

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

2. ACTIVE CENTRE DETERMINATION

By

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ملخص

عند بلورة 4-ميثل بنتين -1- بواسطة العامل المساعد المتكون من كلوريد المغنيسيوم |بنزوات الاثيل| رابع كلوريد التيتانيوم |ثلاثي ايزوبوتيل الالمنيوم ، تم دراسة تأثير تركيب العامل المساعد على عدد المراكز النشيطة ، ثابت سرعة تفاعل الادخال ، سرعة وثابت سرعة انتقال الكيل الالمنيوم الممتص وثابت سرعة امتصاص 4-ميثل بنتين -1- على العامل المساعد . كما تم دراسة ونقاش تأثير تركيز الكيل الالمنيوم على سرعة تفاعل البلمرة وتأثير تركيز بنزوات الاثيل على عدد المراكز النشيطة في العامل المساعد وسرعة انتقال الكيل الالمنيوم .

ABSTRACT

In the polymerization of 4-methylpentene-1- by using the $MgCl_2$ |EB| $TiCl_4$ | $Al(iBu)_3$ catalyst systems, the effect of catalyst composition on the number of active centres, propagation rate constant, rates of transfer and rate constants for transfer with respect to adsorbed aluminium alkyl and monomer have been reported. The role of aluminium alkyl on the rate of polymerization and the effect of ethyl benzoate on the number of active centres and rate of transfer with respect to aluminium alkyl have been discussed .

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INTRODUCTION

In previous work^[1], kinetic studies have been made on the polymerization of 4-methylpentene-1- by using the $MgCl_2$ |EB| $TiCl_4$ - $Al(iBu)_3$ catalyst system.

The polymerization procedure and the method used for catalyst preparation were presented in earlier publications^[1,2].

In this work, the number of active centres C_0 , and the propagation rate constant k_p were determined in order to understand the role of ethyl benzoate, EB, on the rate of polymerization of this catalyst system. We also study the effect of the procedure used to prepare the catalyst on the number of active centres and the effect of catalyst composition on the rates transfer and rate transfer constants. Four distinct methods for active centre determination have been reported in literature^[3,6]. In this work tritium labeling quenching techniques is used since it is the most reliable one.

EXPERIMENTAL

Materials:

Details of catalysts have already been published^[1].

Tritium labeled water: This was supplied by U.K.A.E.A. Radiochemical Centre. Amersham. at an activity of $5 Ci.cm^{-3}$ Tritium labeled methanol: The labelled methanol was prepared by adding $0.1 cm^3$ of tritium labeled water to $25cm^3$ of dried methanol and 8 g of sodium methoxide in a specially constructed $100 cm^3$ single unit fractionation apparatus. Dilution of the active methanol with threefold proportion of

inactive methanol was found to be satisfactory for quenching of the polymerization at a specific activity of about 4.5×10^{11} dpm. mol⁻¹. Scintillation solutions: The NE 221 scintillation gel was purchased from Nuclear Enterprises (G.B.) Lt.d, Edinburgh, and was used for polymer activity measurements. A scintillation solution of 4 g .dm⁻³ PPO, 0.4 g .dm⁻³ POPOP in toluene was used for measuring the activity of the labeled methanol.

Tritium labeled standards: n-hexadecane tritium was supplied from the Radiochemical Centre.

PROCEDURE

Polymerization runs were carried in a long necked 30cm³ flask under high vacuum. The reacting mixture was added in the following order, solvent, catalyst, monomer and aluminium alkyl. This order of addition was found to give better reproducibility. The percentage error in the polymer yield was found $\pm 5\%$.

To ensure complete quenching of the polymerization mixture, a tenfold excess of labeled methanol to aluminium alkyl was found satisfactory. On addition of labeled methanol to the polymerization mixture containing the MgCl₂ -supported catalyst, the colour changed from grey to white. The polymerization mixture was stirred for 10 minutes after quenching to ensure complete reaction.

The decontamination of the polymer samples was achieved by the following procedure,

- a) The polymer was first isolated and dried to constant weight..
- b) The polymer was finely powdered by freezing in liquid nitrogen and grinding with a pestle and mortar.
- c) The powdered polymer was then soxhlet extracted for 24 hours with four exchanges of methanol to ensure complete removal of the excess labeled methanol or other impurities.
- d) Finally the polymer was dried to constant weight in a vacuum oven at 80 °C.

The activities of tritium labeled poly (4-methylpentene-1) samples were determined by dispersing about 0.1 g of the polymer sample in 12 cm³ NE 221 scintillation gel in a transparent vial. Sampling reproducibility was found to be within $\pm 2\%$.

The tritium-labeled methanol was assayed in a scintillation solution previously specified. The percentage error in finding the activity of methanol was found $\pm 3\%$.

All radioactive measurements were made with a PACKARD, TRICARB 300 C and 300 CD Liquid Scintillation System.

KINETIC ISOTOPE EFFECT

The kinetic isotope effect was determined by slow addition of labeled methanol to the polymerization mixture as described previous-

ly^[7]. The isotope correction factor was found to be between 1.7 - 3 depending on the concentration of tritiated methanol and the titanium loading of the supported catalyst.

