Chapter Four

EXPERIMENTAL SETUP AND MODEL VALIDATION

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Experimental Setup and Models Validation

ABSTRACT

This chapter is dedicated to introducing the automated polymerisation reactor and the main methods of characterization used to validate the emulsion terpolymerisation model and the calorimetric soft sensor those have been developed in this thesis. Two different capacity reactors were used to operate the emulsion terpolymerisation processes. A 1L reactor was used to validate the process, while a 5L reactor was operated to validate the ability of the model for scaling up. The methods of characterization are:

- Gravimetric analysis: to measure the monomer conversion of the process.
- Gel permeation Chromatography: to determine the molecular weight and molecular weight distribution of the polymer.
- Polymer laboratory particle size distribution analysis: for evaluation of the particle size distribution and its average.
- Nuclear magnetic resonance: to determine the composition of the terpolymer.
- Differential scanning calorimetry: to measure the glass transition temperature of the polymer.
4.1 EXPERIMENTAL SETUP

Polymerisations were carried out with monomer, water and surfactant added to the reactor and brought to the desired reaction temperature (steady state). They were conducted as follows: an initial charge of monomer (comprising 17.78% of the total amount in the “recipe”) was added to the reactor along with water and surfactant. The polymerisation “recipe” used in these runs is given in table 4.1. The reactor contents were brought to the desired reaction temperature and bubbled with nitrogen to eliminate dissolved oxygen from the system since oxygen is a highly reactive inhibitor that is usually dissolved in the reactants. The pre-heated initiator solution (at the reaction temperature) was then added. Thereafter, the remaining monomer was added continuously to the reactor after a “batch pre-period” of 25 minutes.

The reagents used in this work were obtained from Fluka and Sigma-Aldrich. All the monomers were purified to extract inhibitor using inhibitor extraction columns (Sigma-Aldrich No. 306312 & 306320). Styrene (99% purity, inhibited with 4-tert-butylcatechol), MMA (99% purity, inhibited with hydroquinone) and MA (99% purity, inhibited with hydroquinone monomethyl ether) monomers were obtained from Fluka. Surfactant (sodium dodecyl sulfate), initiator (potassium persulfate) and buffer (sodium bicarbonate) were obtained from Sigma-Aldrich and used as received without further purification. Deionised water was used throughout all the experimental work. Nitrogen purging was used to remove oxygen from the reaction mixture and from the reactor since oxygen is a highly reactive inhibitor that is usually dissolved in the reactants.

Sampling: a sample was directly taken from the reactor each 10min for off-line analysis. The first sample, an exception, was taken after 15min of the progress of the polymerisation reaction. The sample is divided into two portions in which the first portion is diluted by an eluent and used to measure the PSD and its average diameter. The second portion was used for gravimetric analysis in which the dried sample obtained from the gravimetric analysis was used for GPC and NMR analysis.
Batch and semibatch emulsion terpolymerisation reactions of styrene, MMA and MA were carried out in a jacketed 1L glass reactor equipped with an agitation speed controller and three RTD sensors. The details of the reactors setup will be described in section 4.2. With respect to the 5L reactor, the operation was set up the same as that for 1L reactor multiplying the recipe with 5.

Table 4.1 Terpolymer emulsion polymerisation recipe.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Monomers (g)</td>
<td>135</td>
</tr>
<tr>
<td>Water (g)</td>
<td>500</td>
</tr>
<tr>
<td>Initiator-Persulfate K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} (g)</td>
<td>0.37</td>
</tr>
<tr>
<td>Surfactant-SDS (g)</td>
<td>0.9</td>
</tr>
<tr>
<td>NaHCO\textsubscript{3}-Buffer (g)</td>
<td>1.00</td>
</tr>
</tbody>
</table>

For Semibatch

Initial charge of monomers 17.78%

4.2 AUTOMATED REACTORS

4.2.1 One Litre Reactor

Batch and semibatch emulsion terpolymerisation reactions of styrene, MMA and MA were carried out in a jacketed 1L glass reactor equipped with an agitation speed controller and three RTD sensors. The control of the reactor and the Data Acquisition are performed using RS232 interface between the computer and the reactor, such as the temperature sensors (Pt100-RTD), mass input monitoring sensors (Shimadzu BW4200H), metering pumps (ProMinent\textsuperscript{®} gamma G/4b) and cooling-heating circulation unit (Julabo).

The 1L reactor system is provided by Pressure Dynamic Consultants (PDC Machines, Inc.), which is one of the world leaders in the design, engineering, manufacture, installation, commissioning, service, and support of equipment for the
chemical, petrochemical, pharmaceutical, and specialty gas industries. The reactor consists of the reactor vessel, an agitation assembly and supporting aluminum stand which are shown in figure 4.1.

