Poly(dimethyl siloxane) Reactor Experiments

for the Unit Operations Laboratory

by

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Abstract

The Process Simulation and Control Center (PSCC) at Michigan Technological University features a 30-gallon pilot scale autoclave reactor system that is used by the Unit Operations Laboratory course to provide a batch process chemical manufacturing experience to senior-level students. The reactor facility is used by the students to produce Silicone fluid, or poly(dimethyl siloxane). In order to make this experience more meaningful, we incorporate a 1-liter benchscale reactor system that was designed and built in-house based on prior experience in polymerization systems and an industry-inspired solution. Specifically, the benchscale experiment is used to determine the pre-exponential factor in the first-order polymerization rate coefficient. With other kinetic information (order of reaction based on catalyst concentration and activation energy) already given, more effective planning for the pilot scale production reaction run can be done. Also, kinetic information obtained from the benchscale experiment is verified from the pilot scale results.

Keywords: Unit Operations Laboratory, Poly(dimethyl siloxane), silicone, pilot plant operations, benchscale experiment

Introduction

The Process Simulation and Control Center (PSCC) was established in 1991 at Michigan Technological University, in order to provide undergraduate seniors with experience in pilot-scale experimentation. Within the center is a 30-gallon fully automated reactor system that is used for the generation of poly(dimethyl siloxane), or PDMS. Experimentation at this scale is a potential waste generator, and experimental times can take longer than 16 hours if the students are unprepared or if abnormal situations occur. To provide a "chemical manufacturing" experience for the students, it does not suffice for them to be told exactly how to run the facility. Sound engineering and leadership principles must be invoked by the students at the qualitative and quantitative levels.

In order to provide the students a typical new product scale-up experience, a benchscale experiment is designed which is more convenient and economical to operate. Data from the benchscale experiment is used with a kinetic model of the polymerization system, and the rate coefficient is obtained. The rate coefficient is to be used in planning the pilot scale system, which is to be operated at different temperature and catalyst concentration. From an industry perspective, exhaustive benchscale polymerization experiments are typically undertaken before the pilot scale work. Thus, this integrated experimental plan also gives the students a real-world scenario of the development of reaction systems.

Experimental Plan

The experiments require gravimetric and viscometric measurements in order to chaqracterize the reaction kinetics and verify the mass balance. Component data will be used to perform kinetic analysis of the reaction system.

The polymerization reaction is based on ring opening of cyclic siloxanes, using KOH as catalyst [1].

$$[(CH3)_2SiO]_n + KOH <=====> HOSi\text{-----------}SiO^- \ldots K^+$$
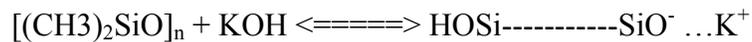
where n is the number of dimethyl siloxane groups in the cyclic. For our system, n has an average value of 5 at the start of the reaction. Thus, the $[(CH3)_2SiO]_n$ will simply be called D_5. At low-to-moderate amount of polymer concentration, the reaction rate is first-order with respect to the cyclic siloxane and half-order with respect to the catalyst. At relatively high polymer concentration, the reaction becomes reversible, due to a "backbiting" mechanism. This results in a value of n to range from 3 to about 100. In order to regulate the molecular weight of the polymer product, a trimethyl endblocker (so-called Endblock A™, or EBA, with chemical formula $-(CH_3)_3SiO_{1/2}$)is added into the reaction mixture. The endblocker reacts with the linear polymer (PDMS) intermediate ($HOSi\text{-----------}SiO^- \ldots K^+$) and releases the K^+ and OH^- ions as well. Other features of the reaction system include [2]:

1. Water (solvent for KOH catalyst) plays no role in the reaction, except to function as an endblocker or to alter the activity of the catalyst.

2. Pressure has no effect on reaction kinetics, unless the cyclics are being stripped.

3. The heat of reaction is zero.

4. The activation energy for reaction is 19 kcal/mol-K

5. The ring-opening reaction with its backbiting mechanism combined with the endblocking reaction causes this system to approach an equilibrium state.

