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Description	

**Effects of Molecular Dispersion State of Surface Ti Species on
Ethylene-Propylene Copolymerization with TiCl₃-based Ziegler-Natta
Model Catalyst**

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Running Head; Ti Dispersion State on Ethylene-Propylene Copolymerization

Abstract

The dispersion state of surface Ti species is one of the most important factors for polymerization properties of MgCl₂-supported heterogeneous Ziegler-Natta catalysts. In this paper, ethylene-propylene copolymerization was conducted using a novel Ziegler-Natta model catalyst having “isolated” and “clustered” TiCl₃ molecules on MgCl₂. At a lower ethylene/propylene feed ratio, the dispersion state of the Ti species was found to strongly affect both the composition and sequence distribution of copolymers. The “isolated” Ti species gave a relatively random copolymer and clustering of Ti species obviously enhanced the blockiness. The addition of an external donor basically deteriorated the random copolymerization character of the “isolated Ti species, but the degree of the deterioration depended on the kind of donors. On the contrary, the balance between the monomer feed and consumption dominated the copolymerization performance at a higher ethylene/propylene feed ratio to obscure the effects of the dispersion state.

Introduction

Ethylene-propylene copolymers (EPCs) have a variety of unique characteristics that are not present in ethylene or propylene homopolymers, in terms of molding processability, transparency, elasticity, impact resistance, and etc. Industrially important EPCs are the random copolymer produced by propylene polymerization in the presence of a small amount of ethylene and the impact copolymer made by sequential copolymerization process. These random and impact copolymers with isotactic sequences of propylene units belong to polypropylene grades and have been dominantly synthesized with MgCl_2 -supported Ziegler-Natta (ZN) catalysts for several decades. Thanks to the industrial significance and long history of the ethylene-propylene copolymerization with ZN catalysts, several problems were identified and have been empirically improved, such as block-wise insertion of monomers and non-uniform chemical composition of produced copolymers attributed to the multiple active site nature of ZN catalysts.^{1,2} However, a rational catalyst design for the improvement of the copolymerization performance have been disturbed owing to the poor understanding of the most fundamental one-to-one relationship between active sites and copolymer structures. The main difficulty is that Ti species as active sites or their precursors are remarkably heterogeneous in terms of their dispersion states, valency, and interaction with the other components such as MgCl_2 , donors and alkylaluminum.³ Alkylaluminum as an activator of the supported TiCl_4 precursor reduces Ti^{4+} to Ti^{3+} and Ti^{2+} , which induces clustering of Ti species as well as extracts donors from MgCl_2 .^{4,5} These heterogeneities have prevented the direct characterization of the active sites or their precursors, systematic alternation of the states of

the active sites, and consequently correlating the active site structures with the produced copolymer structures.

The usage of model ZN catalysts having a reduced heterogeneity of the active sites is one of the most promising approaches for establishing the said one-to-one relationship. Recently, a $\text{TiCl}_3/\text{MgCl}_2$ model catalyst synthesized from a $\text{TiCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$ (Py) complex precursor was found to be highly useful for studying effects of the dispersion states of Ti species on the polymerization performance.⁶ With the $\text{TiCl}_3/\text{MgCl}_2$ model catalyst, we have already reported large impacts of the dispersion state of the Ti species on the propylene polymerization activity, produced polypropylene structures, efficiency of the donors' addition for the stereospecificity improvement, and H_2 response.^{6,7} Briefly, the dispersion state is precisely controllable by means of the Ti content, namely the amount of the introduced $\text{TiCl}_3 \cdot 3\text{Py}$ precursor in the synthesis, and moreover the originally designed dispersion state of TiCl_3 strongly bound on MgCl_2 is likely unchanged during the polymerization. Using this model catalyst, propylene polymerization was precisely examined with varying the Ti content, *i.e.* the dispersion state of Ti species. Below 0.1 wt.-% of the Ti content, all the propylene polymerization properties such as the catalyst activity, as well as stereoregularity, molecular weight and its distribution of polypropylene became constant, indicating the dominance of isolated Ti species free from an interaction with other Ti species. The isolated Ti species was the most active but poorly isospecific, giving short chains. On the other hand, the propylene polymerization properties depended on the Ti content above 0.1 wt.-%, due to the formation of clustered Ti species. The activity monotonically decreased, and the stereoregularity and molecular weight of

polypropylene also monotonically increased for the Ti content.

