

Propene Polymerization with MgCl₂-Supported TiCl₄/Dioctylphthalate Catalyst. III. Effects of Polymerization Conditions on Molecular Weights and Molecular Weight Distribution

CHUN B. YANG and CHENG C. HSU*

Department of Chemical Engineering, Queen's University, Kingston, Ontario K7L 3N6, Canada

SYNOPSIS

In propene polymerization over the MgCl₂-supported TiCl₄/dioctylphthalate (DOP) catalyst, the weight- and number-average molecular weights and the molecular weight distribution (MWD) of polypropene products and of the isotactic and atactic polymer portions were studied. The average molecular weights and MWD were found to be independent of time. The isotactic polymer had higher molecular weight and broader distribution than the atactic portion by almost an order of magnitude. An increase in temperature and cocatalyst/catalyst ratio resulted in lowering molecular weight due to increasing transfer reaction. Alkyl aluminum was used as a cocatalyst, and the molecular weight did not vary significantly with different alkyl groups. Of the three external bases studied, 2,2,6,6-tetramethyl piperidine (TMPiP), dimethoxydiphenyl silane (DMDPS), and *t*-butylmethyl ether (TBME), the addition of a small amount of one of the first two bases caused a substantial increase in both molecular weight and polydispersity of the isotactic polymer. Those increases leveled off quickly with increasing amounts of the external base. On the other hand, both average molecular weights and polydispersity of the atactic polymer decreased with a net increase in the molecular weight of the whole polymer. TBME, however, has no significant effect on either molecular weight or MWD. These effects are discussed in the context of the roles of the external base in propene polymerization. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In the first two parts of this series, we studied the catalytic behavior of the MgCl₂-supported TiCl₄/dioctylphthalate (DOP) catalyst system for the slurry polymerization of propene and the effects of polymerization conditions, particularly the use of different external Lewis bases, on the microstructure of isotactic polymers separated by heptane extraction from polymer products. In this part we examine the effects of polymerization conditions on average molecular weights and molecular weight distribution (MWD).

MWD is one of the most important polymer characteristics that determines the polymer prop-

erties, which ultimately govern the applications of the polymer products. Thus, understanding the factors that regulate molecular weight and MWD in the polymerization process is of paramount importance from industrial as well as academic points of view. Publications on this subject are rather scarce.^{1,2}

One of the academic interests in the MWD of polymers is its close relationship with the polymerization mechanism, particularly the nature of termination, chain transfer, and catalyst deactivation reactions, and the heterogeneity of polymerization sites. It is generally agreed that the broad distribution of molecular weights of polymers obtained from heterogeneous Ziegler-Natta catalysts is due to the existence of multiple sites and to the activity distribution of those sites.

In this study, average molecular weights and MWD of the whole polymer as well as those of isotactic and atactic portions of the polymer were

* To whom all correspondence should be addressed.

Table I Effect of Polymerization Time on Molecular Weights of Polymers

Polymerization Time (min)	Whole Polymer			Isotactic Part ^a			Atactic Part		
	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n
5	3.24	2.17	6.7	4.60	2.21	4.8	0.62	0.24	3.9
10	2.72	1.93	7.1	4.51	1.89	4.2	0.97	0.36	3.7
20	2.91	2.06	7.1	4.70	2.16	4.6	0.90	0.39	4.3
40	3.65	2.70	7.4	5.92	3.07	5.2	0.88	0.35	3.9
60	3.31	2.55	7.7	5.02	2.90	5.7	0.81	0.24	2.9

Polymerization conditions: Catalyst A; [Ti] = 0.12 mmol/L; TEA/Ti = 50; polymerization temperature = 50°C; propene partial pressure = 118 kpa; volume of heptane = 0.2 L.

^a The whole polymer was separated into isotactic and atactic parts by extracting it with boiling heptane.

investigated under different polymerization conditions: polymerization temperature, types of cocatalyst, cocatalyst/catalyst ratios, and external base/catalyst ratios of three different types of bases.

EXPERIMENTAL

Polymerization

Catalysts A, B, and C were synthesized at 80, 95, and 105°C, respectively, as described in part I of this publication.³ The slurry polymerization of propene was also described in part I. The polypropenes obtained were separated into isotactic and atactic polymers by extraction with boiling heptane.

Molecular Weight Determination

High temperature gel permeation chromatography (GPC) was used to determine MWDs of the polypropene samples, from which the number-average (M_n) and weight-average (M_w) molecular weights were calculated. GPC was performed with a Waters 150C (Mississauga, Ontario), equipped with five styrene/divinylbenzene gel columns of 10^4 , 10^5 , 10^6 , 10^7 , and 10^8 Å pore sizes (Shodex GPC AT 803-71s, Waters).