The reproducibility of measuring of the kinetic isotope effect was found within $\pm 12\%$, values between 1 and 3.7 for the correction factor have been reported by different authors.^[8-12]

RESULTS AND DISCUSSION

The concentration of active centres, C_* , and the rate of transfer with respect to aluminium alkyl, R_{tr} , were determined from metal polymer bond values using an extrapolation procedure. The concentration of metal polymer bonds, (MPB), was determined from the equation^[9],

$$[\text{MPB}] = \frac{KAG}{a} \quad \dots(1)$$

where A is the specific activity of the polymer in dpm.g^{-1} , G the yield of polymer at the time of quenching in g. dm^{-3} , a the specific activity of the methanol in dpm.mol^{-1} and K is the correction factor for the isotope effect Figure 1 shows a typical plot of [MPB] versus time for catalyst III.

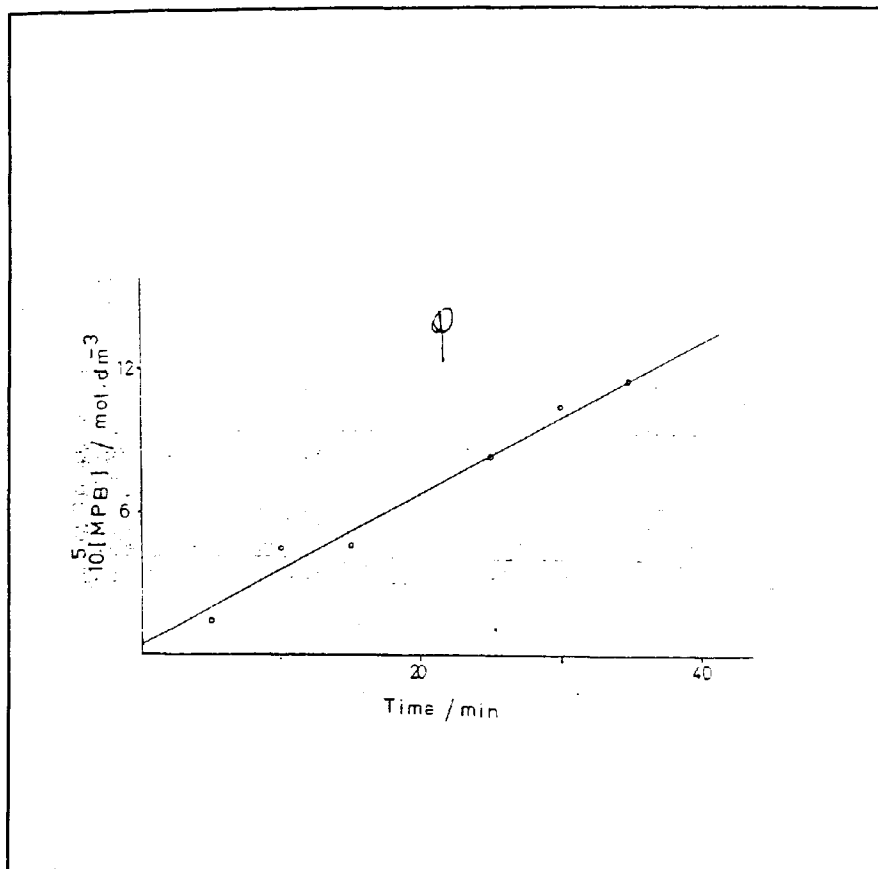


Figure 1: Plot of [MPB] versus time for catalyst III at 40°C.
 [Ti] = 0.028 mmol.dm⁻³; [Al] = 18 mmol.dm⁻³;
 [4MP-1] = 2mol.dm⁻³ ; solvent : heptane.

The increase in [MPB] with time can be attributed to transfer reactions with aluminium alkyl as shown in the following equation^[13],



Therefore R_p was obtained from the slope of the linear plot, whereas C_p^* was determined from the plot of $[MPB]$ versus $\log(100 - \% \text{ conversion})$ rather than polymerization time or $\% \text{ conversion}$. The above plot was preferred due to the initial settling period and to the decrease in monomer concentration with polymerization time, which make the plot of $[MPB]$ versus $\% \text{ conversion}$ non linear.

Figure 2 shows a typical plot of $[MPB]$ versus $\log(100 - \% \text{ conversion})$ for catalyst III.

