# EFFECT OF EXTERNAL LEWIS BASE CONCENTRATION ON THE POLYMERISATION PARAMETERS OF STYRENE USING HIGH ACTIVITY ZIEGLAR-NATTA CATALYST

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## ABSTRACT

[1]Kinetic and active centre investigation were carried out on styrene polymerisation using the $MgCl_2$-supported, high activity Zieglar-Natta catalyst system: $MgCl_2$/Diisobutyl phthalate (DIBP)/$TiCl_4$/Al(i-Bu)$_3$ in toluene at 40°C. Rates of polymerization were followed by dilatometric procedure whereas active centre determinations were performed using a tritium quenching technique. The rate of polymerization was found to vary depending on the concentration of the Al (i-Bu)$_3$ co-catalyst used; and an optimum Al/Ti molar ratio of 500 was found to give the best activity for the catalyst. It was observed also that the rate of polymerisation decreases with increasing concentration of the external Lewis base (DIBP). Active centre studies have shown that the decrease in the rate of polymerisation with increasing concentration of the Lewis base was due to a decrease in the concentration of active polymerisation sites.

## INTRODUCTION

Throughout the history of $\alpha$-olefin polymerisation catalysis, the search for highly-active, well characterised industrial catalysts has been a constant driving force and produced many of the interesting scientific discoveries which have been made over the years. Of greatest significance has been the discovery in 1968 by the Montecatini Edison Company[1] and the Mitsui Petrochemical Industries[2] and also in 1969 by the Hoechst A.G.[3] that catalysts prepared from magnesium chloride, titanium tetrachloride and a Lewis base and activated by a mixture of trialkylaluminium and a Lewis base could polymerise propylene with a high yield and high stereospecificity. The desired characteristics of a good industrial catalyst have been highlighted elsewhere[4].

Due to the higher activity shown by magnesium chloride supported catalysts for $\alpha$-olefin polymerisation, there has been a considerable interest in the determination of active centre concentration and in the evaluation of values for rate constants for chain propaga-

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tion. Progress in these areas has been reviewed by Tait[5-6], Tait and Abu-Eid[7] and Chien et al.[8] for a number of magnesium chloride supported catalyst systems and monomers. For instance Tait[4] has concluded that much of the increased activity shown by the supported catalyst systems when used for the polymerisation of 4-methylpentene-1 arose from the considerable increase in active centre concentration and also from a more modest increase in propagation rate constants.

In this paper, we report the findings of some kinetic and active centre studies in the polymerisation of styrene (ST) using $MgCl_2$/Diisobutyl phthalate/$TiCl_4$/Al(i-Bu)$_3$ in toluene at 40°C.

## EXPERIMENTAL

### Chemicals

The monomer (ST) was supplied by BDH. The inhibitor present in the monomer was removed by extraction with aqueous NaOH (10% w/v) followed by washing with distilled water. After drying over anhydrous sodium sulphate, the monomer was fractionally distilled under reduced pressure. The middle fraction boiling at 40°C (under 20mmHg) was

collected and stored over molecular sieves.

Diisobutylpthalate (DIBP) and Toluene were also supplied by BDH and purified as for styrene.

Triisobutylaluminium in 99% purity was supplied by Aldrich Chemical Company Ltd. and was used without further purification.

Analar grade methanol was fractionally distilled over magnesium turnings using iodine as a catalyst[9]. The middle fraction boiling at 65°C at atmospheric pressure was collected and stored over a type 4A molecular sieves.

Tritium-labelled water was supplied by U.K.A.E.A. Radiochemical Centre, Amersham International Plc. The water had an activity of about 5 Ci cm$^{-3}$ and was diluted ten times by addition of 9cm$^3$ of dry inactive methanol.

Tritiated methanol was prepared by tritium exchange with inactive methanol in the presence of sodium methoxide[10]. Dilution of the active methanol with a three-fold proportion of inactive methanol was found to be satisfactory for quenching the polymerisation mixture.

NE221 scintillation gel was obtained from Nuclear Enterprises Ltd., Edinburgh, and was used for measuring the activities of both tritiated methanol and polymer.

