

Effects of Polymerization Parameters on Activity of Ethylene/Propylene Copolymerization Using $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ Catalyst System

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ABSTRACT

Semi-continuous ethylene/propylene copolymerization is carried out at atmospheric pressure in toluene using $\text{Cp}_2\text{ZrCl}_2/\text{methylaluminumoxane}$ catalyst system. The effects of operating conditions including polymerization temperature, monomer feed composition, catalyst/cocatalyst molar ratio and reaction time (as mean residence time of the catalyst system in reactor) on kinetics of the copolymerization is investigated. The catalyst activity seems to increase with a decrease in catalyst concentration but decreasing with either propylene/ethylene molar ratio in feed or with reaction temperature. Chain transfer to propylene is shown to be the main reason for catalyst deactivation. The rate-time profiles are also shown to be of decaying character after passing a maximum indicating that the deactivation of active growing centre occurs as soon as the catalyst components are mixed in the presence of monomer mixture.

Key Words:

ethylene/propylene copolymerization;
bis(cyclopentadienyl) zirconium dichloride/methylaluminumoxane catalyst; kinetics; reaction conditions.

INTRODUCTION

Random ethylene/propylene copolymers are commercially important elastomers and are presently manufactured in the presence of vanadium-based Ziegler-Natta catalysts [1,2]. The vanadium catalysts are, however, of short lifetime and exhib-

it low productivity[1-3]. Additionally, they do not terpolymerize unconjugated dienes such as 5-ethyliden-2-norbornene or dicyclopentadiene for successive vulcanization purposes [4]. Beside these limitations, there are still a few drawbacks to the use

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of homogeneous vanadium catalysts in producing random ethylene/propylene copolymers. These drawbacks are: (1) at least one of the catalyst components needs to contain a halogen atom, mainly chlorine, (2) they form multiple active centres and causing broadening of molecular weight distribution, (3) high catalyst residues must be removed from final product, (4) and finally they are poisonous and thus restricting application of the product in medical fields. As a consequence of these handicaps, research has long made efforts to develop novel catalysts, being more efficient towards production of desirable polymer structures with high yields and hence elimination of expensive de-ashing processes.

In this connection, catalysts based on cyclopentadienyl compounds of group IV B transition metals have seemed to serve as an attractive alternation[5-8]. Cp_2TiCl_2/AlR_2Cl system was the first homogeneous catalyst examined for olefin polymerization[9-11]. However, the catalyst was found to be of poor activity for ethylene polymerization due to fast Ti reduction. According to a latter achievement, Kaminsky[12] and Even[13] observed 1000-fold increase in ethylene polymerization activity upon using methylaluminumoxane cocatalyst instead of aluminium dialkyl chloride. Sinn et al.[14] discovered that by substituting Zr in place of Ti, highly active catalysts are formed in the presence of methylaluminumoxane as cocatalyst. The super high productivity of such system in ethylene polymerization was reported to be associated with formation of high concentrations of active centres per unit of catalyst and to their longer life time compared to the Ti-based counterparts.

Kinetic studies of olefin polymerization involving the above mentioned catalyst systems and application of radio-quenching techniques have led to determination of the nature of propagating species, the result of which has indicated that only one type of active centre is produced during polymerization giving rise to the production of reasonably narrow molecular weight polymers[15]. An additionally important point of interest in developing metallocene or as sometimes called "Kaminsky-Sinn catalysts" is said to be the academic aim of introducing more simplified systems for mechanistic investigations of olefin polymerization [15-18]. In this respect, the studies of these systems have shed valuable light on the proposed catalytic cycles by mod-

elling some fundamental elementary reaction steps such as olefin insertion and alkyl migration[19].

Although research on metallocene catalyzed olefin polymerization and copolymerization has been the subject of several studies in recent years and Cp_2ZrCl_2/MAO has been described in many publications as a powerful homo and copolymerization catalyst, there seems to be lacking knowledge concerning kinetic factors influencing the catalyst activity and productivity [8,20,21]. It is, therefore, the aim of this work to undertake a careful examination on kinetic behaviour of the mentioned catalyst system when continuously applied to a reactor containing a mixture of ethylene and propylene monomers.