In this study, the novel $\text{TiCl}_3/\text{MgCl}_2$ model catalyst was extended to ethylene-propylene copolymerization in order to elucidate the impact of the Ti dispersion state on the copolymerization performance. It was found that the dispersion state of the Ti species was crucial for a lower ethylene/propylene feed ratio, significantly affecting the copolymer composition and blockiness. Clustering the Ti species lowered the randomness of the insertion. The addition of an external donor also deteriorated the randomness but the deterioration degree depended on the kind of donors.

Experimental Part

Materials. Propylene, ethylene and nitrogen of research grade were used without further purification. Heptane was used after passing through the molecular sieve 4A.

Ethylbenzoate (EB) and cyclohexylmethyldimethoxysilane (CMDMS) were purified by distillation. Anhydrous MgCl_2 with a specific surface area of $65.1 \text{ m}^2 \cdot \text{g}^{-1}$, T-Ti Cl_3 (both donated by Toho Titanium Co.), diethylaluminumchloride (DEAC) and triethylaluminum (TEA, both donated by Tosoh Finechem Co.) were used as delivered.

Preparation of $\text{TiCl}_3/\text{MgCl}_2$ model catalysts. The MgCl_2 -supported TiCl_3 model catalyst was prepared according to the previously reported procedure.⁸ MgCl_2 of 8 g and a specified amount of $\text{TiCl}_3 \cdot 3\text{Py}$ were added in a 300 ml glass flask under N_2 and stirred in

heptane for a few minutes. Then, DEAC (Al/Ti = 78) was added to the slurry and reacted for 3 h at room temperature. Thus obtained model catalysts were adequately washed with heptane. The reaction between DEAC and $\text{TiCl}_3 \cdot 3\text{Py}$ caused an almost complete removal of Py from the powders and immobilization of TiCl_3 species on MgCl_2 at a molecular level.⁹ The quantity of the residual DEAC hardly affected the structure of polypropylenes.¹⁰ To clarify the relationship between the dispersion state of the Ti species and the ethylene-propylene copolymerization performance, two catalysts were synthesized with 0.08 and 0.9 wt.-% of the Ti content, and denoted as Cat-A and Cat-B, respectively. Isolated Ti species was dominant for Cat-A, while clustering of the Ti species was sufficiently progressed for Cat-B. Cat-A and Cat-B were sometimes expressed as the isolated and clustered Ti species in what follows.

Slurry Polymerization. Heptane and TEA ($12.5 \text{ mmol} \cdot \text{L}^{-1}$) were introduced into a 300 ml glass reactor equipped with a magnetic stirrer under nitrogen. Monomers were continuously flown for 30 min at 1 atm, controlling the ethylene/propylene feed ratio with mass flow controllers (KOFLOC Model-3200). The ethylene/propylene feed ratio was set to 0/100, 20/80, 50/50, 80/20, and 100/0 vol%/vol% to obtain an entire picture of copolymerization with the model catalysts. The total feed volume was always kept at $800 \text{ cm}^3/\text{min}$. Then, a specified amount of the $\text{TiCl}_3/\text{MgCl}_2$ model catalyst ($[\text{Ti}] = 1.39 \times 10^{-2}$, 2.78×10^{-2} , $6.94 \times 10^{-2} \text{ mmol} \cdot \text{L}^{-1}$) was added to start the polymerization. The polymerization was conducted under a continuous monomer flow condition at 30°C for 5 min to minimize the reduction of Ti^{3+} to Ti^{2+} , which would produce homopolyethylene.¹¹

