Polymerization of butene-1 with highly active $MgCl_2$– supported $TiCl_4$ catalyst system

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Polymerization of butene-1 was carried out with $MgCl_2/TiCl_4$–Et_3Al/ethylbenzoate (EB) or 2,2,6,6-tetramethylpiperidine (TMP) catalyst systems and the poly(butene-1) obtained was fractionated into n-decane (C_{10}) -soluble and -insoluble portions. By ^{13}C nuclear magnetic resonance analysis, the frequency of the mmmm pentad of each fraction was determined to be 30–34% for the C_{10}-soluble and 78% for the C_{10}-insoluble fractions. EB or TMP enhanced the stereospecificity by selective poisoning for the formation of C_{10}-soluble polymer and increased the molecular weight of each fraction by a maximum 2–3 times without changing the polydispersity. EB was found to be superior to TMP as a stereospecificity improver.

(Keywords: butene-1 polymerization; highly active titanium; stereospecificity; ethyl benzoate; catalyst; magnesium chloride; tetramethylpiperidine)

INTRODUCTION

It is well known[1,2] that $MgCl_2$-supported titanium catalyst systems, $MgCl_2/TiCl_4$–Et_3Al/ethyl benzoate (EB), exhibit a very high activity and high stereospecificity in polymerization of propylene. In previous papers, the determination of the number of active centres by a kinetic method[3,4] and the role of EB[5-10] in polymerization with these catalyst systems have been reported, and it has been concluded that the high activity and the high stereospecificity of these catalyst systems are achieved by the joint effects of increase of concentration of the active centres and propagation rate constant by $MgCl_2$ and the selective poisoning of the non-stereospecific active centres by EB.

In this paper, polymerization of butene-1 was examined with the catalyst system composed of $TiCl_4$ supported on activated $MgCl_2$ by mechanical pulverization in conjunction with Et_3Al/EB or 2,2,6,6-tetramethylpiperidine (TMP) in order to obtain further knowledge on features of $MgCl_2$-supported $TiCl_4$ catalyst systems. By varying the concentration of EB or TMP, changes in the yield of poly(butene-1), the micrstructure, the molecular weight and the molecular weight distribution were investigated, and the function of EB or TMP and the nature of the active centres in this catalyst system were discussed. Some of the results obtained were compared with those of polymerization of propylene.

EXPERIMENTAL

Preparation of catalyst

In a 800 ml stainless-steel pot containing 2.8 kg of stainless-steel balls (15 mm diameter), 20 g of $MgCl_2$ were milled for 6 h under nitrogen. The milled $MgCl_2$ was heated with 200 ml of $TiCl_4$ at 80°C for 2 h in a 400 ml flask. Subsequently, the solid product was separated by filtration and washed seven times with n-decane. Eight milligrams of Ti atoms were contained in 1 g of the resulting catalyst.

Polymerization of butene-1

In a 1 litre glass reactor equipped with a stirrer, 200 ml or 400 ml of n-decane was added and the system was substituted by butene-1. Et_3Al, EB or TMP, and Ti catalyst were added at 50°C in this order ($[Al]=2.5\,mmol\,l^{-1}$, $[Ti]=0.1\,mmol\,l^{-1}$, [EB] or [TMP] variable). Polymerization was carried out under atmospheric pressure at 50°C for 2 min. Butene-1 was supplied continuously, maintaining atmospheric pressure. After 2 min, a small amount of methanol was added to the glass reactor to stop polymerization, and the whole product was poured into a large amount of methanol. The collected polymer was filtered and vacuum-dried at 80°C for 12 h.

Polymerization of propylene

Polymerization of propylene was carried out with $MgCl_2/TiCl_4$–Et_3Al/EB by the same method as for polymerization of butene-1 except for the following conditions: $[Al]=14.375\,mmol\,l^{-1}$, $[Ti]=0.575\,mmol\,l^{-1}$, 200 ml n-decane and polymerization time of 15 min.