EXPERIMENTAL

Chemicals

Toluene of RG grade (from Riedel-de-Haen) and pentamethylheptane known as EC180, (from ICI, plc, now BASF) were used as catalyst preparation and polymerization solvents. The later is a hydrocarbon solvent consisting of two paraffinic isomers, 2,2,4,4,6 and 2,2,4,6,6 pentamethylheptane with a water content of ca. 20 ppm and a boiling point of about 180°C at atmospheric pressure. Before use, both solvents were double distilled over CaH_2 and finally dried by passing through a column containing a mixture of 4A and 13X molecular sieves. The metallocene catalyst, bis (cyclopentadienyl) zirconium dichloride (from Witco) and methylaluminumoxane (from Scherinc) were used after dilution with toluene in a dry box under high purity grade nitrogen atmosphere. The Al content of cocatalyst was said to be 4.5-5.5 wt%. Polymerization grade ethylene and propylene (from Messer-Gniehem) with 99.28% and 99.45% purity, respectively were passed through 4A and 13X molecular sieves before use. Ethylene was further purified just before mixing with propylene and entering the reactor by conducting it through columns containing CuO and Al_2O_3 .

Apparatus and Polymerization Technique

Copolymerizations were performed in pentamethylheptane (EC180) and toluene solvents semi-continuously. A 250 mL jacketed glass reactor fitted with an efficient water-cooled condenser was used to conduct the

copolymerizations. The reactor was of open-ended flange top type to facilitate the multiple addition of catalyst, cocatalyst solutions and pure solvent through individual inlets, whereas, the product mixture was discharged after a predetermined time interval. In such flow method, ethylene and propylene monomers were supplied to the reactor continuously via two restricting valves and a 3-way tap, where part of each monomer was consumed and its remainder was discharged and measured by a wet gas flowmeter. The catalyst and cocatalyst components were fed to the reactor as dilute solutions. Copolymerization experiments were performed within a wide range of temperature, cocatalyst/catalyst molar ratio, propylene/ethylene molar ratio and reaction time to study the effect of each variable on rate of the copolymerization. The product of each set of copolymerization was immediately quenched by blowing off the monomers, adding methanol and stirring in C₂H₅OH/HCl mixture to kill the catalyst residue. They were washed thoroughly with deionized water and dried overnight in vacuum oven at 65°C. The flow sheet of the polymerization system (set up at the Dept. of Chemistry, UMIST, UK) is shown in Figure 1.

Rate and Yield Calculation

The volumetric flow rate of the monomers supplied to the reactor was controlled by means of a system of pressure gauge and calibration of each monomer-orifice combination was carried out by measuring the volumetric flow rates. Propylene/ethylene molar ratios (P/E) of 50/50 to 80/20 were employed in this study. The total monomer volumetric flow rate was always checked at the start of any polymerization run. After purging the system with nitrogen for 20 min, EC180 or toluene was transferred from its reservoirs to the reactor by applying excess of nitrogen gas pressure. Once the temperature of the circulating water around the reactor had reached the required polymerization temperature (in the range 30°C to 60°C), a run was started by switching the nitrogen supply with the monomer gas mixture. After the establishment of steady state conditions in the reactor, a 40 mL polymer solution was collected into a conical flask and was quenched according to the procedure described earlier in experimental part. Generally 3-5 samples were collected for any specific set of polymerization conditions which normally showed almost identical yields (within ±6%). The

mean polymer yield was then calculated as follows:

$$\text{Yield/g(mmol cat)}^{-1} = \frac{\text{Mean polymer yield (g dm}^{-3}\text{)}}{[\text{cat}] \text{ in total liquid stream (mmol dm}^{-3}\text{)}}$$