Polypropene is very difficult to dissolve and is thermally sensitive.⁴ An initial attempt to dissolve polypropene in 1,2,4-trichlorobenzene (TCB) at about 145°C for 35 h with 0.1 wt % antioxidant ([tetrakis(methylene 3,5-di-*tert*-butyl-4-hydroxy hydro cinnamate)] methane) (Irganox 1010, Ciba-Geigy, Mississauga, Ontario) to obtain an aggregate-free solution somehow resulted in a discoloration of the solution. Instead, GPC samples were prepared by dissolving polypropene in prefiltered TCB to

make up 0.05 wt/vol % at 145°C for at least 5 h. GPC operating conditions were as follows:

Elution solvent:	TCB
Flow rate:	1.0 mL/min
Injection volume:	200 μ L
Column temperature:	145°C
Sensitivity:	64
Scale factor:	20

The GPC was calibrated against three polydispersed polypropene standards using the Purdon and Mate method.⁵ The standards with nominal molecular weights 5×10^4 , 20×10^4 , and 35×10^4 were obtained from Polyscience, Inc. (Warrington, PA). The reproducibility of the M_n s and M_w s was estimated by replications to be $\pm 8.7\%$ and $\pm 4.5\%$ standard deviations, respectively.

RESULTS AND DISCUSSION

Variation of Average Molecular Weights and MWD with Polymerization Time

M_n , M_w , and MWD were determined for the isotactic and atactic polymers which were separated by heptane extraction, and for the whole polymer. Polymer samples were collected at the end of various time intervals from a semibatch reactor at 50°C, where monomer was fed continuously to maintain a constant monomer concentration.

The molecular weight data clearly indicate that the M_n and M_w of the atactic polymer are lower than those of the isotactic polymer by almost an order of magnitude, as can be seen in Table I. This difference can be attributed to the difference in activities of the two types of polymerization sites. It should also be noted that atactic sites yield polymers with nar-

Table II Effect of Cocatalyst Type on Molecular Weights of Polymers

Cocatalyst ^a	Whole Polymer			Isotactic Part ^b			Atactic Part		
	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n
Catalyst A									
TEA	3.31	2.55	7.7	5.02	2.90	5.8	0.81	0.24	2.9
TIBA	3.48	2.58	7.4	5.75	3.05	5.3	0.89	0.37	4.2
THA	3.71	2.52	6.8	5.87	2.76	4.7	1.25	0.45	3.6
TOA	3.80	2.43	6.4	6.12	2.57	4.2	1.37	0.48	3.5
Catalyst B									
TEA	2.78	1.91	6.9	4.62	1.54	4.0	0.91	0.28	3.1
TIBA	2.97	1.93	6.5	4.59	1.68	3.7	0.98	0.27	2.8
THA	2.85	1.85	6.5	5.15	1.83	3.6	1.04	0.50	4.8
TOA	3.12	1.93	6.2	5.95	2.01	3.4	1.40	0.64	4.5
IPRA	2.57	1.72	6.7	4.60	1.70	3.7	1.85	0.67	3.6
Catalyst C									
TEA	2.01	1.47	7.3	3.55	1.63	4.6	0.71	0.30	4.2
TIBA	2.75	1.90	6.9	4.90	1.81	3.7	1.11	0.48	4.3
THA	3.21	2.09	6.5	5.82	1.94	3.4	1.57	0.58	3.7
TOA	4.32	2.63	6.1	7.10	2.32	3.3	2.14	0.75	3.5
IPRA	2.67	1.54	5.8	5.40	1.82	3.4	1.43	0.37	2.6

Polymerization conditions were the same as in Table I, except polymerization time = 1 h.

^a TEA = triethylaluminum; TIBA = triisobutylaluminum; THA = tri-*n*-hexylaluminum; TOA = tri-*n*-octylaluminum; IPRA = isoprenylaluminum.

^b The whole polymer was separated into isotactic and atactic parts by extracting it with boiling heptane.