### Catalyst

The catalyst was prepared using a modification of the preparation described in the patent literature[11]. Anhydrous magnesium chloride (35g) was dried for 93h at 205°C under vacuum and ball-milled for 70h at room temperature in the presence of SOCl$_2$ (5% of the weight of the support) and diisobutyl phthalate (MgCl$_2$:DIBP = 13:1). The ball-milled product was then treated with TiCl$_4$ (MgCl$_2$:TiCl$_4$ = 0.67:1), washed several times with 30cm$^3$ portions of dry n-heptane. The catalyst was then dried under vacuum at room temperature. The pale yellow solid catalyst gave the following on analysis: Ti = 3.7; Mg = 14.8; C = 15.5 and H = 5.8 (wt-%).

### Polymerisation procedure

The dilatometric technique was used to follow the course of the polymerisation. The technique has been widely used in the study of the rates of polymerisation[12-14]. In this procedure, it was necessary to prepare all polymerisation components in an identical manner so as to obtain reproducible results. The required amounts of solution were introduced into a previously evacuated dilatometer by means of a graduated syringe. Slurries of catalyst were made up in dry toluene by mixing amounts of catalyst in known volumes of toluene. The total volume of the polymerisation mixture was kept to about 1cm above the dilatometer bulb, stoppered and transferred to a thermostat set at the polymerisation temperature. The contents of the dilatometer bulb were stirred using an under-water magnetic stirrer. The polymerisation was monitored by periodically determining the height of the meniscus in the capillary using a cathetometer reading to ± 0.01mm.

It has been shown that[12,13]:

$$R_p = \frac{\% \text{ conversion } [M]}{t \times 100} \quad \text{.................. (1)}$$

(M) = monomer concentration
t = polymerisation time
$R_p$ = rate of polymerisation.

Thus, plots of % conversion versus time were constructed and rates of polymerisation in terms of % conversion/time were obtained by drawing tangents at appropriate time intervals. The rates in terms of conversion/time were converted into rates in units of mol.dm$^3$min$^{-1}$ when multiplied by the factor [M]/100. A graph of rate versus time was then plotted and the maximum rate ($R_{max}$) was taken as the rate of polymerisation, $R_p$, for a particular run.

Isotactic index (I.I.) values were obtained by extracting the polymer in boiling methyl ethyl ketone (MEK) and the % insolubles was taken as the I.I. of the polymer.

### Active centre determination

The method used for the determination of the active centre concentration is that devised earlier by Feldman and Perry[15] and involved quenching the polymerisation mixture with

tritiated methanol. To achieve a complete quenching of the polymerisation mixture and to have a polymer of sufficiently high activity, a ten-fold excess of tritiated methanol was used. The mixture was stirred for a further 10min after quenching to ensure complete reaction. Decontamination of the polymer was effected by treatment with acidified methanol for 30min. The polymer was then washed with methanol, filtered and then dried to constant weight. The polymer was then ground into a fine powder after freezing in liquid nitrogen and then extracted for 24h using a soxhlet extractor with two charges of methanol. The extracted polymer was then dried at 60°C under vacuum.

Polymer samples were prepared for scintillation counting by dispersing about 0.5g of polymer in NE221 scintillation gel in each counting vial. The radioactive counting was performed using a Parckard Liquid Scintillation Counting System, type TRI-CARB 300C which has the facility for determination of the plymer activity in cpm (count per minute) and the sample channels ratio values.

In this method,

$$[MPB] = \frac{KGA}{a} \quad \ldots\ldots\ldots\ldots (2)^{15}$$

where [MPB] is the concentration (mol dm$^{-3}$) of metal-polymer-bonds; K is a correction for the kinetic isotope effect (K.I.E.); G is the concentration (gdm$^{-3}$) of the polymer at time of quenching; a is the activity (dpmg$^{-1}$) of tritiated methanol and A is the activity of polymer (dpmg$^{-1}$).

