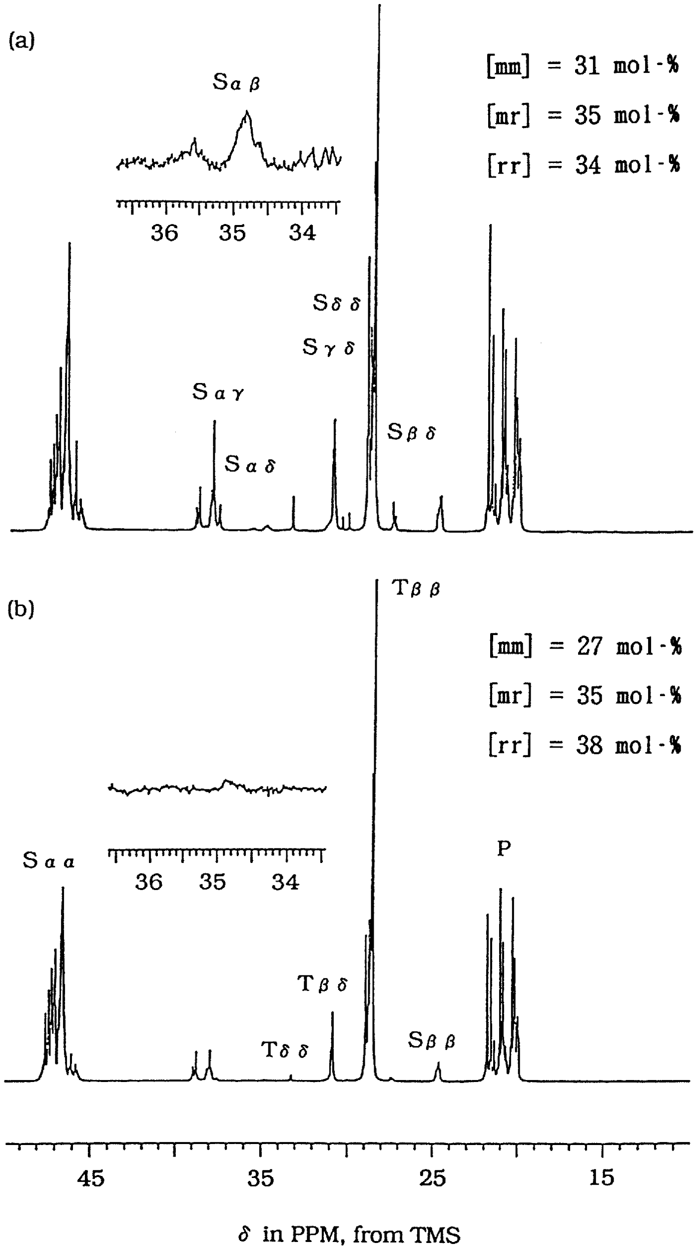
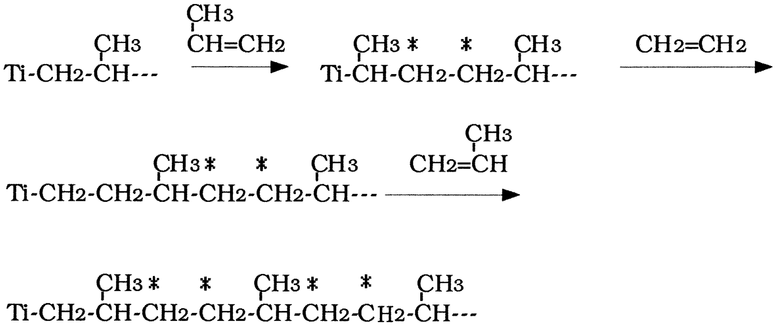


Fig. 1. ^{13}C NMR spectra of diethylether-soluble copolymers obtained with and without ADMB : (a) sample 2, (b) sample 4 in Tab.1. I(S$\alpha\beta$)/I(T$\beta\beta$): 0,027 in (a), 0,0031 in (b)

It should be noted here that such resonances due to the irregular bonding were hardly observed in ^{13}C NMR spectra of the ether-insoluble samples. The aspecific sites were, therefore, said to be different from the stereospecific ones not only in the stereospecificity but also in the regiospecificity. The relative intensity of S α β and T β β carbons : I(S α β)/I(T β β) in Fig. 1-a is 8,7 times higher than that in Fig. 1-b, suggesting that the aspecific sites in the ADMB-containing system are much more regiospecific than those in ADMB-free one.



It is well known that the 2,1-insertion of propene proceeds even in the highly active mgCl$_2$-supported Ti catalysts. Recently, some authors have claimed, on the basis of the results obtained with this type of catalysts, that the 2,1-insertion of propene might slow down the rate of chain propagation in propene polymerization(9). Taking their suggestion into consideration, the results described above implies that the ADMB addition might accelerate the propene polymerization at the aspecific sites formed.

