ABSTRACT

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Micro reactors provide enhanced mass and heat transfer owing to their high surface area to volume ratio. These reactors offer precise control and selectivity and can be used for synthesizing specifically engineered and technically sophisticated olefin polymers. An unsteady state reactor model (using coordination reaction kinetics) was developed to study the concentration profiles of monomer, catalyst, polymer and its molecular weight distribution along the length of the reactor with time. Nano silica particles of diameter 400nm were synthesized as a support for the metallocene catalyst. Heterogeneous ethylene polymerization was carried out in tubular reactors of diameters 800µm, 1mm, and 2.37mm under 2-phase flow conditions. This thesis investigates the effect of operating conditions in a micro reactor on the qualitative and quantitative properties of the polymer. The results can be extended to propose applications for synthesis of polymers with unique morphology using the inherent advantages of these reactors.

HETEROGENOUS ETHYLENE POLYMERIZATION IN A MICRO REACTOR
SYSTEM

By

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Chapter 1: Background on micro reactor technology for polymerization: Literature review

1.1 Introduction

Micro reactors are miniaturized continuous flow reaction systems with lateral dimensions ranging in the micron scale. Micro channel technology offers a unique solution to meet the challenges of the growing chemical industry by providing improved chemistry, energy efficiency and better kinetics.[1]

Due to the high surface area to volume ratio they offer certain integral advantages such as enhanced mass and heat transfer coefficients and a high volumetric productivity. Micro reactors facilitate very precise control over the products of the reaction and their properties. Their laminar flow conditions results in better control over the residence time distribution and extent of back mixing. Highly exothermic, potentially hazardous or unstable reactions can be carried out with ease in a micro reactor due to their small volumes and high heat transfer effects. These reactors have very low manufacturing, operating and maintenance costs and are considerably more energy efficient as compared to traditional reactors. And most importantly micro reactors can be scaled out by numbering up the individual reactor for larger operations.[2, 3]

Over the last decade micro channel technology has been applied in several industries such as petrochemicals, organic chemical synthesis, heat exchangers and pharmaceuticals. There is a constant demand for technically sophisticated polymers with very specific properties for novel applications. Traditional polymers are typically produced in macro reactors in industries on a large scale with limited scope for finer control and innovation in terms of material properties. The need for efficient synthesis and rapidly changing research aspirations make using micro reactors for polymerization an ideal option. This introduction focuses on the existing research on polymerization in micro reactors and the motivation for our research.[1, 3]

Important design issues for a micro reactor requires the knowledge of the extent of the kinetic and transport rates that can be achieved and their dependence on the design choice and other parameters. The following sections discuss the fundamental issues such as flow patterns, mass and heat transfer, reaction kinetics, operating conditions, channel geometry in a micro reactor system specifically with respect to different types of polymerization.[3]

1.2 Flow regimes in micro reactors

Most typical polymerization reactions involve a gaseous monomer, so an analysis of the flow pattern of gas-liquid flow in a micro channel is important. There exists different flow regimes based on the superficial velocities of the gas and the liquid phases. There is a vast literature on flow visualization experiments and CFD models for circular, rectangular and even triangular channels.[4] Many of these have

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been demonstrated for CO_2 in water; however it is useful to extend these results for the case of 2-phase polymerization in micro channels.

Figure.1 shows the different flow regimes that have been analyzed namely, bubbly flow, slug flow, slug- annular, annular flow, churn flow. The studies suggest the dominance of surface tension and laminar flow in micro channels.[5]
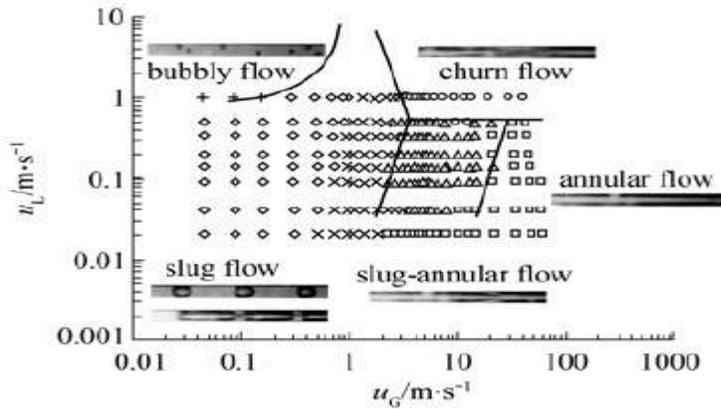
Figure 1 Flow pattern map of CO_2-water in a rectangular micro channel (500μm x1000μm) with respect to gas and liquid velocities. [5]

1.3 Enhanced mass transfer effects in micro reactors

Figure 2 shows the comparison of mass transfer coefficients measured in a rectangular micro channel having cross-section of 500 μm × 1000 μm with other types of gas-liquid contactors.[6] The liquid side mass transfer coefficient, k_{La}, and specific interfacial area, a, in this micro channel exceed those in conventional reactors such as bubble columns, and packed columns by at least one or two orders of magnitude.
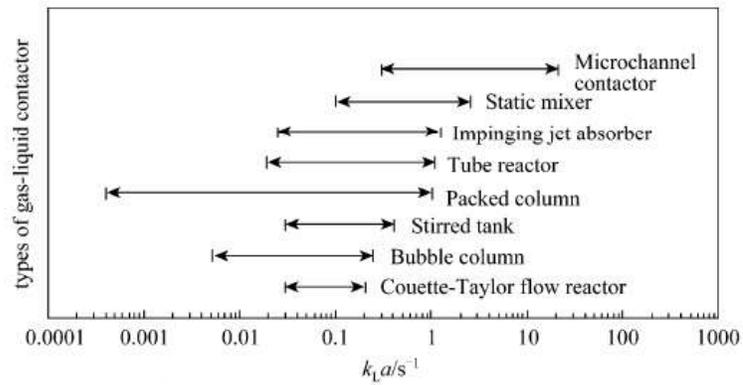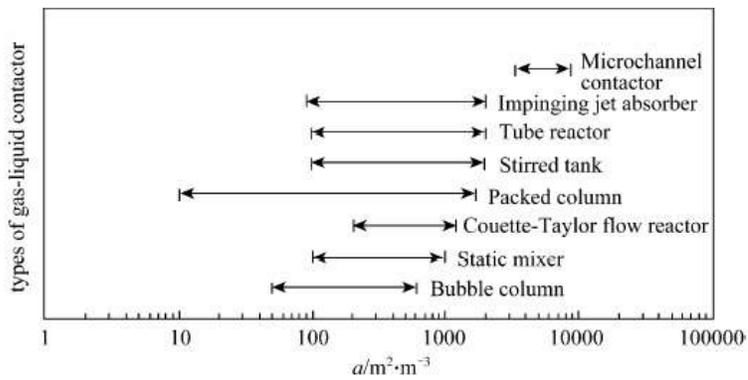
Figure 2 Mass Transfer Coefficient and Interfacial are for different gas liquid contactors.[6]

Taylor flow is a type of gas-liquid flow pattern that consists of elongated bubbles with equivalent diameter usually many times that of the channel diameter, separated by liquid slugs. Most mass transfer studies are focused on Taylor flow patterns.[7] The results suggest that the transfer of gas occurs through the interface between bubble caps and the liquid slug or via the interface between the bubble body and the surrounding liquid film. Mass transfer contributions through these two types of interface are determined by the contact time between the liquid film and the bubble, the mixing extent of the liquid film to the liquid slug, and the Taylor bubble length fraction.

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In a study of CO_2 mass transfer in different fluids in a micro channel devices[8], the bubble size is determined by the injection flow rates and channel geometry. Rate of dissolution of large bubbles depends on fluid pair composition and injection pressure. It is also found for different fluids studied that the rate of dissolution is proportional to the ration diffusion coefficient to Henry's constant.

1.4 Residence time distribution in micro reactors

Studies show that residence time distribution (RTD) curves determined in a micro reactor were typical of laminar flow in long pipes. And the axial dispersion model was used to characterize the non-ideal behavior. This model uses the dispersion number (D/uL), where D is the axial dispersion coefficient, L the length of the tube; u is the mean linear velocity, to determine the extent of the deviation from the ideal plug flow. Values lower than 0.01 are considered as a small deviation from plug flow.

Ouzineb and Muller et al. found similar results in their analysis on tubular reactor under low flow rates, and attributed it to axial mixing.[9,10] They concluded that a secondary flow pattern was introduced because the reactor was coiled.

Some experimental findings show that the flow pattern of the micro channel was a result of the interaction of the laminar velocity profile with radial molecular diffusion, causing a nearly plug flow, despite a laminar flow regime.[11] Due to the narrow diffusion lengths micro reactors have faster mixing. [11]

1.5 Free radical polymerization in micro reactors

Micro reactors have been used more commonly to carry out free radical polymerization reactions, these reactors typically require an initiator which decomposes thermally into radicals and starts the polymerization.

Significant improvement in the molecular weight distribution (MWD) control of the polymers from free radical polymerization in micro reactors has been observed. In one experiment the thermal decomposition of a radical initiator AIBN in a micro reactor is carried out.[12] A plot of the unchanged AIBN versus the residence time based on bath temperature indicates effective heat transfer due to high surface area to volume ratio. The authors performed several reactions, such as polymerizations of Butyl Acrylate (BA), Methyl Methacrylate (MMA), Styrene (St) Benzyl Methacrylate (BMA) and Vinyl Benzoate (VBz). They used a 500µm diameter, 1m stainless tube reactor, and an oil bath at 80 or 100°C.

Effect on poly dispersity index and molecular weight Polydispersity index (PDI) (ratio of weight average to number average molecular weight of the polymer) from the polymerization of BA in the micro reactor was found to be much smaller than a macro reactor because of higher heat removal efficiency. Effect on PDI for BMA and MMA was much less, and Vbz and St had no effect. Therefore a micro reactor is very useful in controlling MWD for highly exothermic free radical polymerization compared to less exothermic reactions. [12]

The styrene free radical polymerization performed in two types of lamination micro reactors was investigated by means of 2D and 3D finite elements numerical

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simulations.[13] It was found that micro reactors and tubular reactors with radii of hundreds of micrometers allow keeping the PDI close to the theoretical value of 1.5 over a wide range of diffusion coefficients. However, as the tube radius increases, there is lesser control over the reaction, and the PDI gets higher than 1.5 as is the case for lab-scale reactors.

In another experiment[14] a 900µm, 5.85 m stainless steel tube was used, heater collar at 60°C, with 2 reactant reservoirs Chemical composition of initial solution and flow rate in the micro tube varied the polymer properties, and polymer of number average molecular weight M_n from 2000 to 20000 g/mol synthesized. The results showed improved average branching efficiency compared to regular reactors. Linear and branched PMA were synthesized and a colloidal solution of polymer nano particles 90-100 nm was formed.

Effect on polymer yield Polymer yield was observed to follow the pattern of St<VBz<MMA<BMA<BA. This is because faster reactions are more exothermic, and BA is fastest and most exothermic reaction and the effect of micro reactor on MWD is greatest for BA. The authors were able to carry out the continuous polymerization for several hours without fouling effect and so the system can be used for industrial polymerization.[12]

Effect of numbering-up a micro reactor In another study[15], a micro chemical pilot plant for radical polymerization of methyl methacrylate (MMA) was constructed and continuous operation was accomplished for 6 days without any issues, indicating that micro flow systems can be applied to relatively large-scale production of polymers. The setup has a numbered up reactor (94 tubes, 510 um, 600

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mm) where the volume of the micro channels is 9.6mL and uses a shell and tube system for heating/cooling of the polymer solution. Table 1 compares the yield and PDI of a laboratory scale reactor to that of single micro channel reactor and a numbered up reactor.[15]

Table 1 Polymerization in single micro tube reactor and numbered up reactor Comparison of yield, M_n, PDI. [15]

monomer	reactor type	reactor volume (mL)	monomer flow rate (mL/min)	AIBN flow rate (mL/min)	residence time (min)	yield (%)	M_n	PDI (M_w/M_n)
MMA	laboratory-scale single microtube reactor	1.8	0.9 0.4	0.9 0.4	1.0 2.3	12.4 25.9	8600 8400	1.80 1.82
	type-1 numbering-up reactor	9.6	4.1 1.9	4.1 1.9	1.2 2.5	12.8 21.2	9300 9800	1.84 1.85
BA	laboratory-scale single microtube reactor	1.8	0.6 0.3	0.6 0.3	1.5 3.0	70.7 84.5	33000 22800	3.63 3.14
	type-1 numbering-up reactor	9.6	2.4 1.6	2.4 1.6	2.0 3.0	66.8 73.2	34500 32000	3.21 3.26

[a] Polymerization temperature 100 °C, cooling temperature 0 °C, [MMA] = 9.4 mol/L (neat), [BA] = 7.0 mol/L (neat), [AIBN] = 0.094 mol/L (MMA conditions), 0.070 mol/L (BA conditions) in toluene, numbering-up reactor i.d. = 510 μm, 500 mm, 94 pieces, single tube i.d. = 500 μm, 9 m (cooling tube i.d. = 500 μm, 1 m)

The residence time was varied by changing the flow rate. The yield, molecular weight, PDI for the polymerization of MMA in the numbered-up reactor was similar to those obtained with the single micro tube reactor. The viscosity of the solution is quite uniform during the polymerization of MMA, since the polymer yield was low. In the case of the polymerization of BA, however, the yield obtained with the numbered-up reactor was smaller than that obtained with the single micro tube reactor in the same reaction time. This can be attributed to the lack of flow uniformity since the channels appeared to clog because of the high viscosity.

Effect of channel diameter Smaller channel diameters offer high mass and heat transfer, and are useful in the initial part of the reaction since there is a high

monomer concentration and a large heat loss. However these small diameters result in high pressure drop as well so their advantage need to be restricted to the early stages of the reaction. By using larger diameters in the later stages of the reaction, the volume increases, resulting in a higher throughput and an increase in the residence time. Another important aspect is to reduce the complexity of the design and ensure that the tube is easily replaceable in case of clogging.

1.6 Emulsion polymerization in micro reactors

Emulsion polymerization has also been successfully carried out in a micro reactor set up. One such research uses PTFE tubing and a pre-emulsion stream and initiator stream at low flow rates (0.5 to 5 ml/min).[16] It is observed that 4 residence times are required for a reactor to achieve steady state. Reactor coil is placed in a hot water bath. Comparison of the results to a batch reactor of same composition show similar kinetics and molar mass properties due to both efficient mixing in MR and good temperature control in a batch reactor.

1.7 Ethylene polymerization using metallocene catalyst in micro reactors

One of the more successful attempts at carrying out the widely popular metallocene catalyzed polymerization in a micro channel reactor was conducted by researchers at Dow.[17] An electro thermal micro reactor with voltage taps along the length of the reactor was used to sense the temperature profile. The system consisted of a preheating zone, a catalyst addition zone and a reaction zone. Upon addition of catalyst, heat pulses can be observed due to the exothermic nature of the reaction. The

entire unit was in a glove box (Fig 3) and utilized pure ethylene and toluene and a channel of ID 1.27mm, 150cm length at 175˚C and 2.8MPa. Low flow rates in the order of 0.05 to 2 ml/min are utilized with Reynolds number well below the turbulent regime. It shows a typical parabolic flow pattern of laminar flow regime with the velocity maximum along the axis.
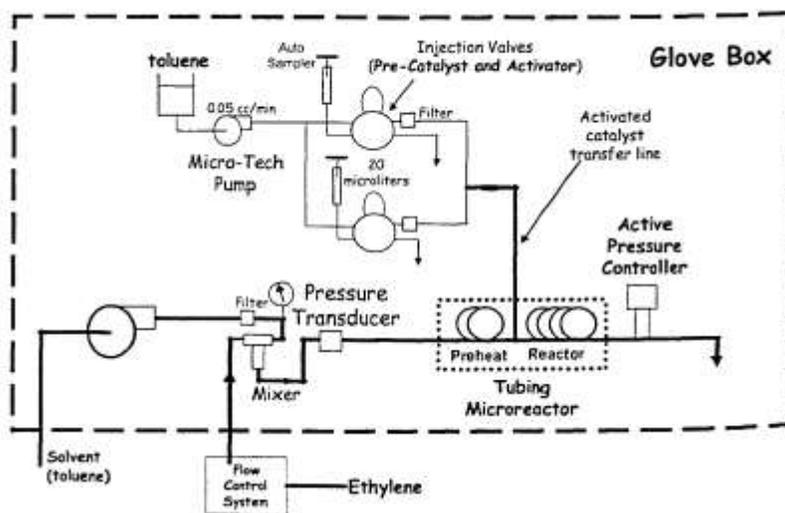
Figure 3 Ethylene Polymerization using a soluble metallocene catalyst in a MR setup.[17]

A different approach to polymerization in similar set up was carried out by Beigzadeh, heating via a hot water bath at 140˚C .[18] The reactor was maintained at 150 psig for 2-phase and 400 psig for single-phase. Low molecular weights in these polymerization experiments were attributed to 1) non isothermal reaction conditions 2) continuous decrease in monomer concentration along the reactor resulting in continuous decrease in instantaneous molecular weight of polymer produced.

Pressure and flow rate is chosen such that 2-phase is maintained along the length of the reactor to minimize variation of ethylene concentration. Widely different viscosities for vapor and liquid may contribute to large pressure fluctuations but

smooth pressure control was possible. A channel of ID 0.05", 145 cm reactor section was used.

Non isothermal behavior Under constant temperature and pressure, as ethylene is being depleted, VLE forces the ethylene in gas phase to replenish ethylene in liquid phase. The authors assume that the rate of polymerization is much lesser than rate of mass transfer. High exotherms corresponded to high catalyst loading, which promote polymerization and hence there is more heat released and more polymer produced. It is also observed that for similar exotherms M_w of the polymer in two phase is much higher than single phase since monomer concentration drops continuously for singles phase.

Near isothermal behavior Increasing catalyst loading results in an increased M_w, M_n. However on doubling the catalyst concentration form 0.0025 M to 0.005 M the polymerization rate increases such that it becomes comparable to mass transfer rate so there is a depletion of monomer and the MW drops since it is now mass transfer controlled. But further increase from 0.005 to 0.01 doesn't have any significant effect .This suggest that at 0.0025M the reaction is controlled by kinetics, but making it 0.005 or higher makes rate of polymerization comparable or higher than mass transfer rate, so increasing catalyst concentration has no effect on kinetics. So at high catalyst concentrations it is better to improve mass transfer by for example increasing surface area between the 2 phases using packing material.

1.8 Clogging in micro reactors

A major disadvantage to the synthesis of solid products within micro reactors is the clogging of the reactor channels. Cummings and Poe report a solution to this problem by using a mono dispersed droplet flow to isolate the solid particles from the walls of the reactor tubing. [19] An immiscible phase is used as the carrier-continuous medium and the chemical reagents are injected. The disperse-phase droplets are used as individual reactors.

1.9 Particle laden flow in micro reactors

In a study on particle laden flow in PDMS micro channels (15μm high, 1mm wide and 3cm long) suspensions containing polystyrene particles of diameter 1.5 or 5 um were forced through the channels and the flow video was recorded and the formation and growth of cluster of particles was noted.[20] The average cluster size seems to be uniform and the number of clusters is more at the inlet compared to center; also the average cluster area grows linearly with time and increases with flow rate and void fraction. For larger particles, there are more clusters with smaller area.

1.10 Motivation for the project

As described in the sections above micro reactor technology has been effectively applied in several kinds of polymerization. The literature review suggests the impact of operating conditions and experimental features on both the qualitative and quantitative properties of the polymer. Our research attempts to study ethylene polymerization using a heterogeneous catalyst to synthesize polymer particles in a micro reactor set up. The study by Dow[17] and Beigzadeh[18] described in Section 1.7

which utilizes a dissolved homogenous catalyst and operates under high temperature and pressure conditions with the entire set up inside a glove box. The properties of polymer produced using a heterogeneous catalyst differ considerably from that of a homogenous catalyst, and offer finer control over the reaction rate and polymer properties at a molecular level. We were able to investigate the polymer morphology synthesized in a micro reactor. Traditional heterogeneous polymerizations have been carried out in macro scale batch or semi batch reactors and packed bed systems, but as it can be seen from the literature, micro reactors offer much better mass transfer compared to these conventional reactors and coupled with the effects of using a supported catalyst with much better activity there is tremendous potential for the properties of polymers that can be produced.

Chapter 2: Preliminary experimental work and theoretical background

2.1 Heterogeneous catalyst for polymerization

Metallocenes are a class of catalysts developed in the 1980s for the production of precisely designed polyolefins and engineering plastics. Based on transition metals such as titanium and zirconium atoms sandwiched between ring structures they have well defined single catalytic sites and well understood molecular structures. The reactive site has been enhanced through the use of a bridging structure, which is used to strictly define and highlight the reactive site.

The ability to design the structure of these catalysts and the flexibility in the catalyst molecule allows the polymerization of many monomers which cannot be produced using Zeigler-Natta catalysts on a commercial scale.

The main catalyst used as the central ingredient here is rac-ethylene-bis (indenyl) zirconium (IV) dichloride (EBI), Methylaluminoxane (MAO) is used as a co-catalyst to activate the active sites of the catalyst (Zirconium center) and maintain optimum reaction conditions.