Actually there was no evidence to indicate the production of homopolyethylene (except 100/0 vol%/vol% of the feed ratio) in DSC and ^{13}C NMR of the obtained copolymers. The polymerization was terminated by adding acidic alcohol. The produced copolymers were dried *in vacuo* for 6 h, and reprecipitated with xylene/cold acetone. To examine the effects of a donor, EB ($1.25 \text{ mmol}\cdot\text{L}^{-1}$) or CMDMS ($1.25 \text{ mmol}\cdot\text{L}^{-1}$) was added as an external donor before the injection of the catalyst.

Polymer Characterization. The chemical composition of the produced copolymers was determined by ^{13}C NMR (Varian Gemini-300 spectrometer) at 120°C using hexachloro-1,3-butadiene as a diluent and 1,1,2,2-tetrachloroethane- d_2 added as an internal lock and reference. From ^{13}C NMR, the monomer reactivity ratio, r_E and r_P respectively for ethylene and propylene, and $r_E \times r_P$ were evaluated. The value of $r_E \times r_P$ becomes 0 for alternating copolymers, 1 for random copolymers, and approaches to ∞ for real block copolymers.

Results and Discussion

Table 1 shows propylene and ethylene homopolymerization activities using the $\text{TiCl}_3/\text{MgCl}_2$ model catalysts with the isolated and clustered Ti species (Cat-A and Cat-B, respectively). The ethylene homopolymerization activities are always much higher than the propylene homopolymerization activities. Moreover, Cat-B is much less active than Cat-A, which is consistent with our previous results for propylene homopolymerization and

attributed to a lower active site concentration for the clustered Ti species. The ratio of the ethylene/propylene homopolymerization activities was 3.9 for Cat-A, and 9.7 for Cat-B, indicating that the clustered Ti species prefer ethylene polymerization more than the isolated Ti species.

The effect of the Ti concentration in the polymerization slurry was examined on propylene and ethylene copolymerization activities of Cat-A, to investigate the balance between the monomer feed and consumption (Figure 1). For all the Ti concentrations examined, the copolymerization activities were always much higher than the homopolymerization activities: the copolymerization activities were above the line connecting the two homopolymerization activities. These phenomena are well known as the activation effect in copolymerization, where two kinds of monomers synergistically enhance the activity, and have widely observed for copolymerization both of ethylene with α -olefins and of propylene with higher α -olefins, being irrespective of employed catalysts (ZN or metallocene catalysts).¹²⁻²² Though it has not been completely clarified yet, various mechanisms for the activation effect have been proposed; i) decrease of crystallinity of formed copolymers due to the incorporation of comonomer to accelerate the diffusion of monomers or alkylaluminum,^{12,13} ii) reactivation of dormant sites by comonomer,¹⁴⁻¹⁶ iii) increase of the active site concentration in copolymerization with the assumption that active sites for ethylene and propylene polymerization might not be identical and that both the active sites work for copolymerization,^{17,18,19} iv) acceleration of catalyst particles disintegration during copolymerization,¹⁸ and so on. Considering that Cat-A gave poorly crystalline polypropylene ($X_c \sim 8$ wt.-%), the mechanism i) was not

likely relevant to the observed activation. The homopolymerization activities hardly depended on the Ti concentration, indicating that the amount of the monomer consumption was negligible compared with that of the monomer feed. On the contrary, the copolymerization activities increased for a lower Ti concentration, suggesting that the monomer feed was more or less insufficient for the copolymerization due to the large activation effect. Copolymerization at a higher ethylene/propylene feed ratio especially suffered from the insufficient monomer feed, showing a greater sensitivity of the copolymerization activity on the Ti concentration. The precise examination for the monomer consumption and feed balance is reported in another paper.²³

The copolymerization activities of Cat-A and Cat-B were shown in Figure 2 in the absence or presence of EB as an external donor, where the Ti concentration was fixed at $2.78 \times 10^{-2} \text{ mmol}\cdot\text{L}^{-1}$. Similar activation phenomena were always observed for all the results. The activation degree from the homopolymerization was slightly higher for the isolated Ti species. EB marginally decreased the activation degree in spite of a large enhancement of the isospecificity (45 mol% increase of *mmmm* in propylene homopolymerization), again suggesting that the crystallinity was not important for the comonomer activation.