6. At equilibrium, there are about 13-18 wt % cyclics.

Equipment

Figure 1 shows the apparatus used in the benchscale polymerization experiment. The reactor is a 1-liter three-necked flask. An agitator mixer is used to keep the fluid at a uniform temperature. A very slow flow of nitrogen gas is used to keep the system under an inert atmosphere. In order to minimize liquid loss by evaporation, the nitrogen flows through a refluxing condenser before it exits through the water bubbler. The control system for the temperature is a PID control unit that is actuated by a pneumatic lift for the heating mantle. When the controller signals a heat-up mode, the mantle is lifted while electrical power is applied to it. When the controller signals a cool-down mode, the air that is used to lift the mantle is diverted to two side nozzles that blow air onto the reactor. This results in the removal of physical contact between the mantle and the reactor flask in addition to forced convection cooling, while electric power is no longer applied into the mantle. This air-driven actuation is made possible by the solenoid valve, using a compressed air source.

This particular reactor design has been formulated based on the experience that heating mantle surfaces are just too hot (temperatures in the order of 200°C), and simply

turning them off does not result in effective temperature control even in conjunction with a PID scheme. We found that the mantle should be physically removed from the bottom of the reactor to effect cooling of the reactor fluid. The automation of this manual operation is inspired by a so-called jack-o-matic system that has been used in an industry lab where one of the authors (G.C.) consulted with. Subsequently, a $100 design is envisioned and fabricated in the machine shop, and test runs have been found to be successful.

The schematic diagram of the pilot-scale reactor system is shown in Figure 2 [3]. The reactor is a jacketed 30-gallon autoclave that is heated by an external fluid. In this case, Syltherm 800™, a heat transfer fluid manufactured by Dow Corning (Midland, Michigan), is continuously flowing through the reactor jacket and heated by condensing steam. The reactor system was operated from a control room using a Honeywell TDC 3000™ distributed control system. Data acquisition is performed using the OSI Software PI™ system. Sampling is done by operating a HaZcor™ sampling valve system (manufactured by the Analytical Systems of the Ethylene Corporation, Murray Hill, New Jersey), which allows the collection of one-ounce fluid samples at any given time.

Data Analysis

For the polymerization reaction that exhibits the above-mentioned kinetic features, the following kinetic expression is obtained [4]

$$\frac{d([D_5]-[D_5]_{eq})}{dt} = -k[Catalyst]^{1/2}([D_5]-[D_5]_{eq}) \tag{1},$$

where $[D_5]_{eq}$ is the concentration of D_5 at equilibrium. The integrated form of Eq. 1 is

$$\ln\left(\frac{[D_5]-[D_5]_{eq}}{[D_5]_o-[D_5]_{eq}}\right) = -k[Catalyst]^{1/2}t \qquad (2),$$

where $[D_5]_o$ is the concentration of D_5 at t=0. If we assume that the system has a constant density and that the proportion of D_5 to EBA is almost the same during the reaction,

$$1 - \frac{[D_5]-[D_5]_{eq}}{[D_5]_o-[D_5]_{eq}} \cong \frac{\omega^{PDMS}}{\omega_{eq}^{PDMS}} \qquad (3),$$

where ω^{PDMS} is the weight fraction of PDMS in the reactor fluid. Alternately, the right-hand side of Eq. 3 is also equal to the relative fractional conversion, X, which is defined as

$$X \equiv \frac{x}{x_{eq}} \qquad (4),$$

where x is the fractional conversion of D_5 to PDMS. Since a particular experiment is done at constant catalyst concentration, we can define the effective rate coefficient k_{eff} as

$$k_{eff} \equiv k[Catalyst]^{1/2} \qquad (5).$$

Based on Equations 1-5 and the definition of the relative fractional conversion, X, the effective rate coefficient, k_{eff}, could be obtained as the negative of the slope of the plot of $\ln(1-X)$ vs. time. Also, the temperature dependence of the rate coefficient, k, can be obtained from the Arrhenius equation

$$k = k_o \exp\left(-\frac{E_a}{RT}\right) \qquad (6),$$

where k_o is the pre-exponential factor and E_a is the activation energy, which is taken to be equal to 19 kcal/mol-K. From the slope of $\ln(1-X)$ vs. time, catalyst concentration, and activation energy, the pre-exponential factor can be obtained. In turn the catalyst concentration can be obtained from the following:

$$[Catalyst] = \rho\left(\frac{\omega}{MW}\right)_{Catalyst} \tag{7},$$

where ρ is the density of the reactor fluid.