2.1.1 Using a nano silica support for the catalyst

Polymerization in a micro reactor is difficult to control when a homogenous catalyst is directly used and the rapidly increasing size of the polymer particle usually results in clogging of the micro reactor. To be able to control the reaction kinetics of

polymerization, the metallocene catalyst has been supported on nano silica particles where the active sites of the catalyst are embedded on the surface of the particle.

2.1.2 Synthesis of nano silica particles

Silica Particles are synthesized using a modified Stöber Process.[21] The molar quantities of the reagents were tuned upon several experiments to determine the exact proportion that would produce silica particles of desired size.

Solution A contains 0.124 moles Tetra ethyl ortho silicate (TEOS, Sigma Aldrich) in 50 ml of ethanol. And solution B contains 6.34 mL of NH_4OH, 11.3 mL distilled water and 32.5 mL of ethanol. Solution A is added to solution B slowly and allowed to react for 1 hour with a stirrer. After 1 hr, an equal volume of dilute HCl Solution is added to neutralize the solution. The solution is filtered and washed with water multiple times and dried in a high temperature oven.

2.1.3 Preparation of Catalyst-MAO-Silica system

The calcined silica particles are treated with piranha solution ($H_2O_2+H_2SO_4$, 1:3), and washed 3 times with methanol, and dried for 24hrs in a vacuum chamber.

The silica is then weighed (0.87g) and treated with MAO (2 ml + 3 ml) based in toluene inside the glove box. It is allowed to react for 24hrs and washed 3 times with toluene. This procedure is repeated once more. The mixture is treated with quantified amount of EBI catalyst (0.0115g) and allowed to react for 24 hours and washed thrice with toluene. Once all the catalyst has been attached to silica, it can be observed that the supernatant toluene is colorless. The concentration of catalyst (0.0087g/ml) can be fixed by adding required amount of toluene (100ml). The amount of catalyst loaded

on the silica particles is measured by analyzing the moles of zirconium in the catalyst; this is done using ICP (Quantachrome).

2.1.4 Catalyst properties

SEM Images of Nano Silica Support Scanning Electron Microscopy Images (using Hitachi SU-70 SEM) of the nano silica particles were taken to ensure uniform size distribution and estimate the diameter of the silica particle. The diameter was found to be 400 nm (Fig 4).
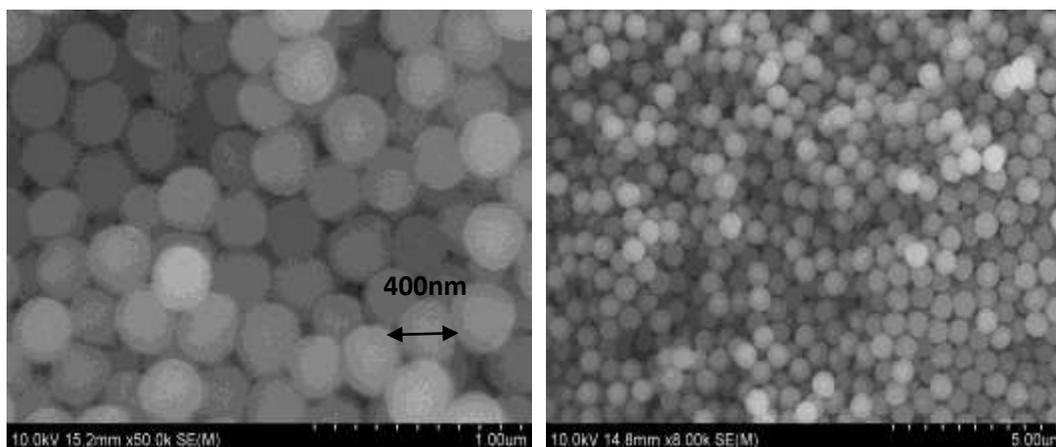
Figure 4 Uniform sized nano silica particles.

B.E.T results of nano silica support B.E.T (Brunauer, Emmet and Teller) Multilayer Isotherm is used to measure surface area of the silica particles. Adsorption and desorption rate constants are same for all layers except the first. Amount of gas adsorbed against the changing relative pressure at a constant temperature is used to estimate the surface area and porosity.

Surface Area: 42 m^2/g

Pore Volume: 0.147 cm^3/g

SEM images of catalyst particles SEM Images of the catalyst particles were taken to visualize the nature of the EBI coating around nano silica support. (Fig 5)
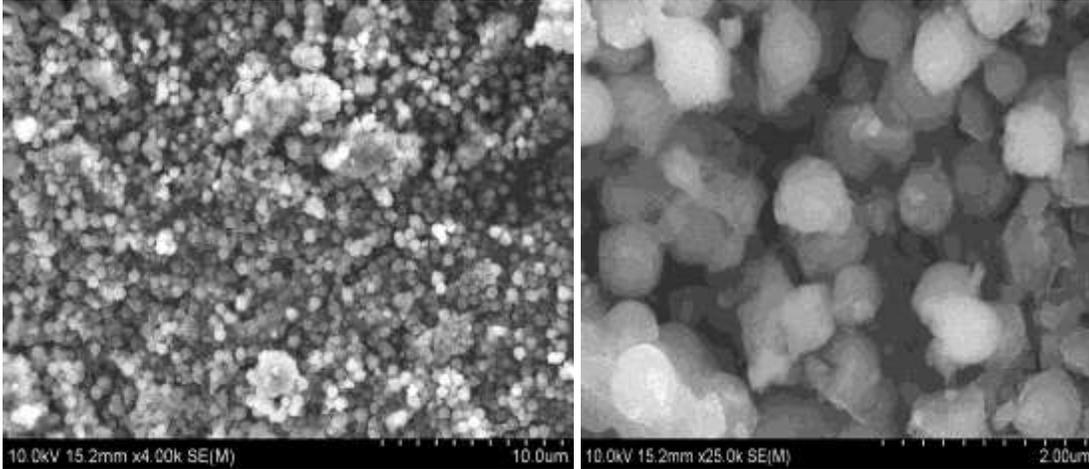
Figure 5 Nano silica supported catalyst

ICP Results of the catalyst Moles of Zirconium loaded per gram of catalyst: 3.17e-5 mol Zr/gCat. The nano silica supports offers high mass transfer rate due its large surface area and hence can accommodate more active catalytic sites.

2.2 Theory of kinetics of polymerization

It is important to understand the reaction kinetics in order to model the polymerization in a micro reactor.

2.2.1 Coordination mechanism of homopolymerization

Equations below describe the individual reactions that comprise the polymerization mechanism using the specific kinetic constants The elementary reactions include activation of the catalyst sites, initiation of activated site,

propagation of polymer chain, chain transfer to monomer, hydrogen and co-catalyst and deactivation of active catalytic site.[22]

1) Catalyst site activation $\quad C_O + MAO \xrightarrow{k_a} C^*$

2) Initiation $\quad C^* + M \xrightarrow{k_i} P_1$

3) Propagation $\quad P_n + M \xrightarrow{k_p} P_{n+1}$

4) Chain transfer to monomer $P_n + M \xrightarrow{k_{tm}} P_1 + M_n$

5) Chain transfer to hydrogen $P_n + H_2 \xrightarrow{k_{th}} M_n + C^*$

7) Chain transfer to Aluminium $P_n + Al \xrightarrow{k_{tAl}} M_n + C^*$

8) Spontaneous Beta Scission $\quad P_n \xrightarrow{k_{t\beta}} M_n + C^*$

6) Deactivation $\quad P_n \xrightarrow{k_d} M_n + D^*$

$$C^* \xrightarrow{k_d} D^*$$
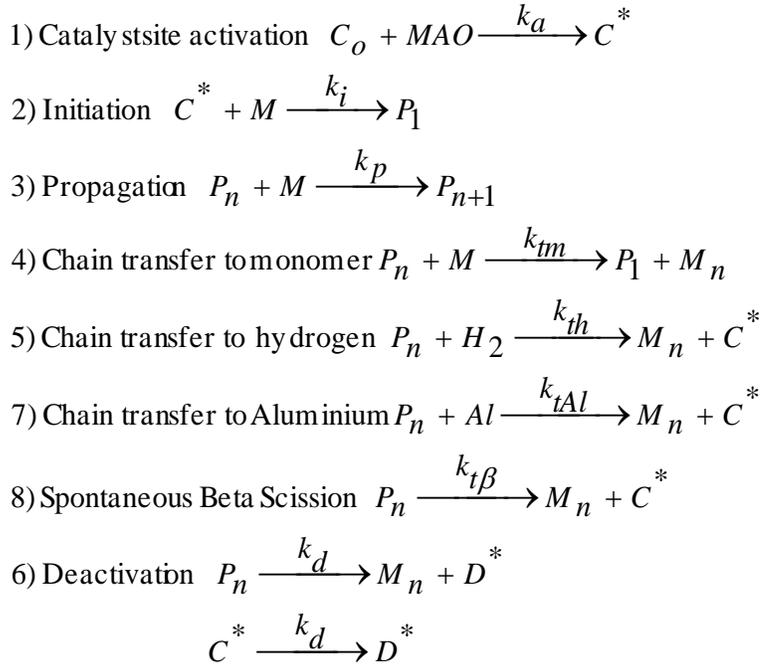
In the above equation C_o represents the catalyst and C^* is the activated catalyst, M is the monomer, P_1 is first unit live polymer, P_n is the live polymer with n units in the chain M_n represents the dead polymer of length 'n' which does not undergo further reaction, k_i represents the rate constants for each reaction, and D^* is the deactivated catalyst that can no longer react with the monomer.

The reaction rates with respect to each of the reactants and products are represented by the following expressions.

$$r_M = -k_i C^* M - k_p PM - k_{tm} PM$$

$$r_{C^*} = -k_i C^* M + k_{t\beta} \sum_{n=2}^{\infty} P_n + k_{th} H_2^p \sum_{n=2}^{\infty} P_n - k_d C^* + k_{tAl}[Al]\sum_{n=1}^{\infty} P_n$$

$$r_{P_1} = k_i C^* M - k_p P_1 M + (k_{t\beta} + k_{th} H_2^p + k_{tAl}[Al] + k_{tm} M)P_1$$

$$r_{P_n} = k_p (P_{n-1} - P_n)M - k_{tm} MP_n - k_{fh} H_2^p P_n - k_d P_n - k_{tAl}[Al]P_n$$

$$r_{H_2} = -k_{th} H_2^p \sum_{n=1}^{\infty} P_n$$

$$r_{M_n} = -k_{tm} MP_n + k_{th} H_2^p P_n + k_d P_n + k_{tAl}[Al]P_n$$

$$r_{D^*} = -k_d C^*$$

$$r_{Al} = -k_{tAl}[Al]\sum_{n=1}^{\infty} P_n$$

2.2.2 Molecular weight moments

Polymer produced from a reaction is distributed over a wide length range of molecular weights and usually a Gaussian distribution is assumed. Weight moments are defined to get a polymer weight distribution based on the polymer chain length.[23]

Live polymer moment

$$\lambda_k = \sum_{n=1}^{\infty} n^k P_n$$

Dead polymer moment

$$\mu_k = \sum_{n=2}^{\infty} n^k M_n$$

The number average (M_n) and weight average (M_w) polymer molecular weights and the polydispersity index (PDI) are commonly defined parameters to assess polymer properties.

$$M_n = M_{seg}\left(\frac{\lambda_1 + \mu_1}{\lambda_0 + \mu_0}\right)$$

$$M_w = M_{seg}\left(\frac{\lambda_2 + \mu_2}{\lambda_1 + \mu_1}\right)$$

PDI is the ratio of M_w to M_n.

The instantaneous chain length distribution for olefin polymerization is given by a single-parameter equation, Flory's most probable distribution (Flory,1953), where w(r) is the weight chain length distribution for polymer chains of length r, and τ is the ratio of all chain transfer rates to the propagation rate.

$$w(r) = \tau^2 r \exp(-\tau r)$$

The chain length distribution function is usually combined with a reactor residence time distribution function to calculate the overall molecular weight distribution in a continuous process.

Rate equations in terms of moments is described below.[24]

$$r_{\lambda_o} = k_i MC^* - [K_T + k_d]\lambda_0 \qquad\qquad r_{\mu_0} = (K_T + k_d)(\lambda_0 - P_1)$$
$$r_{\lambda_1} = k_i MC^* - (K_T + k_d)\lambda_1 + k_p M\lambda_0 \qquad r_{\mu_1} = (K_T + k_d)(\lambda_1 - P_1)$$
$$r_{\lambda_2} = k_i MC^* - (K_T + k_d)\lambda_2 + k_p M(\lambda_0 + 2\lambda_1) \qquad r_{\mu_2} = (K_T + k_d)(\lambda_2 - P_1)$$

Where,

$$K_T = k_{fH} H_2^p + k_{tAl}[Al] + k_{tH} H_2 + k_{tm} M + k_{t\beta}$$

2.2.3 Copolymerization kinetics

Kinetics of copolymerization differ from that of homo polymerization when two or more monomers come together to produce unique chains of different combinations of monomers.[22, 25]

a) In the terminal model, polymerization kinetic constants depend on the type of monomer taking part in the reaction and on the type of monomer at the polymer chain end.

b) The copolymerization of ethylene with alpha-olefins leads to the co monomer rate-enhancement effect, where the overall polymerization rate can increase significantly upon addition of an olefin.

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c) A possible explanation for this phenomenon is given by the trigger mechanism (Yestenes, 1991), whereby the presence of the alpha-olefin has a synergistic effect on the rate of ethylene insertion.

$$\tau = \frac{R_\beta}{R_p} + \frac{R_M}{R_p} + \frac{R_{CTA}}{R_p} + \frac{R_{MAO}}{R_p} = \frac{k_\beta}{k_p[M]} + \frac{k_M}{k_p} + \frac{k_{CTA}[CTA]}{k_p[M]} + \frac{k_{MAO}[MAO]}{k_p[M]}$$

τ is ratio of rate of chain transfer to rate of chain propagation, copolymerization rate equations are shown below

Initiation	Chain transfer to	c) Cocatalyst
$C^* + A \xrightarrow{k_{iA}} P_{1,A}$	a) Monomer	$P_{r,A} + Al \xrightarrow{k_{tAlA}} C^* + M_r$
$C^* + B \xrightarrow{k_{iB}} P_{1,B}$	$P_{r,A} + A \xrightarrow{k_{tmAA}} C^* + M_r$	$P_{r,B} + Al \xrightarrow{k_{tAlB}} C^* + M_r$
Propogation	$P_{r,A} + B \xrightarrow{k_{tmAB}} C^* + M_r$	d) β - Hydrogen
$P_{r,A} + A \xrightarrow{k_{pAA}} P_{r+1,A}$	$P_{r,B} + A \xrightarrow{k_{tmBA}} C^* + M_r$	$P_{r,A} \xrightarrow{k_{\beta A}} M_r + C^*$
$P_{r,A} + B \xrightarrow{k_{pAB}} P_{r+1,B}$	$P_{r,B} + A \xrightarrow{k_{tmBB}} C^* + M_r$	$P_{r,A} \xrightarrow{k_{\beta B}} M_r + C^*$
$P_{r,B} + A \xrightarrow{k_{pBA}} P_{r+1,A}$	b) Hydrogen	Deactivation
$P_{r,B} + B \xrightarrow{k_{pBB}} P_{r+1,B}$	$P_{r,A} + H_2 \xrightarrow{k_{thA}} C^* + M_r$	$P_{r,A} \xrightarrow{k_{dA}} M_r + C_d$
	$P_{r,B} + H_2 \xrightarrow{k_{thB}} C^* + M_r$	$P_{r,B} \xrightarrow{k_{dB}} M_r + C_d$
		$C^* \xrightarrow{k_d} C_d$
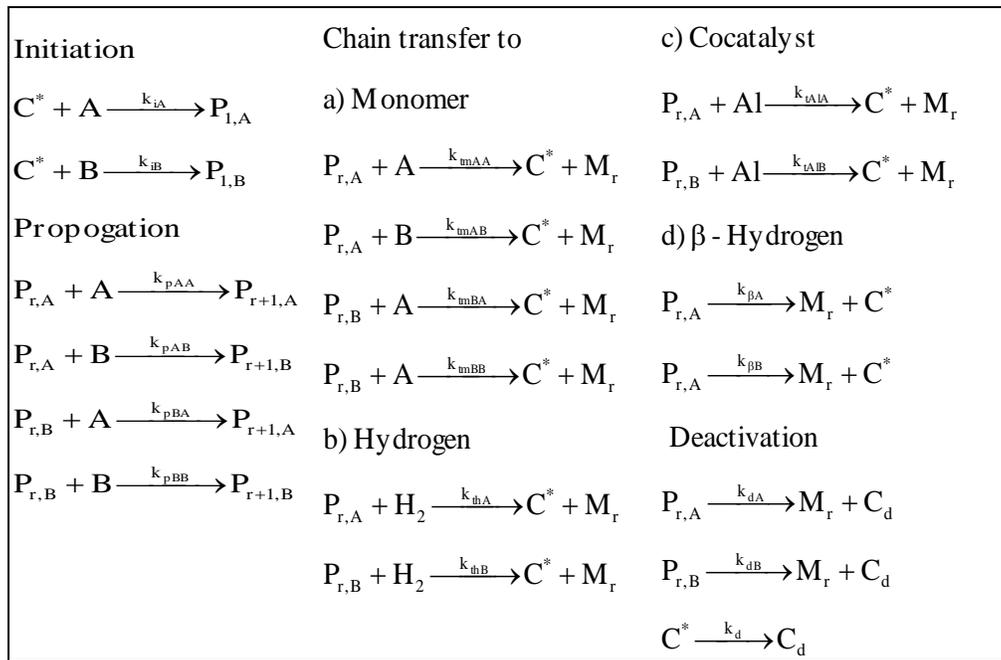
In the above equation C^* represents the activated catalyst, A and B are the monomers, P_r, is the live polymer with r units in the chain, M_r represents the dead polymer of length 'r' which does not undergo further reaction, k_{ij} represents the rate constants for each reaction, and C_d is the deactivated catalyst that can no longer react with the monomer.

Different copolymer chains have varying combinations of monomer components. Copolymerization Composition Distribution can be calculated by the parameters described below.

Reactivity Ratios (r_1 and r_2) are given by the ratio of homo propagation to cross propagation.[26,27]

$$r_1 = \frac{k_{pAA}}{k_{pAB}} \quad r_2 = \frac{k_{pBB}}{k_{pBA}}$$

F_1 represents the instantaneous mole fraction of monomer A in the copolymer and f_1 represents the instantaneous mole fraction of monomer A in the bulk phase

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

Stockmayer's bivariate distribution It describes the instantaneous bivariate distribution of chain length and chemical composition of linear polymers made with single-site-type coordination polymerization catalysts.[28] The distribution is given by the following function.

$$w(r, y) dr dy = r\tau^2 \exp(-r\tau) dr \frac{1}{\sqrt{2\pi\beta/r}} \exp(\frac{y^2}{2\beta/r}) dy$$

$$\beta = \overline{F_1}(1-\overline{F_1})[1 + 4\overline{F_1}(1-\overline{F_1})(r_1 r_2 - 1)]^{0.5}$$

$$y = F_1 - \overline{F_1}$$

The function can be integrated for all possible chain lengths to obtain w(y), where y is difference between the molar fraction of monomer A in the polymer and the average molar fraction of monomer A in the polymer.

2.3 Batch and semi-batch experiments

To establish the kinetics and performance of the catalyst, batch and semi batch polymerizations were carried out to determine k_p and k_d (propagation and deactivation constants) values. Polymerization of ethylene was carried out in a 500 mL stirred glass reactor equipped with a pressure and temperature control unit. The reactor was filled with quantified amounts of solvent, catalyst, MAO inside a glove box unit.

In case of batch polymerization the reactor containing the catalyst and solvent was filled with ethylene to a specified pressure and allowed to react until the ethylene is almost completely utilized. Batch reaction can be described analogous to small unit in the micro reactor with a bubble of ethylene dissolving into the solvent region surrounding the bubble and reacting with the catalyst particles.

Semi Batch polymerization was carried out by continuous inflow of ethylene maintaining the reactor pressure constant, till the catalyst loses its activity and the reaction stops. Thus semi batch reaction provides a good estimate of the life and activity of the catalyst. The polymerization kinetics are simplified to estimate the amount of polymer produced in the reaction.[29]

$$g\text{Polymer} = ([M]_o - [M])w_m V_{solvent}$$

$$\text{Rate of polymerization } (R_p) = \frac{g\text{Polymer}}{g\text{Catalyst.min}}$$

$$R_p = -k_p[M]w_m[C_0^*]e^{-k_d t}$$

$$R_p^0 = -k_p[M]w_m[C_0^*]$$

$$\ln\left(\frac{R_p}{R_p^0}\right) = -k_d t$$

Where [M] is the monomer concentration in mol/L, w_m is the molar weight of the monomer (g/mol), [C^*] is the catalyst concentration in terms of moles of Zirconium per gram of catalyst. The propagation constant is given by k_p (L/mol-min) and the catalyst deactivation constant is given by kd (min^{-1}).