The compositions of the obtained copolymers are plotted against the ethylene/propylene feed ratio in Figure 3. As these curves were convex upward, the ethylene reactivity is higher than the propylene reactivity at all the conditions. The reactivity for ethylene was higher for Cat-B than for Cat-A both in the absence and in the presence of EB. The addition of EB hardly changed the copolymer compositions in spite of improved

isospecificity of the catalysts. Soga et al. have compared ethylene-propylene copolymerization performance of mostly aspecific and mostly isospecific catalysts and concluded that the copolymer composition was independent of the catalyst isospecificity,²⁴ similarly to our results.

The results of the sequence distribution analysis are summarized in Table 2 for 20/80 vol%/vol% of the feed ratio. Increasing the Ti concentration, the ethylene content of the produced copolymers tends to be higher both in the absence and presence of an external donor, suggesting that the feed of ethylene was insufficient compared with the consumption. However, the variation of the ethylene content is within a few mol% in the examined range of the Ti concentration, and thus it is believed that the balance between the feed and consumption hardly affected the copolymer composition at 20/80 vol%/vol%. The copolymers produced with the clustered Ti species contain ethylene 10 mol% more than those with the isolated Ti species, and exhibited a much higher blockiness ($r_E \times r_P$). The increase of the blockiness by clustering of the Ti species was attributed to the increase of the EE sequence, *i.e.* r_E , in line with the fact obtained in Table 1 that the clustered Ti species prefer ethylene polymerization. It is suggested that the blockiness of EPCs produced with ZN catalysts be owing to the formation of clustered Ti species during polymerization. The addition of EB tends to increase the ethylene content, r_E , and $r_E \times r_P$ for both Cat-A and Cat-B. CMDMS also increases these values, but the extent is much larger than EB. Thus, the increase of the blockiness was dependent on the kind of external donors.

Similar results are presented in Table 3 for 80/20 vol%/vol% of the feed ratio. Again,

lowering the Ti concentration partly mediated the insufficiency of the ethylene feed to raise the ethylene content of the copolymers. However, the effects of the Ti concentration on the copolymer composition were far greater for 80/20 vol%/vol% than for 20/80 vol%/vol%. In other words, the copolymerization at a higher ethylene/propylene feed ratio is more susceptible to the balance of the monomer consumption and feed, making it very difficult to extract the effects of the Ti dispersion state on the copolymer composition (the influences of the Ti concentration dominated those of the Ti dispersion state). On the contrary, the effects of the Ti dispersion state on the composition and blockiness of copolymers were successfully extracted at a lower ethylene/propylene feed ratio.

Conclusion

The impact of the dispersion state of Ti species was firstly examined for ethylene-propylene copolymerization using a $\text{TiCl}_3/\text{MgCl}_2$ model catalyst over a wide range of ethylene/propylene feed ratio. Both of the homo and copolymerization activities of “isolated” Ti species were much higher than those of the “clustered” Ti species. The activation phenomena in copolymerization were observed over a full range of the ethylene/propylene feed ratio, irrespective of the Ti dispersion state and catalyst isospecificity. It was suggested that the crystallinity of the polymers are not relevant for the activation. Clustering of the Ti species tended to increase the ethylene content and blockiness of copolymers at a lower ethylene/propylene feed ratio. The “isolated” Ti species gave a relatively random copolymer. The addition of CMDMS as an external

donor significantly enlarged the ethylene content and blockiness compared with EB, suggesting that the copolymerization performance is dependent on the kind of donors rather than the catalyst isospecificity. At a higher ethylene/propylene feed ratio, the consumption of ethylene largely exceeded the feed, dominating the copolymerization performance. Finally, the control of the dispersion state of the Ti species is proposed as meaningful for the development of industrial ZN catalysts for copolymerization.