Fractionation of polymer

One gram of the polymer sample was dissolved in 100 ml of n-decane (C_{10}) at 120°C, cooled to 0°C, and then left overnight at room temperature. Subsequently, the precipitated polymer, that is, C_{10}-insoluble polymer, was separated by filtration and vacuum-dried, while C_{10}-soluble polymer was recovered by pouring the filtrate into a large excess of acetone–methanol.

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Characterization of polymer

^{13}C n.m.r. analysis. The polymer solution was prepared by dissolving 250 mg of the polymer sample at 100°C in a mixture of 2 ml of hexachlorobutadiene and 0.3 ml of deuterobenzene. The ^{13}C n.m.r. spectrum was recorded with a Jeol GX-270 spectrometer operating at 67.8 MHz under proton decoupling in Fourier transform (FT) mode. Instrument conditions were 45° pulse of 6 μs, 5 s repetition rate, 4000 Hz sweep width and 100°C temperature.

Molecular weight and molecular weight distribution. *MW* and *MWD* of the polymer sample were determined by g.p.c. (Waters Associates, model ALC/GPC 150C) using polystyrene gel columns (10^7, 10^6, 10^5, 10^4 and 10^3 Å pore size) and *o*-dichlorobenzene as solvent at 150°C.

RESULTS AND DISCUSSION

Microstructure of poly(butene-1)

Polymerization of butene-1 was carried out with $MgCl_2/TiCl_4$–Et_3Al/EB or TMP catalyst system. The polymers obtained were fractionated by n-decane (C_{10}) into C_{10}-soluble and -insoluble portions, and molecular weight was determined by g.p.c. as listed in *Table 1* with EB and *Table 2* with TMP. In *Figure 1*, the ^{13}C n.m.r. spectra of C_{10}-soluble and -insoluble fractions are shown together with the peak assignments based on previous papers[11–13]. According to the report by Doi *et al.*[14], peaks based on butene-1 unit inversion (head-to-head or tail-to-tail addition) are observed at 41.3, 39.2, 37.5–37.0, 36.8, 33.6, 29.8 and 24.3–23.3 ppm using *o*-dichlorobenzene as solvent. As shown in *Figure 1*, peaks based on 'head-to-head or tail-to-tail bonding' were not found at all. Therefore, it can be concluded that in the $MgCl_2$-supported $TiCl_4$ catalyst system studied, the inversion of butene-1 unit addition in the propagation stage does not take place, at least in homopolymerization of butene-1.

The frequency of mmmm pentad (iso value) of the fractionated polymers was determined using the peaks of side-chain methylene carbon of poly(butene-1) split by the difference of pentad tacticity. In *Figure 2*, as an example, a ^{13}C n.m.r. spectrum of a C_{10}-soluble polymer (run no. 1) is shown together with the peak assignment.

The obtained iso values for the fractionated polymers are listed in *Table 3*. As shown, iso values were 78% for C_{10}-insoluble polymers and 30–34% for C_{10}-soluble polymers, indicating that the fractionation by C_{10} has