2.3.1 Batch and semi-batch polymerization results

The reaction conditions described in Table.2 are maintained the same for both batch and semi batch polymerization. The temperature and catalyst concentrations are varied for different experiments. Monomer concentration is a function of reaction temperature and pressure and is calculated using Henry Gasetz Law[30] given by

$$[M]= P\, H_o \exp (H_1/RT).$$

Where P is the Pressure (bar), T is the Temperature (K), [M] is the monomer concentration in mol/L, H_o and H_1 are experimentally determined constants whose values are 0.00175 mol/L.bar and 10742 J/mol respectively

Table 2 Operating Conditions for Batch and Semi-Batch Polymerization of Ethylene.

Constant Reaction Conditions for Batch and Semi-Batch Polymerization of Ethylene	
Catalyst/Co-Catalyst/Support	EBI/MAO/ Nano Silica Support (400 nm)
Ethylene Reactor Pressure	30 psig
[Ethylene] at 60°C	0.26 mol/L
[Ethylene] at 70°C	0.23 mol/L
[Ethylene] at 80°C	0.21 mol/L
Volume of solvent (toluene)	300 mL
Moles of [Zr]/ g-Catalyst	3.17×10^{-5}

The rate of polymerization measured by instantaneous amount of polymer synthesized per gram of catalyst for a semi batch reaction decreases with time (Fig 6) This is measured using the ethylene flow rate into the reactor to maintain the reactor pressure at set value, which indicates the amount of ethylene consumed in reaction.
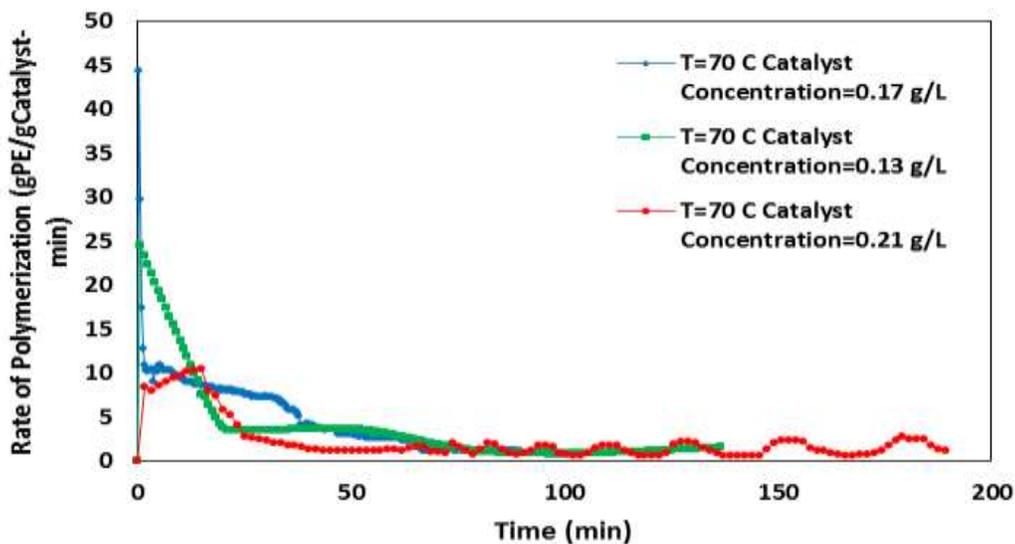
Figure 6 Rate of semi-batch polymerization (gPE/gCatalyst-min) against time (min) for T= 70˚C and different catalyst concentrations.

Instantaneous Activity is similar to rate of polymerization, but is measured in terms of the moles of active site, i.e. Zirconium active centers. The system shows high activity initially and as the active sites decay the activity decreases (Fig 7). Yield is measured by the cumulative grams of polyethylene produced per gram of catalyst every instant and increases initially and gradually reaches a constant value. (Fig 8). The plot shows that the lowest catalyst concentration has very high yield, however a small change in temperature has negligible effect.
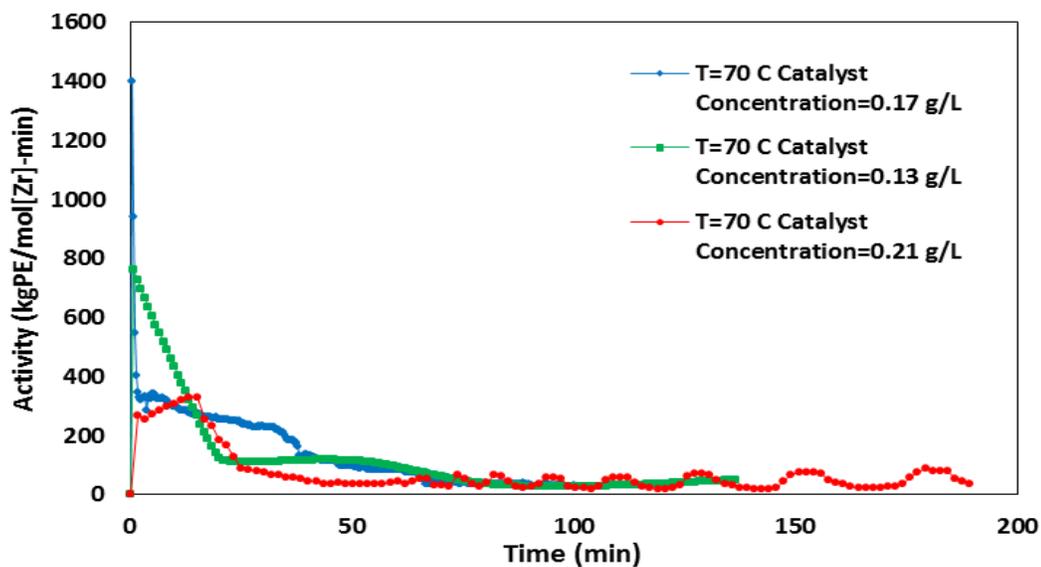
Figure 7 Activity against time for semi batch experiments at T=70˚C and varying catalyst concentrations.
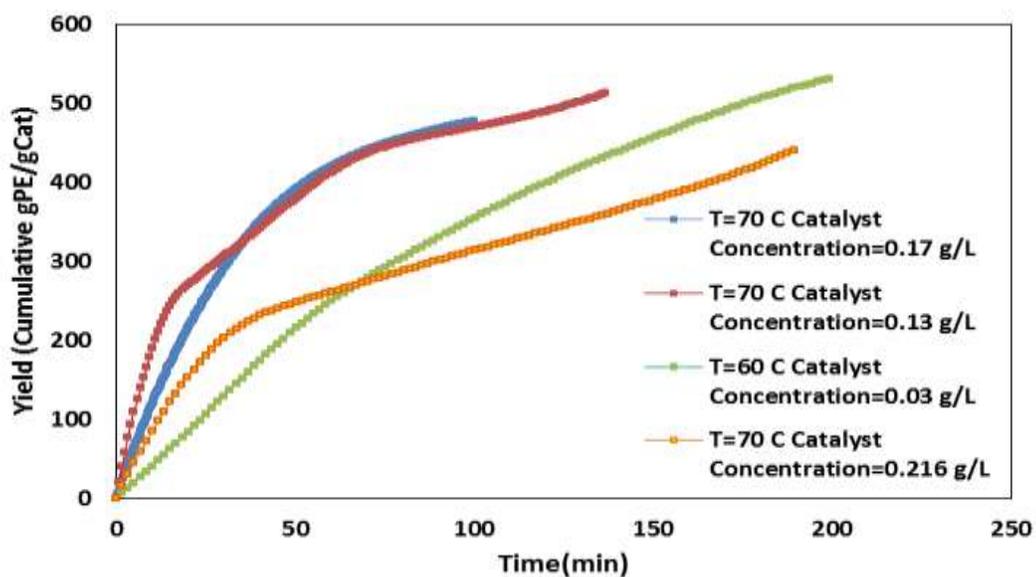
Figure 8 Yield against time for semi-batch experiment at different temperatures and catalyst concentrations.

A deactivation constant of 0.028 min⁻¹ found using the semi-batch experiment indicates much better catalyst properties compared to homogenous catalyst and

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commonly marketed catalyst support. (Fig 9).The slope of the straight line is k_d by the

following equation $-\ln\left(\dfrac{R_p}{R_p^o}\right) = k_d t$

k_d is an indicator of the life of the catalyst and an optimum value is ideal to control the reaction time and rate.
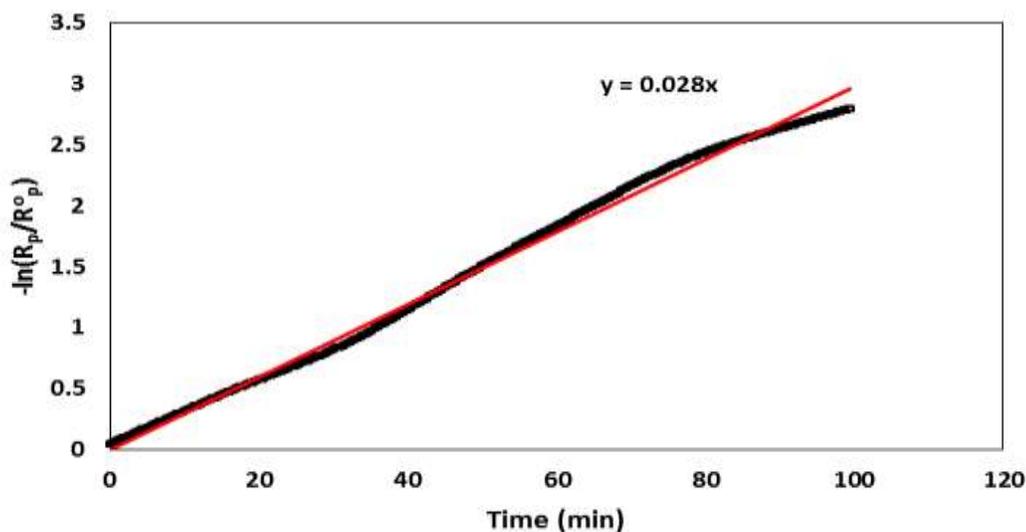
Figure 9 Estimation of k_d: Reaction conditions T=70°C, Catalyst Concentration=0.17 g/L, k_d=0.028min^{-1}.

Batch Experiment

Figure 10 and Figure 11 shows the decrease in rate of polymerization and increase in yield with time for different temperatures while maintaining the other parameters constant. The dissolved monomer concentration is higher at lower temperatures, so the yield is higher; this is probably because the temperature increase is not large enough to impact the rate of polymerization very much.
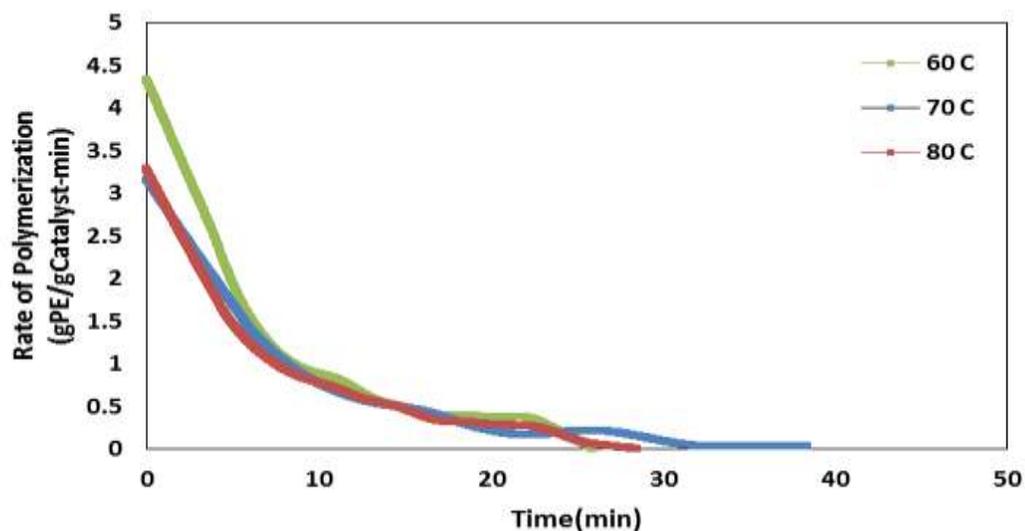
Figure 10 Rate of polymerization (Batch reaction) for 60, 70, 80 ˚C.
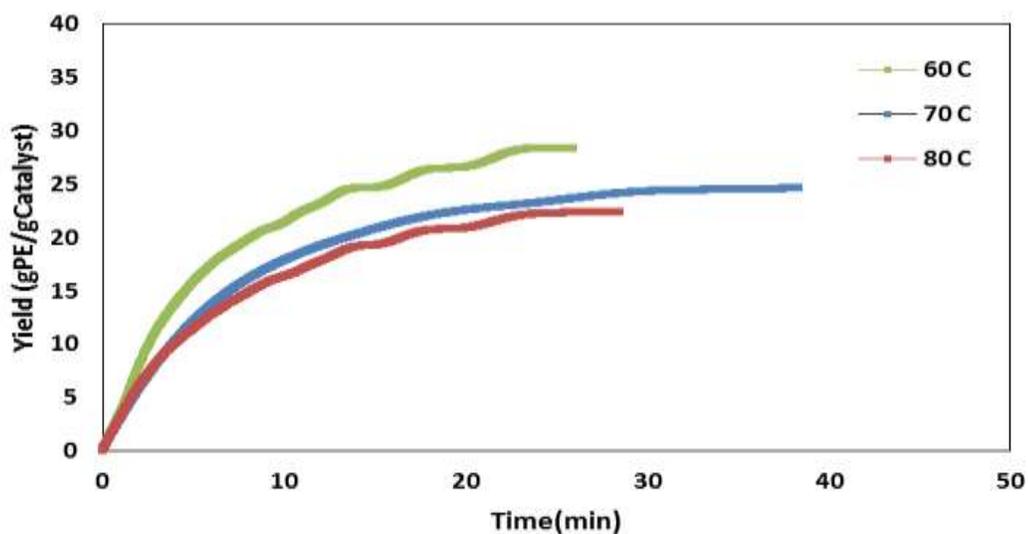
Figure 11 Cumulative yield (gPE/gCat) (Batch Reaction for 60, 70, 80 ˚C).

Simplified kinetics assume Rate of Polymerization to follow a linear relation with the product of [M] and [C*] (Fig 12). The decreasing catalyst concentration is determined using an exponential decay with the k_d value determined in the semi batch experiment. The propagation constant was determined to be 2.4×10^4 L/mol-min.
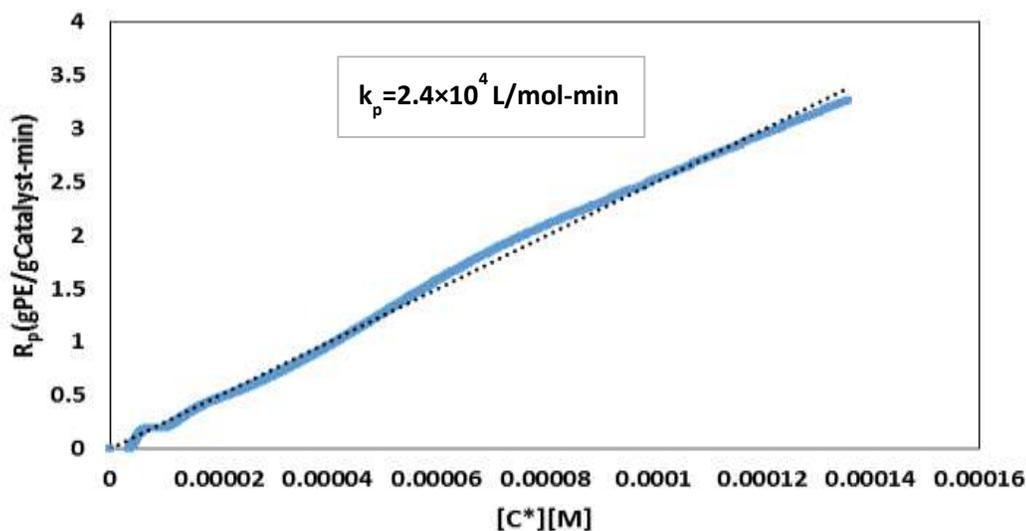
Figure 12 Estimation of k_p using linear fit of $R_p = k_p[C^*][M]$.

2.3.2 Summary of results

Table 3 summarizes the results from batch and semi batch experiments. As the catalyst concentration increases the yield and activity are found to decrease for a semi-batch reaction. In case of a batch reaction the activity and yield decreases from 60 to 70˚C , but there is negligible change oberved for 80˚C. In the range of 60 to 80˚C there is a negligible change in the kinetic constants.

Table 3 Summary of batch and semi batch polymerization results

	Temper-ature (˚C)	Catalyst Concentration (g/L)	Yield (Total gPE/gCatalyst)	Activity (Total kgPE/mol[Zr] -min)	Kinetic Constants estimated
Semi-Batch	70	0.13	512.2	118.29	k_d=0.028 min^{-1}
	70	0.17	495.4	129.9	
	70	0.21	440	62.8	
Batch	60	0.17	28.4	34.5	k_p=2.4×10^4 L/mol-min
	70	0.17	23.5	24.4	
	80	0.17	22.3	24.7	

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2.3.3 SEM Images showing polymer evolution

Polymer samples were collected during different time intervals during the course of a semi-batch reaction to visualize the growth of the polymer particle around the nano silica supported catalyst. It is observed that the polymer chains grow around the catalyst support without disintegrating the catalyst particle As time progresses there is addition of monomer between live polymer chains growing from different catalyst particles and eventually forming an interconnected mass of polymer chains Towards the end of the reaction an entangled mass of chains surround the catalyst particles (Fig 13).

t=1 minute:
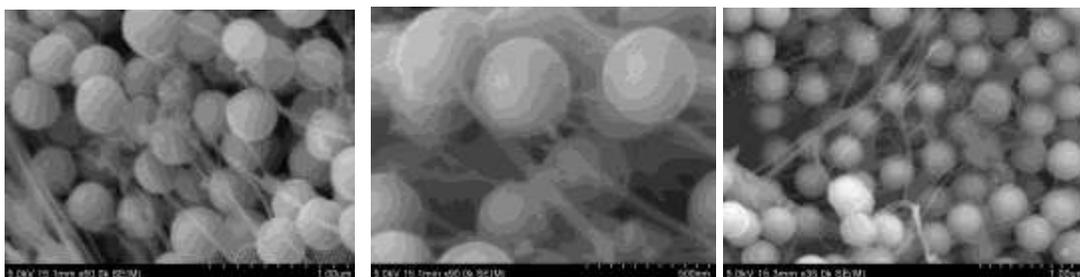
t=3 minutes:
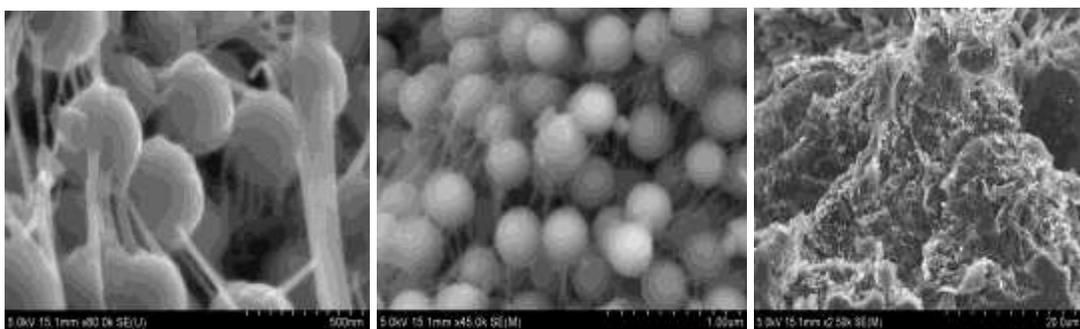
t=5minutes:
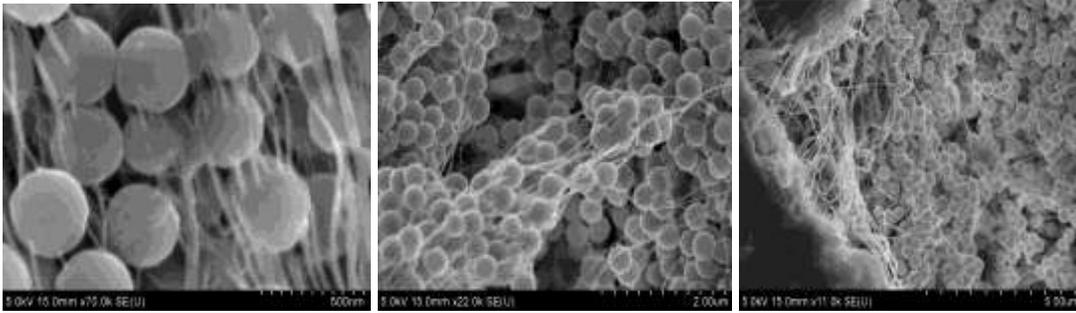
t=10 minutes:
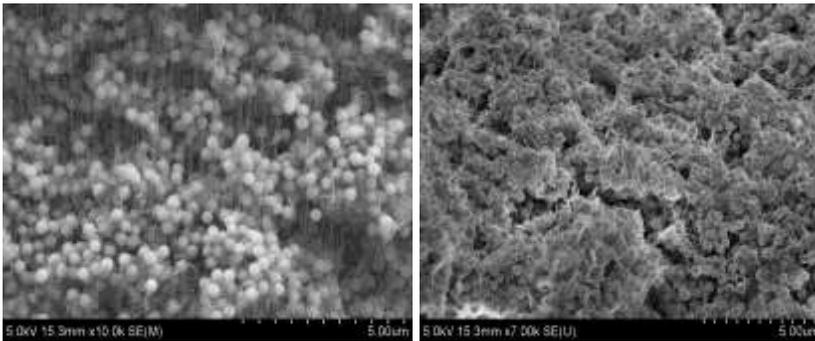
t=20 minutes:
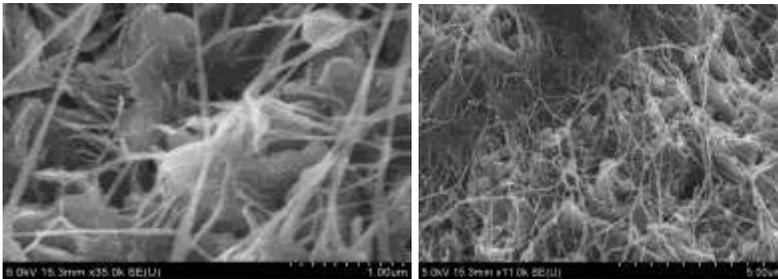
t=30 minutes-End of Reaction
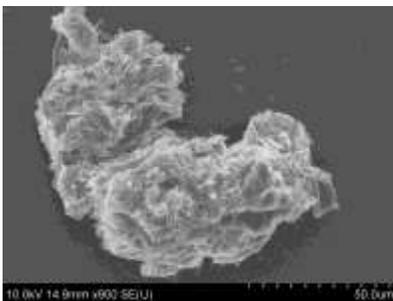
Figure 13 Growing polymer for a batch reaction.