Procedure

At the start of the benchscale reactor run (Figure 1), the airlift control system was tested and the reactor purged with nitrogen gas. The following was then loaded into the reactor: 320 ml Dow Corning 245 fluid (mainly D_5 material), 47 ml Dow Corning Endblock A (EBA), 0.15 ml of 45 wt % KOH in water (corresponding to 200 ppm of KOH). The slow nitrogen flow was applied and the agitator started. The temperature programmer was set to heat the reactor linearly to $140^{o}C$ in 1 hr. Then, the reactor fluid was be maintained at its operating temperature of $140^{o}C$ for 2 more hours. Finally the reactor temperature was dropped to room temperature linearly in 30 minutes. At the start of the heat-up phase to $140^{o}C$, a sample fluid was taken (Sample #1). Additional samples were taken at 15-minute intervals. Sampling was done by stopping the agitator and drawing 5-10 ml of reactor fluid with a syringe. The sample in the syringe was placed in crushed ice to cool it quickly enough before placing it into an aluminum weighing pan. The weight of the fluid was recorded, and the fluid was air dried to constant final weight for a period of 6-7 days. At the end of this period, the pan is assumed to contain PDMS plus a minor amount (about 10 wt %) of nonvolatile nonreactive material that originated from the Dow Corning 245 fluid[*] and possibly from the EBA. The percentage of nonvolatile nonreactive material in the reaction mixture was obtained from the dried Sample #1. Thus, the weight fraction of PDMS at any point during the reaction was

obtained from the weight fraction of the dried sample minus the weight fraction of dried

Sample #1, or

$$\omega^{PDMS} = \omega_{DriedSample} - \omega_{DriedSample\#1} \tag{8}.$$

The pilot scale reactor was initially purged with nitrogen gas. Then, 153 ± 4 lb

Dow Corning 245 fluid and 6.540 ± 0.001 lb End Block A are pumped in. The KOH

catalyst (0.3350 ± 0.0001 lb of 45 wt % KOH in distilled water) was dropped into the

reactor from the catalyst adder. Since the total weight of the reactor charge was 160 ± 4

lb, then the catalyst concentration was 942 ppm. This relatively large catalyst

concentration was used because a relatively low operating temperature could only be

obtained from the system at the time of the experiment. The reactor was then heated to a

temperature of $118^{o}C$ with the Syltherm™ heat transfer fluid using an 85 psig steam.

Throughout the heating stage, samples were taken for both gravimetric and viscometric

measurements. Figure 3 shows the temperature history of the pilot scale and benchscale

reactor systems.

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* According to the Dow Corning product literature for DC 245 fluid, it is only 95% pure D_5.

Results and Discussion

Figure 4a shows plots of the relative conversion, X, vs time for the benchscale reactor run. It can be clearly seen from Figure 4(a) that the rectangular plot is sigmoidal in nature. The inflection area of the plot is where the system is at the operating temperature of 140°C; hence it should follow the predictions of Equation 2. Based on the trendline in Figure 4(b), we find from the slope that the effective rate coefficient, $k_{eff}=k[Catalyst]^{1/2}=0.0431$ min^{-1}. For the 200 ppm KOH used as catalyst, based on Equation 7, we calculate $k(\rho/MW_{KOH})^{1/2}=3.0901$ min^{-1}. For the operating temperature of 140°C and activation energy of 19 kcal/mol-K (using Equation 6), we obtain $k_o(\rho/MW_{KOH})^{1/2}=3.4606\times10^{10}$ min^{-1}. On a more practical note, the value of that $k_{eff}=k[Catalyst]^{1/2}=0.0431$ min^{-1} corresponds to a half-life, $t_{1/2}$, for the reaction of 16.08 min, based on