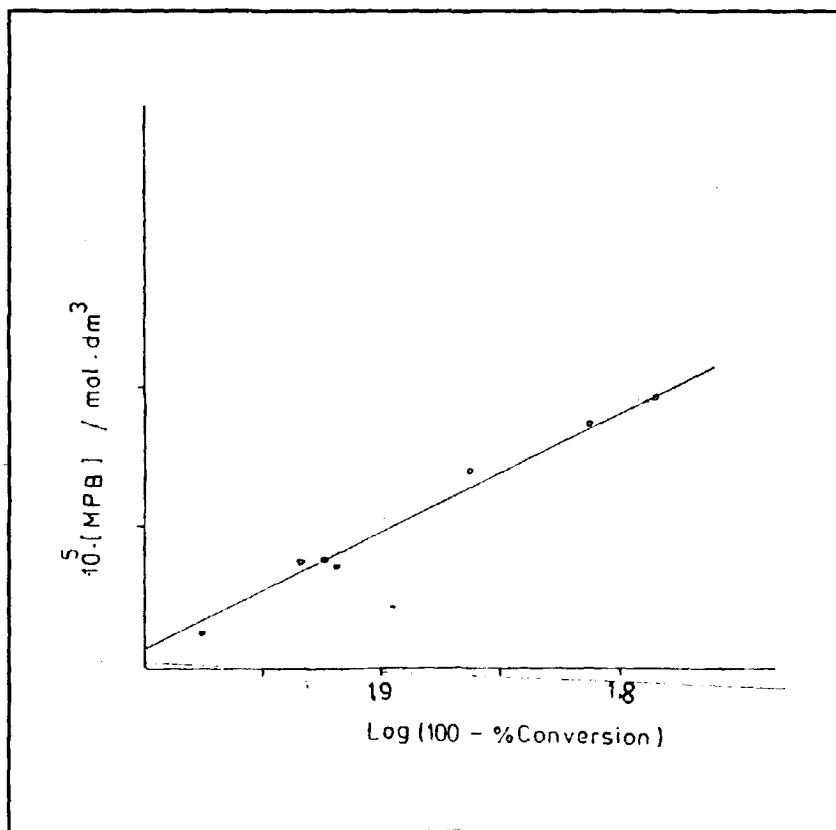


Figure 2: Plot of $[MPB]$ versus $\log(100 - \% \text{ conversion})$ for catalyst III at 40°C .

The apparent values for the rate constant for chain propagation, k_p , can be calculated from the simplified equation^[33],

$$R_p = k_p C_o^* [M] \quad \dots(3)$$

Where R_p represent the rate of propagation and $[M]$ is the concentration of monomer

Effect of the catalyst composition on the C_o^* , R_u and k_p values:

In a previous paper^[1], we have reported that the catalyst activity can increased by a factor of 44 when the catalyst is prepared by the proper method. This series of experiments were performed in an attempt to investigate the effect of the procedure used to prepare the catalyst on the activity and stereoregularity of the polymer and the results are shown in Table 1.

Table 1: Variation of C_o^* , R_u , k_p on the method of catalyst preparation

Catalyst number	Solvent	R_p $[[Ti]]$ mol.min ⁻¹ (mol Ti) ⁻¹	$C_o^* \times$ 10^3 mol. (mol Ti) ⁻¹	$R_u \times 10^7$ mol.dm ⁻³ . min ⁻¹	K_p [dm ³ . min ⁻¹ . mol ⁻¹
I	EC 180	25.1	31.4	1.9	398
II	Heptane	558	190	22	1468
III	Heptane	1111	290	31	1916

(4MP-1) = 2 mol. dm⁻³

temperature = 40°C

It can be seen from Table 1 that by improving the method of preparation of the $MgCl_2$ - supported catalyst, the C_2^* value has increased nine times and the k_p value has increased by a factor of five. Comparing the results of catalysts I and II indicate that the efficient drying of the anhydrous $MgCl_2$ before treatment with ethyl benzoate and titanium tetrachloride, led to increase in both the number and reactivity of the active centres.

However, the results of catalysts II and III illustrate the effect of the molar ratio of $MgCl_2$: $TiCl_4$ on C_2^* and k_p values. The increased catalyst III activity was found also to be due to an increase in both the number and reactivity of the active centres. In catalyst II the amount of $TiCl_4$ added to the $MgCl_2$ /EB support was not enough to replace the ethylbenzoate and to fill all the free $MgCl_2$ crystalline surface vacancies.

Goodall^[14] has reported that during the treatment of the product of ball-milled $MgCl_2$ /EB, with $TiCl_4$ the ethyl benzoate was lost not only from the weakly bonding sites on the lateral faces of the support but also from the strongly co-ordinating corner sites. This conclusion of Goodall^[8] can be used to explain the increase reactivity of the active centres, k_p , with increased amount of $TiCl_4$ added to the support.

Effect of aluminium alkyl concentration on metal polymer-bond concentration:

The polymerization runs were carried out at constant catalyst and monomer concentrations. The reaction times were 40 and 30 minutes for catalysts II and III respectively. The results obtained for catalysts II and III are summarized in Figures 3 and 4.