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Figure Captions

Figure 1. Copolymerization activities of Cat-A. Cat-A is a $\text{TiCl}_3/\text{MgCl}_2$ model catalyst with the Ti content of 0.08 wt.-%, where most of the Ti species are isolated. The Ti concentration in the polymerization slurry was varied: (\diamond) 1.39×10^{-2} , (\circ) 2.78×10^{-2} , (\square) $6.94 \times 10^{-2} \text{ mmol}\cdot\text{L}^{-1}$. The copolymerization was conducted at 30°C under 1 atm for 5 min in heptane with TEA ($12.5 \text{ mmol}\cdot\text{L}^{-1}$).

Figure 2. Copolymerization activities of Cat-A having isolated Ti species (\circ) in the presence or (\bullet) in the absence of EB. Those of Cat-B having clustered Ti species (\square) in the presence or (\blacksquare) in the absence of EB. The copolymerization was conducted at 30°C under 1 atm for 5 min in heptane. $[\text{Ti}] = 2.78 \times 10^{-2} \text{ mmol}\cdot\text{L}^{-1}$, $[\text{Al}] (\text{TEA}) = 12.5 \text{ mmol}\cdot\text{L}^{-1}$ and $[\text{Donor}] (\text{EB}) = 1.25 \text{ mmol}\cdot\text{L}^{-1}$ in heptane.

Figure 3. Copolymer composition curves (\circ) without EB and (\bullet) with EB for Cat-A. Those (\square) without EB and (\blacksquare) with EB for Cat-B. The copolymers were obtained in the same condition with that in Figure 2.

Table 1. Propylene and ethylene homopolymerization activities^a

Cat. ^b	Donor ^c	Activity x 10 ⁻³ (kg-polymer·mol-Ti ⁻¹ ·h ⁻¹ ·[M] ⁻¹)	
		Propylene	Ethylene
A	n/a	9.6	37
A	EB	3.4	34
B	n/a	0.65	6.3
B	EB	0.36	5.0

^aPropylene and ethylene homopolymerization were conducted at 30°C under 1 atm for 5 min. [Ti] = 2.78 x 10⁻² mmol·L⁻¹ and [Al] (TEA) = 12.5 mmol·L⁻¹ in heptane.

^bCat-A: a TiCl₃/MgCl₂ model catalyst with the Ti content of 0.08 wt.-%, where most of the Ti species are isolated. Cat-B: a TiCl₃/MgCl₂ model catalyst with the Ti content of 0.9 wt.-%, where most of the Ti species are clustered.

^c[Donor] (EB) = 1.25 mmol·L⁻¹.

Table 2. ^{13}C NMR analysis of obtained copolymers at the ethylene/propylene feed ratio of 20/80 vol%/vol%

Cat.	Ti concentration ^a (mmol·L ⁻¹)	Donor	Ethylene content (mol%)	r_E^b	r_P^b	$r_E \times r_P$
A	1.39×10^{-2}	n/a	18	8.4	0.21	1.8
A	1.39×10^{-2}	EB	20	11	0.21	2.4
A	1.39×10^{-2}	CMDMS	28	28	0.20	5.6
A	2.78×10^{-2}	n/a	16	6.8	0.23	1.6
A	2.78×10^{-2}	EB	17	9.5	0.30	2.4
B	2.78×10^{-2}	n/a	28	18	0.15	2.7
B	2.78×10^{-2}	EB	34	25	0.12	3.0

^aThe Ti concentration in the polymerization slurry.

^bThe monomer reactivity ratio, r_E and r_P respectively for ethylene and propylene. $r_E = 2EE \cdot EP^{-1} \cdot X^{-1}$ and $r_P = 2PP \cdot EP^{-1} \cdot X^{-1}$, where X is the molar ratio of ethylene/propylene in solvent.