2.4 Flow visualization in micro channels

In order to carry out the reaction in channels of small diameters, the 2 phase flow of the monomer in the solvent is observed to understand the physical mechanics of the reaction progression. Video snapshots of different flow regimes in the micro channel were observed to visualize the flow pattern of ethylene in toluene. In order to maintain a uniform consistent monomer concentration in the reactor and yet have sufficient dissolved monomer, the flow rates of ethylene and toluene needed to be tuned. This provided a basic idea of conditions that would result in at least partial dissolution of ethylene in toluene. The tests were carried out in an 800µm channel (Fig 14).
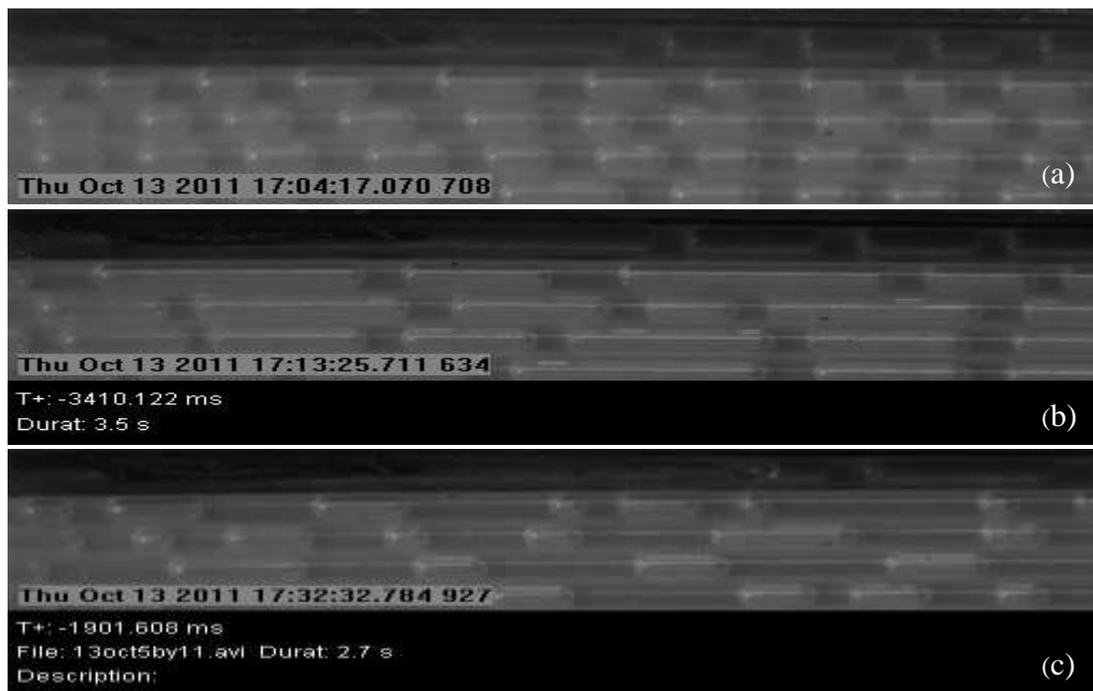
Figure 14 Flow patterns in an 8ooµm channel for the following flow rates;
      (a) Toluene Flow rate=2mL/min Ethylene Flow rate=3.1mL/min
      (b) Toluene Flow rate=2mL/min Ethylene Flow rate=7mL/min
      (c) Toluene Flow rate=5mL/min Ethylene Flow rate=7mL/min

To understand the stability of flow of the larger polymer and catalyst particles and the feasibility of conducting 2 phase polymerization with a solid catalyst in a MR, silica gel particles of 1 to 5 microns (colored with a tracer) was suspended in toluene and injected along with ethylene in the micro channel. A uniform flow of the particles was observed in the liquid region between the ethylene bubbles (Fig 15).
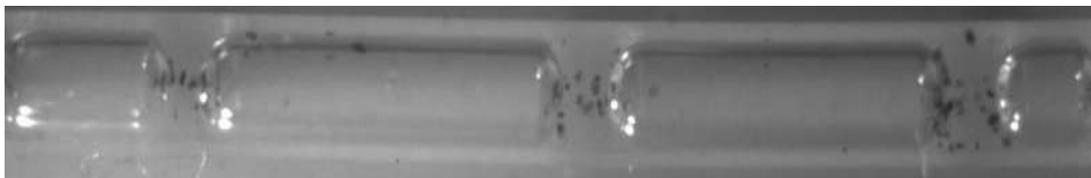
Figure 15 Two phase flow in presence of particles

2.5 Micro reactor experimental setup
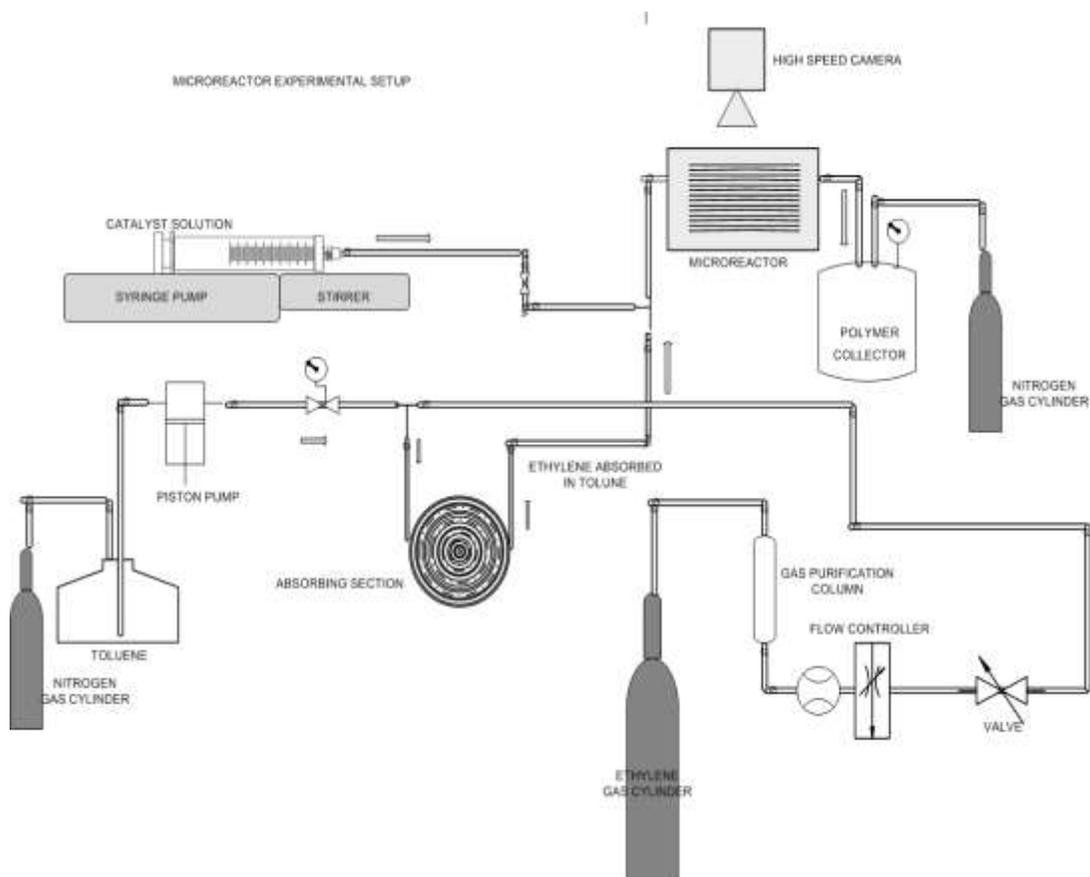
Figure 16 Micro reactor experimental setup.

Over the course of the project, the experimental set up has evolved to overcome the constraints in carrying out polymerization in a micro reactor.

Absorption section This helps in dissolving the ethylene monomer partially in the solvent and thereby allowing faster reaction in the reactor section. The advantage in this set up is that, the undissolved gas bubbles leaving the absorber section acts as a consistent source of monomer in the reactor section.

Catalyst supply The metallocene catalyst used for polymerization is highly sensitive to air and moisture, the catalyst is prepared and extracted into a syringe in a glove box, and the syringe is kept in contact with a stirrer to ensure homogeneity and prevents the particles from settling (Fig 17).
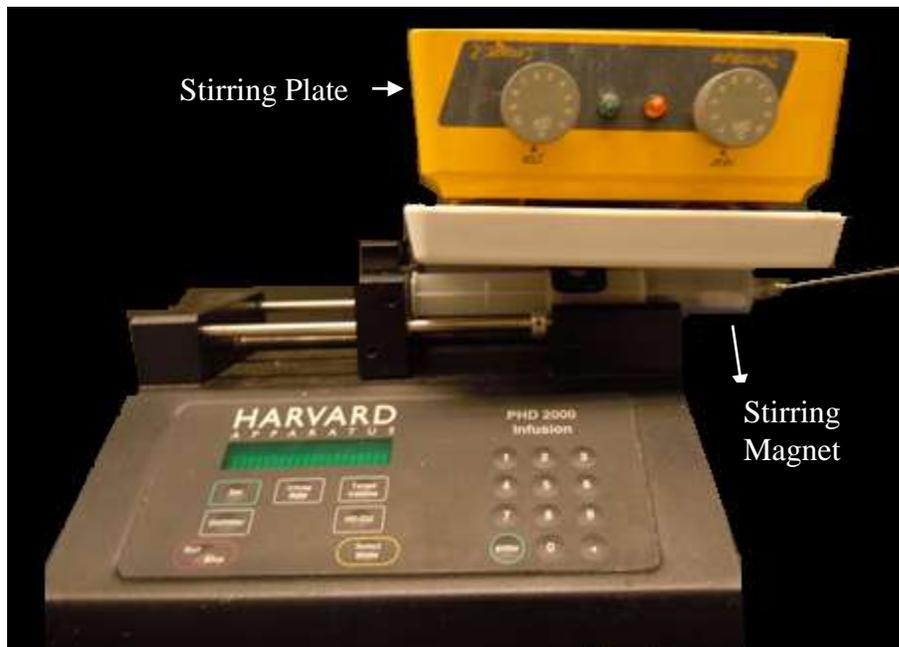
Figure 17 Catalyst supply system with magnetic stirrer.

Gas purification column A gas purification column was built in order to remove any moisture or other impurities from the monomer. It consists of layers of

molecular sieves, activated carbon, neutral alumina, combination of R3-16 Cu-Zn Catalyst, molecular sieves and glass wool.

Reactor section The reactor section consists of a PTFE tubing coiled and heated in a water bath to control the reaction temperature. PTFE tubing work for a wide range of temperatures from -65 to 260 °C and can withstand pressure up to 500 psi and have the right amount of stiffness and flexibility such that it can be coiled to improve mixing. The tubing is very compatible with toluene which tends to react harshly with other materials. They are easy to replace when clogged and reactor lengths can be adjusted without effort and are very economical. They have a smooth surface and low friction that prevents the polymer from sticking to the sides of the tubes. These tubes are also fairly transparent allowing for easy visualization of the process.

Polymer The polymer collected is washed with a solution of methanol and concentrated hydrochloric acid and filtered to recover solid polymer.

Challenges overcome Catalyst and solvent supply without exposing to air and moisture: Solvent was kept in a nitrogen atmosphere and supplied using a piston pump. Catalyst is filled into a syringe inside a glove box with inert atmosphere and taken out with the needle sealed. An absorbing section with smaller diameter compared to the reactor section ensures higher mass transfer of the monomer into the solvent. The dissolved monomer reacts instantaneously in the reactor section and the undissolved monomer acts as a reservoir constantly replenishing the monomer. Valves with small holding volumes are used to prevent the catalyst particles from settling. Maintaining the reactor outlet at a pressure slightly smaller than the inlet

pressure proved more effective compared to maintaining it at atmospheric pressure.

Elevated pressure of the reactor enhances mass transfer.

Chapter 3: Reactor modeling and simulation

3.1 Model Assumptions

The polymerization in the micro reactor is simulated assuming an unsteady state model to study the evolution of the reaction along time and length of the reactor channel.[31,32] The consumption of the gaseous monomer is considered from bubble to liquid phase via dissolution into the solvent and its consequent reaction with active sites on the solid catalyst loaded on nano silica carriers (Fig 18). This is done to establish operating conditions and to predict the results of experiments.
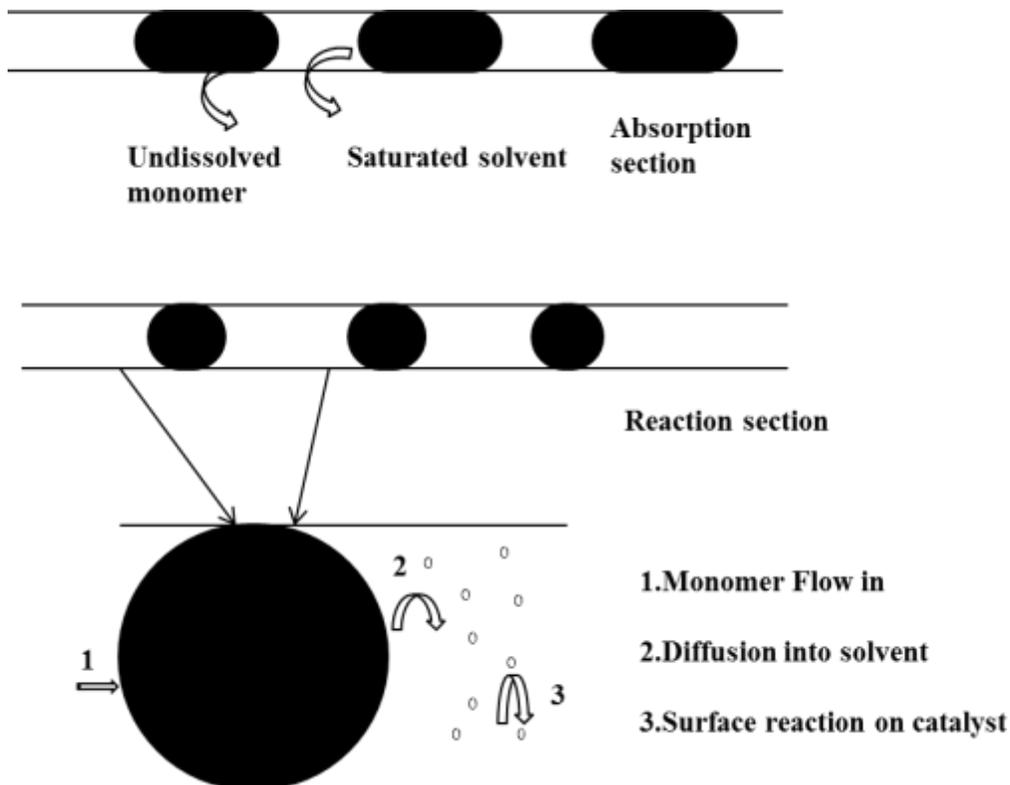
Figure 18 Absorption and reaction mechanism.

A mass balance of the monomer in the solvent takes into account consumption of the monomer in polymerization, monomer transferred from bubble to solvent and the monomer in the flow term.

$$\frac{\partial M_L}{\partial t} = -k_p M_L C_{cat}^0 e^{-k_d t} - v_z \frac{\partial M_L}{\partial z} + k_m (M_g^o - M_L)$$

Initial Conditions
$$M_L(0) = M_L^0 \text{(from Henry's Law)}$$
Boundary conditions
$$\text{At } z = L \quad \frac{\partial M_L}{\partial z} = 0$$

In the above equation M_L is the dissolved monomer concentration in the solvent, M_g is the bubble phase monomer concentration, C_{cat}^o is the catalyst concentration, v_z is the average flow velocity along the length of the reactor (neglecting pressure effects), k_m is the mass transfer coefficient (of the monomer from gas bubble to solvent) calculated using the diffusion coefficient and Sherwood number. The partial differential equation is solved using MATLAB PDEPE solver.

The model generates the monomer concentration at every z, t. This can be used to measured instantaneous grams of polyethylene produced, activity, conversion and other parameters.

3.2 Reactor design conditions for the simulations based on experimental observations

The initial simulations were carried out for smaller channels of diameters 800μm and 1mm, despite the model results giving good activity and conversion, the clogging issue was inevitable in the actual experiments This is because the polymer

particles grow and agglomerate and since the flow rates maintained are low for sufficient residence time, the possibility of clogging is higher at low flow rates. Experiments carried out for channels of 2.37mm were more successful for stable polymerization without clogging.

3.3 Activity and conversion profiles

Net activity is measured by calculating the total polymer produced at the end of the experimental run in the micro reactor and the total moles of Zirconium utilized (i.e. the active sites in the catalyst). Activity described in the following section is

$$\frac{\text{Total (kg) Polymer synthesized}}{\text{(g) Catalyst used} \times \dfrac{\text{moles[Zr]}}{\text{gCatalyst}} \times \text{Run Time (hr)}}$$

Net conversion is estimated using the difference of initial monomer concentration and final monomer concentration. gPE refers to the grams of polyethylene produced.

$$\frac{\text{Total gPE synthesized in the micro reactor} \times 100}{\text{Total g Ethylene inlet}}$$

The simulation is carried out for the following primary conditions with the toluene flow rate, volume of catalyst, [Al/Zr], temperature and pressure maintained constant.