Due to chain transfer reactions with aluminium alkyl, it can be shown[16] that:

$$[MPB]_t = C_o^* + R_{ta} t \quad \ldots\ldots\ldots\ldots (3)$$

where $C_o^*$ is the active centre concentration at time of quenching; $R_{ta}$ is the rate of chain transfer with aluminium alkyl and t is time of quenching. Therefore, when [MPB] is plotted against time, $R_{ta}$ may be obtained from the slope of the linear part of the curve, and $C_o^*$ from the intercept.

## RESULTS AND DISCUSSION

The variation of rate of polymerisation with time for the catalyst system is shown in Fig. 1. It can be seen that the kinetic profiles
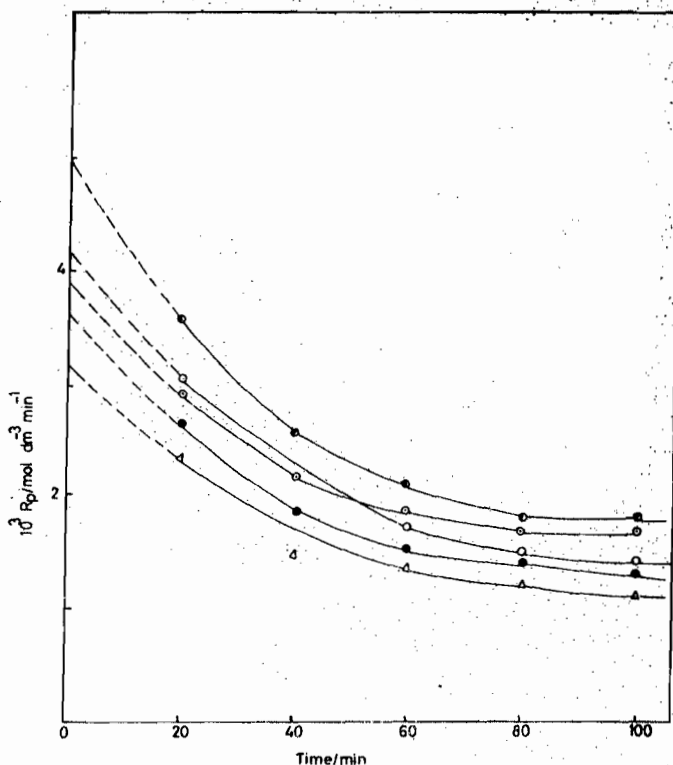
Figure, 1: Polymerization rates at various concentrations of Al(i-Bu)$_3$ [Al(i-Bu)$_3$]mmol dm$^{-3}$ 30(θ); 40(0); 50 (0); 55 (●) and 60(▲): (Ti) = 0.100 mmol dm$^3$ :(ST) = 2.0mol dm$^3$. Solvent = Toluene, Temperature = 40°C

are of decay type, which are characterised by high initial rates of polymerisation followed by a gradual decrease as the polymerisation time increased. Similar results have been reported by other workers[17] for the polymerisation of propylene and 1-decene using MgCl$_2$-supported catalysts. The decay in rate of polymerisation with time has been attributed to both physical and chemical[17,18] processes occurring during the polymerisation. The physical causes for the rate decay have been based on the concept of catalyst encapsulation by the growing polymer building a diffusion barrier to the monomer molecules[19]; whereas chemical causes, such as reduction of active centres by aluminium-alkyl, spontaneous breakage of metal-polymer bonds and interaction between the active centres and other components of the catalyst system, etc, have been identified as contributing to the overall catalyst chemical deactivation of polymerisation centres. It is important to point out that the degree of conversion of monomer to polymer (less than 30% in most cases) achieved during the course of the present in-