Table 3. ^{13}C NMR analysis of obtained copolymers at the ethylene/propylene feed ratio of 80/20 vol%/vol%

Cat.	Ti concentration ($\text{mmol}\cdot\text{L}^{-1}$)	Donor	Ethylene content (mol%)	r_E	r_P	$r_E \times r_P$
A	1.39×10^{-2}	n/a	80	6.3	0.18	1.2
A	1.39×10^{-2}	EB	84	8.8	0.23	2.1
A	2.78×10^{-2}	n/a	75	5.9	0.40	2.4
A	2.78×10^{-2}	EB	79	6.5	0.26	1.7
B	2.78×10^{-2}	n/a	89	13	0.15	1.9
B	2.78×10^{-2}	EB	92	19	0.12	2.2

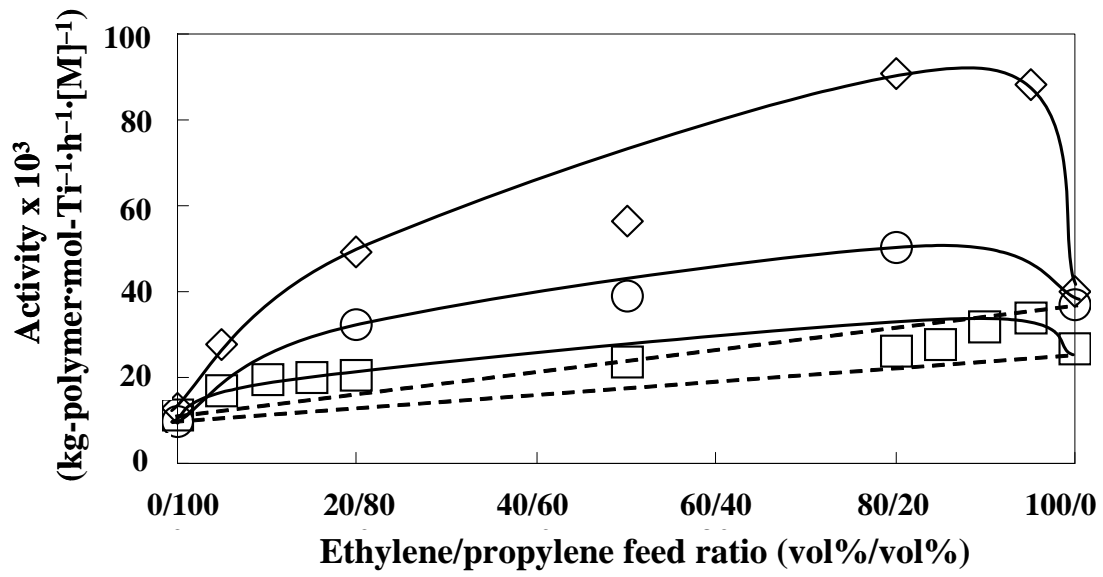


Figure 1. Taniike et al.