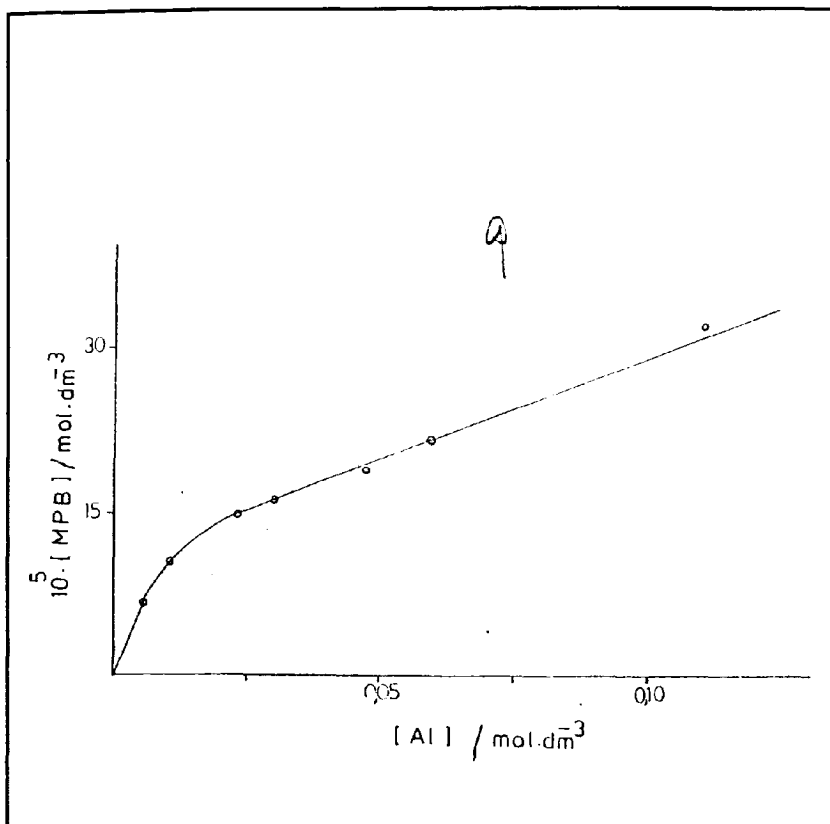


Figure 3: Plot of $[MPB]$ versus $[AI]$ for catalyst II at 40°C .
 $[Ti] = 0.036 \text{ mmol} \cdot \text{dm}^{-3}$; $[4MP-1] = 2 \text{ mol} \cdot \text{dm}^{-3}$
solvent : heptane.

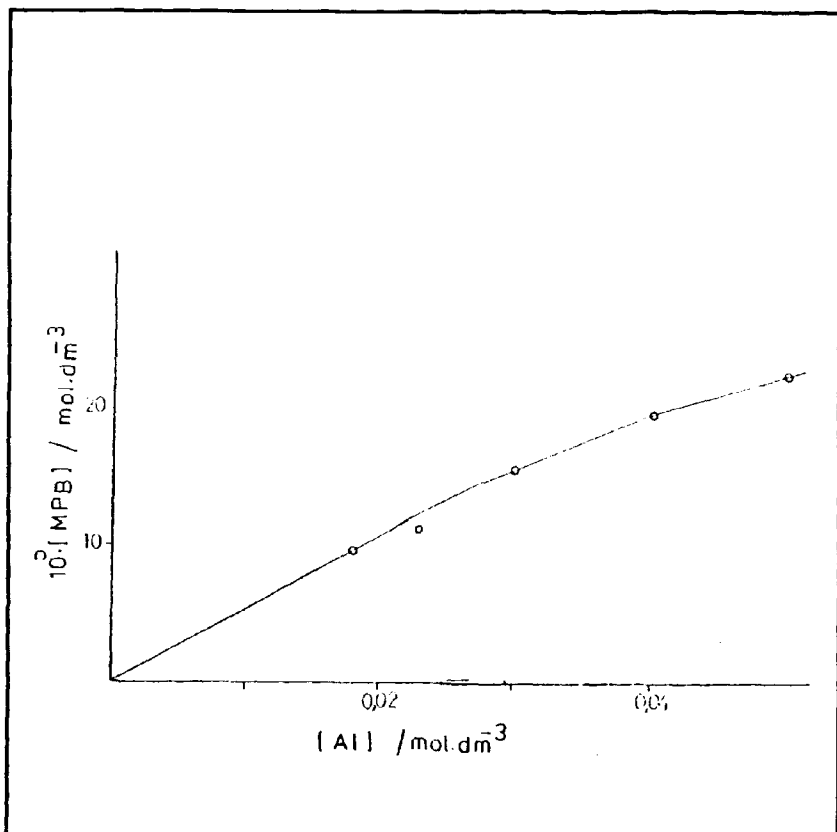


Figure 4: Plot of [MPB] versus [Al] for catalyst III at 40°C.

[Ti] = 0.028 mmol.dm⁻³; [4MP-1] = 2 mol.dm⁻³;

solvent : heptane.

The non linear plot obtained in figures 3 and 4, indicate that the rate of transfer with aluminium alkyl was not directly proportional to the aluminium alkyl concentration in the solution.