vestigation, was too low to suggest any major physical change as limiting the rate of polymerisation. The effect of Al/Ti molar ratio on kinetic behaviour of the catalyst system is depicted in Fig. 2 and it is quite evident that
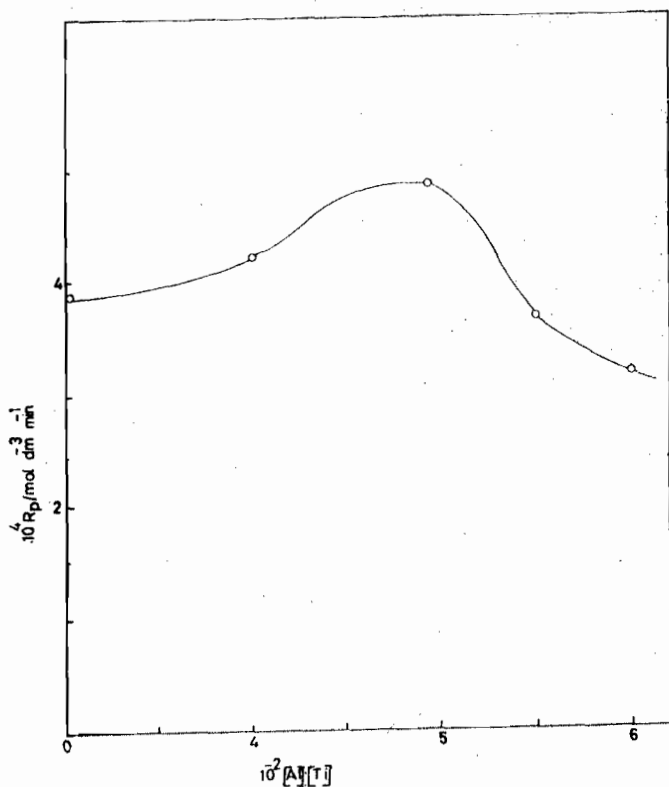


Figure 2: Variation of $R_p$ with $[Al]:[Ti]$ molar ratio.

the rate of polymerisation increased with increasing Al/Ti ratio up to a maximum value and then decreased with further increase in the Al/Ti ratio. Increase in $R_p$ at low Al/Ti molar ratio has been thought to be due to progressive activation of potential polymerisation centres by interaction with the aluminium alkyl[20] On the other hand, decrease in rate when the Al/Ti ratio increases beyond a certain limit is believed to be due to over-reduction of the transition metal by the aluminium alkyl[21]

The effect of the Lewis base on the rate/time kinetic profiles is shown in Fig. 3. Comparison of Figs. 1 and 3 shows that addition
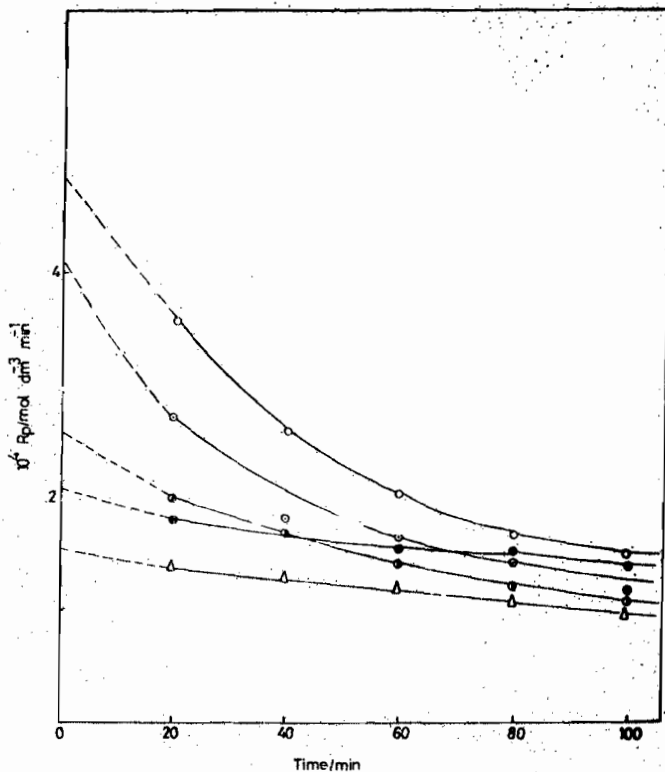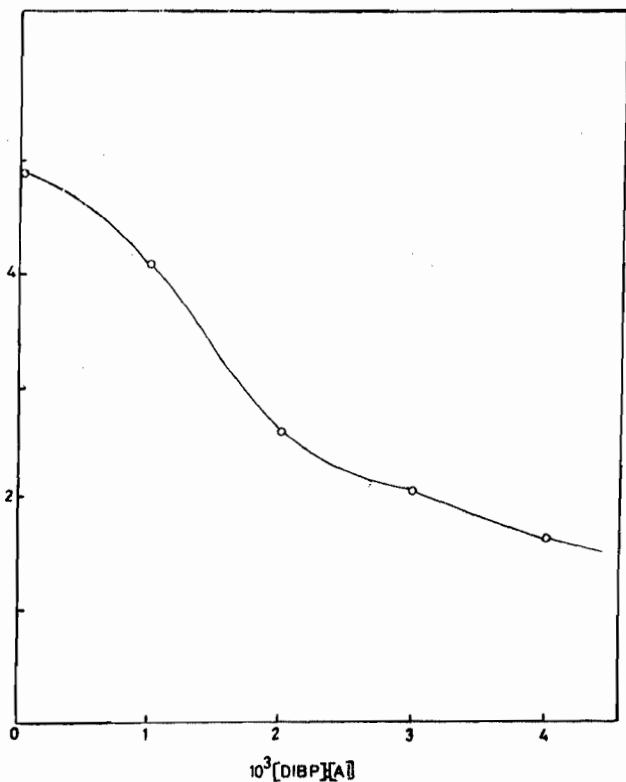


