POLYMERIZATION OF 4-METHYLPENTENE -1- BY THE $MgCl_2|EB|TiCl_4|Al(iBu)_3$ CATALYST SYSTEM

1. KINETIC INVESTIGATIONS

By

M. A. Abu-Eid[1], P. J. Tait[2]

ملخص

لقد تم تحري ميكانيكية تفاعل بلمرة ٤ ميثل بنتين -١- مع المحفز المتكون من كلوريد المغنيسيوم|بنزوات الاثيل|رابع كلوريد التيتانيوم|ثلاثي ايزو بيوتيل الالمنيوم ولقد تم مناقشة الظروف والاحتياجات المناسبة لتحقيق أفضل سرعة تفاعل بلمرة وأفضل خصائص فراغيه للبوليمر المحضر. بالاضافة لهذا فلقد تم ذكر تأثير الكيل الالمنيوم وبنزوات الاثيل على سرعة التفاعل والخصائص الفراغيه للبوليمر .

ABSTRACT

The kinetics of the polymerization of 4-methylpentene-1- with the $MgCl_2|EB|TiCl_4|Al(iBu)_3$ catalyst systems have been investigated. The conditions and

1 Chemistry Department, An-Najah N. Universtiy, Nablus-West Bank
2 UMIST, Chemistry Department, Sackville Street Manchester, U.K.

requirements to achieve the highest activity and stereospecificity of the $MgCl_2$-supported catalyst systems were discussed. Moreover, the role of aluminum alkyl and ethyl benzoate on the activity and stereoregularity of the polymers have been reported.

INTRODUCTION

Many studies[1-8] have appeared in the published scientific literature concerning the procedure used to prepare the $MgCl_2$-supported catalyst system and it's use in the polymerization of ethylene and propylene. But no article of these publications gives a detail study about the conditions and requirements needed to achieve a highly active and stereospecific catalyst.

In our earlier publications[9-11], we have reported some important results showing the differences in kinetic behaviour between the polymerization of 4-methylpentene-1 and propylene using stauffer AA and $MgCl_2$ - supported catalysts. In this paper more kinetic studies concerning the polymerization of 4-methylpentene-1- with $MgCl_2|EB|TiCl_4|Al(iBu)_3$, catalyst system have been reported. The effect of ethyl benzoate concentration, aluminum alkyl concentration and the procedure used to prepare the $MgCl_2$-supported catalysts on the polymerization activity and stereoregularity of the polymer have been discussed.

EXPERIMENTAL

Preparation of $MgCl_2$/EB/$TiCl_4$ catalysts

Three $MgCl_2$ - supported catalysts were prepared as follows:

For catalyst I, the commerical anhydrous $MgCl_2$ (surface area = 3.1 m^2/g) was dried at 120°C in a vacuum oven for 48 h, whereas fo catalysts II and III the $MgCl_2$ support was dried at 120°C for 120 h then mixed with $SOCl_2$ to form a mixture with a molar ratio of $MgCl_2$: $SOCl_2$ = 20:1. the mixture was ball-milled for 1 h. For the three catalysts ethyl benzoate was added to the mill by a molar ratio of $MgCl_2$: EB = 6.5 : 1. The grinding times of the supported mixtures for catalysts I,II and II were 48, 120 and 120 h respectively. The BET surface area of the $MgCl_2$/EB supports were measured and found equal to 30.5, m^2/g for catalyst I and 8.8 m^2/g for catalysts II and III.

After grinding, a portion of the treated support was transferred under nitrogen atmosphere to a glass flask equipped with a magnetic stirrer, and then treated with a given amount of $TiCl_4$ to form a molar ratio of $MgCl_2$:$TiCl_4$ = 0.12:1, 0.97:1 and 0.32:1 for catalysts I, II and III respectively. The mixtures were stirred vigrously at 80°C for 2 h to form the catalysts. After the soluble part was filtered out, the supported catalysts were washed five times with n-pentane before drying under vacuum at room temperature. A pale yellow catalysts were formed with %Ti by mass equal 10.9, 2.6 and 3.4 for catalysts I,II and III respectively.

