Polymer Bulletin 11, 485-489 (1984)

Polymer Bulletin

Polymerizations of α-Olefins and Styrene with $MgCl_2$-Supported Titanium Catalyst System: $MgCl_2/TiCl_4/PhCO_2Et$ with $AlEt_3PhCO_2Et$

Norio Kashiwa and Junichi Yoshitake

Research Center, Mitsui Petrochemical Industries, Ltd., Waki-cho, Kuga-gun,
Yamaguchi-ken, Japan 740

SUMMARY

Kinetic analysis was performed in a short time polymerizations of 1-butene,4-methyl-1-pentene and styrene by using a catalyst system composed of $MgCl_2/TiCl_4/PhCO_2Et$ with $AlEt_3/PhCO_2Et$ which is known as a highly active and highly stereospecific catalyst system in olefin polymerization. The concentration of the active centers,$[C^*]$, the propagation rate constant,k_p, and the chain transfer rate, r_{tr}, were determined for each monomer. It was found that the values of $[C^*]$ were almost same for every monomer, but the values of k_p changes widely in the following order: propylene>1-butene>4-methyl-1-pentene$\gg$styrene.

INTRODUCTION

It is well known(1) that the catalyst system which is incorporated with the $MgCl_2$-supported titanium catalyst($MgCl_2/TiCl_4/PhCO_2Et$), triethylaluminium and ethyl benzoate($AlEt_3/PhCO_2Et$) exhibits a very high activity and high stereospecificity in propylene polymerization. In a previous paper(2), we have reported a kinetic study on propylene polymerization with the above catalyst system. In this report, kinetic analysis was performed with short time polymerizations of 1-butene, 4-methyl-1-pentene and styrene, in which the values of the concentration of the active titanium centers, $[C^*]$, the propagation rate constant, k_p, and the chain transfer rate, k_{tr}, were determined for each monomer.

EXPERIMENTAL

Preparation of $MgCl_2$-supported titanium catalyst; Preparation of the $MgCl_2$-supported titanium catalyst was carried out as described in the previous paper(2).

1-Butene polymerization; 1-Butene slurry polymerization was carried out in a 1l glass-made flask using decane as solvent. Decane(500ml) was put into the flask, which was filled with 1-butene. Triethylaluminium, ethyl benzoate, and the solid catalyst were added, then , the polymerization was performed under atmospheric pressure for 15-240sec. at 10°C. After completion of polymerization, a small amount of ethanol was added to the system to stop the polymerization and , then, the whole slurry was poured into a large quantity of methanol. The obtained solid polymer was collected , washed with HCl-methanol solution , and dried in vacuo.

Polymerization of 4-methyl-1-pentene and styrene; 4-Methyl-1-pentene and styrene slurry polymerizations were carried out in a 1l glass-made flask without added solvent. Other polymerization conditions were the same with those of 1-butene polymerization.

Characterization of polymer; Isotactic index(I.I.) for poly-1-butene and poly-4-methyl-1-pentene was given by the weight fraction insoluble in decane at room temperature;,i.e., 1*g* of polymer was dissolved in 100*ml* of decane at 150°*C*, cooled to room temperature, and allowed to stand for one night. The precipitated polymer was separated, dried and weighed. The number average molecular weights, $\bar{M}_n$, of the poly-1-butene and styrene were determined by GPC(Waters Associates, Model ALC/GPC 150), using polystyrene gel colums(10^7, 10^6, 10^5, 10^4 and 10^3Å pore size) and *o*-dichlorobenzene as solvent at 135°*C*. The number average molecular weight, $\bar{M}_n$, of the poly-4-methyl-1-pentene were calculated using Hoffman's relationship(3)

$$[\eta] = 1.94\times10^{-4}\,\bar{M}_n^{\,0.81} \qquad (1)$$

where the intrinsic viscosity, [η], of the polymer was obtained in decaline at 135°*C*.

RESULTS AND DISCUSSION

Short time(5-300*sec*) polymerizations of 1-butene, 4-methyl-1-pentene, and styrene were performed with the catalyst system($MgCl_2/TiCl_4/PhCO_2Et$ with $AlEt_3/PhCO_2Et$) at 10°*C*. The results are given in Table 1.