$$t_{1/2} = \frac{\ln 2}{k_{eff}} \qquad (9).$$

A rule-of-thumb we normally use to estimate the reaction time is 5 times the half-life.[+] In the benchscale system, the reaction time is obtained at about 80 minutes. This means that the allotted time of 2 hrs at 140°C for the experiment is more than enough to effectively end the reaction. Using a catalyst composition of 942 ppm and operating temperatures of 110-120°C for the pilot scale system, the above equations predict a

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[+] Based on $X=1-\exp(-k_{eff}t)$ and $k_{eff}=0.693/t_{1/2}$, at $t=5t_{1/2}$, we obtain $X=0.97$. This means that for a first order system, the reaction is 97% complete after 5 times the half-life.

reaction time in the range of 120-227 min. This is valuable information for the planning the pilot scale experiment.

Based on the pilot scale run, the slope of ln(1-X) vs time (Figure 4(b)) indicates a value of k_{eff} of 0.0222 min^{-1}. This corresponds to a half-life (using Eq. 9) of 31.2 min and a reaction time of 156 min. This is reflected in the relative fractional conversion-time plot in Figure 4(a), i.e., once the system reached its operating temperature range it took about 156 minutes for it to attain its equilibrium conversion. Based on the catalyst composition of 942 ppm and the pre-exponential factor obtained from the benchscale run, the effective operating temperature in the pilot scale run was 115°C. This is within the range of operation of 113-118°C actually used in the system (Figure 3).

By successfully integrating benchscale and pilot scale experimentation in a polymerization reactor system, we have provided our Unit Operations laboratory students with an experience that is balanced in science, engineering, project planning, and teamwork. A notable feedback from the students is that in the benchscale system it was good to be able to see the materials and their physico-chemical transformation due to polymerization reaction before moving on to the pilot-scale experimental system.   In course evaluations of the Unit Operations laboratory by the students, this integrated experimental system has always been cited as a high point in their learning experience.

Conclusion

Integration of benchscale polymerization experimentation with state-of-the-art pilot scale work in the Unit Operations laboratory has been successfully implemented at Michigan Technological University. The benchscale experiment was introduced not only for the purpose of acquiring experience with the materials used in the experiments, but also as a means of gathering kinetic data that can be used in planning the pilot scale work. Such an experimental methodology provides the students a glimpse of the developmental process used by industry in scaling up of polymerization reaction systems.

References

1. Buchalski, D.L. and Caspary, D.W., "Polydimethylsiloxane Polymerization Reaction Process: Process Package", a handout by the Process Simulation and Control Center of Michigan Technological University, Nov. 30, 1994.

2. Voronkov, M.G., Mileshkevich, V.P., and Yuhelevskii, Yu.A., "The Siloxane Bond: Physical Properties and Chemical Transformations", Consultants Bureau, New York & London, 1978, ISBN 0-306-10940-9.

3. Caspary, D.W., "Michigan Technological University Offers Experience", *The Journal for Industrial Automation and Control* Technology, Volume 6, No. 1, March, 1999.

4. Smith, J.M., "Chemical Engineering Kinetics", McGraw-Hill Book Co., New York, 1981, pp. 71-72.

Acknowledgements

Nomenclature

E_a – activation energy, cal-mol^{-1}

k - rate coefficient, L-mol^{-1}-min^{-1}

k_o – pre-exponential factor, L-mol^{-1}-min^{-1}

k_{eff} – effective rate coefficient, min^{-1}

MW – molecular weight, g-mol^{-1}

R – Universal gas constant, 1.987 cal-mol^{-1}-K^{-1}

t - min

$t_{1/2}$ – half life of reaction, min

T – absolute temperature, K

x – conversion, dimensionless

X – relative conversion, dimensionless

Greek Letters

ρ - density, g-L^{-1}

ω - weight fraction, dimensionless

Subscripts

eq – equilibrium condition

o – initial condition

Epilogue

The experiments described in this paper were conducted in the 1995-96 academic year. Since that time substantial changes have been made to the chemical engineering undergraduate curriculum at Michigan Tech and to the PDMS reaction process.