It is more likely however, that transfer would be with adsorbed metal alkyl, where the rate of chain transfer can be described by a Langmuir adsorption isotherm as suggested by Tait et al^[13]. Thus,

$$R_{ta} = k_a Q_A C^* \quad \dots (4)$$

where, k_a is the rate constant for chain transfer with adsorbed aluminium alkyl, and

... (5)

$$Q_A = \frac{K_A [A]}{1 + K_A [A] + K_M [M]}$$

where $[M]$ and $[A]$ are the equilibrium concentrations for monomer and metal alkyl, and K_A and K_M are the equilibrium constants for the respective adsorption equilibrium. Hence.

... (6)

$$\frac{C^*}{R_{ta}} = \frac{1}{k_a} + \frac{1 + K_M [M]}{K_a K_A [A]}$$

Figures 5 and 6 show that the plots of $\frac{C^*}{R_{ta}}$ versus $\frac{1}{[A]}$ for catalysts

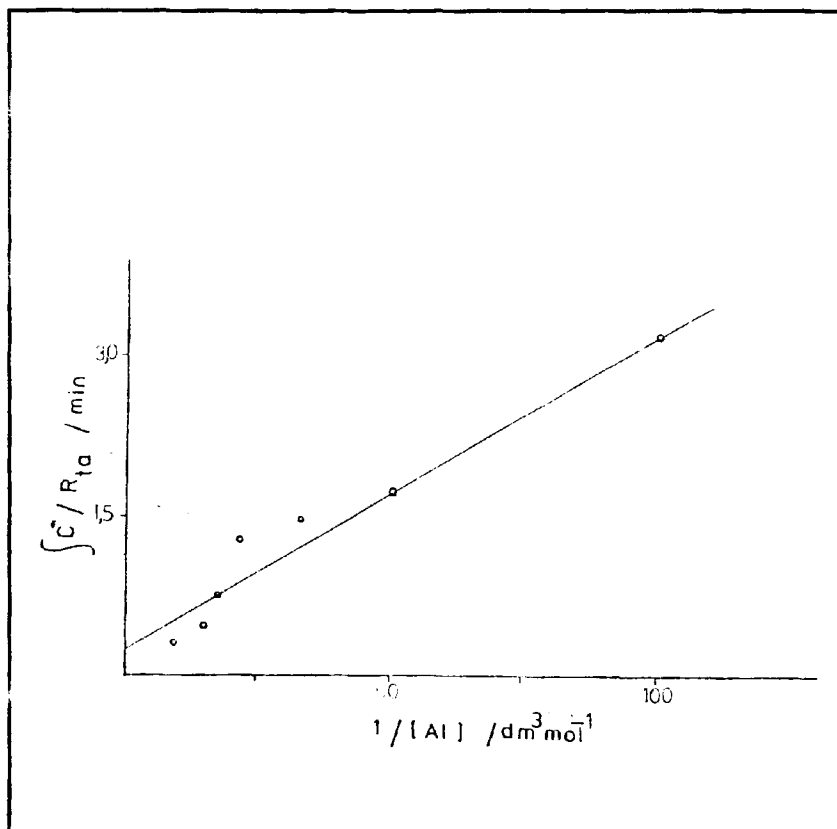


Figure 5: Plot of $\int \frac{C_a^*}{R_a}$ versus $\frac{1}{[Al]}$ for catalyst II at 40°C.

II and III are linear and with positive intercept, thus confirming that adsorption of aluminium alkyl may be described by a Langmuir type isotherm.

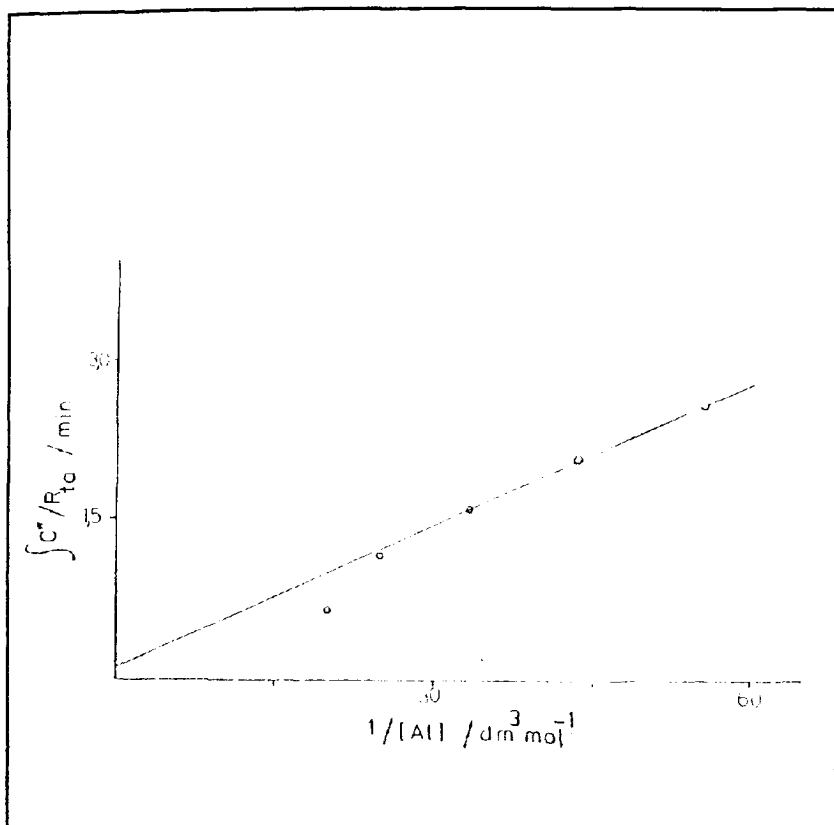


Figure 6: Plot of $\int \frac{C^*}{R_{p0}}$ versus $\frac{1}{[Al]}$ for catalyst III at 40°C.