![Figure 4.1 Schematic view of the reactor system (Pdc Machines Inc.).](image)

The parts of the reactor vessel are the 1-litre glass cylinder with a jacket around the circumference held together between two steel plates. The glass reactor is a complete system including the glass vessel, supporting stand, agitation assembly which includes magnetic stirrer, drive motor, belt, belt guard and impeller, multiple process connection ports, drain port, sample tube, temperature sensor, cooling coil, gas line and a rupture disc assembly along with an agitation control panel to adjust and monitor the speed of the stirrer. The maximum operating pressure and temperature of the reactor are 0.6 MPa and 200°C respectively.

The reactor vessel has a pneumatic actuation system that can be used to lower the vessel for cleaning and maintenance purposes. Three Pt-100 RTDs (i.e. resistance temperature detectors) were installed to the reactor for on-line temperature monitoring. Moreover, the reactor vessel had a six-blade impeller for adequate mixing and a proper agitation rate to minimize coagulation. A mass input monitoring
sensors (Shimadzu BW4200H), metering pumps (ProMinent® gamma G/4b) and cooling-heating circulation unit (Julabo) were connected with the reactor. The control of the reactor and the Data Acquisition are performed using RS232 interface between the computer and the reactor.

Figure 4.2 Schematic diagram of the 1L reactor system

4.2.2 Five Litre Reactor

Our 5L reactor system includes an agitation assembly and a supporting metal stand as shown in figure 4.3. It is supported with simple bolted closure, liquid sampling, internal cooling, over-pressure and over-temperature protection, temperature sensor and custom control systems. The design pressure is up to 2.07 MPa, and the design temperature is up to 200°C. The reactor is floor mounted. The magnetic drivers utilise a design where an outer magnet turns and is magnetically coupled with an inner magnet. The high energy between these two magnets results in torque transmission via a lower shaft.
The 5L reactor is a complete system including the vessel, supporting stand, agitation assembly (magnetic stirrer, drive motor, belt, belt guard and impeller), multiple process connection ports, drain port, sample tube, temperature sensor, cooling coil, gas line and a rupture disc assembly along with an agitation control panel to adjust and monitor the speed of the stirrer. The reactor vessel can also be lowered from the locked position, via a pneumatic actuation system, for cleaning and maintenance. Three Pt-100 RTDs (i.e. resistance temperature detectors) are installed to the reactor for on-line temperature monitoring, one inside the reactor, and the other two for the inlet and outlet jacket temperature measurement. Moreover, a four-pitched blade impeller was designed to create adequate mixing inside the reactor. A proper agitation rate of 350 rpm was used to minimise the formation of coagulum during polymerisation. Four mass input monitoring sensors (Shimadzu BW4200H), four metering pumps (ProMinent® gamma G/4b) and a cooling-heating circulation unit (Julabo) were connected to the reactor.
4.3 METHODS OF CHARACTERISATION

4.3.1 Gravimetric Analysis

Gravimetry is a technique for determining, by weighing, the amount of a particular substance present in a sample. It usually involves the conversion of the test substance into a compound of known molecular weight that can be easily isolated and purified. Since gravimetric analysis is an absolute measurement, it is the principal method for analysing and preparing primary standards.

Monomer conversion is a key indicator of product property and composition, and is defined as the ratio of the polymer mass formed in the reactor to the total monomer fed until time \( t \) (Araujo et al., 2001). It was obtained experimentally by taking samples directly from the reactor. These samples were dried, the solids contents were determined and the conversion \( (X) \) was obtained as follows:
\[
X = \frac{\text{mass of dried sample}}{\text{mass of sample initial solid fraction}} / \frac{\text{mass of monomer fraction in reactor}}{\text{mass of sample initial solid fraction}}
\] (4.1)

### 4.3.2 Gel Permeation Chromatography

Gel permeation Chromatography (GPC), also called size exclusion Chromatography (SEC) or gel-filtration, is considered to be one of the most important methods for the determination of molecular weight (MW) and molecular weight distribution (MWD) of polymer. It uses porous particles to separate molecules of different sizes. A dilute polymer solution containing a broad molecular weight distribution of polymer chains, oligomers and even un-reacted monomers is allowed to flow through a column packed with finely divided particles under high pressure to accelerate the separation process.

Figure 4.5 Schematic diagram of GPC.

Molecules that are smaller than the pore size can enter the particles and therefore have a longer path and longer transit time than larger molecules that cannot enter the particles. Molecules larger than the pore size can not enter the pores and elute together as the first peak in the chromatogram. This condition is called total exclusion. Molecules that can enter the pores will have an average residence time in the particles depending on the molecules size and shape. Different molecules therefore have different total transit times through the column. Molecules that are
smaller than the pore size can enter all pores, and have the longest residence time on the column and elute together as the last peak in the chromatogram. This last peak in the chromatogram determines the total permeation limit. The separation process is illustrated in figure 4.6.