Figure. 3 Polymerization rates at various concenration DIBP
DIBP / mmol $dm^3$ = 0.0 (0) 0.05 (⊖) 0.10 (⊙) 0.15 (●) 0.20 (△) :
(Ti) = 0.10 mmol $dm^{-3}$ [Al (i-Bu)$_3$] = 50 mmol. $dm^{-3}$
(ST) = 2.0 mol $dm$ solvent = Toluene temprature 40°c

of external Lewis base stabilizes the rate/time curves though at the expense of catalyst activity; i.e. the rate of decay in $R_p$ with time of polymerisation (Fig. 1) is reduced as increasing concentrations of the base are added (Fig. 3). Fig. 4 illustrates the relationship between $R_p$ and base/Al molar ratio: and it is readily observed that the overall rate of polymerisation decreases with increase in the concentration of the external Lewis base (the decrease in rate being markedly higher at low DIPB/Al molar ratios). The decrease in rate with increasing Lewis base concentration is attributable to one or both of the following:

i.   decrease in alkylation of $TiCl_4$ as a result of complex formation between the base and the Al-alkyl, leading to a depletion of free Al-alkyl, especially at equimolar amounts
ii.  competitive adsorption of the Lewis base with monomer at active polymerisation sites.

In order to explain the observed deactivation effect of the base, $NEt_3$ on the polymerisation of 4-MP-1 at high base con-

4: Variation of $R_p$ with [DIBP]:[Al] molar ratio.



Figure 5: Influence of [DIBP] on $\overset{*}{C}_o$ and $K_p$ in the polymerization of Styrene

is interesting to compare Figs. 4 and 5 which show the variation of $R_p$ and $C_o^*$ with Lewis base concentration. Since rate of polymerisation was shown to be governed by the following equation[22]:
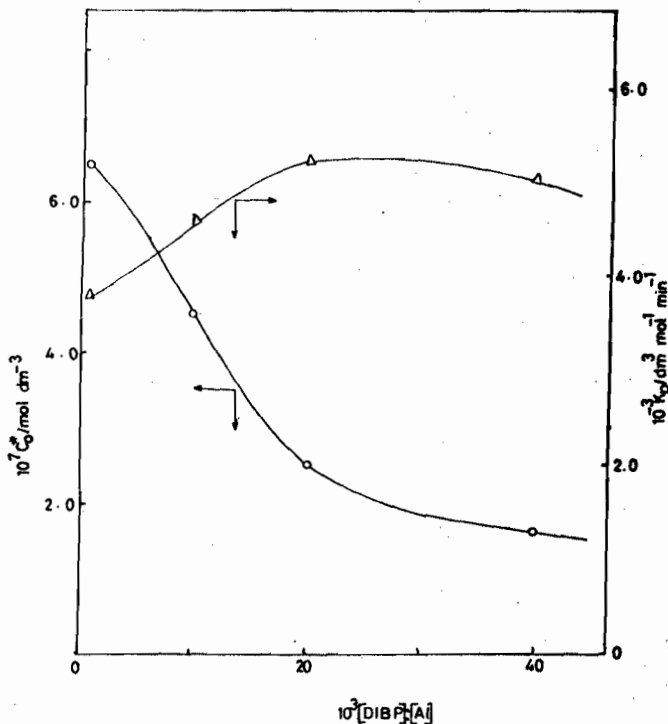
$$R_p = k_p \theta_M C_o^* \quad \text{.....................} \quad (4)$$