Table 4 Micro reactor operation conditions for ethylene polymerization

Reactor Conditions for Ehylene Polymerization in a Micro Reactor	
Reactor Length	7m
Reactor Diameter	2.37 mm
Ethylene Pressure	50 psi
Temperature	75˚ C
Toluene Flow rate	1 ml/min
Catalyst Concentration	0.418 g/L
Catalyst Volume	20 mL
[Al/Zr]	3189

3.3.1 Effect of change in residence time

In Fig 19 the simulation results show Activity (kgPE/mol[Zr]-hr) plotted against varying residence time (by changing the catalyst flow rate) and for different ethylene flow rates. As the catalyst flow rate decreases, despite the increased reaction time available , the amount of polymer produced is lesser due to fewer active catalytic sites available at a given instant.
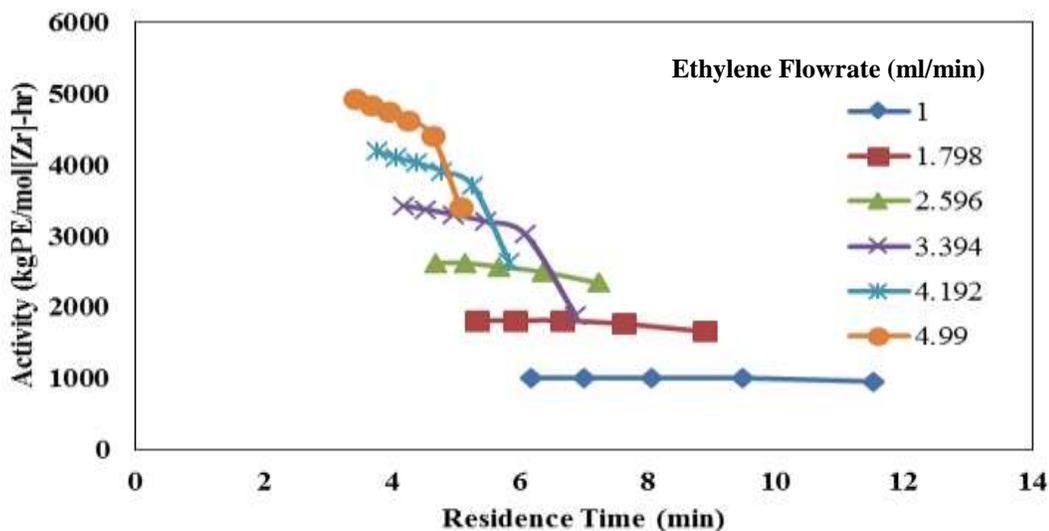
Figure 19 Activity against residence time for varying ethylene flow rates.
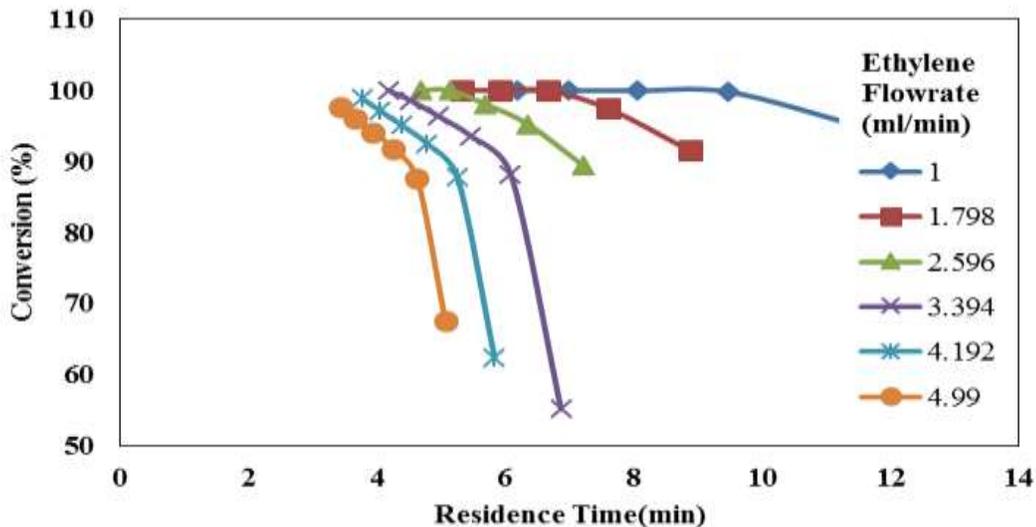
Figure 20 Conversion against residence time for varying ethylene flow rates.

There is an unusually steep decrease in conversion at higher ethylene flow rates with a slight increase in residence time. At lower ethylene flow rates the conversion is higher for the larger residence time since there is more reaction time (Fig 20).

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3.3.2 Effect of change in catalyst flow rate
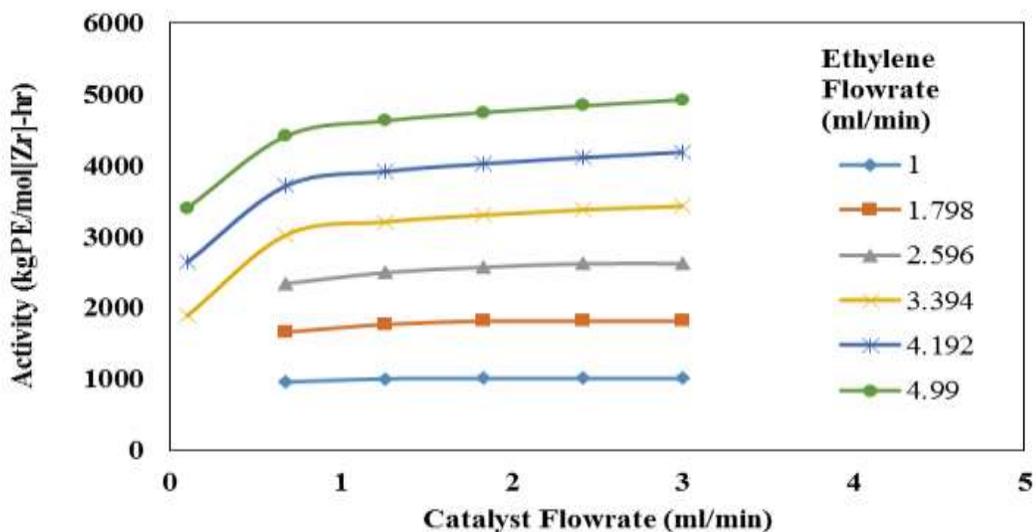
Figure 21 Activity against catalyst flow rate for varying ethylene flow rates.

As in Fig 21 activity is found to increase at lower catalyst flow rate and evens out at flow rates more than 1.5 ml/min at lower ethylene flow rates. At higher ethylene flow rates there is a very gentle increase in activity. This pattern can be attributed to unreacted catalytic active sites.
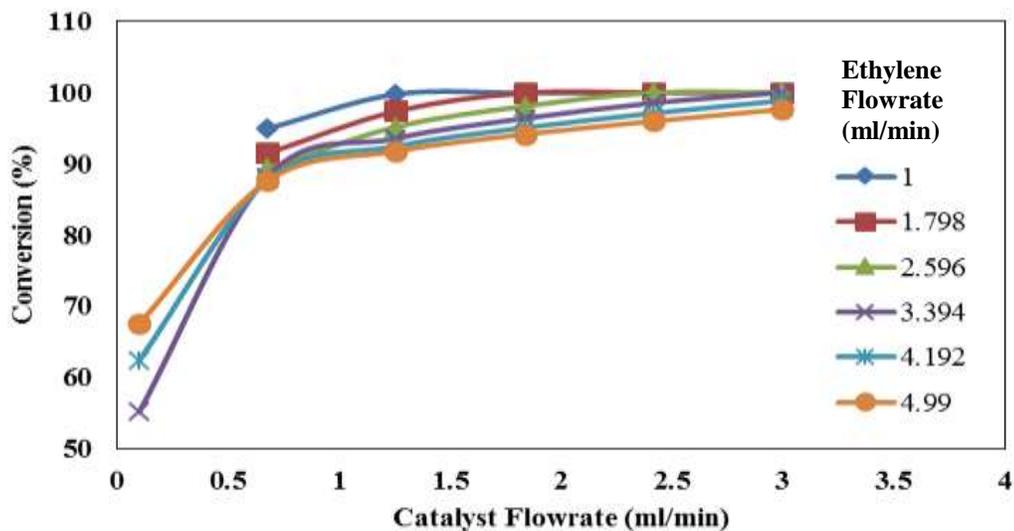
Figure 22 Conversion against catalyst flow rate for varying ethylene flow rates.

There is a steep increase in conversion with increase in catalyst flow rate at higher ethylene flow rates, since conversion solely depends on the unreacted monomer presence of a certain optimum catalytic sites at a given instant is desirable. Beyond that the influence of catalyst flow rate is balanced out by the residence time (Fig 22).

3.3.3 Effect of change in ethylene flow rate
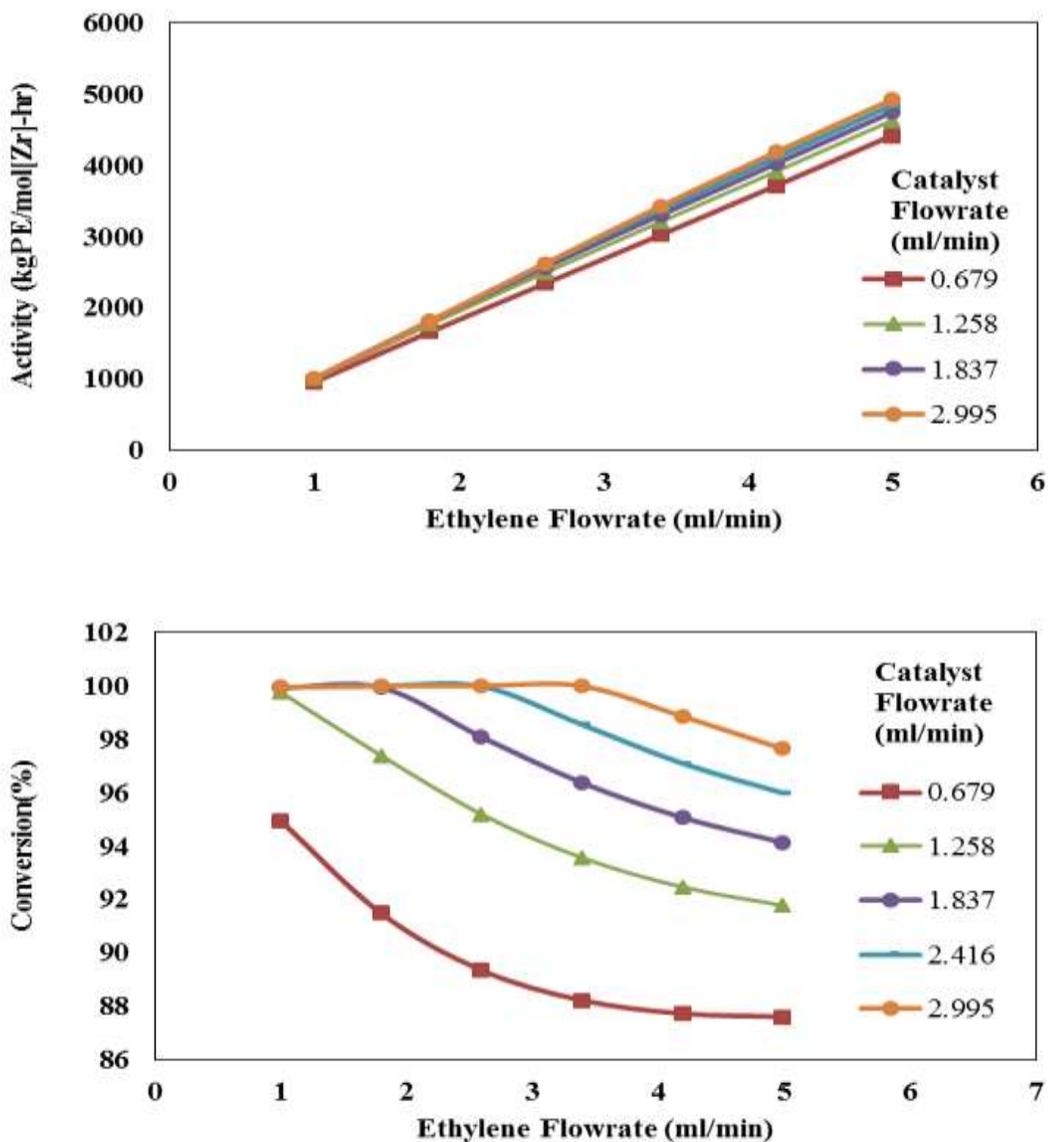
Figure 23 Activity and conversion against ethylene flow rate for varying catalyst flow rate.

Activity increases with increasing ethylene flow rate on the other hand

conversion decreases and follows a logical pattern since activity is a function of both

gPE and runtime.

3.3.4 Effect of change in catalyst concentration

Activity decreases with catalyst concentration and is higher for higher catalyst

flow rates and considers the effect of both molZr and residence time. Conversion

increase with catalyst concentration is higher for higher catalyst flow rates (Fig 24).
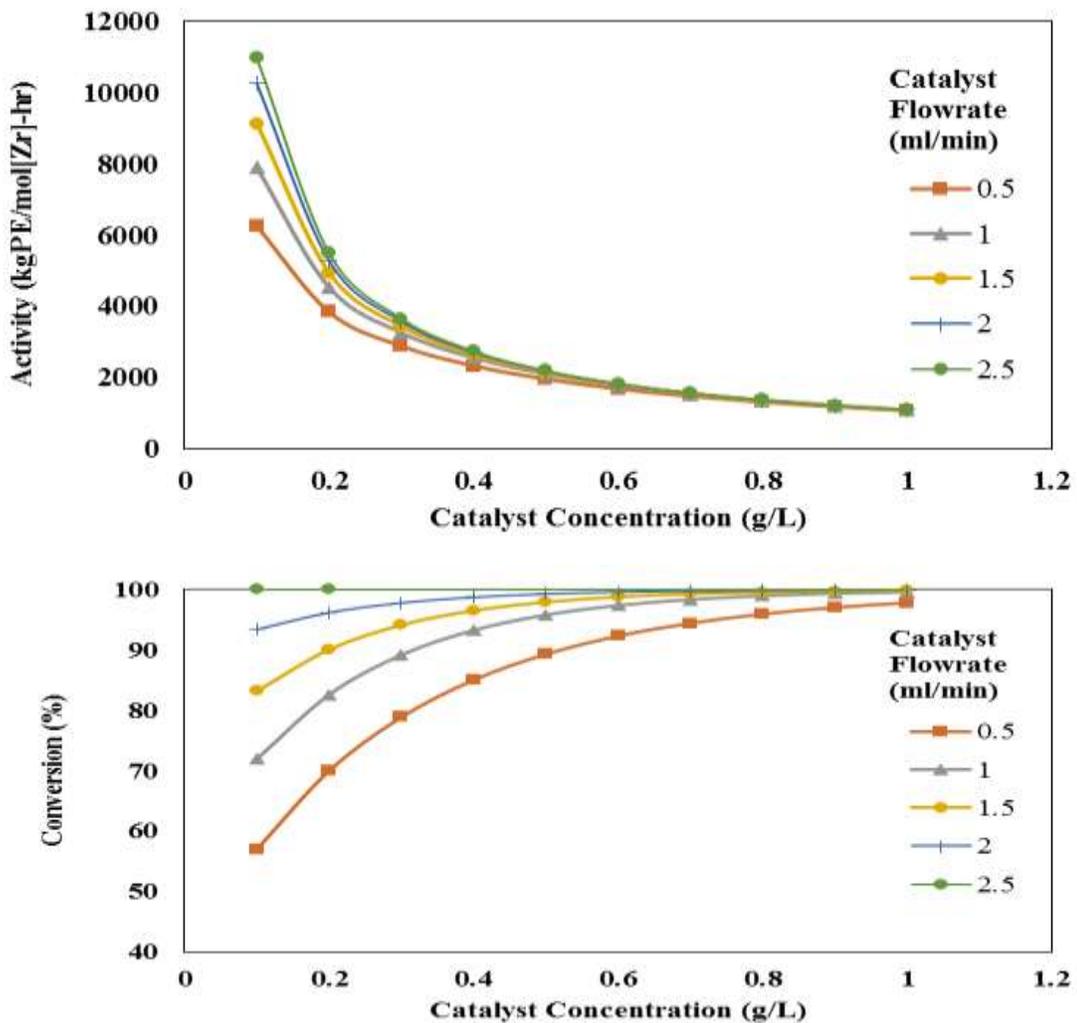
Figure 24 Activity and conversion against catalyst concentration for varying catalyst flow rate.

3.4 Concentration profiles along reactor length and reaction time

The PDE solver generates instantaneous monomer concentration for every z and t, this can be used to calculate instantaneous conversion, rate of polymerization and polymer concentration.

Table 5 Reactor conditions for ethylene polymerization in a micro reactor

Reactor Conditions for Ehylene Polymerization in a Micro Reactor	
Reactor Length	7m
Reactor Diameter	2.37 mm
Ethylene Pressure	50 psi
Temperature	75˚ C
Ethylene Flow rate	2.6 ml/min
Toluene Flow rate	1 ml/min
Catalyst Flow rate	1.25 ml/min
Catalyst Concentration	0.418 g/L
Catalyst Volume	20 mL
[Al/Zr]	3180

Figures 25 and 26 show the profile of Monomer Concentration, gPE/L, Conversion, Rate of polymerization along different points on the reactor length and the time duration of reaction. Monomer concentration decreases along different points of reactor and as the rate of polymerization decreases with time the monomer concentration becomes higher as the active sites of the catalyst decreases.
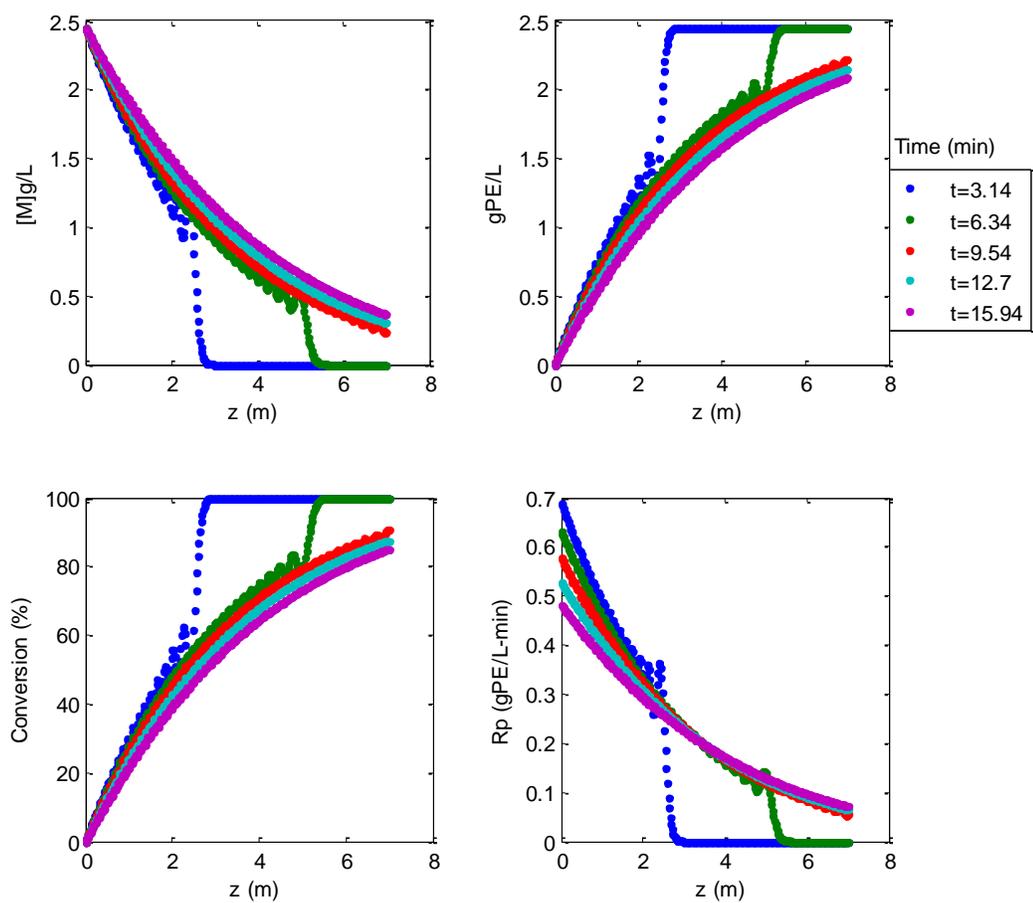
Figure 25 Concentration profiles of monomer, polymer, conversion, rate of polymerization against reactor length.
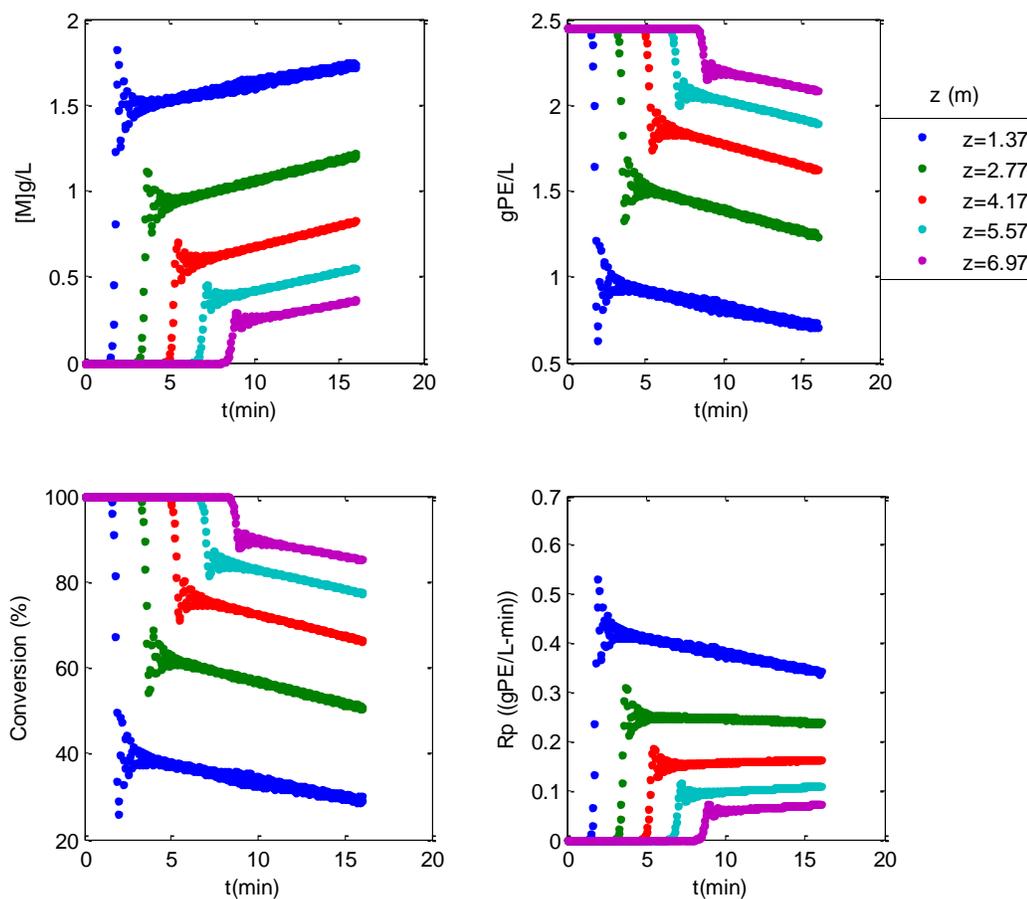
Figure 26 Concentration profiles of monomer, polymer, conversion, rate of polymerization against reaction time.