Effect of monomer concentration on the metal polymer-bond concentration.

This study was carried out at constant catalyst, aluminium alkyl concentration and reaction times. Figure 7 shows the plot of [MPB] versus [4Mp-1] for catalyst II.

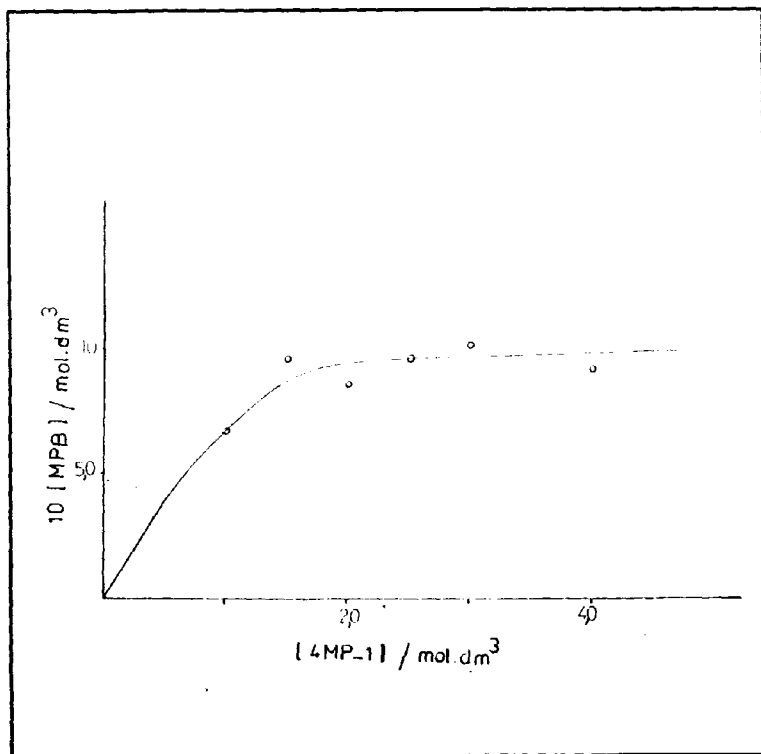


Figure 7: Plot of [MPB] versus [4MP-1] for catalyst II at 40°C.

$[Tl] = 0.036 \text{ mmol.dm}^{-3}$; $[Al] = 10 \text{ mmol.dm}^{-3}$,

solvent : heptane.

In both catalysts, the [MPB] fell sharply at low monomer concentration as found previously^[13] for the $VCl_3|AlR_3|4MP-1|$ benzene catalyst system.

In order to evaluate K_A and K_M , the following equation was used^[9],

....(7)

$$\text{pecific activity} = \frac{D[1 + K_M[M] + (1 + K_a t) K_A[A]]}{K_M[M]}$$

where D is a constant.

The plots of specific activity versus $1/[4MP-1]$ for catalysts II and III are linear as shows in Figures 8 and 9.

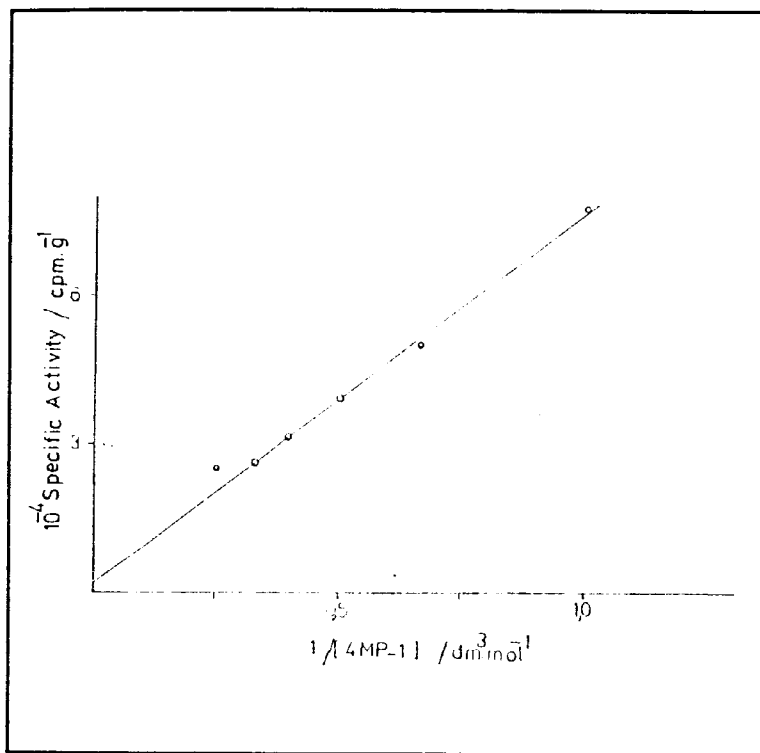


Figure 8: Plot of the specific activity of Polymer versus $\frac{1}{[4MP-1]}$

for catalyst II at 40°C.