The calculated rates were found to be closely distributed about their mean value, with a variation of about ±3%. Also good temperature control was achieved with a deviation of only 0.5°C. Catalyst concentrations below 2×10⁻⁶ mol dm⁻³ were not possible to use this continuously charged reactor due to low reproducibility. For sake of higher reproducibility, better heat control, higher stirring speeds and eliminating mass transfer effect, catalyst concentrations in rang of (2-13)×10⁻⁶ mol dm⁻³ were used in the proceeding parts of this work. Values of the polymerization rate, R_p, under steady state conditions were calculated using the following expression:

$$R_p = \frac{\text{Mean polymer yield (g dm}^{-3}\text{)}}{\text{Mean time (s)} \times [\text{cat}] \text{ in total liquid stream (mol dm}^{-3}\text{)}}$$

The rate has then units of gmol⁻¹s⁻¹. The reproducibility of the method for determination of yield and rate was checked via conducting two parallel polymerization

Table 1. Result of replicated ethylene/propylene copolymerization using CP₂ZrCl₂/MAO catalyst.

| Mean residence time (min) | Yield (g dm ⁻³) | R _p /EP (mol s) ⁻¹ /g | [Zr] × 10 (mol dm ⁻³) |
|---------------------------|-----------------------------|---|-----------------------------------|
| 10 | 2.62 | 2187 | 2 |
| 10 | 2.55 | 2129 | 2 |
| 10 | 2.45 | 2044 | 2 |
| 5 | 2.57 | 1713 | 5 |
| 5 | 2.63 | 1754 | 5 |
| 5 | 2.52 | 1675 | 5 |
| 2 | 10.40 | 1294 | 6.7 |
| 20 | 11.16 | 1388 | 6.7 |
| 20 | 10.69 | 1330 | 6.7 |

Condition; E/P molar ratio= 50/50, [Al]/[Zr] = 3000, temp= 40°C, solvent = toluene, and total monomer pressure = 1 atm.