3.5 Molecular weight distribution modeling

The number and weight average molecular weight ,polydispersity index are plotted along the reaction time and along different points on the reactor .It is found to increase gradually and even out to a constant value. The PDI decreases with time from 2 to a value of around 1.25 (Fig 27).
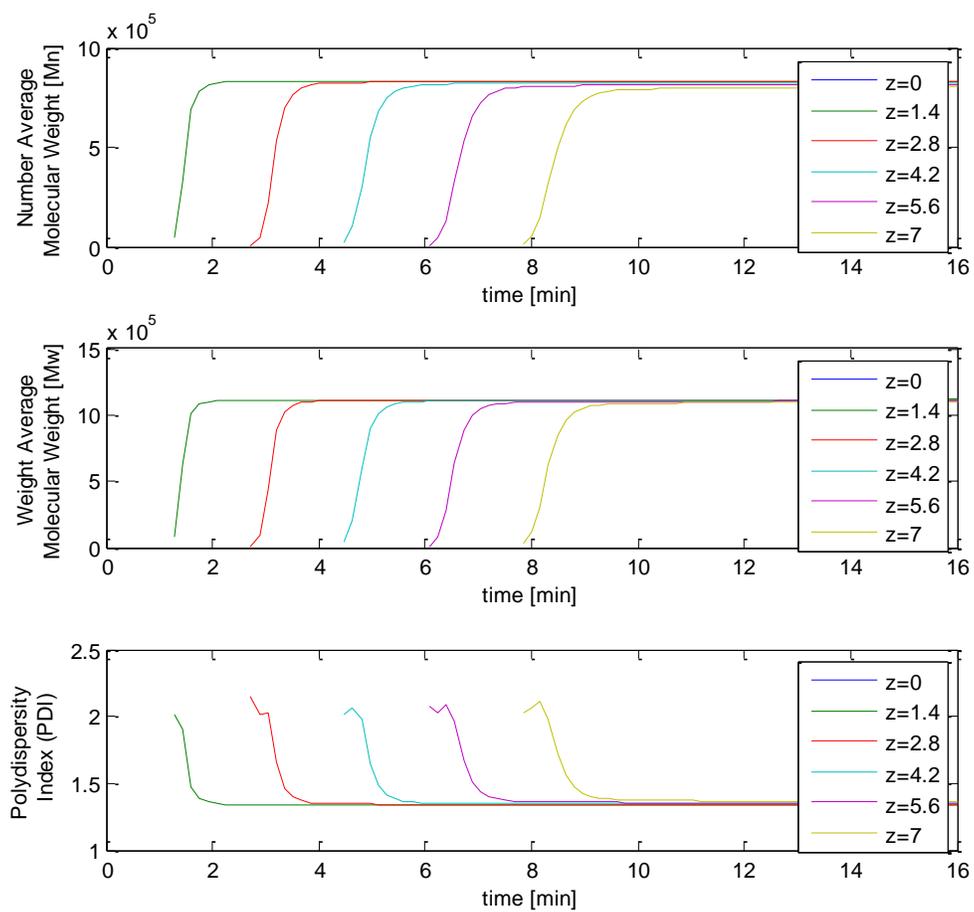
Figure 27 Variation of M_n, M_w, PDI with time

The weight fraction plotted against the chain length gives the molecular weight distribution at the reactor exit, the MWD gets narrower towards the end of the reaction and higher molecular weight polymer is produced in the beginning of the reaction (Fig 28).
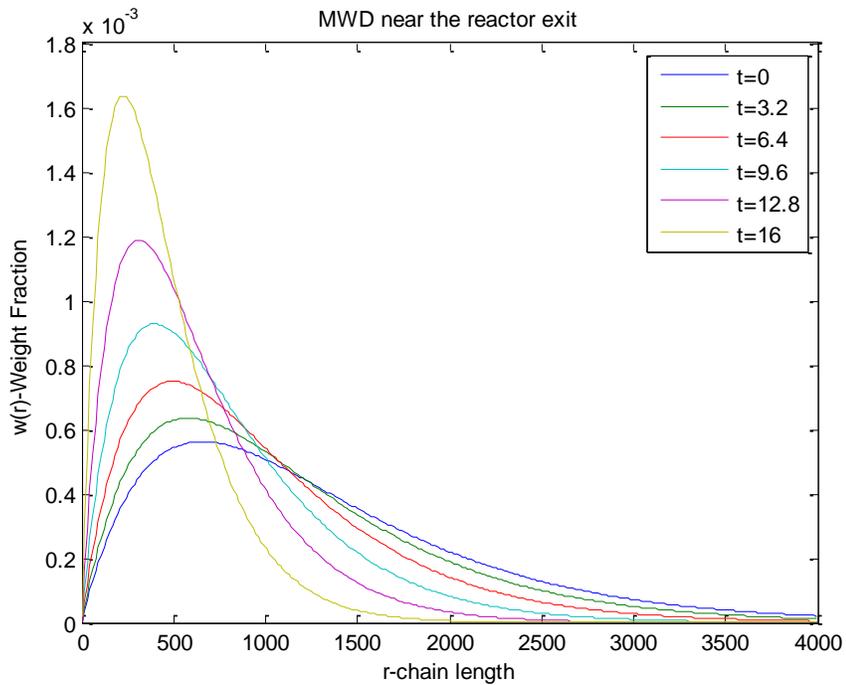
Figure 28 Molecular weight distribution near the reactor exit.

Figure 29 shows the MWD along different points of the reactor .The MWD is broader near the very inlet of the reactor and there is a higher fraction of high molecular weight polymer .Towards halfway through the reactor there is a very narrow MWD. And the weight fraction of the low molecular weight fraction decreases towards the end of the reactor.
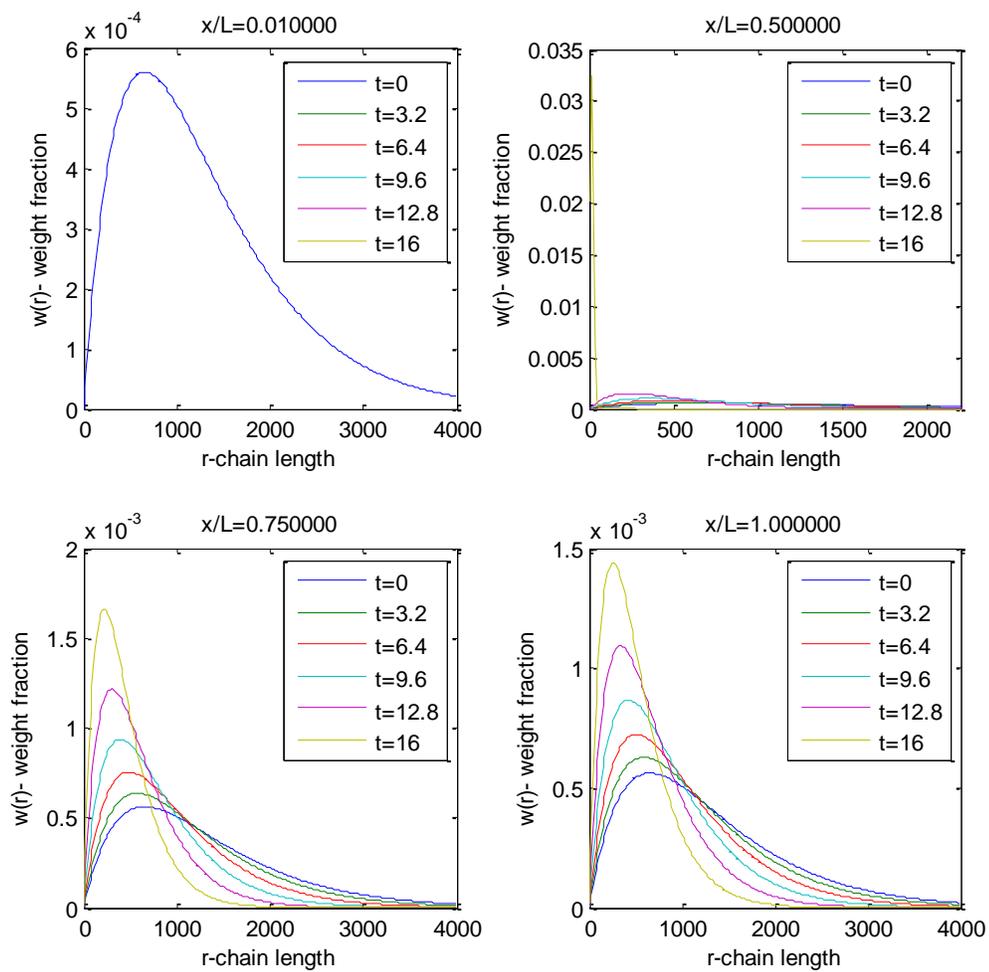
Figure 29 Molecular weight distribution along the reactor length (at x/L=0.01, 0.5, 0.75, 1).

The weight fraction of higher molecular weight polymer decreases with time, and the MWD gets narrower towards the end of the reaction (Fig 30).
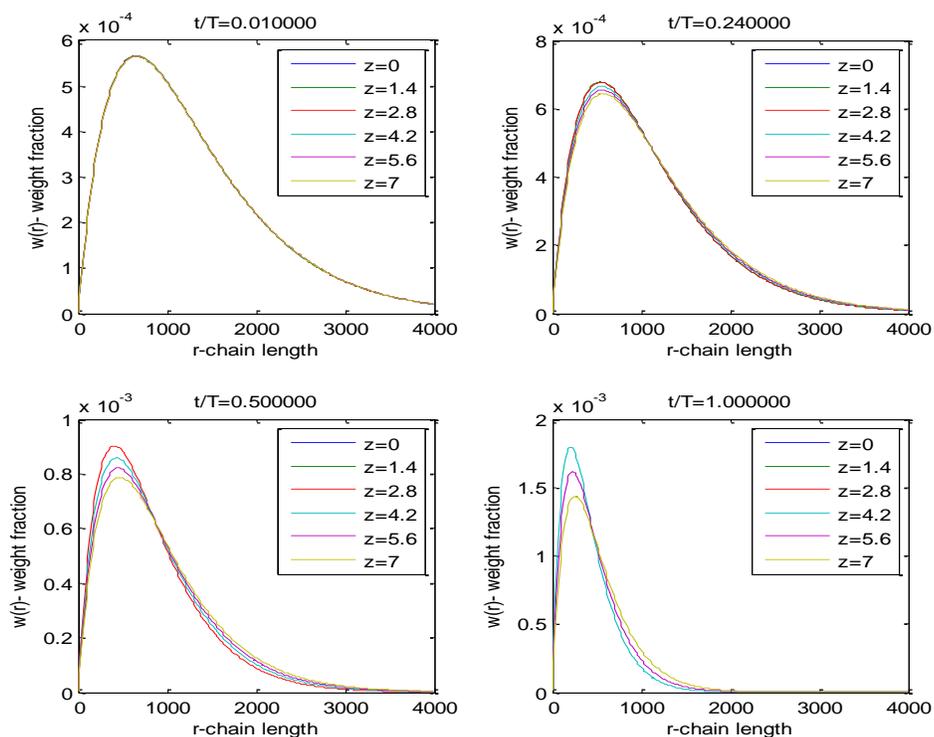
Figure 30 Molecular weight distribution along reaction time (at t/T=0.01, 0.25, 0.5, 1).

3.6 Effect of operating conditions on MWD

As the ethylene flow rate decreases the distribution gets narrower ,there is lesser ethylene concentration and the rate is dependent on mass transfer and the molecular weight drops [33] (Fig 31). As the catalyst flow rate increases MWD becomes narrower since new and shorter polymer chains are formed, as opposed to lower catalyst flowrates where there is sufficient time for the polymer to grow and utilize the effects of high mass transfer (Fig 32). As catalyst concentration increases rate of polymerization becomes very high and the bubble phase ethylene

concentration drops and this makes the reaction mass transfer controlled causing a

drop in molecular weight (Fig 33).
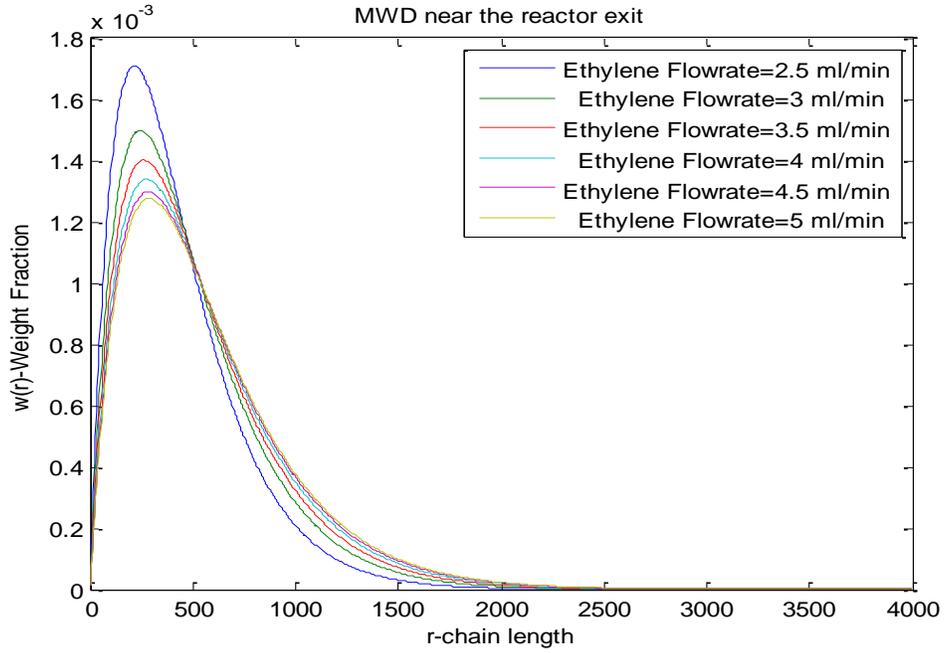
Figure 31 Molecular weight distribution for varying ethylene flow rate.
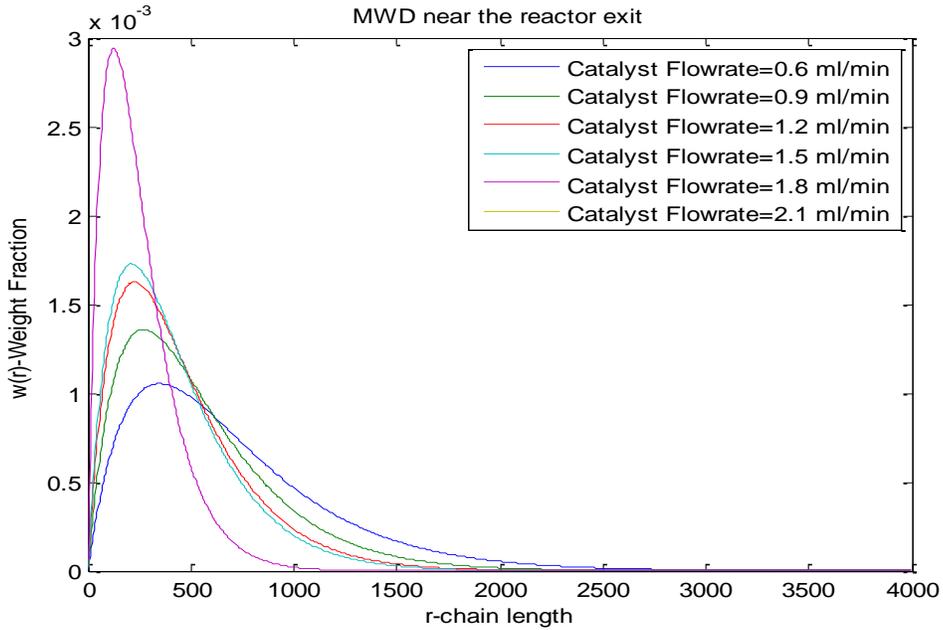
Figure 32 Molecular weight distribution for varying catalyst flow rate.
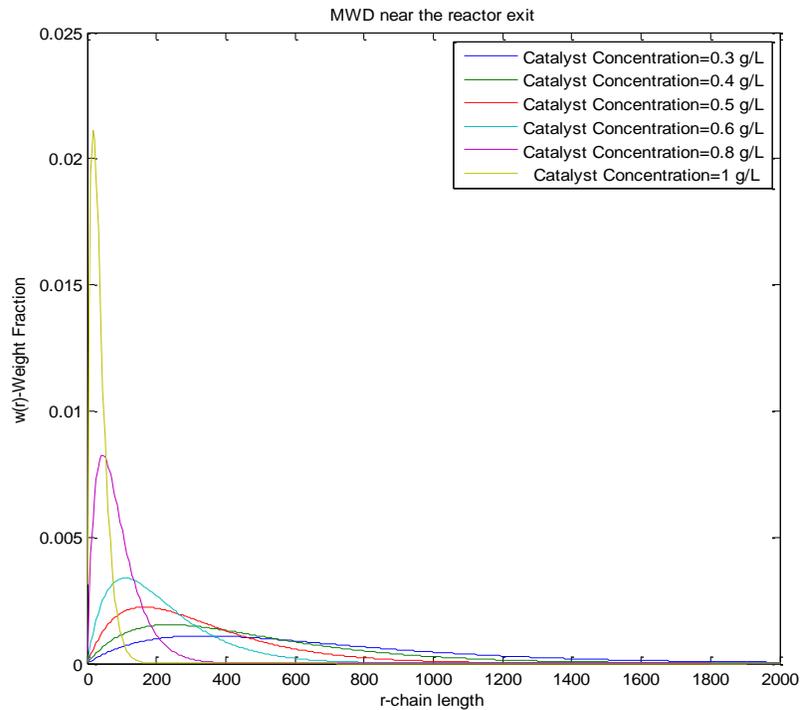
Figure 33 Molecular weight distribution for varying catalyst concentration.

Table 6 summarizes the effects of the operating conditions on activity, conversion

and MWD. This helps in determining experimental conditions that maximize the

activity and the conversion. The MWD helps to determine the quality and density of

the polymer that is desired.

Table 6 Summary of effect of operating conditions on activity, conversion and MWD of the polymer

Effect of Increasing	Activity (kgPE/mol Zr-hr)	Conversion (%)	Molecular Weight Distribution
Ethylene Flow rate	Increases	Decreases	Broader
Catalyst Flow rate	Increases	Increases	Narrower
Catalyst Concentration	Decreases	Increases	Narrower
Residence Time	Decreases	Decreases	

Chapter 4: Micro reactor experimental results

4.1 Quantitative results

4.1.1 Comparison of experimental to theoretical results

Ethylene Polymerization was carried out in the set up described in Section 2.5. After several experiments the reaction parameters were tuned to ensure the yield and activity was maximized and clogging minimized. The initial experiments were performed using reactor channels of diameters 800µm and 1mm, however the intensity of the reaction rate was difficult to control under such conditions and more often resulted in clogging owing to the high mass transfer rate in small channels. Some of the results are summarized below and compared with the theoretical model.

Table 7 Experiment and theoretical activity and conversion for different reactor dimensions [Residence Time =6 min, Activity (kgPE/mol [Zr]-hr), Conversion (%)]

Reactor Length (L) Diameter (D)	$V_{ethylene}$ ml/min	$V_{catalyst}$ ml/min	$V_{toluene}$ ml/min	Theoretical		Experimental	
				Activity	Conversion	Activity	Conversion
L=15m D=0.8mm	0.5	0.25	0.25	548	54	101	18
L=10m D=1mm	0.5	0.3	0.5	650	64.4	250	29
L=7m D=2.37mm	2.5	1	1.5	4865	96.3	4600	85
L=3m D=1mm +L=1.5m D=2.37mm	2	0.5	1	2270	56.2	3300	65

Table 7 summarizes theoretical and experimental results for reactor sections of different dimensions for a constant residence time of 6min. For very small channels of diameters 0.8mm and 1mm, very long channels and small flow rates were required to have sufficient reaction time. Due to the small channel diameters and large surface area for mass transfer the growth of the polymer particle is hindered by clogging. Hence the resulting experimental conversion and activity are lower due to inability to complete the reaction after the channel was clogged. More successful results were obtained for channel of diameter 2.37mm and a series combination of 1mm and 2.37mm channels. The model under predicts the effect of using a combination of channel diameters since it does not take into account the better heat transfer of the smaller section since isothermal behavior is considered for simplicity.