Table III Effect of Aluminumalkyl/Ti Ratio on Molecular Weights of Polymers

Al/Ti (Molar Ratio)	Whole Polymer			Isotactic Part ^a			Atactic Part		
	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n
TEA/Ti									
33.4	3.69	3.03	8.2	5.62	3.29	5.9	0.75	0.34	4.5
50.0	3.31	2.55	7.7	5.02	2.90	5.8	0.76	0.32	4.2
70.9	3.23	2.36	7.3	4.88	2.64	5.4	0.58	0.23	3.9
91.7	2.66	1.97	7.4	4.02	2.29	5.7	0.59	0.23	3.9
200.0	1.83	1.37	7.5	3.03	1.70	5.6	0.50	0.18	3.6
TIBA/Ti									
33.4	3.69	2.87	7.8	6.46	3.03	5.0			
50.0	2.71	2.00	7.4	5.75	3.05	5.3			
70.9	2.91	2.06	7.1	5.43	2.46	4.5			
91.7	2.57	1.82	7.1	5.15	2.15	4.2			
200.0	2.51	1.76	7.0	4.62	1.93	4.2			

Polymerization conditions were the same as in Table II, except with Catalyst A.

^a The whole polymer was separated into isotactic and atactic parts by extracting it with boiling heptane.

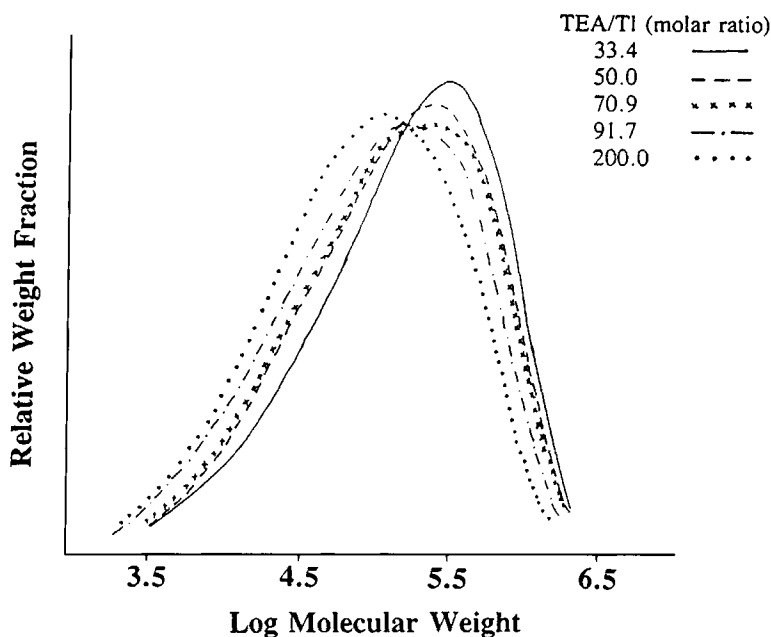


Figure 1 The effect of TEA/Ti ratio on the MWD of isotactic polypropene obtained with $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4$ -TEA catalyst. Polymerization conditions are indicated in Table III.

rower MWD. This is consistent with the hypothesis that the catalyst contains two different isotactic sites, one more isotactic than the other. The polydispersity of the whole polymer is about 7.0, which falls in the general range of 5–8 for heterogeneous Ziegler–Natta catalysts.

For a 1-h polymerization, M_n , M_w , and MWD remained practically unchanged. Similar findings were reported by Keii et al.¹ for MgCl_2 /ethylbenzoate (EB)/ TiCl_4 catalyst. Polydispersities of the whole and isotactic polymers seem to increase slightly toward the end of polymerization, but due to experimental error in molecular weight measure-

ments no definite conclusion can be drawn, even though a slight increase in polydispersity at long polymerization time, due to catalyst deactivation, is understandable.

Effects of the Type and Concentration of Cocatalyst on M_n , and M_w , and MWD

The three catalysts, A, B, and C, were prepared by reacting TiCl_4 at 80, 95, and 105°C, respectively, with MgCl_2 support, pretreated by cogrinding with DOP as the internal Lewis base. As previously communicated,^{6,7} the content of phthaloyl

Table IV Effect of Polymerization Temperature on Molecular Weights of Polymers

Temperature (°C)	Whole Polymer			Isotactic Part ^a			Atactic Part		
	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n
20	4.61	3.32	7.2	7.00	3.50	5.0	0.97	0.32	3.3
30	3.96	3.01	7.6	6.01	3.40	5.6	0.92	0.27	2.9
40	3.85	2.89	7.5	5.20	3.00	5.8	0.86	0.27	3.1
50	3.31	2.55	7.7	5.02	2.92	5.8	0.81	0.26	2.9
60	1.80	1.42	7.9	3.12	1.80	5.8	0.56	0.22	3.9
70	1.50	1.12	7.5	2.67	1.61	6.0	0.46	0.17	3.7

Polymerization conditions were the same as in Table III, except temperature.

^a The whole polymer was separated into isotactic and atactic parts by extracting it with boiling heptane.