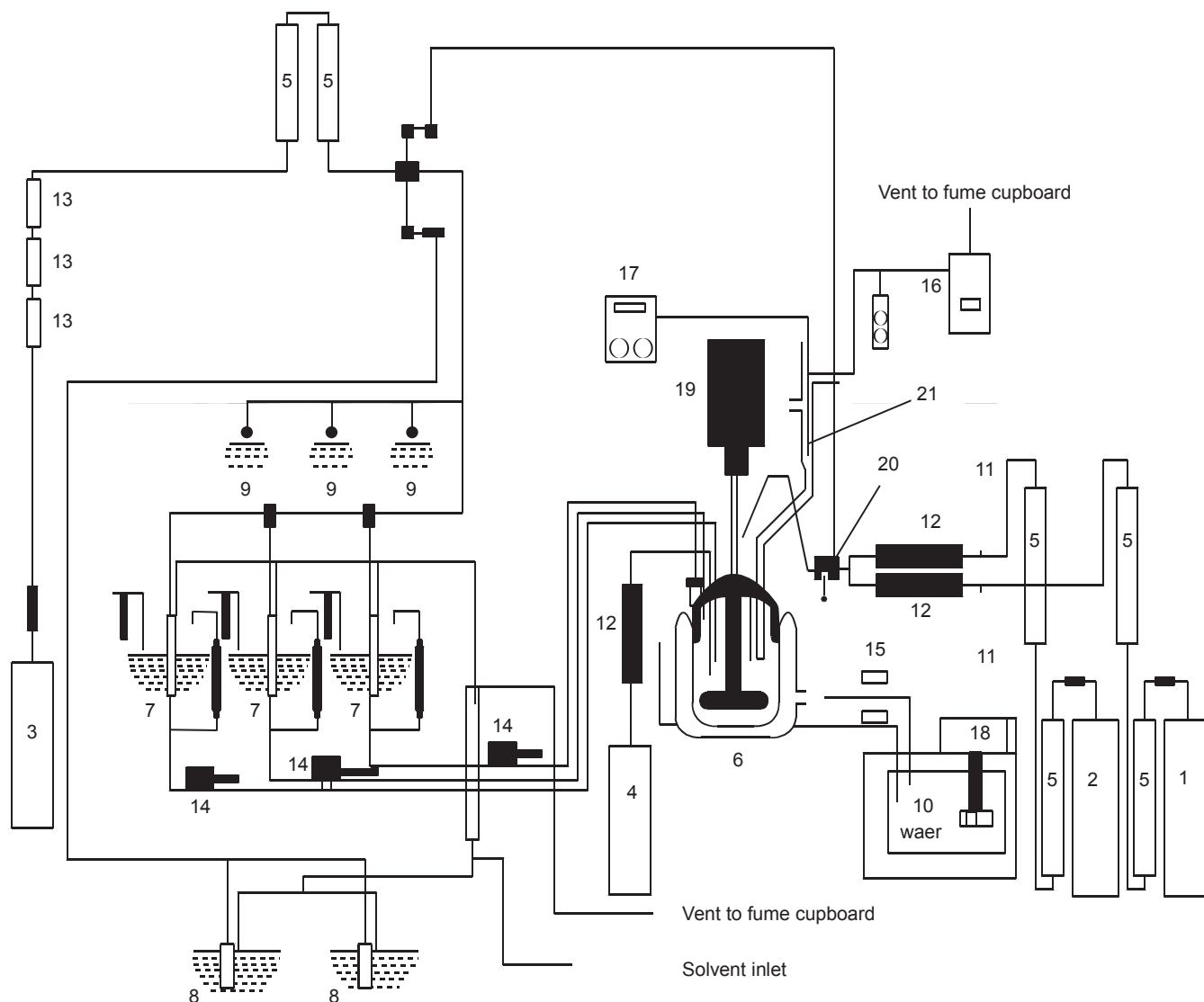


Figure 1. Flow sheet of the reaction system used in ethylene/propylene copolymerization: (1) Ethylene cylinder; (2) Propylene cylinder; (3) Nitrogen cylinder; (4) Hydrogen cylinder; (5) Drying columns (4A & 13x); (6) Reactor; (7) Reactor solution reservoir; (8) Solvent reservoir; (9) Stock solutions; (10) Thermostat bath; (11) Pressure gauges; (12) Restricting valves; (13) Drying bottles; (14) Metering pumps; (15) Circulating pump; (16) Wet gas flowmeter; (17) Digital thermocouple; (18) Control unit; (19) Motor shaft; (20) 3-Way tap; (21) Condenser and glass pocke.

runs for each set of reaction conditions. The data obtained from the test method are collected in Table 1 and they confirm that the method is accurate and valid.

RESULTS AND DISCUSSION

Effect of Solvent

Employing the apparatus and techniques described in

experimental section, ethylene and propylene were copolymerized with the catalyst under study. It was first intended to perform the process in EC180, however, due to low activity and hence low yield at several different reaction conditions, it was decided to follow the catalyst behaviour in toluene. The comparison of the activity of catalyst system in the two solvents is shown in Figure 2. Both activity and the shape of rate-time profile change drastically by substituting EC180

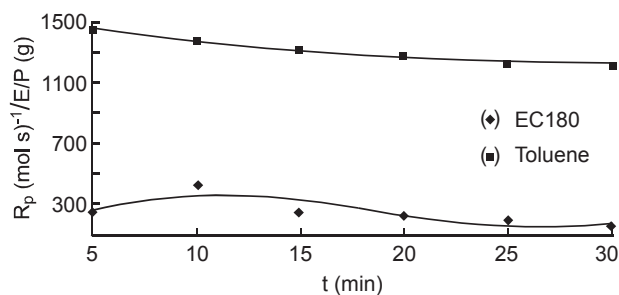


Figure 2. Effect of polymerization solvent on rate of E/P copolymerization conditions; $[Zr] = 6.7 \times 10^{-6} \text{ mol dm}^{-3}$, $[Al]/[Zr] = 3000$, P/E molar ratio = 50/50, temp = 40°C , and total monomer pressure = 1 atm.