POLYMERIZATION PROCEDURE

The rate of polymerizations was determined by a dilatometric technique as have been described previously[12]. In the majority of cases polymerization resulted in 30-50% conversion of monomer to polymer, therefore, the rate of polymerization was corrected with the decrease in

monomer concentration during the time of polymerization. All glassware used in the polymerization experiments was carefully cleaned, dried at 150°C and finally flamed out under vacuum. The polymerization mixtures were prepared in an identical manner to follow the sequence, solvent/ catalyst/monomer/EB-$Al(iBu)_3$.

MEASUREMENT OF STEREOREGULARITY

The stereoregularity of the poly (4-methylpentene-1) polymer was measured by the procedure developed by Natta et al[13] which depends on measuring the percentage, by weight, of insoluble polymer after boiling with n-heptane for 24 hours.

MEASUREMENT OF MOLECULAR WEIGHT

Molecular wights of poly (4-methylpentene-1) were determined from measuring the intrinsic viscosity by using the relationship derived by Hoffman et al[14], which can be expressed by the equation.

$$[\eta] = 1.94 \times 10^{-4} (\bar{M}_n)^{0.81}$$

RESULTS AND DISCUSSION

Effect of catalyst preparation procedure on the activity and stereospecificity of the $MgCl_2$ - supported catalyst systems.

The kinetic results and the experimental conditions for the three $MgCl_2$ - supported catalysts are listed in Table (1).

Table (1): Variation of the catalyst activity and stereospecificity with the method of catalyst preparation

Catalyst Number	[Ti]/ m mol dm^{-3}	[Al] / [Ti]	R_p/[Ti] mol min^{-1} $(mol\ Ti)^{-1}$	Solvent	isotacticity %
I	0.175	86	25.1	EC 180	50
II	0.036	278	558	heptane	45
III	0.028	643	1111	heptane	42

[4MP-1] = 2 mol dm-3
Temp. = 40°C
EC = 2,2,4,4,6, Pentamethyl heptane

These results show that the polymerization activities of the supported catalyst systems vary drastically with the conditions of catalyst preparation. The large differences in activities between catalysts I and II or III can be attributed to :

i) The nature of solvent :- In previous work [15], it was found that the polymerization activity of the $MgCl_2$|EB|$TiCl_4$|$Al(iBu)_3$-EB|4MP-1

catalyst system increased by a factor of 4 when using heptane as a solvent rather than EC 180.

ii) The effective drying of the anhydrous $MgCl_2$ during the catalyst preparation :- The role of $SOCl_2$ in increasing the activity of the $MgCl_2$-supported catalyst is due to its effective drying of the anhydrous $MgCl_2$ as indicated by :-

1) The absence of sulphur in catalysts II and III as confirmed by the results of the microanalysis.

2) The surface area of the $MgCl_2$ |$SOCl_2$ support was found higher than that of the $MgCl_2$ support by a factor which lies within experimental error[10].

The results show also that for catalysts II and III (the same drying conditions) the activity of $MgCl_2$-supported catalysts depended largely on the molar ratio of $MgCl_2$: $TiCl_4$

When the $MgCl_2$: $TiCl_4$ molar ratio increased from 0.32 : 1 in catalyst III to 0.67 : 1 in catalyst II , the activity decreased from 1111 mol min^{-1} (mol Ti)$^{-1}$ to 558 mol min^{-1} (mol Ti)$^{-1}$. The increase in catalyst III activity was found to be due to an increase in both the number and reactivity of the active centers[16]. This would seem to indicate that in catalyst II the amount of $TiCl_4$ added to the $MgCl_2$ |EB support was not enough to replace the ethyl benzoate and to fill all the free $MgCl_2$ crystallite surface vacancies.

In conclusion, the condition necessary to achieve the highest activity were found to be as follow :-

1. The anhydrous $MgCl_2$ should be efficiently dried by heating in a vacuum oven and then treated with $SOCl_2$

2. The dried $MgCl_2$ should be ball-milled with ethyl benzoate for 48 h to achieve the maximum surface area[10].

3. The products of ball-milling, should be treated with excess undiluted $TiCl_4$ at temperatures within the range 80 - 90°C for 2 h.