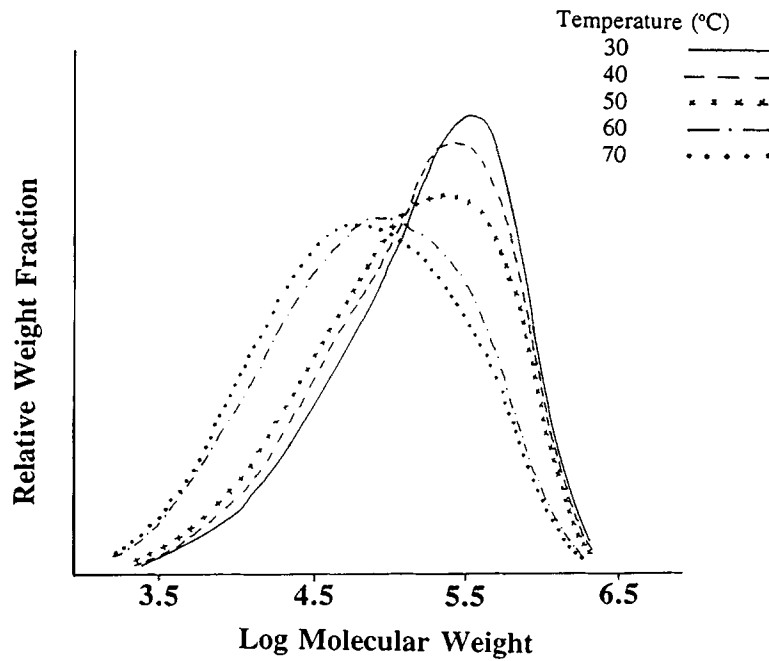


Figure 2 The effect of polymerization temperature on the MWD of isotactic polypropene obtained with $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4\text{-TEA}$ catalyst. Polymerization conditions are indicated in Table IV.

chloride (POC) (a reaction product of DOP and TiCl_4 which increases with reaction temperature from 0.16 mmol/g at 80°C to 0.27 mmol/g at 105°C) has a profound effect on catalyst activity

and stereospecificity. The level of POC could affect both the total number of active sites and how the active sites are distributed among different types. However, from Table II we can see that neither

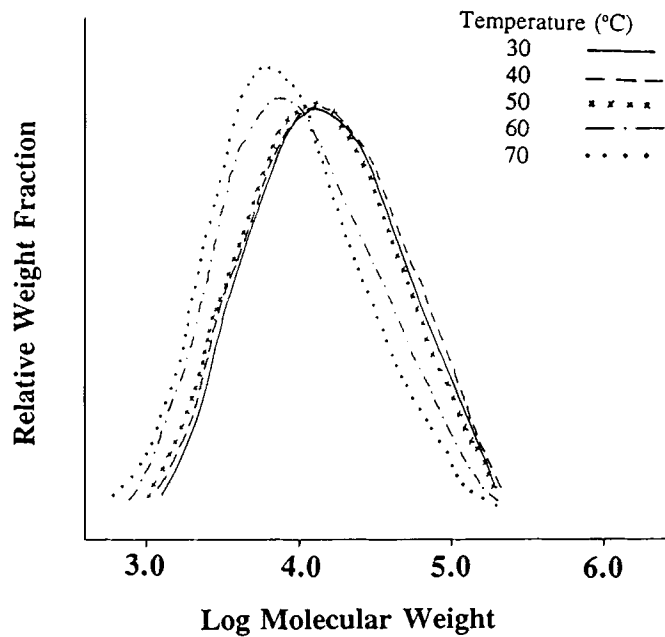


Figure 3 The effect of polymerization temperature on the MWD of atactic polypropene obtained with $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4\text{-TEA}$ catalyst. Polymerization conditions are indicated in Table IV.

Table V Effect of TMPIP/TEA Ratio on Molecular Weights of Polymers

TMPIP/TEA (Molar Ratio)	Whole Polymer			Isotactic Part ^a			Atactic Part		
	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n
0	2.01	1.47	7.3	3.55	1.63	4.6	0.71	0.30	4.1
0.013	3.53	2.51	7.1	4.51	2.72	6.0	0.62	0.18	2.9
0.025	3.14	2.45	7.8	4.53	2.77	5.0	0.59	0.19	3.2
0.038	3.35	2.58	7.7	4.50	2.61	5.9	0.57	0.17	3.0
0.05	3.66	2.74	7.5	5.11	3.07	6.0	0.60	0.16	2.7
0.2	3.92	2.90	7.4	5.67	3.28	5.8	0.61	0.16	2.6
0.4	3.75	2.86	7.6	5.60	3.25	5.8	0.57	0.17	2.9

Polymerization conditions were the same as in Table II, except with Catalyst C.