with toluene. The polymerization in the aromatic solvent showed a maximum rate (1438 g/mol. s) at the start of the polymerization after which it followed a gradual decay pattern and reached to about 85% of its initial value (1200 g/mol. s) with 30 min reaction time. With EC180 the situation was considerably different. The initial low rate (235 g/mol. s) passed a pick at 10 min (420 g/mol. s) and dropped rather quickly to half of its initial value after the end of the run. Such a marked difference in catalyst behaviour is certainly attributed to the enhance solubility of MAO in toluene compared to its solubility in the saturated hydrocarbon. This is in consistence with the work of Tsutsuu and Kashiwa. These authors studied the homopolymerization of ethylene with the same catalyst and reported a ten-fold increase in reactivity by substituting toluene for n-decane [22]. They believed the effect to be attributed to the formation of solid catalyst particles in aliphatic hydrocarbons and concluded that the higher the solubility of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, the greater the solubility of active species and thus the higher the activity of the catalyst.

Effect of $[\text{Cp}_2\text{ZrCl}_2]/[\text{MAO}]$ Molar Ratio

The effect of Cp_2ZrCl_2 and MAO concentrations on the behaviour of the polymerization was studied by holding the former constant while varying the latter and vice versa. As Figure 3 indicates, a notable influence on rate per unit catalyst is exerted by increasing the $[Al]/[Zr]$ molar ratio by keeping the amount of MAO constant but decreasing the Cp_2ZrCl_2 concentration. The decay nature of the rate-time curve also takes acceleration by using dilute catalyst solution. These observations mean that the formation of active centre is

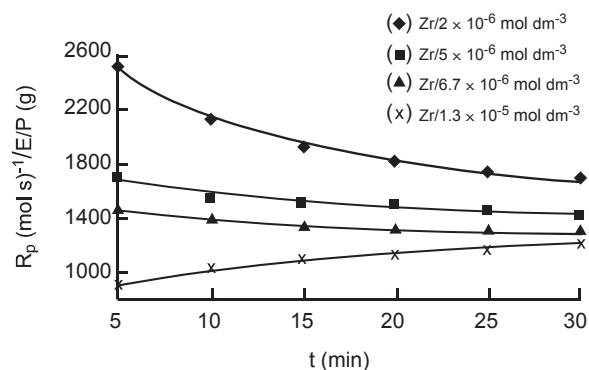


Figure 3. Effect of Cp_2ZrCl_2 concentration on rate. Conditions; $[\text{MAO}]$ in terms of $[Al] = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$, P/E molar ratio = 50/50, temp = 40°C , total monomer pressure = 1 atm, and solvent = toluene.

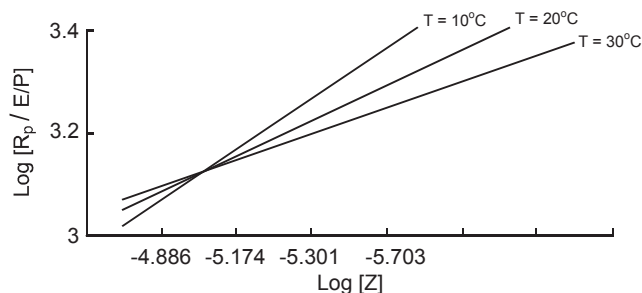


Figure 4. Effect of Cp_2ZrCl_2 concentration on rate of E/P copolymerization at three different temperatures. Other conditions are those mentioned for Figure 3.

not complete when more concentrated catalyst solutions are used and the initially higher R_p at low $[Zr]$ means that either active site formation occurs faster or site destruction is slower at low concentrations. A combination of the two effects is also probable. Plots of R_p versus $\log[Zr]$ are shown for polymerization temperatures of 10, 20 and 30°C in Figure 4. They are almost linear with average slope of -0.6. This means that the copolymerization rate is proportional to $[Zr]^{-0.6}$. Such dependency of rate with catalyst concentration is shown to be of the order of $[Zr]^{-0.8}$ for ethylene homopolymerization with the same catalyst system [23,24].