Table 1 Polymerization of butene-1 with $MgCl_2/TiCl_4$–Et_3Al/EB catalyst

		Whole			C_{10}-insoluble fraction				C_{10}-soluble fraction			
		Productivity										
Run no.	EB/Ti (mol/mol)	(g)	(g/mmol Ti)	*II*[a] (wt%)	Productivity (g/mmol Ti)	$\bar{M}_w$ ($\times 10^{-5}$)	$\bar{M}_n$ ($\times 10^{-5}$)	$\bar{M}_w/\bar{M}_n$	Productivity (g/mmol Ti)	$\bar{M}_w$ ($\times 10^{-5}$)	$\bar{M}_n$ ($\times 10^{-5}$)	$\bar{M}_w/\bar{M}_n$
1	0	13.8	690	27.2	188	5.61	1.10	5.01	502	2.50	0.51	4.90
2	0.25	13.0	650	30.4	198	7.62	1.53	4.98	452	3.53	0.67	5.81
3	0.50	11.2	560	35.7	200	5.89	1.11	5.32	360	2.41	0.48	4.99
4	0.75	9.3	465	44.3	206	4.91	1.10	4.45	259	2.54	0.46	5.53
5	1.0	8.5	425	49.2	209	5.56	1.13	4.91	216	2.55	0.53	4.80
6	2.5	6.2	308	55.2	170	7.69	1.62	4.74	138	4.09	0.70	5.83
7	5.0	4.2	210	62.7	132	6.99	1.59	4.39	78	3.39	0.60	5.63
8	7.5	3.3	165	74.5	123	8.29	2.05	4.05	42	3.38	0.64	5.29
9*	10	4.7	118	68.0	80	9.51	1.95	4.87	38	4.52	0.70	6.49
10*	15	4.8	120	70.9	85	9.35	1.79	5.23	35	4.85	0.92	5.28
11*	20	4.5	114	73.4	84	11.66	2.80	4.17	30	6.25	0.96	6.51
12*	25	1.0	25	85.3	21	14.31	3.20	4.47	4	—	—	—

Polymerization conditions: 50°C for 2 min under atmospheric pressure, 0.1 mmol l^{-1} of Ti and 2.5 mmol l^{-1} of Et_3Al in 200 ml (* 400 ml) of n-decane
[a] Weight fraction of n-decane-insoluble polymer

Table 2 Polymerization of butene-1 with $MgCl_2/TiCl_4$–Et_3Al/TMP catalyst

		Whole			C_{10}-insoluble fraction				C_{10}-soluble fraction			
		Productivity										
Run no.	TMP/Ti (mol/mol)	(g)	(g/mmol Ti)	*II*[a] (wt%)	Productivity (g/mmol Ti)	$\bar{M}_w$ ($\times 10^{-5}$)	$\bar{M}_n$ ($\times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	Productivity (g/mmol Ti)	$\bar{M}_w$ ($\times 10^{-5}$)	$\bar{M}_n$ ($\times 10^{-5}$)	$\bar{M}_w/\bar{M}_n$
1	0	13.8	690	27.2	188	5.61	1.10	5.01	502	2.50	0.51	4.90
13	0.25	9.8	490	46.2	226	5.94	1.10	5.40	264	2.71	0.56	4.87
14	0.50	9.4	470	46.7	217	5.05	0.82	6.16	253	2.29	0.51	4.46
15	0.75	9.5	474	45.4	215	6.17	0.95	6.48	259	2.58	0.46	5.59
16	1.0	9.6	480	45.2	217	6.56	1.19	5.52	263	2.55	0.54	4.71
17	2.5	8.0	400	47.9	192	6.80	1.17	5.83	208	2.33	0.45	5.17
18	5.0	7.6	380	48.2	183	5.75	0.90	6.39	197	2.49	0.50	5.02
19	7.5	6.8	340	53.0	180	6.48	1.10	5.87	160	2.49	0.55	4.57
20	10	5.7	285	52.7	150	7.56	1.32	5.71	135	3.28	0.53	6.21
21	15	4.5	225	56.9	128	7.95	1.17	6.47	97	3.41	0.64	5.33
22*	20	6.5	163	52.0	85	10.0	1.65	6.06	78	4.05	0.76	5.30
23*	25	5.2	130	51.7	67	11.3	1.76	6.43	63	4.50	0.73	6.13

Polymerization conditions: 50°C for 2 min under atmospheric pressure, 0.1 mmol l^{-1} of Ti and 2.5 mmol l^{-1} of Et_3Al in 200 ml (* 400 ml) of n-decane
[a] Weight fraction of n-decane-insoluble polymer

been made mainly by the difference of the microtacticity of poly(butene-1).

Productivity

In *Figure 3*, the relative productivity of the fractionated poly(butene-1) was plotted as a function of EB or TMP/Ti molar ratio, in which the productivity of C_{10}-insoluble polymer produced with $MgCl_2/TiCl_4$–Et_3Al catalyst system was defined as 1.