^a The whole polymer was separated into isotactic and atactic parts by extracting it with boiling heptane.

the molecular weight data of the whole polymer nor that of the isotactic and atactic polymers reflect such an effect.

Table II also shows the effects of cocatalysts on molecular weights. For both isotactic and atactic polymers, the molecular weights increased as the alkyl group in the cocatalyst changed from ethyl to octyl. This observation is in agreement with that of Lynch et al.⁸ for ethylene polymerization with a SiO₂/MgCl₂-supported TiCl₄ catalyst. The increase in M_w appeared to be less pronounced than that of M_n . Therefore, the polydispersities of the whole and isotactic polymers decreased with increasing bulkiness of the alkyl group in the cocatalyst.

The molecular weight data at different aluminum alkyl concentrations are given in Table III, whereas MWDs are plotted in Figure 1. As expected, both M_n s and M_w s of the isotactic and atactic polymers decreased with increasing alkyl concentration, resulting from chain transfer reaction with aluminum

alkyl. However, as compared to literature data, the exact nature of the chain transfer reaction seems to depend somewhat on the catalytic system. Keii et al.¹ found that for the MgCl₂/EB/TiCl₄ catalyst system, M_n and M_w of both isotactic and whole polymers decreased rapidly with increasing TEA concentrations between Al/Ti = 2.3 and 11.4; beyond Al/Ti = 22.8, the molecular weights only decreased slowly with increasing TEA concentrations. Chien and Kuo,² however, showed that for their CW catalyst (MgCl₂/EB/*p*-cresol/AlEt₃/TiCl₄ supported catalyst), between Al/Ti = 42 to 334, the TEA concentration essentially had no effect on M_n and M_w of either whole or isotactic polymer.

One possible explanation for a rapid reduction of molecular weight at low Al/Ti ratios and then a leveling off as Al/Ti reaches high values is the fact that active sites see only those alkyls adsorbed on the catalyst surface, which reaches a saturation point at high alkyl concentration.

Table VI Effect of DMDPS/TEA Ratio on Molecular Weights of Polymers

DMDPS/TEA (Molar Ratio)	Whole Polymer			Isotactic Part ^a			Atactic Part		
	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n
0	2.01	1.47	7.3	3.55	1.63	4.6	0.71	0.30	4.1
0.013	3.75	2.96	7.9	5.55	3.34	6.0	0.67	0.30	4.5
0.025	3.73	2.91	7.8	5.75	3.36	5.8	0.63	0.27	4.2
0.038	4.49	3.14	7.0	5.60	3.47	6.2	0.62	0.18	2.9
0.05	5.67	4.02	7.1	7.18	4.45	6.2	0.59	0.19	3.2
0.2	5.30	3.81	7.2	7.01	4.28	6.1	0.53	0.17	3.3
0.4	5.28	3.91	7.4	7.26	4.32	6.0	0.55	0.16	2.7

Polymerization conditions were the same as in Table II, except with Catalyst C.

^a The whole polymer was separated into isotactic and atactic parts by extracting it with boiling heptane.

Table VII Effect of TBME/TEA Ratio on Molecular Weights of Polymers

TBME/TEA (Molar Ratio)	Whole Polymer			Isotactic Part ^a			Atactic Part		
	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	M_w/M_n
0	2.01	1.47	7.3	3.55	1.63	4.6	0.71	0.30	4.1
0.029	1.82	1.38	7.6	3.70	1.58	4.6	0.82	0.37	4.5
0.043	1.52	1.17	7.7	3.65	1.58	4.3	0.89	0.43	4.8
0.05	1.87	1.36	7.2	3.90	1.79	4.6	0.87	0.34	3.9
0.057	1.91	1.51	7.9	4.17	1.75	4.2	0.96	0.41	4.3
0.72	1.81	1.34	7.4	4.04	1.93	4.8	0.76	0.34	4.4

Polymerization conditions were the same as in Table II, except with Catalyst C.

^a The whole polymer was separated into isotactic and atactic parts by extracting it with boiling heptane.

Within experimental error, no significant changes in MWD with alkyl concentration can be detected. Keii et al.,¹ however, reported a narrowing effect of MWD on the whole polymer at low concentrations of aluminum alkyl ($Al/Ti < 4.56$). No such low ratios of Al/Ti were used in our study. The narrowing effect at low Al/Ti ratios is understandable. As shown by Dusseault and Hsu⁹ in their model study, when the Al/Ti ratio was lowered, active sites became more and more uniform.