Effect of Cocatalyst Concentration

In another series of experiments, the catalytic activity was determined for a wide range of MAO concentra-

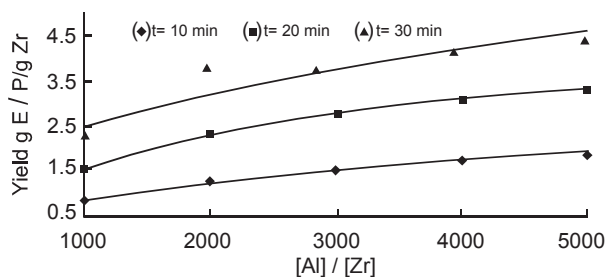


Figure 5. Effect of $[Al]/[Zr]$ molar ratio on yield of E/P copolymerization. Polymerization time (a) 10, (b) 20 and (c) 30 min. E/P molar ratio= 70/30, temp= 40°C, $[Zr]= 5 \times 10^{-6}$ mol dm⁻³, total monomer pressure=1 atm, and solvent= toluene.

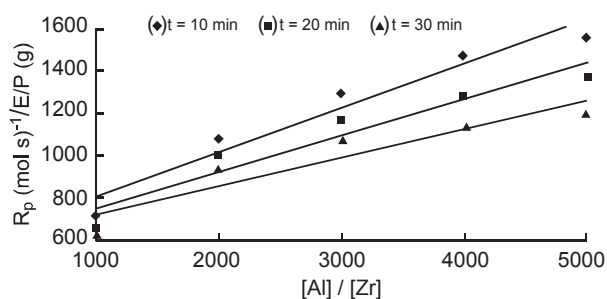


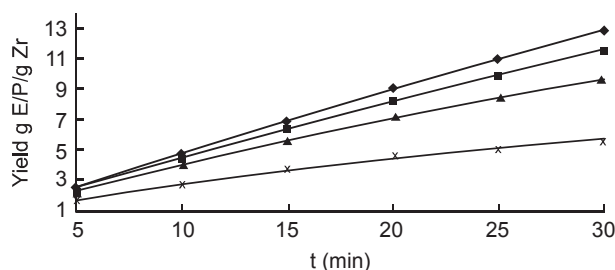
Figure 6. Effect of $[Al]/[Zr]$ molar ratio on rate of E/P copolymerization. Conditions are those of Figure 5.

tion at constant $[Zr] = 2 \times 10^{-6}$ mol dm⁻³. A critical $[Al]/[Zr]$ molar ratio of 180 was detected below which there did not form any measurable product at 40°C and P/E molar ratio of 70/30 in gas feed mixture. The rate and hence yield increased steadily and almost linearly with increase in MAO concentration. This is shown in Figures 5 and 6 for polymerization times of 10, 20 and 30 min. The rate profiles of Figure 5 show that increasing $[MAO]$ by 5-fold, increases R_p by 2-fold meaning that R_p is proportional to $[MAO]^{0.5}$. Therefore, the overall dependence of catalytic activity of the catalyst system under study for EP copolymerization is of the form $[Al]^{0.5}/[Zr]^{0.6}$, or nearly $([Al][Zr])^{1/2}$. Chien and Razzavi [24] found an overall dependence of $([Al]^{0.75}/[Zr]^{0.5}$ for ethylene homopolymerization initiated by bis-Neomenthyl cyclopentadienyl) zirconium dichloride/MAO catalyst system.