Table 1. Polymerization Results with $MgCl_2/TiCl_4/PhCO_2Et$ with $AlEt_3/PhCO_2Et$ as Catalyst System

Run	Polymerization conditions(a)				Results					
	Monomer	[*M*] (*mol/l*)	[Ti] (*mmol/l*)	Time (*sec.*)	Polymer yields (*mol/mol*Ti)	I.I. (%)	[η] (d*l*/*g*)	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ $\times10^{-4}$	$\bar{P}_n$ $\times10^{-3}$
A-I	I-Butene	3.20	0.4	I5	1.07×10^2			3.29	34.7	6.20
2				30	2.68			3.29	48.0	8.57
3				60	4.54			3.63	61.4	11.0
4				90	8.21			3.63	60.3	10.8
5				120	8.57	91		3.64	69.8	12.5
6				240	14.1			3.79	85.3	15.2
B-1	4-methyl-1-pentene	8.00	0.4	30	0.714×10^2		3.76		19.4	2.30
2				60	1.79		4.54		24.4	2.90
3				90	3.33		4.74		25.8	3.07
4				120	3.81		4.98		27.4	3.25
5				150	6.55	89	4.95		27.2	3.23
6				180	6.30		5.28		29.4	3.49
C-1	Styrene	8.71	6.6	5	2.91			14.3	0.867	0.0832
2				10	4.36			13.5	1.11	0.107
3				20	5.82			12.4	1.22	0.117
4				40	11.6			15.8	2.46	0.236
5				120	55.2			17.6	3.57	0.342
6				240	127			21.9	3.50	0.336
7				300	166			16.6	4.59	0.441
D-1	Propylene	(b) 0.71	0.55	5	23.8				5.33	1.27
2				10	34.8				7.37	1.75
3				15	43.8				7.53	1.79
4				60	117	99			11.6	2.76
5				120	197				14.8	3.52

(a) Other polymerization conditions are given in Fig.1.

(b) This data is reported in Ref.(2).

For the purpose of comparison, the results of propylene polymerization with the same catalyst system(2) are also given in Table 1. The values of the isotactic index of the polymers are quite high(about 90%) also with 1-butene and 4-methyl-1-pentene. Fig.1 shows the relation between the polymer yield and polymerization time. In every monomer polymerization, a linear relationship was obtained. Thus, the polymerization rate, R, expressed by the slope was constant against polymerization time. Therefore, the concentration of the active centers, $[C^*]$, could be regarded to be constant under the investigated conditions. From above results, polymerization rate, R, and the number-average degree of polymerization, $\bar{P}_n$, measured for short polymerization time(Table 1) were expressed as follows(4),

$$R = k_p[C^*][M] \qquad (2)$$

$$\bar{P}_n = R \times T/([C^*] + R_{tr} \times T) \qquad (3)$$

where k_p is the propagation rate constant, $[M]$ is the monomer concentration, T is the polymerization time and R_{tr} is the chain transfer rate. Substitution of Eq.(2) into Eq.(3) gives Eq.(4)(next page).

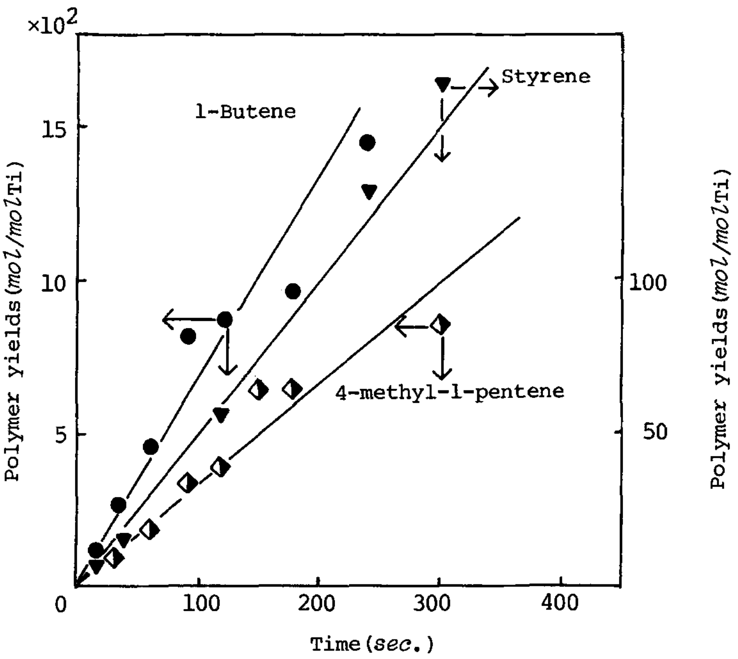

Fig.1 Time Dependence of Polymer Yield in the Polymerizations of 1-Butene, 4-Methyl-1-pentene and Styrene with $MgCl_2/TiCl_4/PhCO_2Et$ with $AlEt_3/PhCO_2Et$ Catalyst System.
Polymerization conditions; Temp: 10°C, [1-butene]=3.2mol/l, [4-methyl-1-pentene]=8.00mol/l, [styrene]=8.71mol/l, mole ratio Al/Ti=25, (●):1-butene, (◆):4-methyl-1-pentene, (▼):styrene.