Effects of Polymerization Temperature on Molecular Weights and MWD

The dependence of molecular weights of isotactic and atactic polymers on polymerization temperature

is presented in Table IV. Their MWDs at different temperatures are plotted in Figures 2 and 3. At low temperatures, 20–50°C, the M_n and M_w of both isotactic and atactic polymers decreased slowly with increasing temperature, but the rate of decrease accelerated with increasing temperature. These results are in agreement with those from polypropenes obtained with unsupported catalysts.^{11,12}

The decrease of molecular weight with temperature can be attributed mainly to the increasing rate of the chain transfer reaction and to a lesser extent the deactivation of active sites. The higher activation energy of the termination reaction compared to that of the propagation reaction is the reason for the high rate of molecular weight reduction at high temperatures.

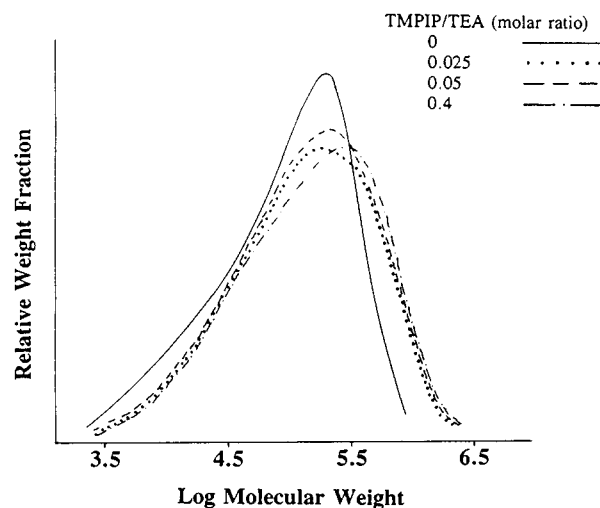


Figure 4 The effect of TMPIP/Ti ratio on the MWD of isotactic polypropene obtained with $MgCl_2/DOP/TiCl_4$ -TEA catalyst. Polymerization conditions are indicated in Table V.

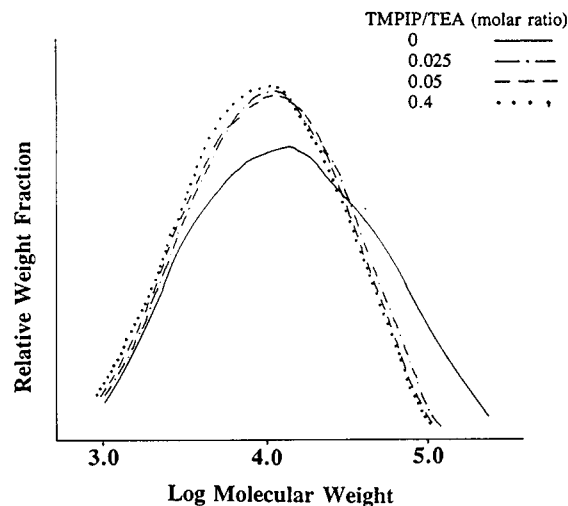


Figure 5 The effect of TMPIP/Ti ratio on the MWD of atactic polypropene obtained with $MgCl_2/DOP/TiCl_4$ -TEA catalyst. Polymerization conditions are indicated in Table V.

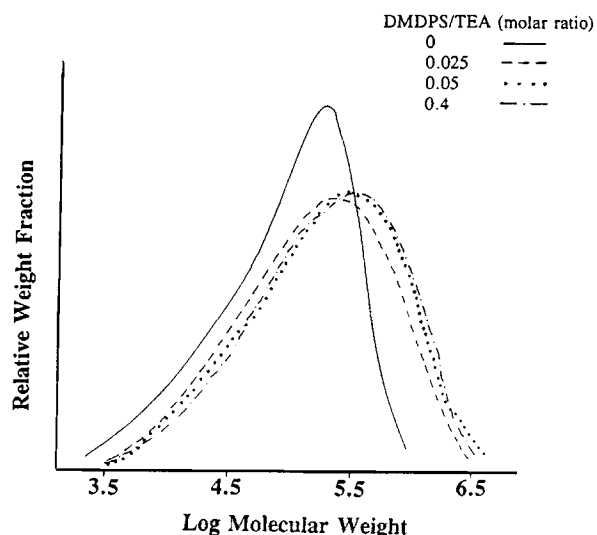


Figure 6 The effect of DMDPS/Ti ratio on the MWD of isotactic polypropene obtained with $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4\text{-TEA}$ catalyst. Polymerization conditions are indicated in Table VI.