![Figure 4.6 Separation in a GPC column.](image)

Differential refractometer (DRI) system is the most commonly employed GPC detector. According to DIR method, the difference in the refractive index between the eluted solution and the pure solvent is proportional to the concentration of the polymer chains. The polymer concentration in the analyte is measured as a function of elution volume or time.

GPC is a relative method for determining the molecular weight. Thus a calibration curve, that relates the elution volume of a given molecule to its molecular size, is required. For a homologous series of polymers and assuming constant flow rate, the molecular size is proportional to Log molecular weight. A series of narrow dispersity polymers from the same homologous series were dissolved in the eluent and injected on the column set. Each of the standards should have known molecular weight average values. The elution volumes are recorded for each of the peaks and then a plot of Log molecular weight via elution volume is constructed as the calibration plot.
Assuming that the known molecular weights of the polymer standards are precise, it is now feasible to derive a function of the form:

\[ \log(M) = F(V) \]  \hspace{1cm} (4.2)

Thus the molecular weight corresponding to any elution volume can be accurately predicted according to Eq 4.2.

The MWD and its averages of the polymer samples were determined off-line by gel permeation chromatography (PL-GPC 120, version 1.0), which is an integrated GPC/SEC system combined with IR detector and High Resolution Data Acquire System (PL Data Stream).

The samples for the GPC were prepared by dissolving dried polymer latex in tetrahydrofuran (THF) to a concentration of 1 mg/mL. Analysis was carried out using two PLGel (Mixed-C) columns (Polymer Laboratories) at 40 °C using THF as an eluent at a flow rate of 1mL/min. Calibration curves were generated using Narrow-distribution polystyrene standards with molecular weight ranges between 580 and $7.5 \times 10^6$ g mol$^{-1}$. The injection volume was 100 µL. Data was processed through the Cirrus GPC software package (PL).
4.3.3 Particle Size Distribution Analysis

The PL-PSDA particle size distribution analyser is an integrated, automated system for the rapid determination of particle size distribution of colloidal dispersions. It operates on the principle of packed column hydrodynamic chromatography (HDC). PL-PSDA measures complex particle size distributions with high precision and accuracy, independent of particle chemistry, making it ideal for narrow distribution, multi-modal or polydisperse samples. The automated features and user friendly software combine to deliver remarkable ease of operation which, together with the high resolution of the technique, makes it as an instrument suitable for both quality control and research applications.

Particle size can have a fundamental effect on the physical properties of colloidal dispersions. The PL-PSDA operates on the principle of packed column hydrodynamic chromatography (HDC), a technique for separating particles based on their size, eluting in the order largest to smallest. Fractionation techniques, including packed column HDC, offer advantages over non-fractionation techniques for particle sizing in that the method produces information about the average particle size and the distribution of particle size. Non-fractionation techniques are less well suited for the analysis of multi-modal samples or samples with broad particle size distributions due to the low resolution of the method (Polymer_Laboratories, 2003).

Separation Mechanism

The sample flows through the cartridge, which contains a packed bed of non-porous particles. The interstitial channels in the packed bed can be visualized as a series of small capillaries and within each capillary and a velocity gradient exists described by a parabolic flow profile. Larger particles are less mobile and tend to remain in the central region of flow in the capillary, while smaller particles tend to migrate to the wall. The fractionation is therefore based on the different eluent velocity experienced by particles of different size particles eluting from the system in order of decreasing size. The dynamic range of the separation depends on the particle size of the packing media in the cartridge.
In the PL-PSDA, a proprietary water-based eluent is continuously pumped through the system at a constant flow rate. An auto-sampler enables multiple sample vials to be loaded and sampled for continuous, unattended operation. The sample under investigation and a small molecule marker solution are introduced into the system via a two position, electrically actuated valve such that the eluent flow is not interrupted. The PL-PSDA contains a separating 'cartridge'. The standard system has a dynamic operating range from 20nm to 1.2µm, with alternative cartridges available to cover specific size ranges up to 2µm. The ultra violet (UV) detector response is used to calculate the concentration of particles of different sizes present in the sample. The subsequent computation of particle size distribution simply requires a calibration procedure employing latex particle size standards (Polymer_Laboratories, 2003).