The productivity of C_{10}-soluble polymer with $MgCl_2/TiCl_4$–Et_3Al catalyst system was more than twice as high as that of C_{10}-insoluble polymer, but decreased very rapidly not depending on C_{10}-insoluble polymer on addition of a small amount of EB or TMP to the catalyst system, and continued to decrease rather moderately with further addition of EB or TMP.

EB or TMP seem to act in almost the same way, although the efficiency to decrease C_{10}-soluble polymer

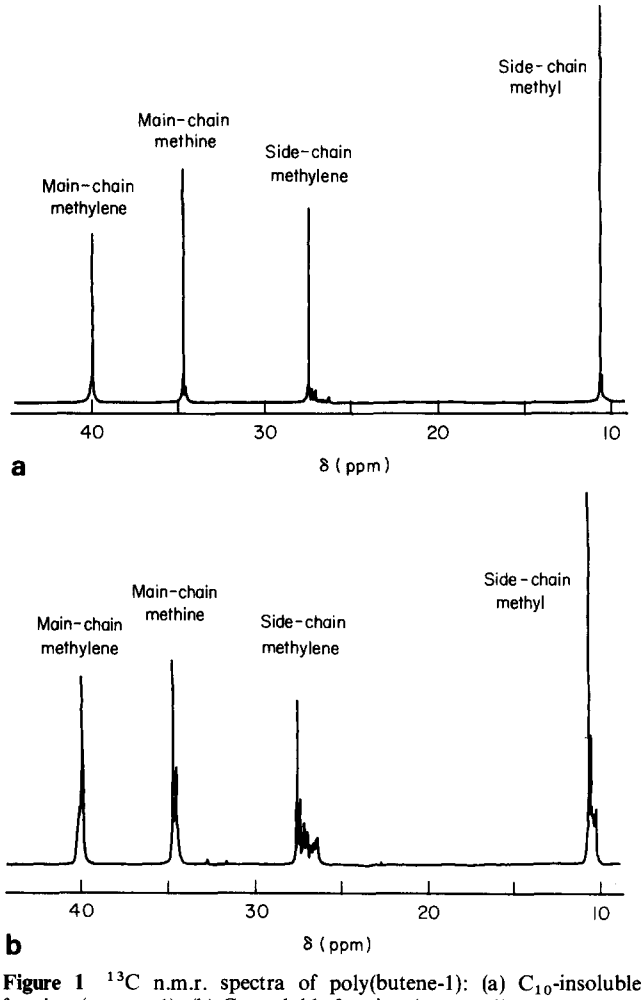

Figure 1 ^{13}C n.m.r. spectra of poly(butene-1): (a) C_{10}-insoluble fraction (run no. 1); (b) C_{10}-soluble fraction (run no. 1)

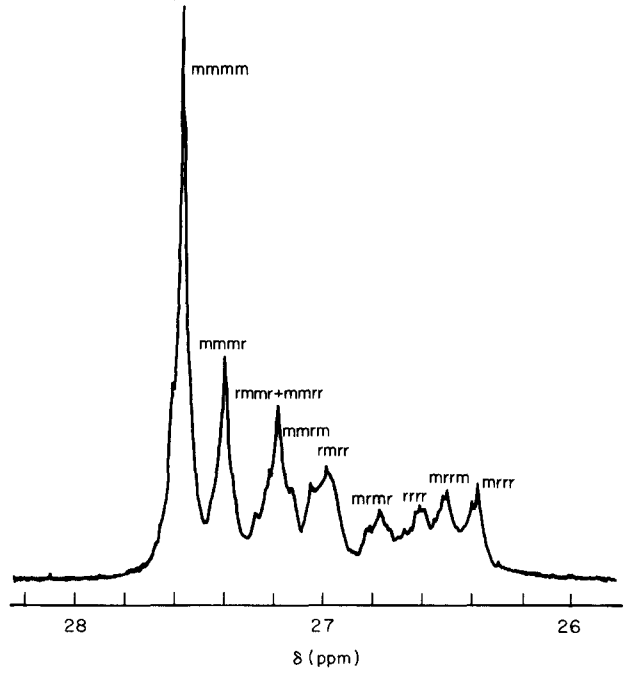

Figure 2 ^{13}C n.m.r. spectrum of C_{10}-soluble poly(butene-1) (run no. 1)