The MWDs of both isotactic and atactic polymers, on the other hand, show (within experimental error) no noticeable changes with temperature. With unsupported catalysts, however, the MWD was usually found to become broader with decreasing temperature.¹⁰⁻¹³

Effects of External Bases on Molecular Weights and MWD

In our previous studies,^{3,13} we examined the effects of three different types of external bases on activity

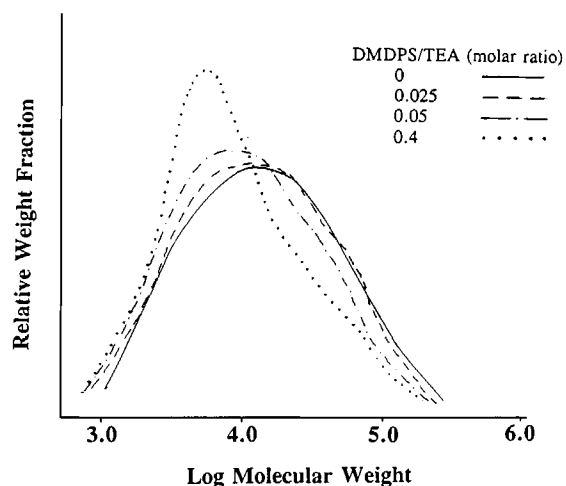


Figure 7 The effect of DMDPS/Ti ratio on the MWD of atactic polypropene obtained with $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4\text{-TEA}$ catalyst. Polymerization conditions are indicated in Table VI.

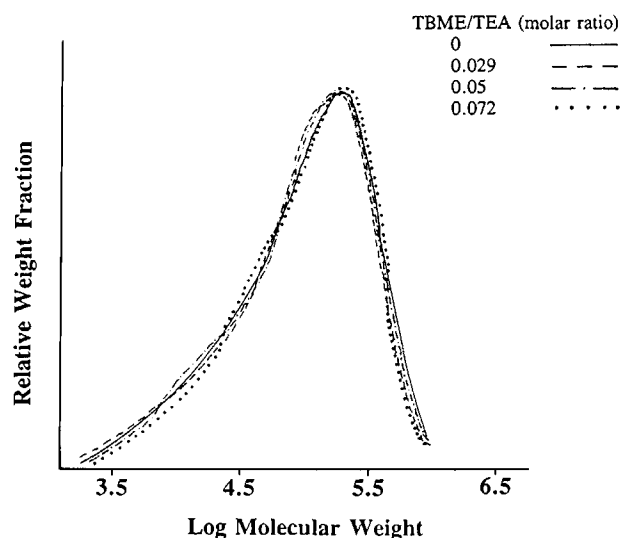


Figure 8 The effect of TBME/Ti ratio on the MWD of isotactic polypropene obtained with $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4\text{-TEA}$ catalyst. Polymerization conditions are indicated in Table VII.

and stereospecificity for catalyst obtained at 105°C (catalyst C), which is supposed to contain relatively high POC. The external bases studied were TMPIP, DMDPS, and TBME. Their effects on molecular weights are tabulated in Tables V, VI, and VII, and MWDs are plotted in Figures 4-9.

In Tables V and VI, molecular weights and polydispersities are given as a function of the base/cocatalyst ratios with the concentration of the cocatalyst (TEA) kept constant (see also Figure 10).

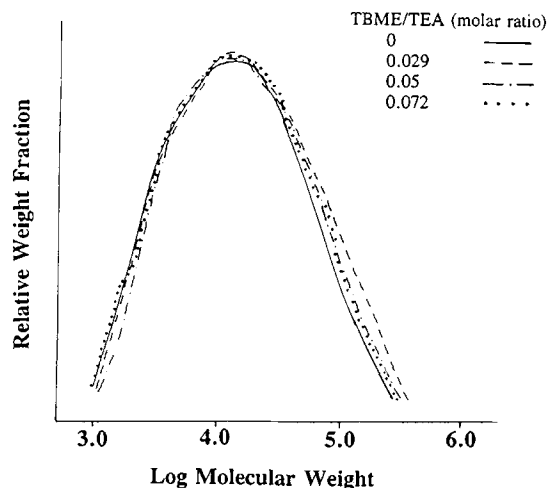


Figure 9 The effect of TBME/Ti ratio on the MWD of atactic polypropene obtained with $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4\text{-TEA}$ catalyst. Polymerization conditions are indicated in Table VII.