The PL-PSDA Windows compatible software provides system control, data acquisition, data analysis and reporting through one user friendly, intuitive graphical user interface. Individual screen views are easily accessed from the familiar style shortcuts toolbar. The main Control view indicates the status of all the system components and facilitates the input of sample details for up to 87 vial positions in the auto-sampler carousel. Samples do not necessarily have to be run sequentially in the carousel, and urgent samples can be assigned higher priority at any time. The auto-sampler graphic in the Control view uses colour coding to indicate the status of
each vial position. The Calibration view permits creation and review of column calibration files. Once a calibration has been performed, the calibration file is logged with the sample results for full traceability.

Figure 4.9 Schematic screen window of the instrument main control.

Figure 4.10 Schematic screen window of the calibration.
4.3.4 Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) is a branch of spectroscopy in which electromagnetic radiation (usually of radiowave frequency) is absorbed by molecules possessing nuclei with nonzero spins. NMR spectroscopy is a powerful method used in the determination of the type and structure of unknown organic compounds. The utility of NMR spectroscopy for structural characterization arises because different atoms in a molecule experience slightly different magnetic fields and therefore transitions at slightly different resonance frequencies in an NMR spectrum. Furthermore, splitting of the spectra lines arise due to interactions between different nuclei, which provide information about the proximity of different atoms in a molecule. NMR technique can provide quantitative and qualitative information about the functional group analysis, bonding connectivity and orientation, through space connectivity, molecular conformation and chemical dynamics.

**Principles of NMR**

When a nucleus with a non-zero spin is placed in a magnetic field, the nuclear spin can align in either the same direction or in the opposite direction as the external magnetic field. A nucleus that has its spin aligned with the external field will have a lower energy than when it has its spin aligned in the opposite direction to the field. Thus, those two nuclear spin alignments have different energies.

Nuclear magnetic resonance (NMR) spectroscopy uses the transition between those levels to detect and quantify nuclei. The magnitude of the energy splitting between these levels for nuclei in a strong magnetic field is in the range of radiofrequency (RF) radiation. Absorption of the RF radiation causes nuclear spins to realign or flip in the higher-energy direction. After absorbing energy, nuclei will reemit RF radiation and return to the lower-energy state.

The energy (and thus frequency) of an NMR transition depends on the magnetic-field strength, the nature of each nucleus and the local atomic environment around a given nucleus in a molecule. Every isotope has a particular combination of protons and neutrons in its nucleus. The nuclear structure largely determines the value of the
resonance frequency. Thus every isotope displays a basic resonance frequency. $^{13}$C nuclei will have a different basic resonance frequency compared to that of $^1$H etc.

Superimposed on the basic resonance frequency is an effect due to the local atomic environment in which an isotope is situated. The precise value of the resonance frequency of a $^1$H nucleus in a particular compound will depend upon the atoms it is bonded to and surrounded by. The nucleus is surrounded by electrons which may be viewed as moving electrical charges with associated magnetic fields. These electrons act as a source of magnetic shielding for the nucleus. The extent of the shielding will depend on the precise local atomic environment. The size of typical local field variations (which will result in a frequency variation) will depend on the isotope and the strength of the magnetic field in which the sample is placed.

NMR signals are usually plotted as spectra and analysed with respect to two features, frequency and intensity. It is conventional in NMR to plot frequency on the horizontal axis. The frequency yields qualitative information regarding the local atomic environment. The integrated intensity of a signal is a measure of signal strength and is determined by integrating the area under the signal peak. The integral will be directly proportional to the number of nuclei contributing to a signal at a particular frequency (if all nuclei are equally excited) and hence will provide quantitative information regarding chemical structure. The variation in precise resonance frequency is referred to as the “chemical shift”. The resonance frequency is shifted by the effect of neighbouring atoms and in particular the extent of magnetic shielding from local electrons discussed earlier. The size of the shift is normally measured in ppm relative to the trimethylsilane (TMS) peak which is referenced to 0 ppm.

The basic arrangement of an NMR spectrometer is shown in figure 4.11. The sample is positioned in the magnetic field and excited via pulsations in the radio frequency input circuit. The realigned magnetic fields induce a radio signal in the output circuit which is used to generate the output signal. Fourier analysis of the complex output produces the actual spectrum. The pulse is repeated as many times as necessary to allow the signals to be identified from the background noise.
In its simplest form, an NMR experiment consists of four steps:

1. Prepare the sample in an appropriated solvent.
2. Place the sample in a static magnetic field.
3. Excite nuclei in the sample with a radio frequency pulse.
4. Measure the frequency of the signals emitted by the sample.

The polymer sample is dried under nitrogen atmosphere at 200°C in order to remove the water traces present in the sample. Then 12mg of the sample is dissolved in 1mL of deuterium chloroform (CDCl$_3$). The sample solution is then put in the NMR tube and the tube is installed in the NMR spectrometer. The analysis of the sample was carried out at 35°C. A Bruker AM 400 spectroscopy (400 MHz) was used to determine the terpolymer composition through $^1$H-NMR spectra.