Effect of Feed P/E Molar Ratio

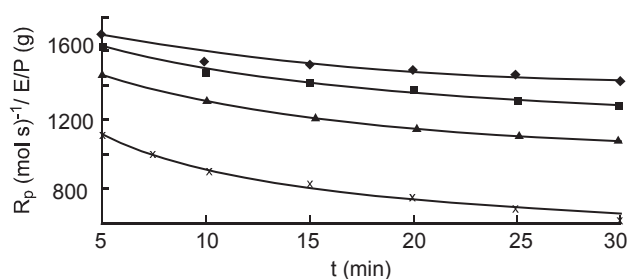
Effect of P/E molar ratio in feed mixture from 50/50 to

80/20 is shown in Figures 7-9. All other operating conditions were kept constant. The yield and activity are dependent on this ratio since they declined continuously with variation of propylene mole fraction from 50% to 80%. On the other hand, the polymerization time gives rise to a significant increase in the amount of copolymer formed per unit catalyst. The rate-time profiles depicted in Figure 8 are only slightly of decay type at low P/E ratios and take acceleration in decay by increasing the fraction of propylene. This is in contrast to higher solubility of propylene than ethylene in toluene and hence, the decrease in R_p in the presence of higher amounts of propylene is clearly due to enhanced reactivity of ethylene. Such behaviour of zirconium-based polymerization catalysts in E/P copolymerization was observed by Kaminsky and Miri [7] for Cp_2ZrCl_2/MAO under comparative P/E molar ratio.



(—◆—) C3/C2 = 50/50; (—■—) C3/C2 = 60/40; (—▲—) C3/C2 = 70/30; (—×—) C3/C2 = 80/20.

Figure 7. Effect of P/E molar ratio on yield. Conditions; $[Zr]= 5 \times 10^{-6}$ mol dm⁻³, $[Al]/[Zr]= 3000$, temp= 40°C, solvent= toluene, and total monomer pressure= 1 atm.



(—◆—) C3/C2 = 50/50; (—■—) C3/C2 = 60/40; (—▲—) C3/C2 = 70/30; (—×—) C3/C2 = 80/20.

Figure 8. Rate data at different P/E molar ratios and temperatures. Conditions, $[Zr]= 5 \times 10^{-6}$ mol.dm⁻³, $[Al]/[Zr]=3000$, tem= 40°C, solvent = toluene, and total monomer pressure= 1 atm.

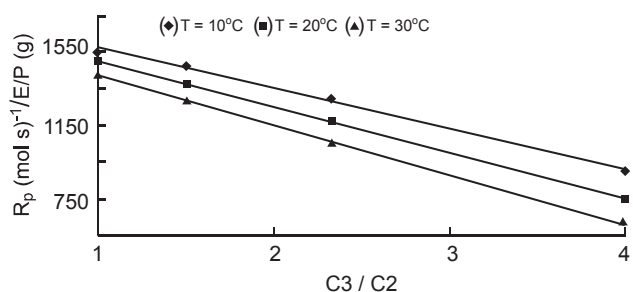


Figure 9. Effect of temperature on rate : Conditions; $[Zr]=5 \times 10^{-6} \text{ mol dm}^{-3}$, $[Al]/[Zr]=3000$, $[P/E]$ molar ratio= 65/25, solvent= toluene, and total monomer pressure= 1atm.

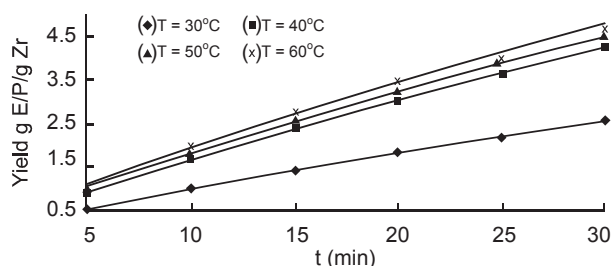


Figure 10. Effect of temperature on yield: Conditions; $[Zr]=5 \times 10^{-6} \text{ mol dm}^{-3}$, $[Al]/[Zr]=3000$, $[P/E]$ molar ratio = 65/25, solvent= toluene, and total monomer pressure= 1atm.