A result of our continuous improvement program was the addition of an on-line viscometer for the PDMS pilot plant. This allows the students to track the reaction without continuous sampling and eliminates the variation in viscosity measurements due to operator technique. A new (in 2001) Rockwell Automation ProcessLogix control system is used to control the processes, and the OSI Software, Inc. PI-3 system is used for data archival/retrieval as well as real-time process management. A steam generator, producing 125 psig steam allows us to run the pilot plant at higher temperatures. This past 2001-2002 academic year, we replaced the endblocker (EBA) with a 1.5 CSt Dow Corning® 200 Fluid™. This is a distilled PDMS product with a very uniform molecular weight and has reduced much of the variation in our product molecular weight distributions.

For the 2002-03 academic year, an Emerson Process Management DeltaV system will also used for process control along with a number of Fisher-Rosemount Foundation Fieldbus instruments.

Figure Captions

Figure 1. Schematic diagram of the benchscale polymerization system

Figure 2. Schematic diagram of the pilot scale polymerization system

Figure 3. Temperature histories of the benchscale and pilot scale reactor systems

Figure 4. Relative conversion-time plots for the benchscale and pilot scale systems. Part (a) provides actual relative conversion-time plots, while Part (b) are semi-logarithmic plots that is used to determine effective rate coefficients from the slopes of data points.
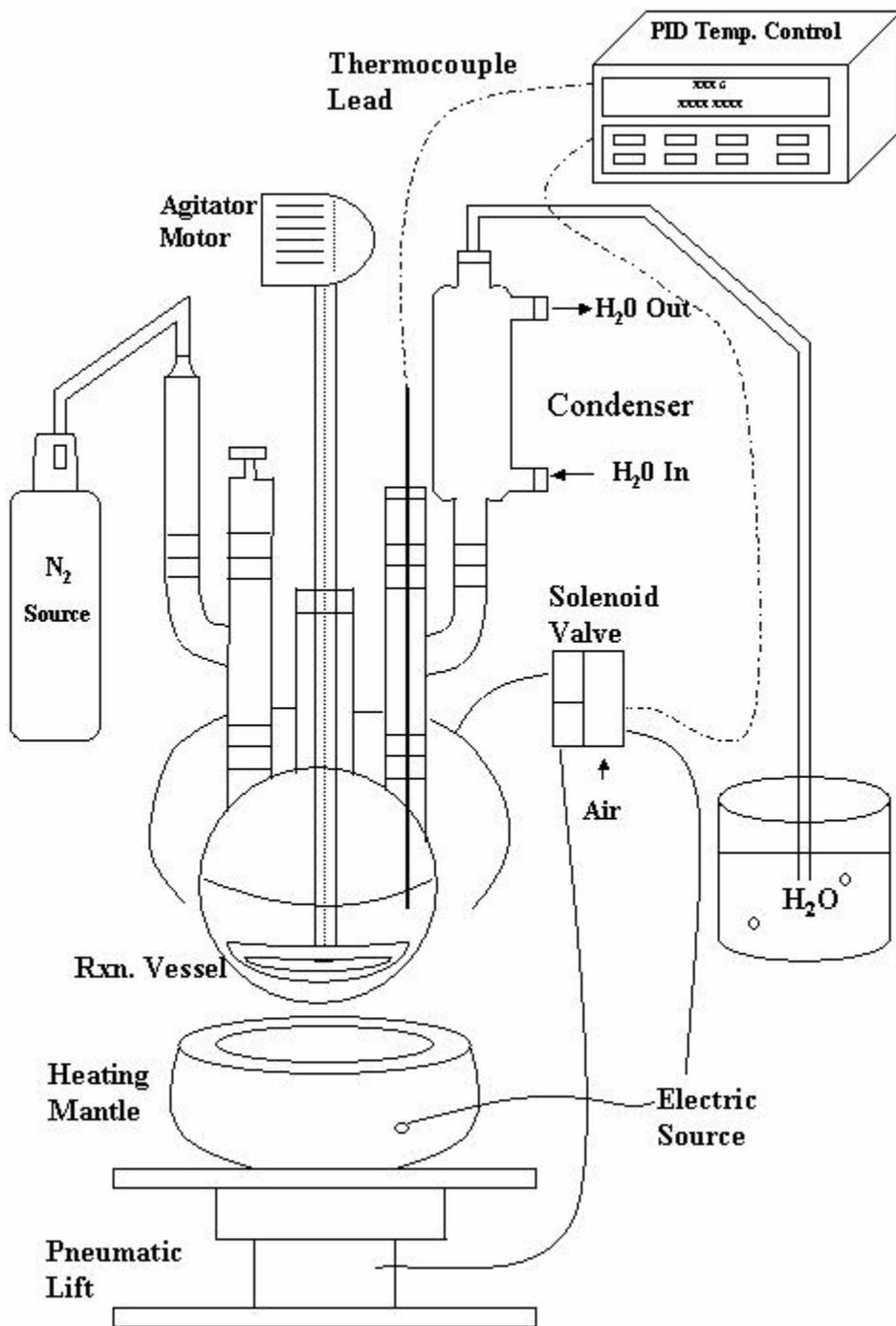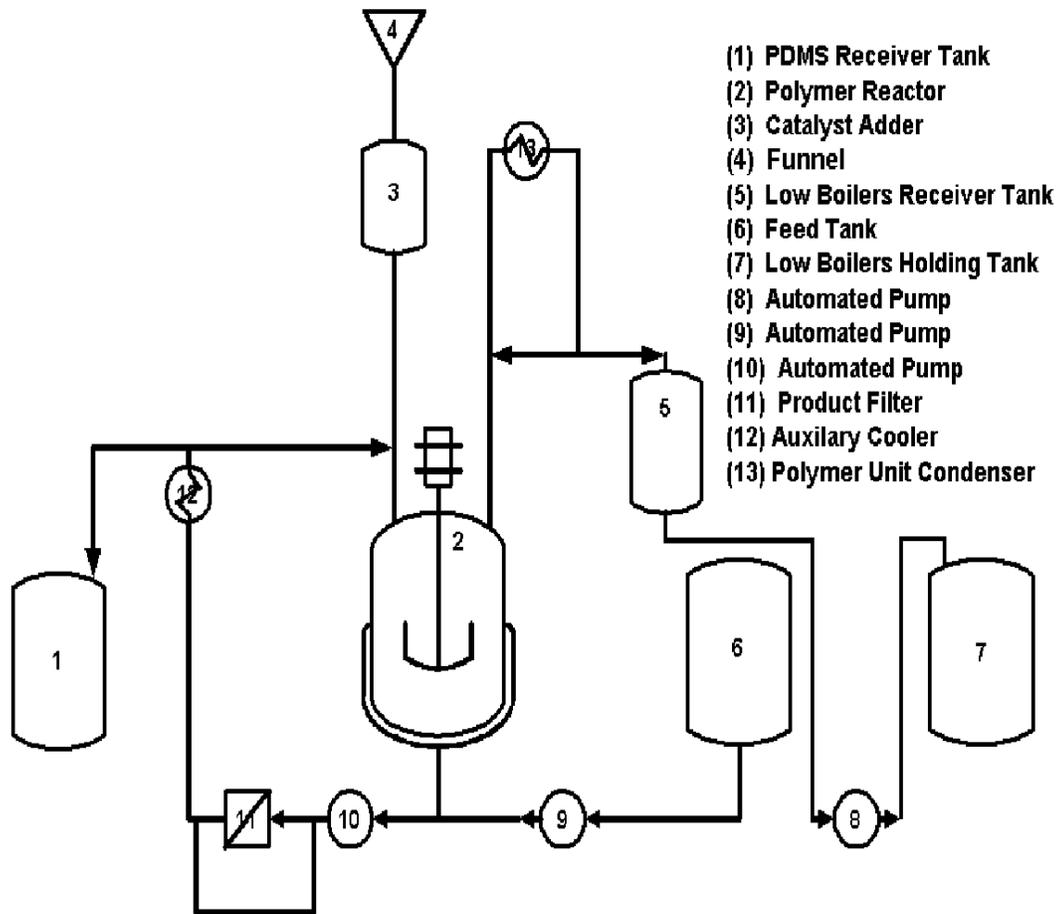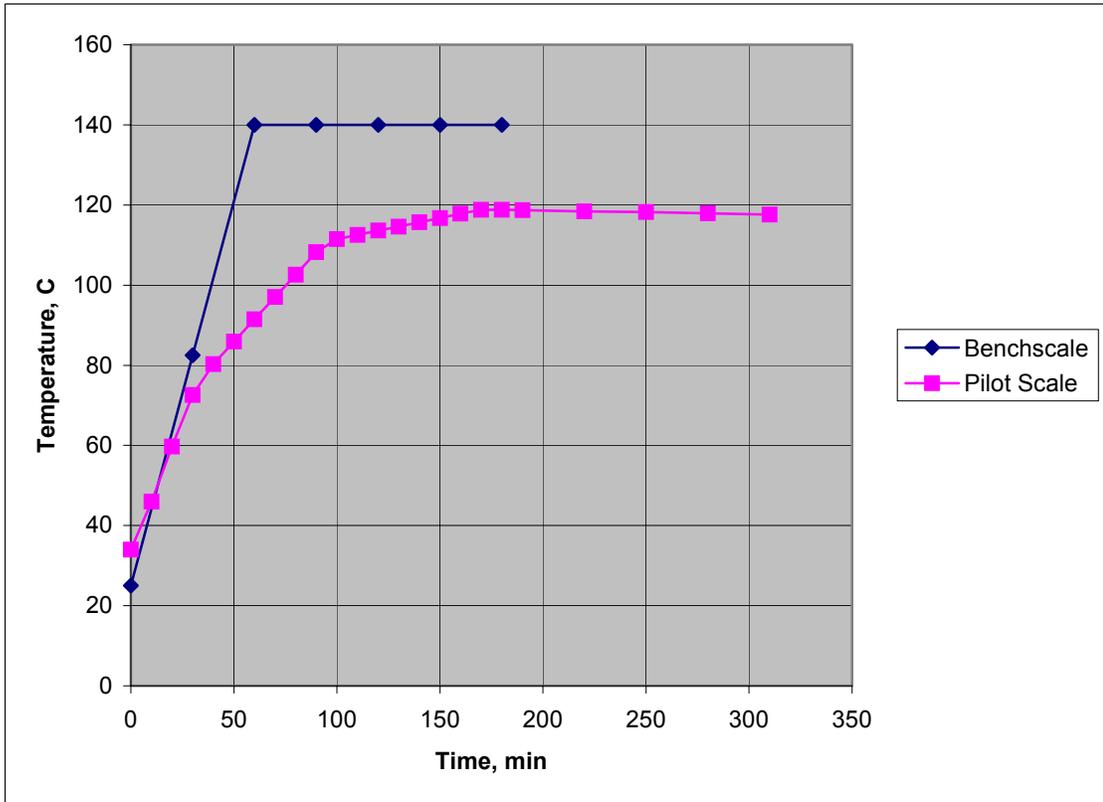
Figure 1

Figure 2

(1) PDMS Receiver Tank
(2) Polymer Reactor
(3) Catalyst Adder
(4) Funnel
(5) Low Boilers Receiver Tank
(6) Feed Tank
(7) Low Boilers Holding Tank
(8) Automated Pump
(9) Automated Pump
(10) Automated Pump
(11) Product Filter
(12) Auxilary Cooler
(13) Polymer Unit Condenser

Figure 3

Figure 4(a)

Figure 4(b)