Figure 4.12 shows the NMR spectrum we obtained for a sample of our terpolymer. We encountered a few challenges in analysing the NMR spectrum. First was the overlapping of CH$_2$ peaks of surfactant with that of MMA and MA. This problem was solved by using the extraction process. The dried polymer was dissolved in a chloroform-water mixture. The molecules of surfactants remain at the surface contact between the water-chloroform mixture, while the polymer dissolves in chloroform.
Then the chloroform was collected and dried. The other problem was the presence of water molecules in the polymer in which its peak overlaps with that of CH$_2$. The sample was dried at 180°C for 1h under nitrogen atmosphere in order to remove water from the polymer. Since MMA and MA both are sensitive to moisture due to hydrogen bonds with water molecules, the samples were saved in a desiccator after drying.

To determine the ratio of each component in the terpolymer, the areas of four peaks were integrated: Aromatic peak (ar) which is due to the phenyl group of styrene molecule; Aliphatic peaks (al) which is for all the protons in the polymer except that in the phenyl group, methyl (α-CH$_3$) peak which comes only from MMA and methoxy (OCH$_3$) peak which relates to both MMA and MA. The ratios were calculated from Equations 4.3, 4.4 and 4.5. Equation 4.6 is to confirm the calculations because the peaks of CH and CH$_2$ may overlap. All these challenges have now been successfully overcome and we are ready to carry out further analyses.

\[
F_S + F_{MMA} + F_{MA} = 1 
\]

\[
\frac{A_{ar}}{A_{ar} + A_{al}} = \frac{5F_S}{5F_S + 8F_{MMA} + 6F_{MA}} \tag{4.4}
\]

\[
\frac{A_{ar}}{A_{ar} + A_{CH_3}} = \frac{5F_S}{5F_S + 3F_{MMA}} \tag{4.5}
\]

\[
\frac{A_{ar}}{A_{ar} + A_{OCH_3}} = \frac{5F_S}{5F_S + 3F_{MMA} + 3F_{MA}} \tag{4.6}
\]
4.3.5 Differential Scanning Calorimetry

Differential scanning calorimeter (DSC) is a powerful technique for analysing the thermal transitions in materials. It provides information on the temperature at which transitions occur as well as quantitative measurement of the heat associated with the event. It determines the temperature and heat flow associated with material transitions as a function of temperature and time. DSC can also provide data on the amount of heat absorbed or emitted by the material during transitions which are caused by heat-related changes such as glass transition, crystallinity, melting, specific heat, heat of fusion, oxidation, reaction kinetics and phase changes. This information helps the user to identify processes and ultimately qualify performance. Two different differential scanning calorimeters, DSC 2920 Modulated, manufactured by TA Instruments and Seiko DSC 6100 system, were used in this work to measure the glass transition temperatures of the polymer samples. Figure 4.13 shows the schematic diagram of the DSC setup.

DSC consists of two sample holders which are thermally isolated from one another and which contain the sample S and reference substance R which are both heated in
parallel according to a linear temperature programme. For each measurable temperature difference between R and S, the corresponding amount of energy is immediately compensated with variable filament power. The filament power is recorded. The integration of the measured peak area gives the measured heat energy directly.

![Schematic diagram of DSC setup.](image)

DSC technique utilises a software package for the thermal analysis. This software allows the glass transition, specific heat capacity, change and enthalpy as well as crystallinity and melting to be calculated directly. A useful feature of this software is the overlay command where up to eight DSC curves can be placed together to aid comparative efforts.

Before any accurate readings can be measured for multipolymers, it is standard research practice to calibrate all equipment to a known reference material. For DSC, tin and indium was supplied by the manufacturers as the reference material of choice. DSC reading for the melting temperature ($T_m$) of tin was determined to be 234.8°C before calibration which is slightly higher than the literature value of 232.0°C. Similarly, $T_m$ for indium was also higher than expected before calibration at 162°C (literature value 156.6°C). Note that for indium, DSC curves have been normalised as an overlay to better distinguish the effect of calibration.
The DSC instrument uses a sinusoidal PID signal to measure heat flow against temperature. The corrected calibration parameters are recorded in table 4.2 below. After implementing the calibration parameters, reference materials were retested to obtain $T_m$ of 231.74°C and 153.1°C for tin and indium respectively.