Variation of overall rate of polymerization with time :-

The profiles of the rate of polymerization verus time graphs for the $MgCl_2$-supported catalyst systems were found to have a curve of the acceleration type as shown in Fig 1 and not of the decay type often characterize the $MgCl_2$ supported catalyst systems.

The maxima in overall polymerization rates were observed at 90, 25 and 5 minutes for catalysts I, II and III respectively. The variation in the settling periods can be attributed to different ball-milling time of $MgCl_2$|EB supports during the catalysts preparations and also to the Al: Ti molar ratios in the supported catalyst systems. The settling periods were found to be decreased by increasing the grinding time of the

$MgCl_2$|EB supports and by increasing the Al : Ti molar ratio.[10]. The

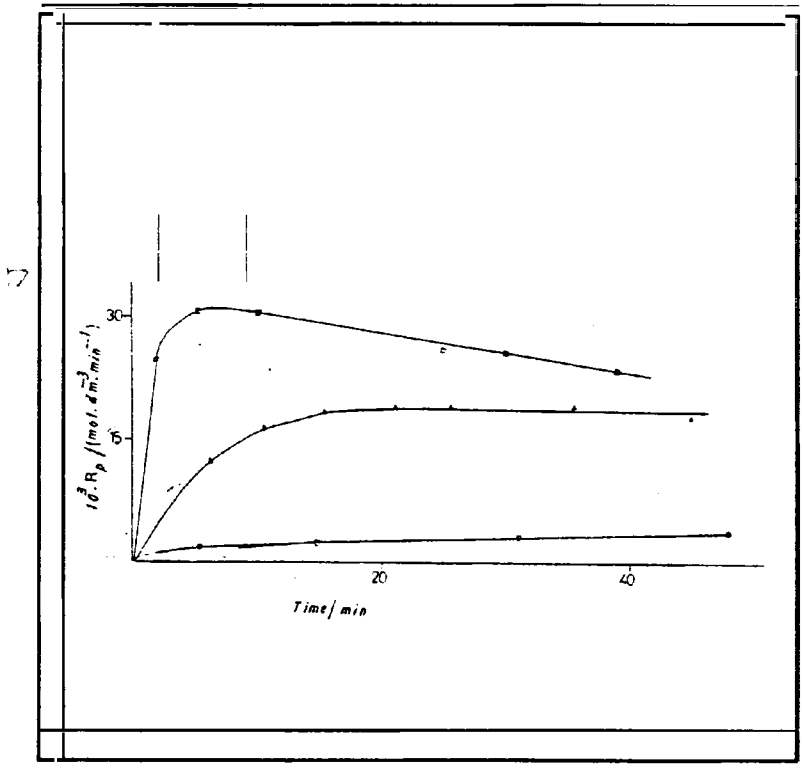

Figure 1 : Polt of rates of polymerization versus time.

o : Catalyst I, [Ti] = 0.175 mmol.dm^{-3}; [Al] = 15 mmol.dm^{-3}. Solvent : EC 180.

Δ : Catalyst II, [Ti] = 0.036 mmol.dm^{-3}; [Al] = 10 mmol.dm^{-3}. Solvent : heptane.

□ : Catalyst III, [Ti] = 0.028 mmol.dm^{-3}; [Al] = 18 mmol.dm^{-3}. Solvent : heptane.

temperature = 40°C, [4MP-1] = 2 mol.dm^{-3}

observed kinetic behaviour in the Mg Cl_2|EB|$TiCl_4$|$Al(iBu)_3$ |4MP-1 catalyst systems suggests the presence of stable active centers which are responsible for the nearly constant rate of polymerization after the maximum.

Variation of the overall rate of polymerization with aluminuim alkyl concentration:

For the three catalysts, a series of polymerization runs were carried out in which the concentration of aluminium alkyl was varied whilst the concentrations of catalyst and monomer were kept constant. Fig. 2 shows a plot of the maximum rate of polymerization for catalysts II and III against aluminium alkyl concentration.