[Ti] = 0.036 mmol.dm⁻³, [Al] = 10 mmol.dm⁻³, solvent : heptane.

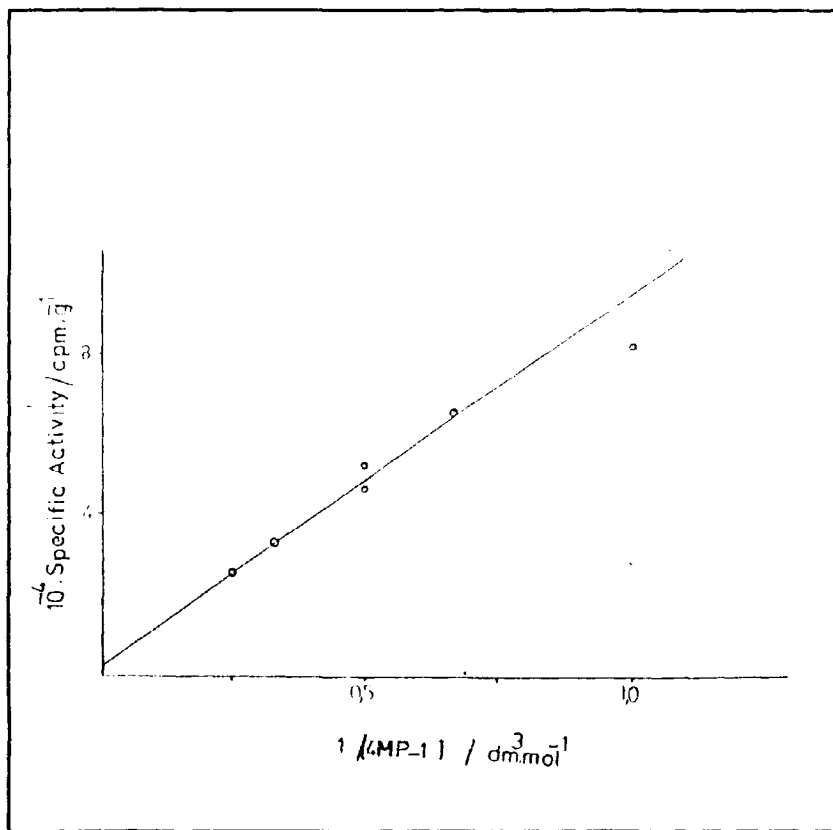


Figure 9: Plot of the specific activity of Polymer versus $\frac{1}{[M.P-1]}$

for catalyst III at 40°C.

$[T] = 0.028 \text{ mmol.dm}^{-3}$; $[Al] = 18 \text{ mmol.dm}^{-3}$, solvent : heptane.

Equations 6 and 7 were used to evaluate K_A and K_M for catalyst II and III. The calculated values of K_A and K_M allows the determination of Q_A and Q_M for each catalyst. Table 2 show the calculated values of K_A , K_M , Q_A and Q_M for catalyst II and III. These results indicate the importance of the procedure used to prepare the catalyst on the values of Q_M and K_A .

Table 2 : Effect of catalyst composition on k_p , K_A , K_M , Q_A and Q_M values

Catalyst System	k_p min ⁻¹	K_A dm ³ .mol ⁻¹	K_M dm ³ .mol ⁻¹	Q_A	Q_M
II	4.0	30.0	1.48	0.07	0.69
III	10.0	12.6	2.59	0.035	0.81

Variation of rate of Polymerization with aluminium alkyl concentration:

It was suggested in an earlier paper^[1] that the decrease in the maximum rate of polymerization with increase in metal alkyl concentration was due to competitive adsorption of aluminium alkyl with monomer. Thus, if the rate of polymerization is related to adsorbed monomer, then

$$R_p = K_p Q_M C_* \quad \dots(8)$$

where K_p is the true propagation constant.

The effect of aluminium alkyl concentration on Q_M , Q_A and R_p is shown in Table 3 for catalysts III.

Table 3 : Variation of Q_M with $[Al(iBu)_3]$

$[Al]$ mmol. dm^{-3}	$10^3 - R_p$ mol. dm^{-3} .min $^{-1}$	Q_M	Q_A	$10^6. R_{ts}$ mol $^{-3}$ min $^{-1}$
18	31.1	0.81	0.035	3.1
23	29.0	0.80	0.045	3.6
30	3.0	0.79	0.058	5.2
40	29.0	0.77	0.075	6.5
50	19.0	0.76	0.093	7.6

Catalyst III (3.4 % Ti)

$[Ti] = 0.028 \text{ mmol.dm}^{-3}$; $[4MP-1] = 2 \text{ mol.dm}^{-3}$

temperature = $40^\circ C$; solvent : heptane

It can be seen that when the concentration of aluminium alkyl increased the values of Q_A and R_{ts} increased, while the value of Q_M decreased.