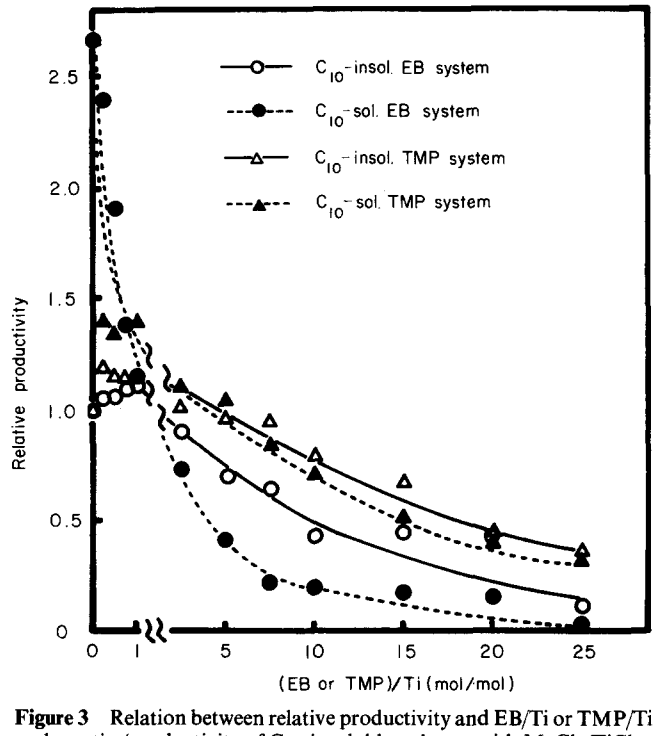

Figure 3 Relation between relative productivity and EB/Ti or TMP/Ti molar ratio (productivity of C_{10}-insoluble polymer with $MgCl_2/TiCl_4$–Et_3Al is defined as 1)

Table 3 Iso value[a] and frequency of pentad for C_{10}-insoluble and C_{10}-soluble poly(butene-1)

Run no.		Iso value	mmmm	mmmr	rmmr +mmrr	mmrm +rmrr	mrmr	mrrm	mrrr	rrrr
1	C_{10}-insol.	77.8	77.8	5.9	5.9	3.3	1.6	2.5	1.5	1.6
	C_{10}-sol.	30.4	30.4	13.7	15.7	13.7	6.8	6.0	6.2	6.8
5	C_{10}-insol.	77.7	77.7	5.7	5.8	3.0	2.4	2.5	1.5	1.4
	C_{10}-sol.	33.0	33.0	11.3	16.4	11.9	6.8	5.6	7.0	8.0
9	C_{10}-insol.	78.3	78.3	6.6	6.6	2.1	1.7	2.0	1.6	1.3
	C_{10}-sol.	34.0	34.0	10.8	15.3	11.3	7.1	5.7	6.9	9.0

[a] The frequency of mmmm pentad

with TMP was considerably poorer than with EB at higher concentration.

The observed profile for C_{10}-soluble polymer suggests that there would be a rather broad distribution of non-stereospecific centres having different acidity in this $MgCl_2/TiCl_4$–Et_3Al catalyst system. The non-stereospecific centres having stronger acidity would be selectively and easily inactivated by a small amount of EB or TMP, but those having weaker acidity would hardly be inactivated, especially by TMP.