The GPC/FT-IR chromatograms of the ether-soluble portions in sample 2 and 4 are illustrated in Fig. 2, where the number-average molecular weight($\overline{M}n$) and the ratio of weight- to number-average molecular weight $\overline{M}w/\overline{M}n$) determined by GPC are also depicted. The broader molecular weight distribution ($\overline{M}w/\overline{M}n$) of the fractions indicates that there are several kinds of aspecific sites which gives the stereoirregular polymers having different chain lengths. It is obvious from Fig.2 that the addition of ADMB brought about a drastic increase in $\overline{M}n$ as well as a significant decrease in $\overline{M}w/\overline{M}n$ in the ether-soluble fraction. Such changes in both $\overline{M}n$ and $\overline{M}w/\overline{M}n$ by the ADMB addition resulted in a drastic reduction in the lower molecular weight polymers, i.e., the weight fraction of polymers less than 10^4 in molecular weight in Fig.2-b were clearly lower than that in Fig.2-a. The ADMB-containing catalytic system might, therefore, be very effective for the production of copolymers having less content of sticky by-products. The comonomer distribution of the fraction , on the other hand, hardly affected by the ADMB addition under the present copolymerization conditions.

In conclusion, it was found that ADMB as an external donor caused a decrease in ethylene content of the propene-ethylene copolymers formed not only on the stereospecific sites but also on the aspecific ones in the $TiCl_4$/DBP/$MgCl_2$ catalyst activated by Al(i-C_4H_9)$_3$. Furthermore, it was clarified from the detailed analysis of the copolymers fractionated with boiling diethylether that the ADMB-containing system gives ether-soluble polymers with higher molecular eight and narrower molecular weight distribution as well as less content of

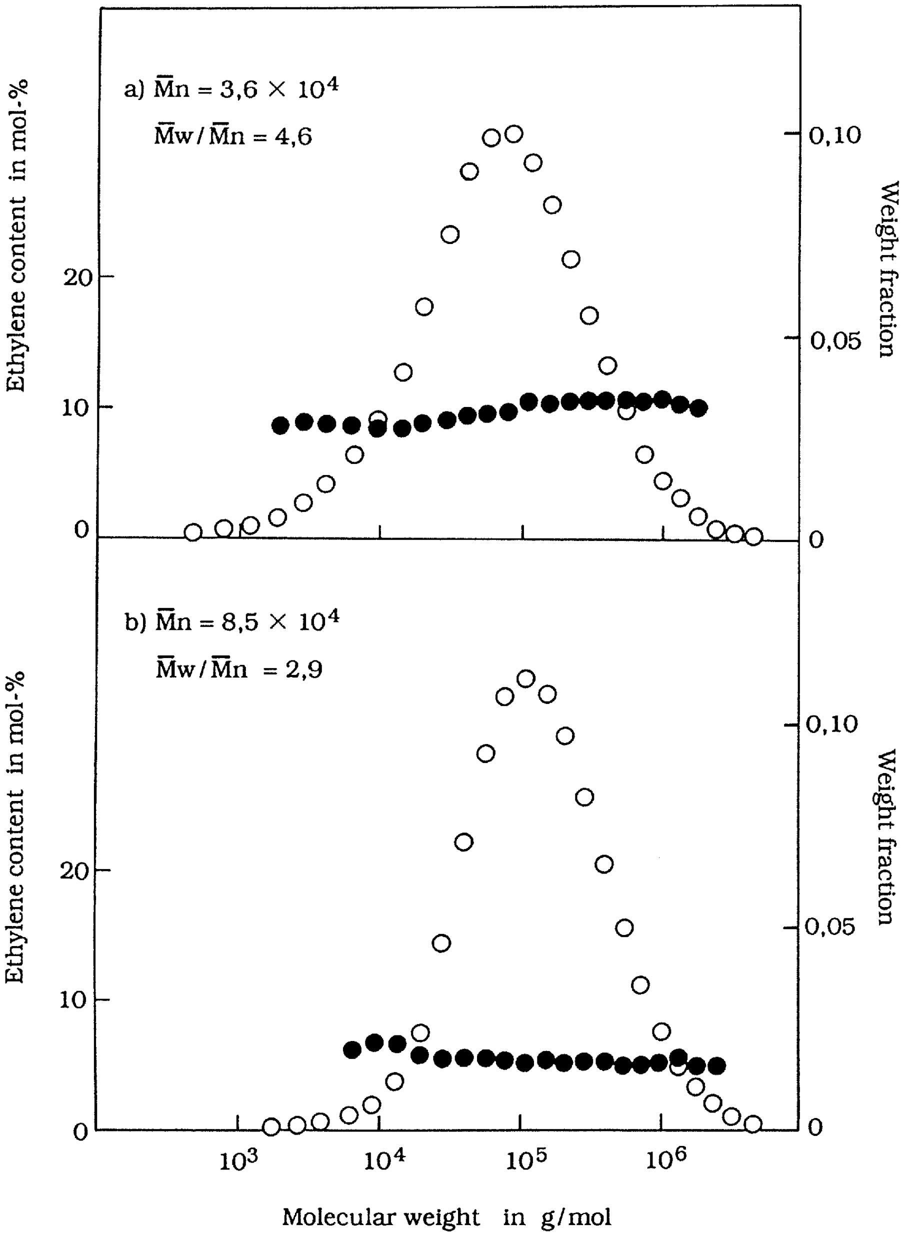


Fig. 2. GPC/FT-IR chromatograms of the ether-soluble copolymers: (a) sample 2, (b) sample 4 in Tab.1. ● and ○ represents the ethylene content and the weight fraction of polymers, respectively.

regioirregular sequences of propene. Such changes in the microstructures implies that ADMB might affect the copopymerization mechanism on the aspecific sites formed. A further study is, however, necessary to discuss a more detailed mechanism of the copolymerization. A more precise study is , therefore, being carried out with the present catalyst by changing the monomer feed ratio and the results will be reported in another paper.

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