Maxima in the rate of polymerization at molar ratios of Al : Ti of about 86, 277 and 643 were obtained for catalysts I,II and III respectively. Then for the three catalyst systems, the maximum rate decreased with further increase in the Al : Ti molar ratio.

Variation of the tri-isobutyl aluminium concentration can bring about profound changes in rate -time profiles as is shown in Fig. 3.

It can be seen from Fig. 3 that by increasing the concentration of the aluminium alkyl, the decay in rate after the maximum value increased. The behaviour shown in Fig. 2, can be attributed to two reasons, one due

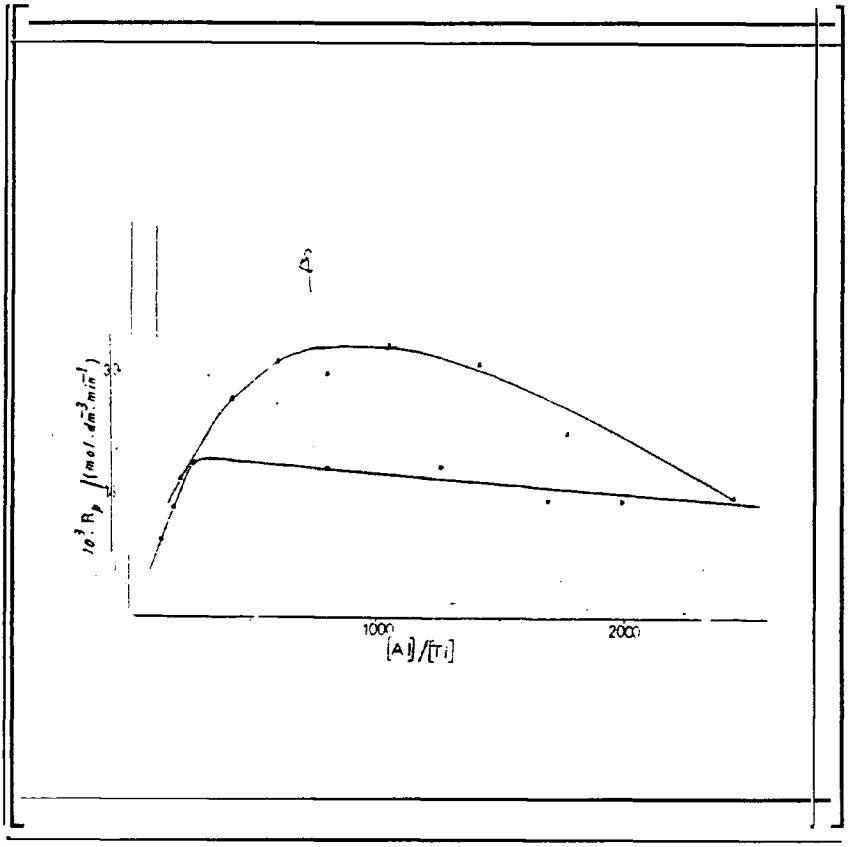

Figure 2 : Plot of rates of polymerization versus [Al]/[Ti]

o : Catalyst II,

Δ : Catalyst III.