On the other hand, the productivity of C_{10}-insoluble polymers, in contrast, was increased a little by a small amount of EB or TMP, then passed through a maximum, and was decreased by further addition, but more slowly compared with C_{10}-soluble polymer. This interesting profile of C_{10}-insoluble polymer can be explained by assuming that EB or TMP would have both positive and negative effects on the productivity of C_{10}-insoluble polymer. As a positive effect, EB or TMP would transform the non-stereospecific centres into stereospecific ones by saturating one or two vacant coordination sites in the non-stereospecific centres, or would increase the propagation rate constant at the stereospecific centres. As a negative effect, EB or TMP would inactivate the stereospecific centres by saturating the single vacant coordination site.

The competition between these two opposing effects would result in the peak and the mild decay of the productivity in the profile of C_{10}-insoluble polymer.

The comparison of EB and TMP in *Figure 3* makes it clear that TMP has a poorer capability for poisoning the active centres and also for distinguishing the difference in the stereospecificity of the active centres.

Stereospecificity

Figure 4 shows the relation between isotactic index (*II*) expressed by the weight fraction of C_{10}-insoluble polymer and EB or TMP/Ti molar ratio.

The very low stereospecificity of the $MgCl_2/TiCl_4$–Et_3Al catalyst system, 30% expressed by *II*, could be enhanced remarkably to 50–60% by addition of a small amount of EB or TMP, and the increase of *II* reached a plateau at 80% for EB and 55% for TMP, indicating the superior capability of EB and the limitation as stereospecificity improver in this $MgCl_2$-supported $TiCl_4$ catalyst system.

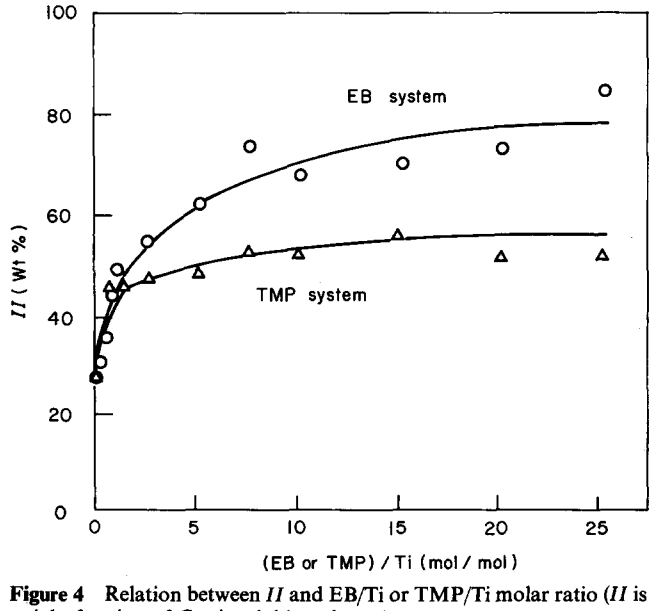

Figure 4 Relation between *II* and EB/Ti or TMP/Ti molar ratio (*II* is weight fraction of C_{10}-insoluble polymer)

Table 3 shows iso values of three kinds of C_{10}-soluble and C_{10}-insoluble poly(butene-1).

For the syntheses of these polymers, the EB/Ti molar ratio in polymerization was 0, 1 and 10, and consequently a large change of *II*, 27.2%, 49.2% and 68.0%, respectively, was observed. However, as seen in *Table 3*, iso values were almost unchanged in spite of the large changes of the polymerization condition and *II*.

This fact gives us important information about the nature of the active centres in this catalyst system.

First, for C_{10}-soluble polymers, the yield decreased to less than one-tenth (comparison of run no. 9 and no. 1) without changing the iso value, indicating that there is no large different in the degrees of stereoregularity among the non-stereospecific centres having different acidity in this catalyst system.

Secondly, for C_{10}-insoluble polymers, iso values were around 80%, rather low for the stereospecific polymer, probably due to the presence of a considerable amount of the 'stereospecific polymer' having rather lower iso values, and were also unchanged by EB, suggesting a broad distribution of stereoregularity among the stereospecific centres as reported in the polymerization of propylene[15] with the same catalyst system, and no influence of EB on the distribution.