**Table 4.2 Calibration parameters for DSC using reference tin and indium.**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg Before</th>
<th>Tg After</th>
<th>Tg Theory</th>
<th>P</th>
<th>I</th>
<th>D</th>
<th>0th order</th>
<th>1st order</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin</td>
<td>234.80</td>
<td>231.74</td>
<td>232.00</td>
<td>10</td>
<td>500</td>
<td>10</td>
<td>-11.88</td>
<td>1.04</td>
<td>40</td>
</tr>
<tr>
<td>Indium</td>
<td>162.15</td>
<td>153.10</td>
<td>156.60</td>
<td>10</td>
<td>500</td>
<td>10</td>
<td>-11.88</td>
<td>1.04</td>
<td>40</td>
</tr>
</tbody>
</table>

**General operating instructions:**

- Weigh about 10mg of a dry polymer sample and enclose it in the pan.
- Load encapsulated sample pan (ensuring good contact between pan and DSC cell).
- Enter experiment information using ‘set sample condition’ menu.
- Select thermal method using ‘temperature program setting’ menu.
- Then set temperature range between 40 to 350°C, rate set to 10°C/min, 5min holding.
- Press ‘run’ from the main menu.
- Wait until DSC finishes heating and then allows cooling back to room temperature.
- Press ‘hold’ until DSC heat flow reading is near zero and then press zero.
4.4 DYNAMIC MODEL VALIDATION

The aim of the model development was to enable simultaneous prediction of the global and individual conversions, terpolymer composition, glass transition temperature, molecular weight distribution, the number- and weight-average molecular weights and particle size distribution and the average particle diameter and concentration versus the process operating conditions (i.e., temperature, surfactant, initiator and monomer concentrations).

Development of a rigorous mathematical model for a polymerisation reactor makes it able to predict both the dynamics of the reactor and the properties of the polymer product. But the reliability of the model depends on the model parameters (Canegallo et al., 1993). In addition, well-estimated model parameters can enhance the performance of computer simulation, optimisation and control.

There are a number of rate coefficients within the kinetics equations of emulsion polymerisation. These parameters refer to rate coefficients of volume growth, entry rate to the particle and the micelles, transfer rate, propagation rate in the particle and the aqueous phase and dissociation rate of the initiator. The parameters in our kinetic, transport, and equilibrium equations for emulsion homopolymerisation and copolymerisation were obtained independently from the literature (Table 4.3).