The rate decay with time is also reported by Kaminsky in ethylene homopolymerization using the same catalyst under study and was said to be partly due to side reactions occurring between two adjacent zirconium propagating species giving rise to production of inactive structures of the type shown below [12]. Since the copolymerization rates observed in this work fall steadily with propylene mole fraction, formation of such inactive species may be facilitated when propylene, the last unit incorporated into the polymer chain, is via chain transfer reactions.

Effect of Temperature

The variation of rate with reaction temperature was investigated using a P/E ratio of 65/35 in range 30–60°C the results of which are shown in Figures 9 -12. The copolymers obtained under this gas feed molar ratio were hard solids allowing work-up of the product easily. Figures 9 and 10 show that the catalyst yield and activity increased considerably when the reactor temperature rose from 30°C to 60°C, indicating that the propagation rate constant is a direct function of temperature. In addition the rate of new active site forma-

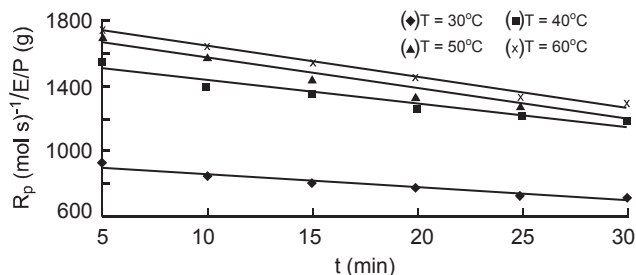


Figure 11. Effect of temperature on rate. Conditions are those shown in Figure 10.

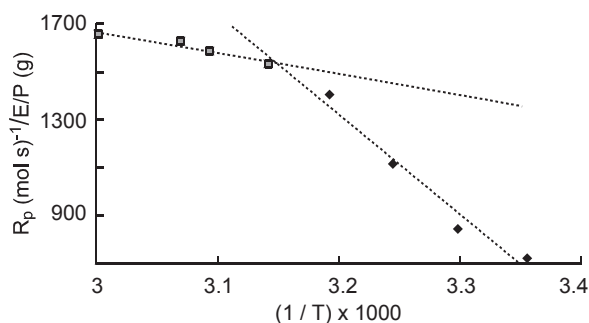


Figure 12. Arrhenius plot of catalyst activity versus $1/T$. Conditions; $[Zr]=5 \times 10^{-6} \text{ mol dm}^{-3}$, $[Al]/[Zr]=3000$, $[P/E]$ molar ratio= 65/25, solvent= toluene, polymerization time= 10 min, and total monomer pressure= 1atm.

tion at higher temperatures in the range used is higher than the site deactivation or lower activation energy requirement at higher temperatures. The Arrhenius plot of the catalyst shown in Figure 12 shows unusual behaviour observed for most generations of Ziegler-Natta catalysts. They show maximum activity at nearly 40°C and decrease were rapid at its either side. From the slope of Figure 12, the overall activation energy was found to be $7.3 \text{ kcal mol}^{-1}$. Taking into account the temperature dependency of the solubility of monomers in toluene, a rough value of $9.4 \text{ kcal mol}^{-1}$ is estimated for the average activation energy of propagation. This value is not very far from those found for homogeneous catalysts in homopolymerization of ethylene and propylene [25].

CONCLUSION

This study has been able to show the following kinetic features of E/P copolymerization with the catalyst system $\text{Cp}_2\text{ZrCl}_2 / \text{MAO}$.

-The rate-time profiles are characterized by initial

maximum rates which occur as soon as the reaction components are mixed followed by a decrease and take acceleration in decay with time.

- An increase in polymerization temperature from 20°C to 60°C enhances both the initial rate and the catalyst productivity

- An increase in P/E molar ratio in the gas feed mixture led to a decrease in the initial value of R_p followed by a faster decay

- On increasing the [MAO]/[Zr] molar ratio from 1000 to 5000, the activity of the Cp_2ZrCl_2 catalyst towards the copolymerization initially increased sharply and then it became very smoothly.

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