Thus the decrease in the rate of propagation when the aluminium alkyl concentration is increased can be attributed to the decrease in the Q_M value. Whereas the increase in the R_{ts} value can be explained by the increase in the Q_A value.

Effect of catalyst composition on the rate constant for chain transfer with adsorbed monomer:

The rate of transfer with monomer, R_{tm} , and the rate constant of transfer with monomer, K_{tm} , for catalysts II and III were determined

from interpretation of the molecular weight results on the basis of the theory described previously^[7,14] and the results are listed in Table 4.

Table 4: Effect of catalyst composition on the values of molecular weight and chain transfer constant

	$\bar{M}_n \times 10^{-5}$	$M_{n_T} \times 10^5$	$R_m \times 10^7$ mol. dm ⁻³ min ⁻¹	K_m min ⁻¹
Catalyst II	0.88	3.58	109.9	3.08
Catalyst III	1.12	5.65	161.9	3.11

The number average molecular weight of poly (4-methylpenten-1), M_{n_T} , was obtained by assuming that each labeled chain contained one tritium atom. Then the following relation was used,

$$\bar{M}_{n_T} = \frac{\text{specific activity of quenching methanol (dpm. mol}^{-1}\text{)}}{\text{specific activity of polymer (dpm. g}^{-1}\text{)} \times K} \dots (9)$$

where K is the correction factor for the kinetic isotope effect.

Experimentally and theoretically determination values of the molecular weights of polymers obtained from catalysts II and III are recorded in Table 4. The results show that the experimentally determined values of the average molecular weights are lower than the molecular weights calculated from tritium data. This is to be expected since the later determination ignores transfer with monomer. Therefore, the results in Table 4 confirm the validity of the active center

determination method, which has been used for studying the $MgCl_2$ - supported catalyst systems.

The effect of ethyl benzoate on the $MgCl_2$ |EB| $TiCl_4$ |Al (iBu)₃ |4MP-1 catalyst system.

The effect of ethyl benzoate concentration on the number of active centres was studied for catalyst III. The number of active centres was determined for ethyl benzoate concentration of 0, 0.05, 0.25 and 0.49 mmol. dm⁻³. Whilst the concentration of catalyst, aluminium alkyl and monomer were kept constant. The results obtained are shown in Table 5.

Table 5 : Effect of [EB] on the value of C^* and R_p

[EB] mmol.dm ⁻³	$R_p \times 10^3$ mol. dm ⁻³ .min ⁻¹	$C^* \times 10^3$ mol (mol Ti) ⁻¹	$R_p \times 10^7$ mol.dm ⁻³ .min ⁻¹
0.00	31.1	290	31.0
0.055	49.1	320	24.8
0.250	18.9	82	8.3
0.490	13.3	45	3.3

Catalyst III % Ti = 3.4

[Ti] = 0.028 mmol.dm⁻³,

[Al] = 18 mmol.dm⁻³

[4MP-1] = 2 mol .dm⁻³,

temperature = 40°C.

Solvent : heptane

It can be seen that the concentration of active centres increased from 29 mol % Ti to 32 mol % Ti with slight addition of ethyl

benzoate and then decreased from 32 mol % Ti to 4.5 mol % Ti with further increases in ethyl benzoate concentration. The initial increase in the number of active centres is very small and can be considered to be within the limits of experimental errors.

Since the rate of polymerization is governed by equation 8, then the observed increases in the activities of the supported catalyst system with small additions of ethyl benzoate are probably due to an increase in the value of Q_M and K_p . The increase in the value of Q_M can be attributed to removal of the adsorbed aluminium alkyl species from the catalyst surface by complexation with ethyl benzoate. The results in Table 5 show also that the decrease in activity with increase in ethyl benzoate concentration is mainly due to the decrease in the number of active centres.

On the other hand, Table 5 shows that the rate of transfer with aluminium alkyl, R_{tr} , decreases sharply with increase in ethyl benzoate concentration.

According to equation 4, the decrease in the value of R_{tr} can be attributed to a decrease in the concentration of aluminium alkyl adsorbed and to the decrease in the number of active centres as is confirmed by Table 5. However, it was found previously^[1] that the increase in ethyl benzoate concentration led to an increase in the molecular weights of the polymers produced by the $MgCl_2$ -supported catalyst. Therefore, the effect of ethyl benzoate in increasing the molecular weights of the polymers can be explained by a decrease in the concentration of adsorbed aluminium alkyl. Moreover, the interaction between esters and aluminium alkyl has also been investi

gated by some workers^[12, 14-17], and they reported that such interaction leads to a decrease in the concentration of adsorbed aluminium alkyl.

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