For the current model, we developed the remaining equations for terpolymerisation from emulsion homopolymerisation and copolymerisation by applying the fundamentals of kinetics, thermodynamics and equilibrium formalism. Thus we developed the kinetic models, dynamic models, and a model-based integrated framework for process simulation, optimisation and control. Molecular averages of the kinetics parameters used in our model adapting the homopolymerisation and copolymerisation values in the literature are molar ones. Polymerisation reactions occur between monomer molecules and so molar average is appropriate to compute the parameters. Table 4.3 shows the parameters used in developing the emulsion terpolymerisation model for Styrene, MMA and MA system.
Table 4.3 Parameters used in the kinetic model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Styrene (1)</th>
<th>MMA (2)</th>
<th>MA (3)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{po,i} ) (L/mol.s)</td>
<td>( 1.99 \times 10^7 e^{-30.78/RT} )</td>
<td>( 4.92 \times 10^5 e^{-18.1/RT} )</td>
<td>( 6.71 \times 10^{6} e^{-29.678/RT} )</td>
<td>(Davis et al., 1990)</td>
</tr>
<tr>
<td>( k_{eq,i} ) (L/mol.s)</td>
<td>( 1.703 \times 10^9 e^{-9.46386/RT} )</td>
<td>( 9.8 \times 10^7 e^{-2.93158/RT} )</td>
<td>( 1.703 \times 10^9 e^{-9.46386/RT} )</td>
<td>(Nomura et al., 1981, Nomura et al., 1983, Schoonbrood et al., 1995)</td>
</tr>
<tr>
<td>( k_{er,i} ) (L/mol.s)</td>
<td>( 10^{0.658} k_{po,i} e^{-23.8/RT} )</td>
<td>( 4 \times 10^{3.8} e^{-45.9/RT} )</td>
<td>( 1.25 \times 10^{-4} \times k_{p,0.3} )</td>
<td>(Clay and Gilbert, 1995, Park et al., 2000)</td>
</tr>
<tr>
<td>( k_{eq,p,i} ) (L/mol.s)</td>
<td>( 2 k_{p,i} )</td>
<td>( 3.15 k_{p,2} )</td>
<td>( 3.15 k_{p,3} )</td>
<td>(Clay and Gilbert, 1995)</td>
</tr>
<tr>
<td>( k_{eq,q,j} ) (L/mol.s)</td>
<td>( 1.753 k_{p,1} )</td>
<td>( 2 k_{p,2} )</td>
<td>( 2 k_{p,3} )</td>
<td>(Clay and Gilbert, 1995)</td>
</tr>
<tr>
<td>( r_{ij} )</td>
<td>( r_{12} = 0.468 )</td>
<td>( r_{21} = 0.461 )</td>
<td>( r_{31} = 0.19 )</td>
<td>(Schoonbrood et al., 1996)</td>
</tr>
<tr>
<td>( j_{crit} )</td>
<td>3</td>
<td>5</td>
<td>18</td>
<td>(Clay and Gilbert, 1995, Schoonbrood et al., 1995)</td>
</tr>
<tr>
<td>( z )</td>
<td>5</td>
<td>10</td>
<td>41</td>
<td>(Clay and Gilbert, 1995, Van Doremaele, 1990)</td>
</tr>
<tr>
<td>( C^\text{sat}_{i,j} ) (mol/L)</td>
<td>( -1.514 + \frac{1259}{T+273} )</td>
<td>0.15</td>
<td>0.6</td>
<td>(Schoonbrood et al., 1996, Gilbert, 1995)</td>
</tr>
<tr>
<td>( D_{w,i} ) (m²/s)</td>
<td>1.55 \times 10^{-7}</td>
<td>1.7 \times 10^{-7}</td>
<td>1.9 \times 10^{-7}</td>
<td>(Coen et al., 1998, Schoonbrood et al., 1995)</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.74 \times 10^{-9}</td>
<td>0.69 \times 10^{-8}</td>
<td>0.69 \times 10^{-8}</td>
<td>(Clay and Gilbert, 1995)</td>
</tr>
<tr>
<td>( cmc ) (mol/L)</td>
<td>3 \times 10^{-3}</td>
<td>3 \times 10^{-3}</td>
<td>3 \times 10^{-3}</td>
<td>(Gilbert, 1995)</td>
</tr>
<tr>
<td>( n_{agg} )</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>(Gilbert, 1995)</td>
</tr>
<tr>
<td>( a_{i} ) dm²</td>
<td>42 \times 10^{-18}</td>
<td>42 \times 10^{-18}</td>
<td>42 \times 10^{-18}</td>
<td>(Clay and Gilbert, 1995)</td>
</tr>
<tr>
<td>( \sigma_{j} ) (dm)</td>
<td>0.60 \times 10^{-9}</td>
<td>0.59 \times 10^{-8}</td>
<td>0.59 \times 10^{-8}</td>
<td>(Clay and Gilbert, 1995)</td>
</tr>
<tr>
<td>( d_{m,1} ) (kg/L)</td>
<td>923.6-0.887T</td>
<td>965.4-1.090T-9.7 \times 10^{-4} T²</td>
<td>976.5-1.15T</td>
<td>(Clay and Gilbert, 1995, Park et al., 2000)</td>
</tr>
<tr>
<td>( d_{p,1} ) (kg/L)</td>
<td>1050.1-0.621T</td>
<td>1.178</td>
<td>1.2</td>
<td>(Clay and Gilbert, 1995)</td>
</tr>
<tr>
<td>( M_{i} ) (kg/mol)</td>
<td>0.104</td>
<td>0.10013</td>
<td>0.08609</td>
<td>(Brandrup and Immergut, 1989)</td>
</tr>
<tr>
<td>( T_{gl} ) (°C)</td>
<td>100</td>
<td>115</td>
<td>9</td>
<td>(Park et al., 2000, Hoppe et al., 2005)</td>
</tr>
</tbody>
</table>

\(^a\) The equation is derived from data taken from references (Park et al., 2000, Schoonbrood et al., 1995).

\(^b\) The values of MA are taken as that of MMA.
The population balance equations were discretised with respect to radius in order to convert them from partial-integro-differential equations into ordinary differential equations. Backward finite difference approximation method is used in discretisation process. The models were programmed within gPROMS to simulate the process and compare with experimental data obtained in our laboratory. The experiments were carried out in both 1L and 5L reactors in order to demonstrate the capability of the model for scaling up. The experimental results for the key process characteristics and polymer properties were compared with the model simulations.

### 4.4.1 Monomer Conversion

In figure 4.14, the experimental results for overall conversion show good agreement with the model simulation. The first sections of figures 4.14b, 4.14c, 4.14d and 4.14e [first 1500sec] show batch reaction for seeding. Then the overall conversion dropped at the instant of feeding the monomer. This is due to the fact that most of the monomers were polymerised and thus adding monomers to the reactor will increase its ratio in the system causing a drop in the overall reaction. Then, the monomers start to propagate converting to a polymer.