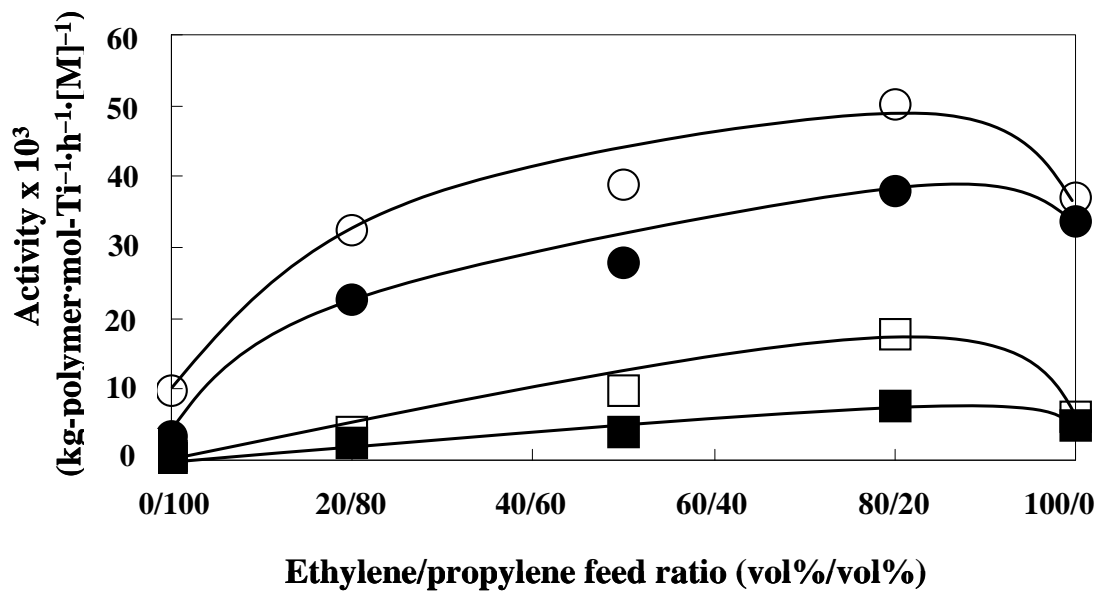


Figure 2. Taniike et al.

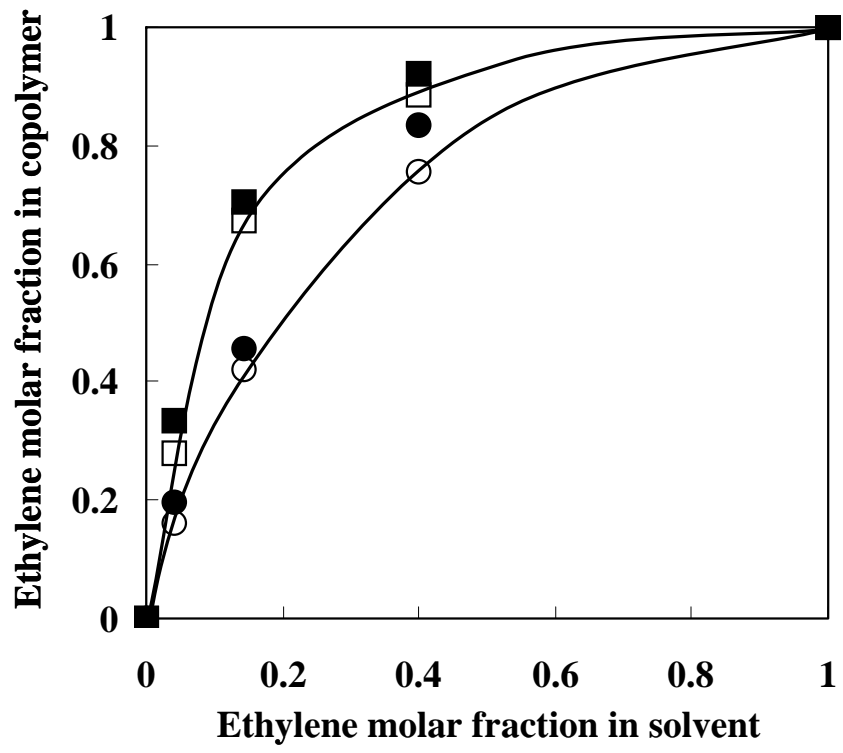


Figure 3. Taniike et al.

Table of Content

Effects of Molecular Dispersion State of Surface Ti Species on Ethylene-Propylene Copolymerization with TiCl₃-based Ziegler-Natta Model Catalyst

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Ethylene-propylene copolymerization was carried out using TiCl₃/MgCl₂ model catalysts. The dispersion state of the Ti species on MgCl₂ was found to be significant for the copolymer blockiness and composition.