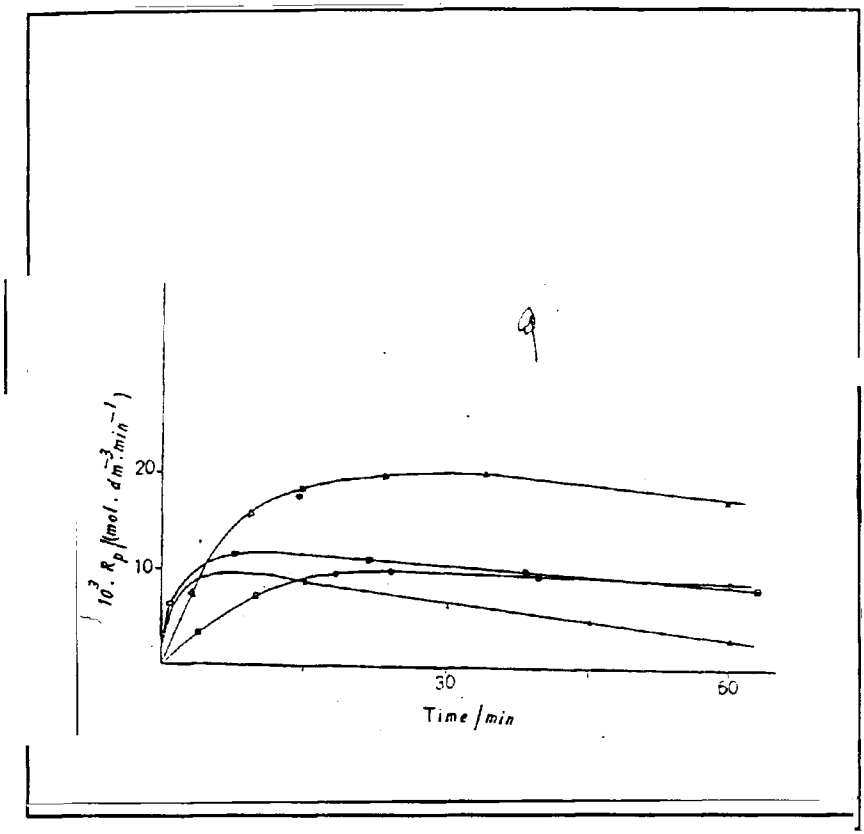

Figure 3 : Plot of rates of polymerization versus time for catalyst II at different alkyl concentration
o : [Al] = 5 mmol.dm^{-3} ; Δ : [Al] = 10 mmol.dm^{-3};
□ : [Al] = 59 mmol.dm^{-3} ; x : [Al] = 117 mmol.dm^{-3}
[Ti] = 0.036 mmol.dm^{-3} ; temperature = 40°C,
Solvent : heptane.

to the production of active centres and the other to the competitive adsorption of the monomer and the aluminium alkyl.

The role of ethyl benzoate in $MgCl_2|TiCl_4|$ EB-$Al(iBu)_3$ |4MP-1 catalyst systems

Effect of ethyl benzoate on activity and stereospecificity:

The effect of ethyl benzoate on the rate of polymerization at constant aluminium alkyl, catalyst and monomer concentration was studied for the three $MgCl_2$-supported catalyst systems and the results are summarized in Table 2.

Maximum values of activities are shown at Ti : Al : EB molar ration of 1 : 86: 4.6, 1 : 278 : 1.1 and 1: 643 : 2 for catalysts I,II and III respectively. Further increase in the ethyl benzoate concentration after the maximum value had been obtained, resulted in a decrease in the catalyst activity for the three catalyst systems. However, it can be seen also from Table 2, that before reaching the maximum, the trend of varying the overall rate of polymerization with ethyl benzoate concentration is different for each catalyst system.

Table (2): Effect of ethyl benzoate concentration on the catalysts activity and stereospecificity

Catalyst no.	[EB]/ mmol. dm^{-3}	$R_p \times 10^3$ mol. dm^{-3}. min^{-1}	% isotacticity
I (a)	0	4.4	50
	0.4	2.5	58
	0.8	5.4	60
	1.4	3.3	52
	2.0	1.1	40
	2.8	0.3	-
II (b)	0	20.1	45
	0.02	14.4	51
	0.04	18.8	54
	0.27	13.4	42
	0.40	8.4	34
III(c)	0	31.1	42
	0.055	49.1	36
	0.063	44.5	48
	0.130	23.2	40
	0.250	18.9	41
	0.490	13.3	43
	0.760	10.8	40

a) [Ti] = 0.175 mmol dm^{-3}; [Al] = 15 mmol dm^{-3}; solvent = EC 180
b) [Ti] = 0.036 mmol dm^{-3}; [Al] = 10 mmol dm^{-3}; solvent = heptane
c) [Ti] = 0.028 mmol dm^{-3}; [Al] = 18 mmol dm^{-3}; solvent = heptane
[4MP-1]=2mol. dm^{-3}, temp. = 40°C