Next, as a comparison, data for two samples of commercial-grade homopoly(butene-1), M801N (Mitsui Petrochemical Ind., Japan) and M4110 (Shell Chemical Co., USA) are listed in *Table 4*. Iso values of 93–94% for C_{10}-insoluble fraction are much higher and 28% for C_{10}-soluble fraction a little lower than those (78% for C_{10}-insoluble, 30–34% for C_{10}-soluble) of the corresponding fractions with the $MgCl_2$-supported $TiCl_4$ catalyst system in this paper.

From these results, one can conclude that the active centres in the commercially used catalyst systems would be very finely divided into the highly stereospecific and the non-stereospecific groups with a narrow distribution. On the other hand, the $MgCl_2$-supported $TiCl_4$ catalyst system in this paper would have a continuous and broad distribution of active centres having different stereospecificity, or essentially would not have the highly stereospecific centres in the commercially used catalyst systems, and EB would increase the relative concentration of the stereospecific centres.

Molecular weight and molecular weight distribution

In *Tables 1* and *2*, the number-average molecular weight ($\bar{M}_n$) and the molecular weight distribution ($\bar{M}_w/\bar{M}_n$) of the fractionated polymers are listed. $\bar{M}_n$ of both C_{10}-insoluble and -soluble polymers were increased

Table 4 Iso value[a] for C_{10}-insoluble and C_{10}-soluble fractions of commercial-grade homopoly(butene-1)

Commercial grade	Iso value	
	C_{10}-insol.	C_{10}-sol.
M801N	94	28
M4110	93	28

[a] The frequency of mmmm pentad

by a maximum 2–3 times by the addition of EB or TMP. This could be explained by saying that the value of k_p/k_{tr} ratio would be increased in the existing active centres after reaction with EB or TMP, where k_p is the propagation rate constant and k_{tr} is the chain transfer rate constant.

On the other hand, the shape of g.p.c. curves and the values of $\bar{M}_w/\bar{M}_n$ seem to be almost unchanged by the addition of EB or TMP as shown in *Figure 5* and *Table 1*, supporting the previous description that the distribution in the nature of both the stereospecific and non-stereospecific centres would not be affected by the addition of EB or TMP.

Comparison with polymerization of propylene

Table 5 shows the results of polymerization of propylene with $MgCl_2/TiCl_4$–Et_3Al/EB catalyst system. The values of *II* of polypropylene (PP) evaluated by C_{10} fractionation as well as poly(butene-1) were considerably higher, 60% at EB/Ti = 0 and 96% at EB/Ti = 15, than for poly(butene-1).

In *Figure 6*, the relative productivity for the fractionated PP was plotted as a function of EB/Ti molar ratio together with the results for poly(butene-1) described earlier.

With increase in the concentration of EB, the productivity of C_{10}-soluble PP decreased rapidly, while