the decrease in $R_p$ observed in the present study was therefore due to a decrease in values of $C_o^*$. On the other hand, the rate of transfer with Al-alkyl, $R_{ta}$, decreased drastically with increasing concentration of the Lewis base. Since the concentration of Al-alkyl will be expected to decrease with increasing concentration of the Lewis base (as a result of complex formation), this may mean that chain transfer to the Al-alkyl will also decrease, thus decreasing the concentration of Al-alkyl adsorbed on the catalyst surface, $\theta_A$. It has been also shown that the rate of chain transfer is governed by the following[22]:

$$R_{ta} = k_a \theta_A C_o^* \quad \text{...........................} \quad (5)$$

Therefore a decrease in both $C_o^*$ and $\theta_A$ could then lead to a decrease in $R_{ta}$ as was indeed observed in the present study (Table 1).

centration. Tait et al.[22] proposed that competitive adsorption of the base with 4-MP-1 at the catalyst sites was responsible.

In order to gain a more complete understanding of the kinetic and mechanistic features of the catalyst system under study, a knowledge of the number of active centres present is quite essential.

Thus the effect of the Lewis base concentration on the number of plymerisation centres. $C_o^*$. and propagation rate constant, $k_p$. was investigated for the polymerisation system. This was performed by varying the concentration of the Lewis base while keeping the concentrations of the catalyst, Al-alkyl, and monomer constant. At each DIPB concentration. the concentration of active centres was determined from the intercept of the linear region of the plot of [MPB] versus time (equ. 3): whereas the rate of chain transfer with Al-alkyl. $R_{ta}$. was found from the slope of such a plot. Figure 5 shows variation of $C_o^*$ and $k_p$ with Lewis base /Al-alkyl ratios. It can be seen that $C_o^*$ decreases with increasing concentration of DIPB, but $k_p$ values increase with increasing concentration of the Lewis base. It

Table 1: Influence of DIBP on rate of chain transfer to Al-alkyl, $R_{ta}$.

| $10^3$ DIBP [Al(i-Bu)$_3$] | $10^8 R_{ta}$/moldm$^{-3}$min |
|---|---|
| 0.00 | 5.2 |
| 1.00 | 2.3 |
| 2.00 | 1.5 |
| 4.00 | 0.6 |

Conditions of polymerisation are:
[Ti] = 0.100mmoldm$^{-3}$; [ST] = 2.0moldm$^{-3}$
MeOT Activity = 1.24 x $10^{12}$dpm mol$^{-1}$
Kinetic Isotope Effect (K.I.E.) = 1.92.
Solvent = Toluene; and Temperature 40°C.

## CONCLUSION

The present study has revealed the following:

i. stabilisation of rate/time kinetic profiles by addition of external Lewis base;

ii. the decrease in rate of polymerisation with polymerisation time was due to a decrease in values of active centre concentration;

iii. increase in DIBP concentration led to a decrease in rate of transfer with Al-alkyl and an increase in the values of propagation rate constant.

The results provide valuable information concerning the factors controlling polymerisation of styrene by the MgCl$_2$ supported Ziegler-Natta catalyst system.

## ACKNOWLEDGEMENT

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