4.1.2 Comparison of micro to macro reactors

Ethylene polymerization carried out under similar conditions for micro and macro reactors (laboratory scale batch and semi batch reactors) at 75°C, 40 psi, catalyst concentration of 0.42 g/L and for the same reaction time.

Reactor type	Volume of reactor (mL)	Activity (kgPE/mol[Zr]-hr)	Activity (kgPE/mol[Zr]-hr-volume of reactor)
Microchannel	30.8	4600	149.3
Microchannel	6.6	1923.3	291.4
Batch	500	4822.5	9.6
Semi-batch	500	9920	19.84

The activity per unit reactor volume of the micro channel reactor is significantly higher than the macro reactors due to the higher mass and heat transfer.

4.1.3 Effect of ethylene flow rate and reactor dimensions

Reactor Dimensions	Catalyst Concentration	Temperature	Pressure	[Al/Zr]	Volume of Catalyst
D=2.37mm	0.42 g/L	75˚C	50 psi	3189	8mL

The experimental activity plotted for the above reaction conditions against ethylene flow rate shows a similar increasing profile to the theoretical activity simulated from the model. (Fig 34 and Fig 35). The experimental values are smaller however, this can be attributed to the uncertainties such as catalytic activity, homogeneity, clogging, and maintaining constant temperature. Also, the amount of ethylene dissolved in toluene is lower than what is obtained by theoretically assumed mass transfer rates and constants. And hence, less ethylene is available in dissolved phase for reaction.
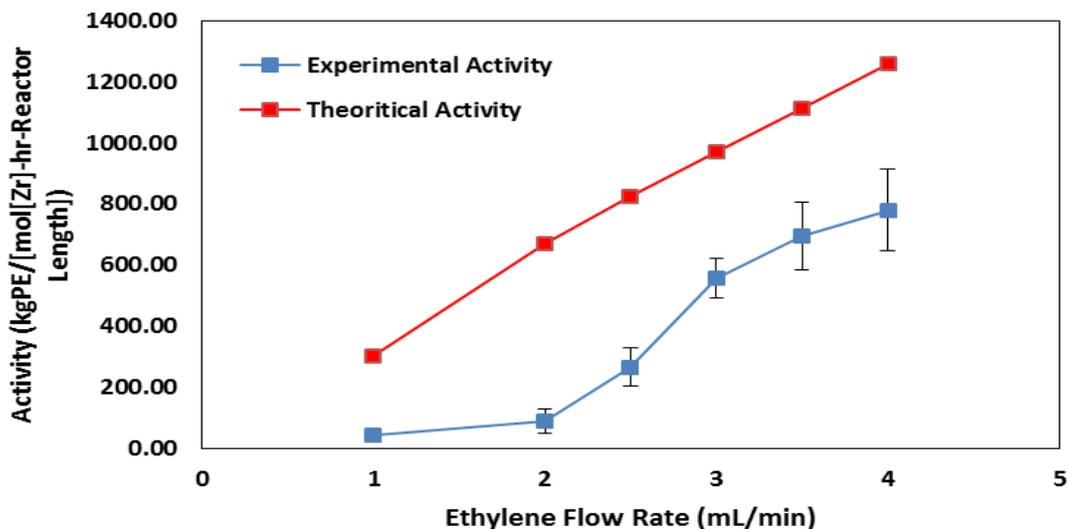
Figure 34 Experimental and theoretical activity for varying ethylene flow rate (Reactor length=7m).
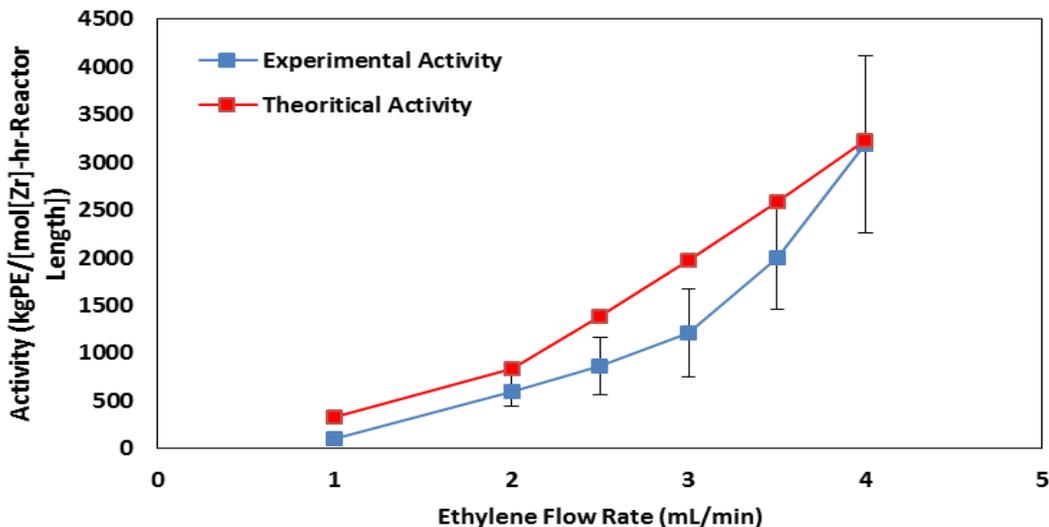
Figure 35 Experimental and theoretical activity for varying ethylene flow rate (Reactor length=1.5m).

Comparison of Figures 34&35 shows activity per unit length of reactor for reactor of length 7m to be lower than that of 1.5m,due to the longer reaction time available. A similar profile is observed for conversion. (Fig 36)
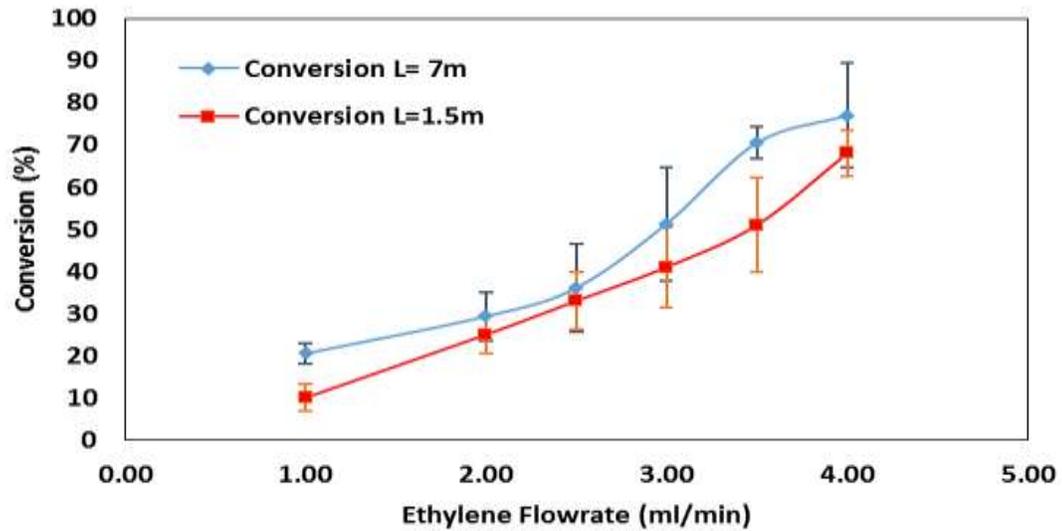
Figure 36 Experimental conversion against ethylene flow rate for different channel lengths

Another experiment was carried out with the initial part of the reactor of smaller diameter (1000µm) and later part (2.37mm), this was effective in reducing clogging problem despite utilizing the advantages of high rate of polymerization in the micro channel section of the reactor (Fig 37).
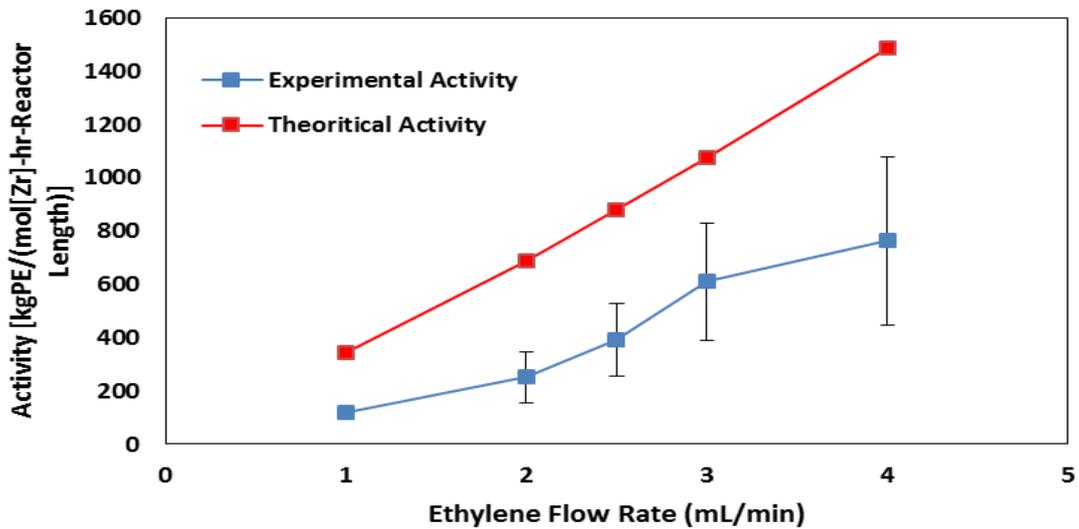
Figure 37 Experimental and theoretical activity for combination of reactor diameters 1mm, 2.37mm.

For larger diameter channels residence time has limited effect on the amount of polymer produced, but for smaller channels the effect of residence time due to mass transfer is more predominant, so extremely small flow rates are needed.

The limitations with maintaining large residence times in small reactor is a) small flow rate are difficult to control b) maintain isothermal conditions is difficult c) very long channels maybe needed causing high pressure drop.

However the activity and conversion are quite high and comparable to traditional macro reactors. This suggests the possibility of stepping up series of micro/mini reactors to produce a consistent yield in a short period of time and yet manipulate the finer properties of the polymer.

Micro reactor set up owing to their high mass transfer rate shows high activity in the order of 5000kgPE/mol[Zr]-hr as it utilizes lesser catalyst compared to macro reactors.

4.2 Qualitative results

On analysis of the polymer samples from experiments carried out for different conditions under a scanning electron microscope distinctive morphology was observed. This section describes the nature of the polymer formed with respect to its structure at a particulate level.

Samples 1 through 3 were synthesised in the micro reactor in which the first 3m of the length(L) are 1mm in diameter (D) and the next 1.5m are 2.37mm in diameter.

Reactor Dimensions	Catalyst Concentration	Temperature	Pressure	[Al/Zr]
(L=3m D=1mm) + (L=1.5m D=2.37mm)	0.4 g/L	75˚C	50 psi	3189

Residence Time Sample-1	Residence Time Sample-2	Residence Time Sample-3
1.5 min	1.28 min	2.15 min

Sample-1

Observations Polymer layer is formed around catalyst support are spheres of size 550 to 630nm.Smaller particles embedded on the surface of catalyst support of size 100nm
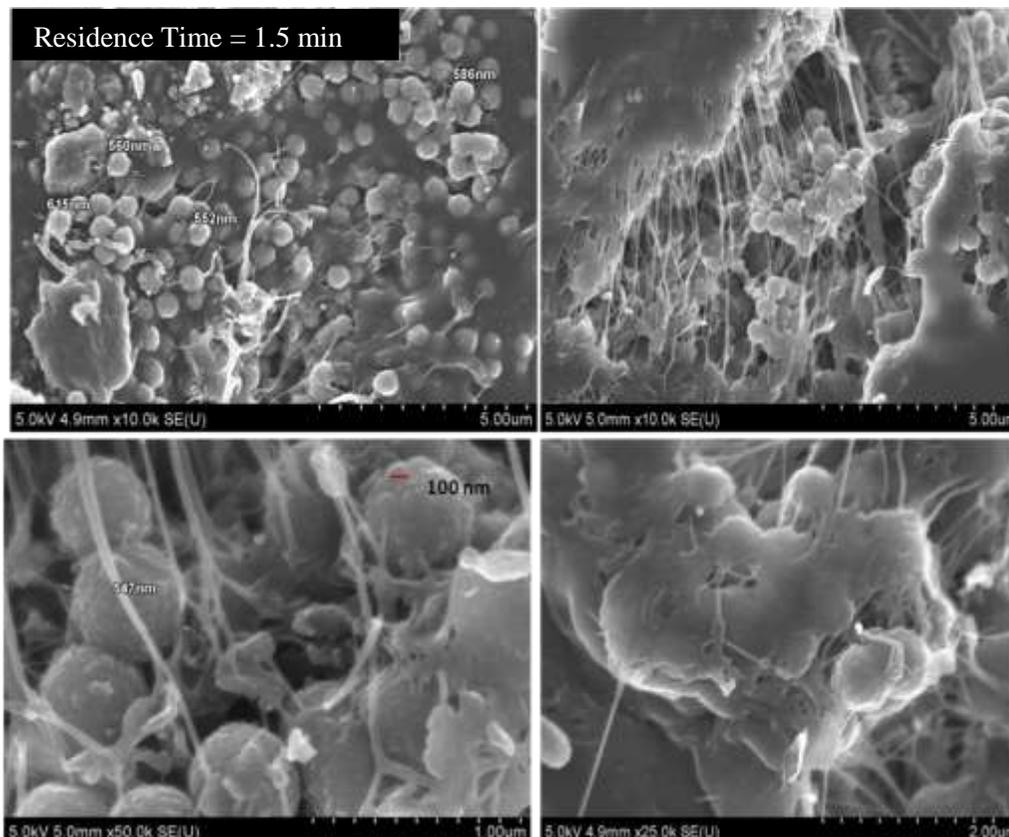
Sample- 2

Observations Polymer layer formed around catalyst support grow into spheres of size 550 to 600nm with several branching polymer chains. Smaller particles are embedded on the surface of catalyst support of size 50nm
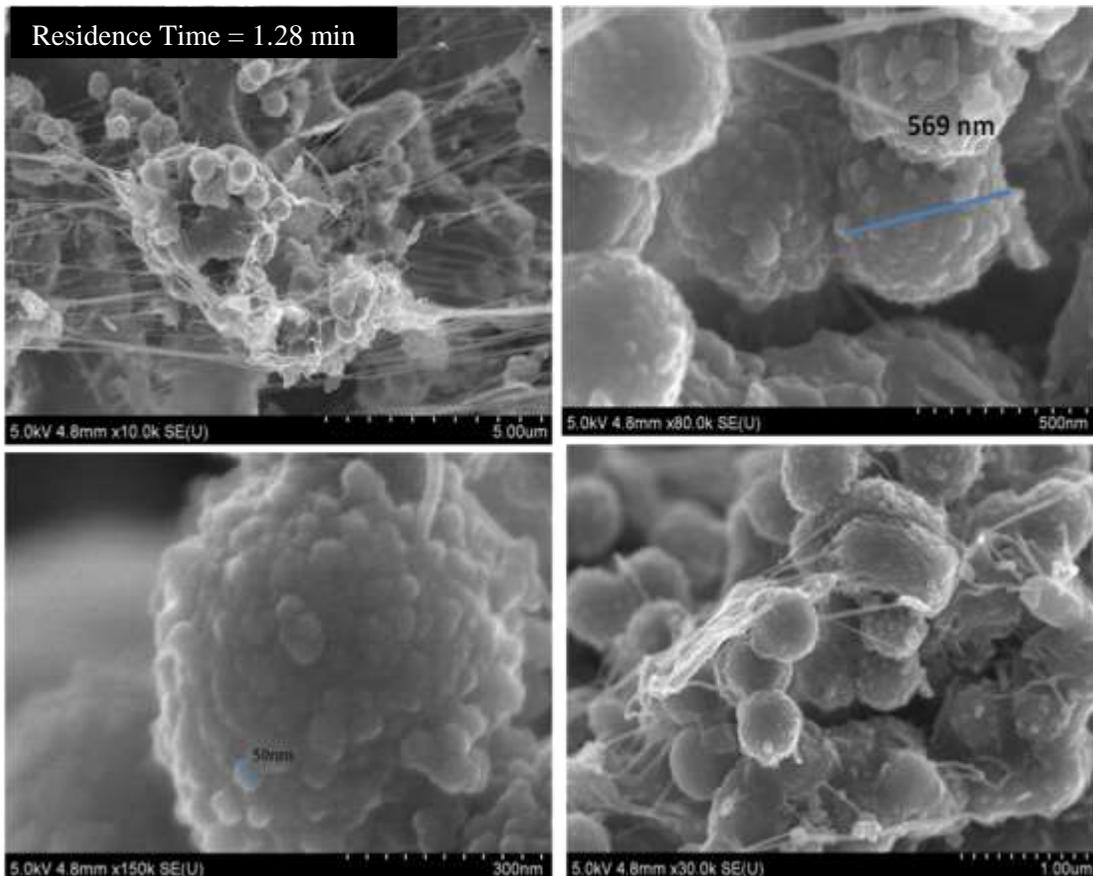
Sample- 3

Observations Polymer layer formed around catalyst support grow into spheres of size 550 to 600nm with fewer thicker fibres. Smaller particles embedded on the surface of catalyst support of size 100-200nm.

Residence Time = 2.15 min
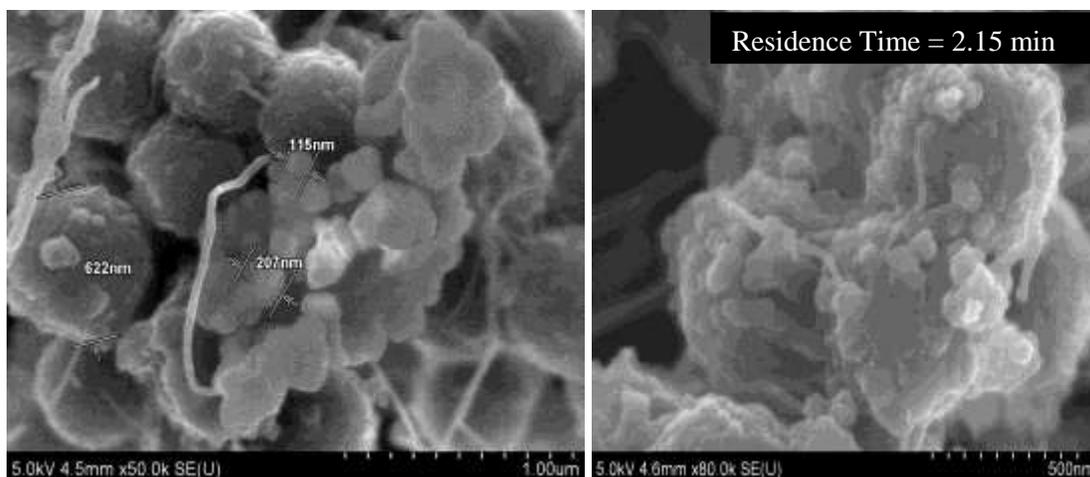
Comparison of samples 1 to 3

Larger residence times have more polymer particles embedded on catalyst support and thicker layer of polymer. In case of smaller residence times there is more branching of polymer fibers. The combination of smaller and larger channel diameter provides both high mass transfer in the initial section and sufficient residence time in the latter section.