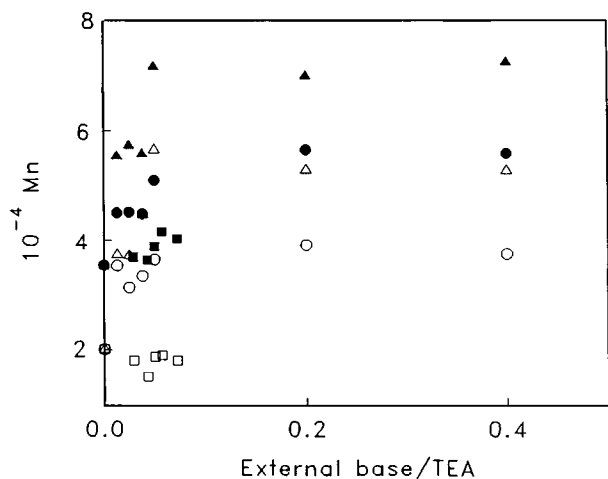


Figure 10 The effect of external base/TEA ratio on Mn of whole (○, △, □) and isotactic (●, ▲, ■) polymers. External base: TMPIP (○, ●); DMDPS (△, ▲); TBME (□, ■). Polymerization conditions were the same as in Table VII.

One can see that by the addition of a small amount of TMPIP or DMDPS, molecular weights of the whole and isotactic polymers were increased by almost a factor of two. Further addition of the base seems, however, to have no clear effect on the molecular weights. On the other hand, M_n and M_w of the atactic polymer decreased slightly with increasing base/TEA ratios.

The MWD, as shown in Figures 4 and 6, broadened and shifted toward higher molecular weight with the addition of the external base, TMPIP and DMDPS, respectively. These results imply a strong interaction between TMPIP (or DMDPS) and isotactic Ti species.¹⁴ The MWD curves of the atactic polymers shift gradually toward a lower range with increasing concentrations of TMPIP (Fig. 5) or DMDPS (Fig. 7). The presence of either base resulted in narrower MWD, but the amount of the external base seems to have little effect on the distribution.

Unlike TMPIP or DMDPS, TBME, as shown in Table V and Figures 8 and 9, had no obvious effects on either the molecular weights or MWD of the whole polymer or the isotactic and atactic polymers.

A variety of roles for the external base have been suggested in the propene polymerization with $MgCl_2$ -supported $TiCl_4$ catalysts: (a) selective poisoning of nonstereospecific sites¹⁵⁻¹⁷; (b) increasing the number of active sites^{15,18-20}; and (c) conversion of nonstereospecific sites into stereospecific sites.^{15,20-22} In this context, two different isotactic sites were thought to exist in the presence of

an external base^{18,23}: (a) low isospecific sites with a single vacancy, producing polymers of relatively low isotacticity and molecular weight; and (b) high isospecific sites with a base associated, producing polymers of higher isotacticity and molecular weight.

We have seen an increase in isotacticity when employing TMPIP or DMDPS as an external base.³ Along with the increase in the molecular weight of the isotactic polymer and the decrease in the molecular weight of the atactic polymer, as found in this study, it is reasonable to say that the principle role of TMPIP or DMDPS is the transformation of nonstereospecific sites into stereospecific sites.

On the other hand, TBME has been shown to enhance the catalytic activity of the catalyst (about 22–32% at the optimum TBME/TEA ratio) without significantly affecting stereospecificity. The enhancement of activity seems to be due to the activation of more active sites in the presence of TBME, but detailed mechanisms of this activation reaction are not yet clear.

CONCLUSION

The study of the influence of the cocatalyst on the average molecular weights and MWD of polypropenes produced with the $MgCl_2$ -supported $TiCl_4$ /DOP catalyst and that of the isotactic and atactic portions of the polypropene separated by heptane extraction has led us to conclude that the active sites are more homogeneous at low cocatalyst/catalyst ratios than at high ratios. The polydispersity increases with the Al/Ti ratio due to the transfer reaction to the cocatalyst. The cocatalyst, as expected, plays a significant role as a chain transfer agent. From the point of view that the internal Lewis base is usually associated with isotactic sites, the steric effect becomes more pronounced in the transfer reaction when the bulkiness of the alkyl group in the cocatalyst increases. The net result is the increase in the average molecular weights of the isotactic polymer. Due to higher activation energy of the transfer reaction compared to that of the propagation reaction, the molecular weight decreases with temperature.

Of the three external Lewis bases studied (TMPIP, DMDPS, and TBME), a sudden increase in the average molecular weights of the isotactic polymer was observed in the presence of a small amount of TMPIP or DMDPS, but the increase leveled off quickly. For the atactic polymer, the effect is exactly the opposite. The effects can be well explained using a three-site model: that TMPIP or

DMDPS converts atactic sites into isotactic sites. Unlike TMPIP and DMDPS, TBME has no obvious effect on either the molecular weight or MWD.

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