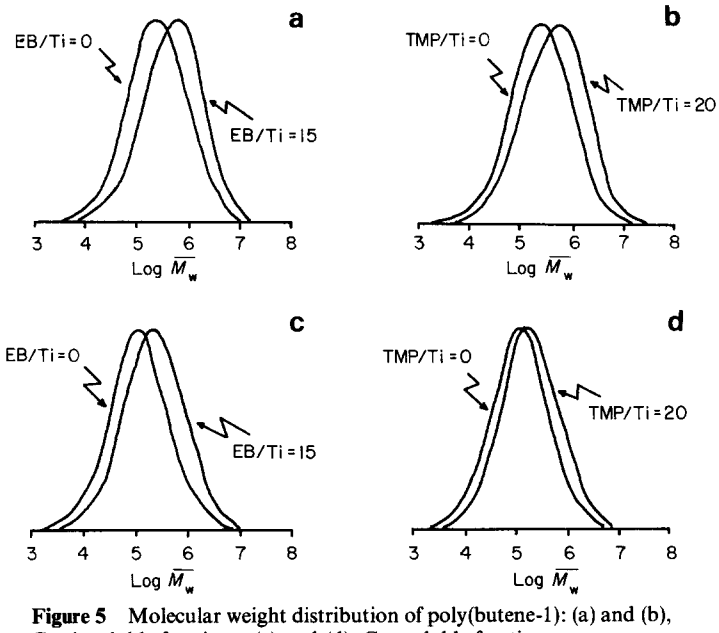

Figure 5 Molecular weight distribution of poly(butene-1): (a) and (b), C_{10}-insoluble fractions; (c) and (d), C_{10}-soluble fractions

Table 5 Polymerization of propylene with $MgCl_2/TiCl_4$–Et_3Al/EB catalyst

Run no.	EB/Ti (mol/mol)	Whole Productivity (g)	Whole Productivity (g/mmol Ti)	Whole *II*[a] (wt%)	C_{10}-insol. Productivity (g/mmol Ti)	C_{10}-sol. Productivity (g/mmol Ti)
24	0	26.5	230	60	138	92
25	2.5	25.9	225	78	176	49
26	5.0	22.4	195	84	164	31
27	10	20.4	177	92	163	14
28	15	12.0	104	96	100	4

Polymerization conditions: 50°C for 15 min under atmospheric pressure, 0.575 mmol l^{-1} of Ti and 14.375 mmol l^{-1} of Et_3Al in 200 ml of n-decane

[a] Weight fraction of n-decane-insoluble polymer

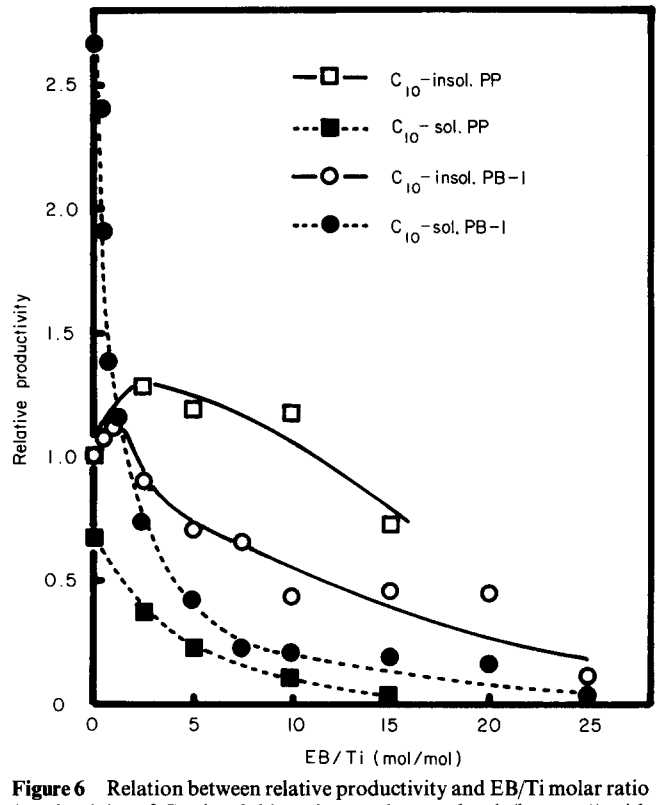

Figure 6 Relation between relative productivity and EB/Ti molar ratio (productivity of C_{10}-insoluble polypropylene and poly(butene-1) with $MgCl_2/TiCl_4$–Et_3Al each defined as 1)

that of C_{10}-insoluble PP increased significantly and, after reaching a maximum, gradually decreased. All these behaviours are similar to the polymerization of butene-1, although a considerable difference in the magnitude of the effect due to EB can be seen.

Therefore, the nature of the active centres and the function of EB in polymerization of butene-1 seem to be more or less similar to those in polymerization of propylene from the point of view discussed.

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