Reactor Dimensions	Catalyst Concentration	Temperature	Pressure	[Al/Zr]
L=1.5m D=2.37mm	0.4 g/L	75C	50 psi	3189

Residence Time Sample-4	Residence Time Sample-5	Residence Time Sample-6	Residence Time Sample-7
1.1 min	1.3 min	1.65 min	2.2 min

Sample-4

Residence Time = 1.1 min

Sample- 5
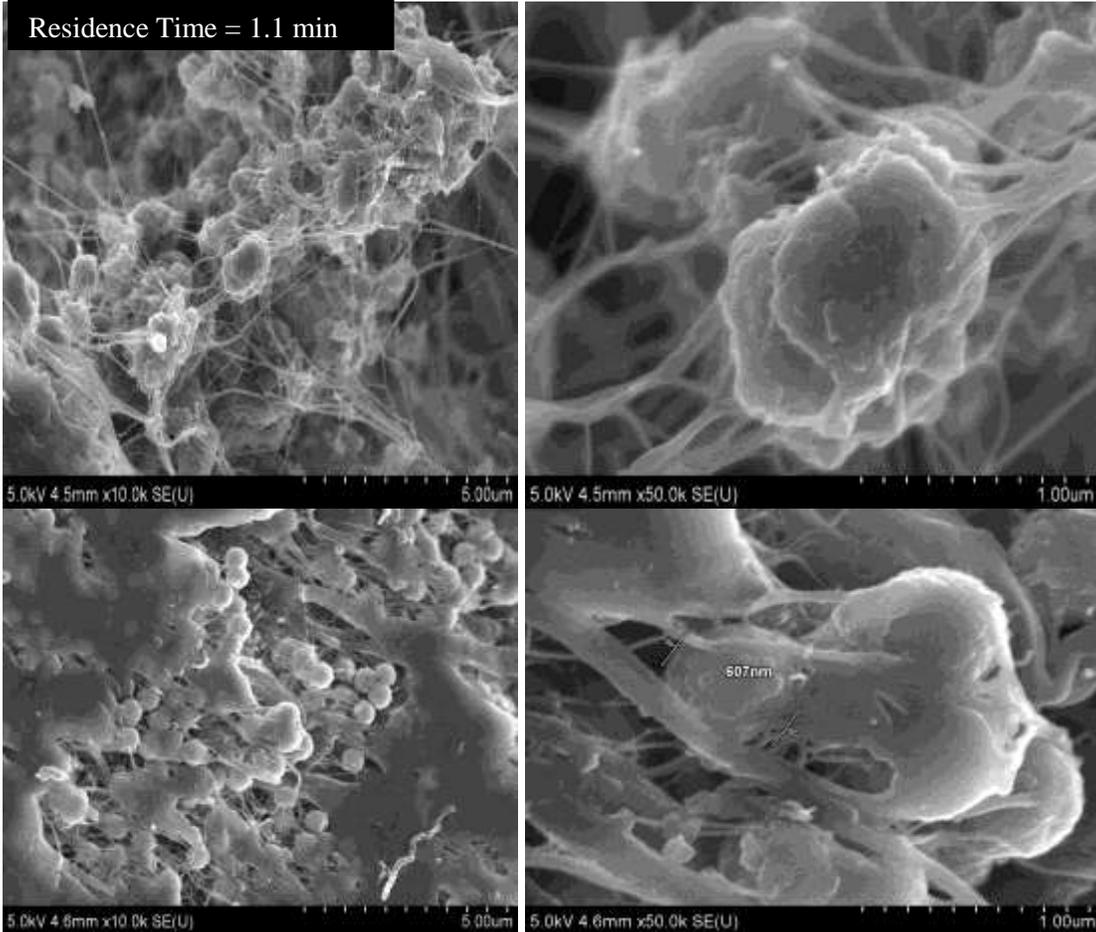
Residence Time = 1.3 min
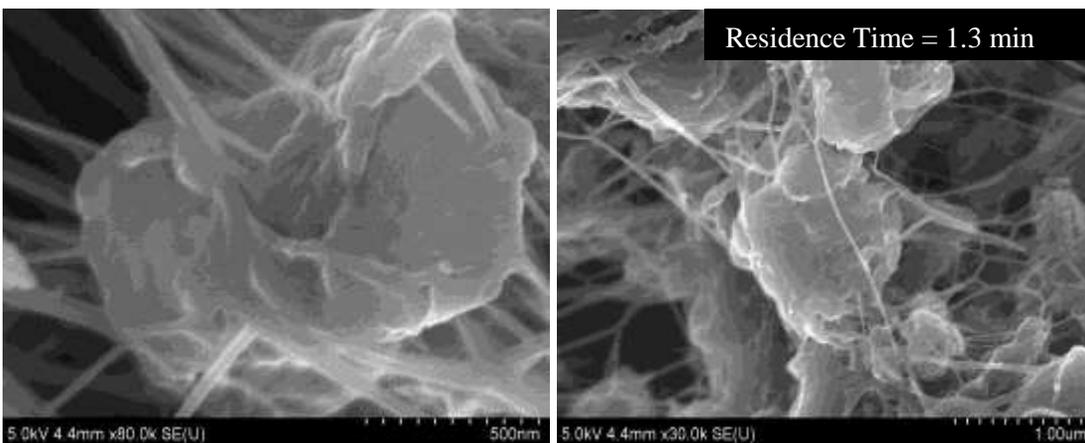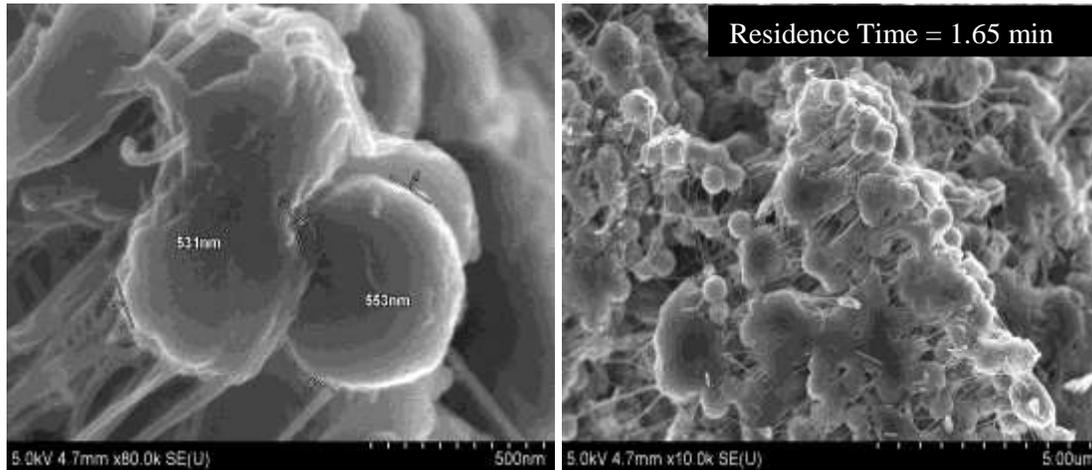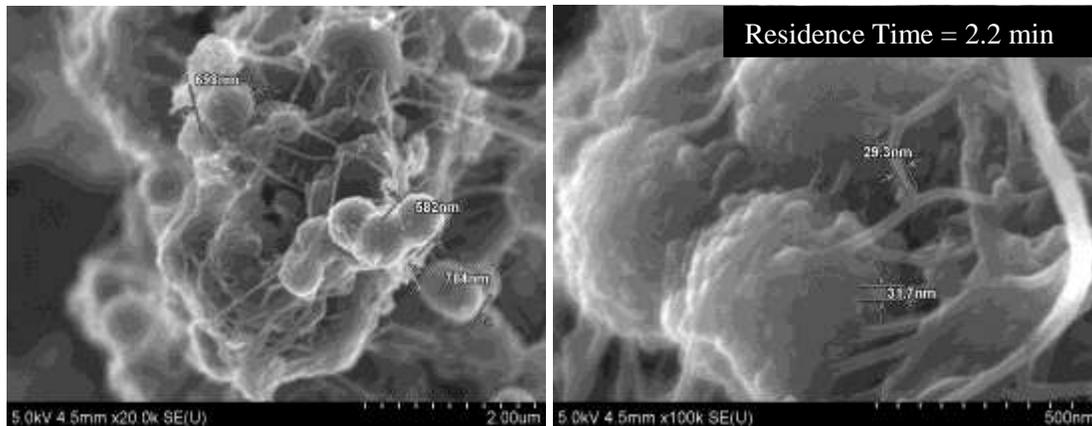
Sample- 6

Sample-7

Comparison of samples 4 to 7

Particles of size 550to 600 nm are formed. Small residence has thinner and denser polymer fibers (10-20nm). Larger residence time has thicker fewer chains. Samples synthesized for smaller residence times have a gelatinous sheet like layer of polymer on the surface of the catalyst support.

Reactor Dimensions	Catalyst Concentration	Temperature	Pressure	[Al/Zr]
L=7 m D=2.37mm	0.4 g/L	75C	50 psi	3189

Residence Time Sample-8	Residence Time Sample-9	Residence Time Sample-10
6.8 min	5.6 min	4.7 min

Sample-8

Residence Time = 6.8 min

Sample-9

Residence Time = 5.6 min
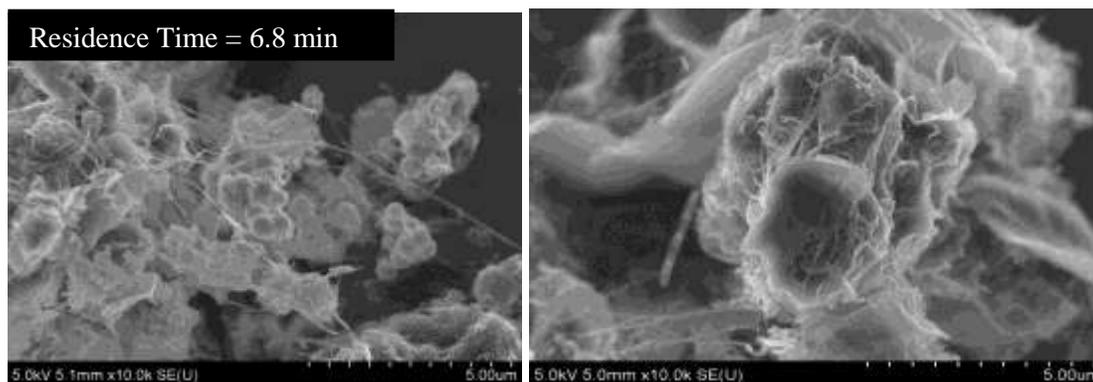
Sample-10
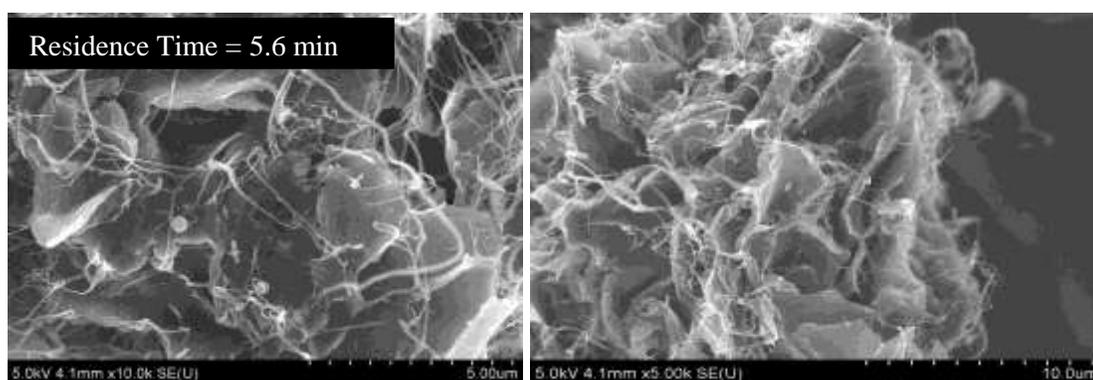
Residence Time = 4.7 min
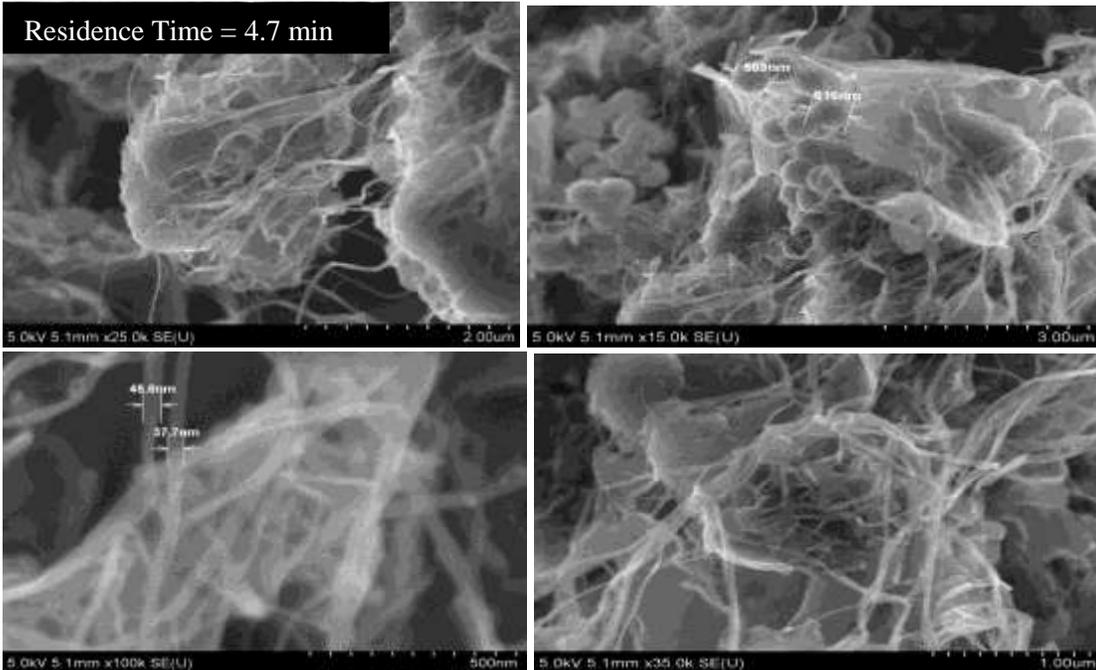
Comparison of samples 8 to 10

Samples 8 to 10 have decreasing residence time. Samples obtained from polymerization in a longer reactor with bigger channel diameter and higher activity, hence more agglomeration is observed. Combination of particles linked by polymer chains forming larger ones of about a micron in size is formed in case of the largest residence time. Higher activity reaction polymers have sheets of polymers. Higher conversion lower activity sample has denser thin polymer chains.

Reactor Dimensions	Catalyst Concentration	Temperature	Pressure	[Al/Zr]
L=7 m D=2.37mm	0.3 g/L	75C	50 psi	3189

Residence Time Sample-11	Residence Time Sample-12
5.6 min	4.7 min

Sample-11

Residence Time 5.6 min

Sample-12
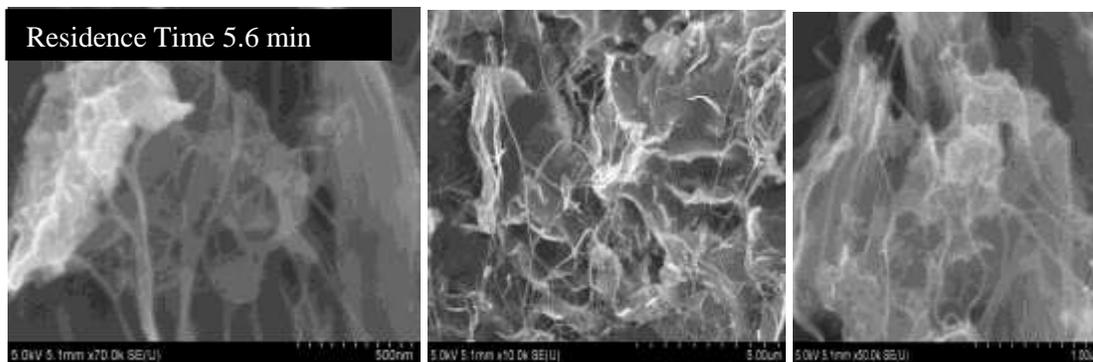
Residence Time 4.7 min
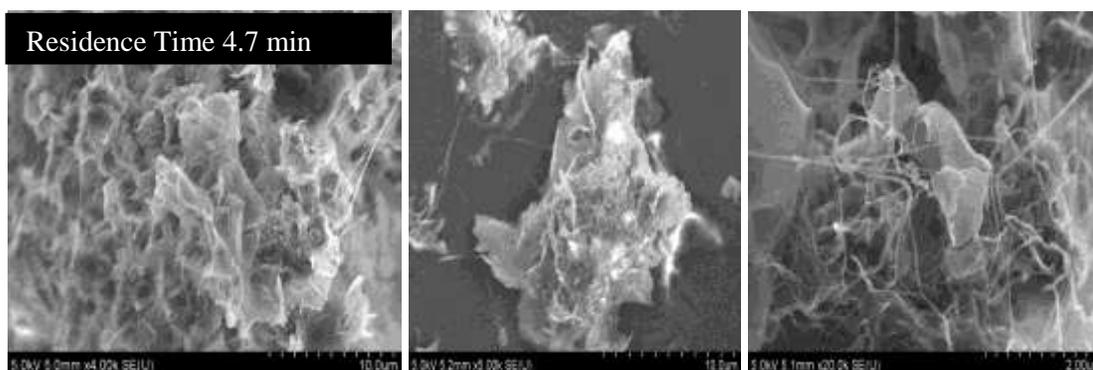
Sample-13

Reactor Dimensions	Catalyst Concentration	Temperature	Pressure	[Al/Zr]	Residence Time
L=7 m D=2.37mm	0.2 g/L	75˚C	50 psi	3189	5.6 min

Residence Time = 5.6 min
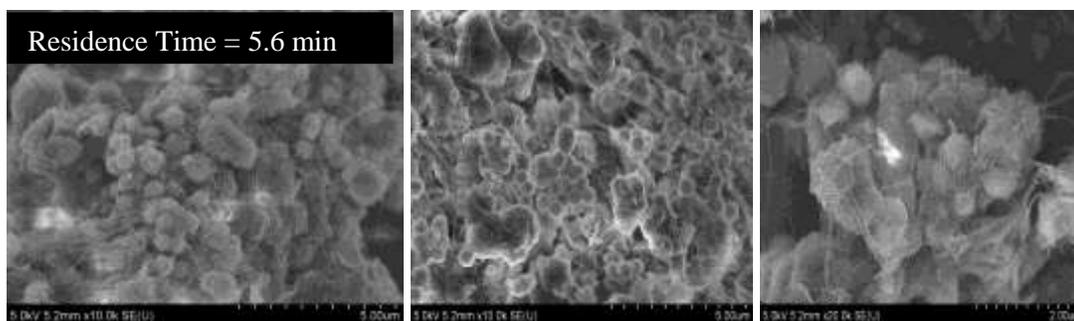
4.2.1 General observations on the nature of polymer produced from a micro reactor

Polymer surrounding the catalyst support has diameters from 500nm to 1µm. Polymer fibers of thickness ranging from 20-40nm are found to entangle between different catalyst particles. The catalyst support particles have smaller polymer grains of diameter 50-100nm embedded on its surface. In some cases sheets of layers of polymer are also observed for higher yield. Some literature show fragmentation of the support occurring due to the internal pressure exerted by the growth of the polymer chains for batch reaction systems[34]. However in the case of micro reactors, the low porosity support used shows no fragmentation indicating growth of polymer around the support.

Effect of residence time due to change in ethylene flow rate, catalyst flow rate, channel dimensions: Longer residence times produce a thicker layer of polymer around the catalyst support, which can be observed by the larger size of the particles in the SEM Images. Higher Ethylene flow rate results in more branching fibers. Lower catalyst flow rate results in a denser polymer layer. Bigger channel dimensions produce larger polymer particles.

Effect of change in catalyst concentration For a given residence time higher catalyst concentration results in a more clustered polymer, at lower concentration distinct particles can be observed (comparing samples 9,11 and 13 with catalyst concentrations 0.4,0.3,0.2 g/L respectively for a residence time of 5.6 min). When more active sites are present the rate of polymerization increases and the reaction is controlled by mass transfer of ethylene from the bubble phase, platelet like structures are observed.

Chapter 5: Conclusion

The results show that micro reactor technology is viable for uniform synthesis of polymer particles. The polymer properties can be tuned by varying the reaction parameters such as flow rate, residence time, pressure, temperature, catalyst concentration. Clogging issues were avoided for the larger channels (1mm and 2.37mm) by adjusting the [Al/Zr] ratio, catalyst concentration and maintaining optimum residence time and uniform heating. The ethylene bubbles dissolve partially in absorber section and polymerize in the reactor section, the undissolved ethylene bubbles provide a consistent source of monomer in the reactor. The nano silica supported metallocene catalyst act as regulators of the rate of polymerization and a uniform base for the growth of polymer chains. The activity and yield obtained from the micro reactors (to the order of 3000 kgPE/mol-Zr-hr)are higher than conventional reactor systems when numbered-up as revealed by the comparison of laboratory scale macro reactors to micro reactors under the same conditions (Sec.4.1.2). ,. The SEM images of the polymer produced show significant difference from traditional polyethylene produced on supported catalysts. The fine variations in properties of the polymers by tuning of the reaction parameters can be useful in synthesizing novel olefin polymers.

Chapter 6 Future work and potential applications

There is a growing demand in the energy and petrochemical industries to use the end products of the refineries for niche applications such as novel polymers without compromising on the manufacturing costs.

Carrying out olefin polymerization in a micro reactor system can produce polymers of the desired unique characteristics. Chemical processing advantages from better control over the size, morphology, thermal and rheological properties of molecules in advanced micro systems can result in innovative polymers that are otherwise not possible to obtain with conventional systems.

As shown in the experimental and modeling results even minor changes to the reaction parameters affect the activity, the amount of polymer produced, its molecular weight distribution, size of the molecules and the morphology of the polymers. This can be extended to suggest the direct effect on short-chain and long-chain branching, crosslinking, stereoregularity ,polymer particle size distribution, morphology that influence a polymer's physical, chemical, thermal, mechanical, and rheological properties such as melting point and viscosity. Further, the content of the organonmetallic component from the catalyst found in the polymer can be regulated to a minimum in case of micro reactor polymerization.

Studies show molecular weight distribution to have a significant influence over the rheological and viscoelastic properties of a polymer.[35] If we compare two samples with same average molecular weight, one with a broad MWD will display

dramatically different melt behavior compare to one with a narrow MWD. It also affects the processability of the polymers

The results suggest future work should include analyzing the polymer synthesized in the micro reactor using gel permeation chromatography for molecular weight distribution, melting point and thermal analysis using a differential scanning calorimetry, viscoelastic properties using a rheometer, internal structure of the polymer using a transmission electron microscope.

Analyzing the feasibility of copolymerization and developing catalysts that can function better for smaller micro channels is an ideal step forward.

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