$$1/\bar{P}_n = [C^*]/(R\times T) + R_{tr}/k_p[M][C^*] \qquad (4)$$

According to Eq.(4) a linear relationship was actually obtained between $1/\bar{P}_n$ and $1/(R\times T)$ (Fig.2). $[C^*]$ were determined from the slope of Fig.2. Next, R could be obtained from the slope of the straight lines in Fig.1, and consequently the values of k_p were determined from Eq.(2). R_{tr} could be obtained from the intercept in Fig.2, which is $R_{tr}/k_p[M][C^*]$. The rate of chain transfer, R_{tr}, can be expressed as follows,

$$R_{tr} = r_{tr}[C^*] \qquad (5)$$

where, r_{tr} is the rate of chain trnsfer at an active center.
The average lifetime of the polymer chain, t, could be obtained from $t=1/r_{tr}$. All of the obtained values are listed in Table 2. As shown in Table 2, the values of $[C^*]$ and t are almost same for every monomer, but the values of k_p($l/mol\cdot sec$) widely vary in the order: propylene(200)>1-butene(160) >4-methyl-1-pentene(30)>styrene(1.9). The order of k_p values of three α-olefins(propylene, 1-butene and 4-methyl-1-pentene) may be rationalized by the magnitude of steric hindrance. The k_p values obtained here are quite significant from both scientific and industrial viewpoints. However, the analysis according to the mechanism of the so-called "coordination polymerization" requires further studies.

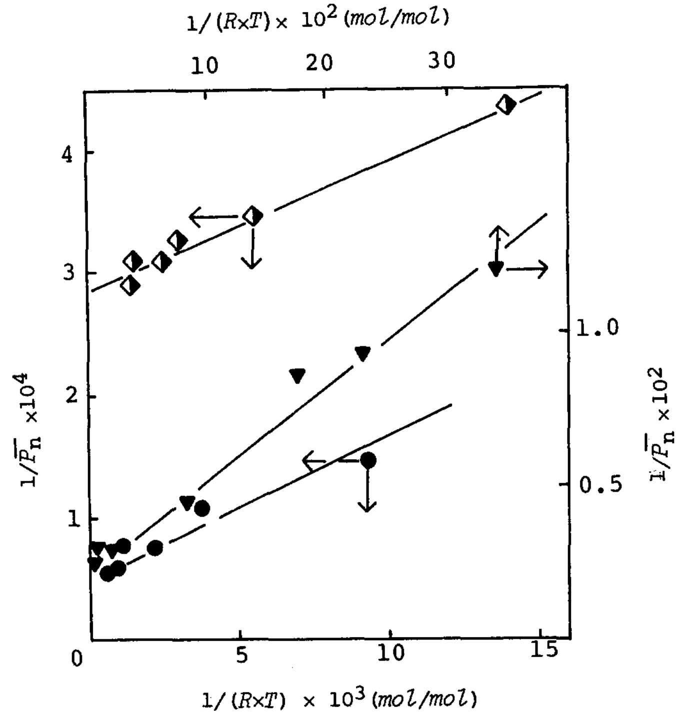

Fig.2 Relation between $1/\bar{P}_n$ and $1/(R\times T)$

Table 2. Kinetic Data

Monomer	$[M]$ (mol/l)	R (mol/molTi$\cdot sec$)	$[C^*]\times 10^2$	k_p ($l/mol\cdot sec$)	k_{tr} (min^{-1})	t (min)
Propylene[a)]	0.71	1.82	1.3	200	2.14	0.47
1-Butene	3.20	6.68	1.3	160	1.37	0.73
4-Methyl-1-pentene	8.00	3.37	1.4	30	3.70	0.27
styrene	8.71	0.512	3.0	1.9	2.40	0.42

a) This data has been reported in Ref.(2).

REFERENCE

1. Japan Kokai: 75-126590, Mitsui Petrochemical Industries, inventors: A.Toyota, N.Kashiwa; Chem. Abstr. 84 122575w; Japan Kokai: 77-151691, Montedison S.P.A. and Mitsui Petrochemical Industries, inventors: L.Luciani, N.Kashiwa, C.Barbe, A.Toyota
2. N.Kashiwa, J.Yoshitake Preceding paper of this Bulletin.
3. A.S.Hoffman, B.A.Fries and P.C.Condit, J. Polym. Sci, Part C 4 109('63)
4. P.J.T.Tait."Transition Metal Catalyzed Polymerizations", MMI press, Harwood Academic Publishers, New York p.115('83)

Accepted April 3, 1984