This observation can be attributed to the difference in the percentage of titanium and to the different procedures used to prepare the catalysts.[16] The results in Table 2 have shown also that the stereoregularity of the polymers produced by the three catalyst systems increased to maximum value with increasing ethyl benzoate concentration, then further increase in ethyl benzoate concentration led to a decrease in the stereoregularity of the polymers. The observed increase in activity and of the supported catalyst systems with small addition of ethyl benzoate are probably due to an increase in the values of the concentration of active centres and the propagation rate constant[17]. However, the decreases in activity and stereospecificity can be attributed to a decrease in the number of active centres as a result of the poisoning of atactic and isotactic active sites by the adsorption of ethyl benzoate and to the decrease in the alkylation of the titanium chloride. Fuller analysis of the role of ethyl benzoate on the activity and stereospecificity of the $MgCl_2|EB|TiCl_4|Al(iBu)_3|4MP\text{-}1$ catalyst system will be presented in a later publication[17].

Effect of ethyl benzoate on the molecular weight of poly(4-methylpentene-1) :-

The effect of ethyl benzoate concentration on the molecular weight was studied for polymers which had been prepared by using supported catalyst III and the results are shown in Table 3. On the basis of these results, the molecular weight was found to increase with increasing ethyl benzoate concentration which indicates that the ethyl benzoate decreased the rate of chain transfer with aluminium alkyl.

Table (3): Variation of the polymer molecular weight with ethyl benzoate concentration

[EB]/ mmol dm^{-3}	$[\eta]$/dl g^{-1}	$\bar{M}_n \times 10^{-5}$
0	2.38	1.12
0.25	4.20	2.25
0.49	4.62	2.53

Catalyst III : [Ti] = 0.028 mmol dm^{-3};
[Al] = 18 mmol dm^{-3}; [4MP-1] = 2 mol dm^{-3}
temperature = 40°C, solvent: heptane;
time of polymerization = 30 minutes.

REFERENCES

1. Mitsui Petrochemicals Ind., Ltd, U.S.A. Patent, 3, 642, 746, 1968.
2. Hoechst AG., Belgian Patent, 755, 185, 1969.
3. Montecatini, Belgian Patent, 744, 221, 747, 864, 1969.
4. U. Giannini, Makromol. Chem., Suppl. 5 , 216, 1981.
5. T. Keii, Makromol. Chem., 183, 2285, 1982.
6. N. Kashiwa and J. Yoshitake, Makromol. Chem, Rapid Commun., 4, 41 1983.
7. P. Galli, Proc. IUPAC Macro 1982, 28th Makromol Symposium, Amherst, MA,July, 12 - 16, 1982.
8. B.L. Goodal, in "Transition Metal Catalysed Polymerization" R.P., Quirk et al, Ed., Harwood academic publishers, New York, 355, 1983.
9. P.J. Tait and M.A. Abu-Eid, A.C.S. Meeting, Seattle. 1983.
10. P.J. Tait and M.A. Abu-Eid, Proc. X, Iberoamerican Symposium on catalysis, Lisbon, Vo. 1, 163, 1984.
11. P.J. Tait, Future Aspects of Olefin Polymerization , Yokohama, Japan, July 4 - 6, 1985.
12. I.D. Mckenzie, P.J. Tait and D.R. Burfield, Polymer, 13, 307, 1972.
13. G. Natta and I. Pasquon, Adv. Catalysis, 11, 1959.
14. A. Hoffman, B. Frier and P. Condit, J. Polym. Sci., C4, 109, 1963.
15. P.J. Tait, M. A. Abu-Eid and A.E. Enenmo, Am. Chem. Soc. Meeting, Chicago, U.S.A., 309, 1985.

16. Keii, T., Suzuki, E., Tamurm, M. And Doi, Y., International Symosium, Transition Metal Catalysed Polymerization Unsolved Problem, Michigan, Aug. 17-21, 1981.

17. M. Abu-Eid, P.J. Tait, An-Najah J. Research (1992), in Press.