In figure 4.14e where the temperature of process was 83°C, the agreement between experimental value and model prediction is less than that in figures 4.14a, 4.14b, 4.14c and 4.14d. This is due to the values of parameters, which were taken from the literature and fitted in Arrhenius equations between 50°C to 70°C. But the agreement is still good, since the temperature of the process is not so far from the fitting ones in the literature.
Figure 4.14 Experimental [●] and simulated [—] results of the conversion of emulsion terpolymerisation with 5/3/2 styrene/MMA/MA at:  

a) Batch at 75°C; b) Semibatch at 75°C and 0.034g/sec feed rate; c) Semibatch at 75°C and 0.064g/sec feed rate; d) Semibatch at 83°C and 0.034g/sec feed rate; e) Semibatch at 65°C and 0.034g/sec feed rate; f) Semibatch at 75°C, 1/1/1 monomers mixture ratio and 0.034g/sec feed rate.

### 4.4.2 Particle Size Distribution and Average Diameter

The particle size distribution is an important measurement for latexes. Figures 4.15 and 4.16 show good agreement between experimental values and model predictions for diameter average and PSD. An amount of 17.78% of the total amount of monomers was used in the batch section of the reaction for seeding. So the particles were produced and then monomers were fed. At that moment, the monomers were
added and entered into the particles which allows for continuing the polymerisation reaction and increasing the particle size until stopping the monomers feeding. This is because polymer growth continues in progress as there are monomers in the particle phase.

The experimental values of average diameter and PSD in figure 4.15c and 4.16c have less agreement than those in figure 4.15 and 4.16. These small differences between model predictions and experimental values are due to the reliability of parameter values at the operational conditions. The Arrhenius equations of the rate coefficient parameters were derived from experiments carried out at 70°C. Thus the reliability of parameter values depends on the temperature of the reactions which is over than 95% (goodness) for temperatures 60-90°C. Figure 4.16d depicts the growth of PSD with time.

Figure 4.15 Experimental [●] and simulated [—] results of the average diameter of polymer particles of in emulsion process with 5/3/2 styrene/MMA/ MA at: a) Batch at 75°C; b) Semibatch at 75°C and 0.034g/sec feed rate; c) Semibatch at 83°C and 0.034g/sec feed rate; d) Semibatch at 65°C and 0.034g/sec feed rate.
Figure 4.16 Experimental [●] and simulated [—] results of particle size distribution of emulsion process with 5/3/2 styrene/MMA/MA for operation in the following modes: a) Batch at 75°C; b) Semibatch at 83°C and 0.034g/sec feed rate; c) Semibatch at 65°C and 0.034g/sec feed rate; d) Semibatch at 75°C and 0.034g/sec feed rate.

4.4.3 Molecular Weight Distribution and Averages

The other key polymer properties tested were the molecular weight distribution (MWD), number average molecular weight ($M_n$), weight average molecular weight ($M_w$) and molecular weight polydispersity index (MWPI) at different temperatures, feed rate and monomer feed composition. The results showed a good agreement between the simulation and the experimental results. Figures 4.17 and 4.18 show that $M_n$ and MWPI were significantly affected by temperatures and monomer feed composition, while monomer feed rate has moderate effect on them.

Figure 4.17a shows that $M_n$ decreases as conversion increases in a batch-process. This is because the monomer concentration decreases as well as the rate coefficient of polymerisation with the increase of viscosity. The first sections of figures 4.17b, 4.17c, and 4.17d and 4.17e [first 1500sec] show batch reaction for seeding and its
Mn trend is similar to that of batch. Then Mn increases sharply at the instant of feeding the monomer. This is due to the fact that most of the monomers were polymerised and thus adding monomers to the reactor will increase its concentration in the system causing increases in Mn.

Figure 4.17 Experimental [●] and simulated [—] results of Mn in an emulsion terpolymerisation with 5/3/2 styrene/MMA/ MA for operation in the following modes: a) Batch at 75°C; b) Semibatch at 75°C and 0.034g/sec feed rate; c) Semibatch at 65°C and 0.034g/sec feed rate; d) Semibatch at 75°C and 0.0173g/sec feed rate; e) Semibatch at 75°C, and 1/1/1 monomers ratio and 0.034g/sec feed rate; f) Semibatch at 75°C, 3/2/5 monomers mixture ratio and 0.034g/sec feed rate.

Figures 4.17b and 4.17c reveal that Mn increases with a decrease in the temperature. This is because the transfer rate coefficient is lower at lower temperatures. Moreover, it can be clearly seen from figures 4.17b, 4.18e and 4.17f that the molecular weights
are greater at 5/3/2 Sty/MMA/MA monomer ratio, compared to 1/1/1 and 3/2/5 Sty/MMA/MA monomer feed composition This is due to the fact that the transfer rate coefficient of MA is about 100-50 times that of styrene and MMA, even though the propagation rate coefficient of MA is moderately larger. The model predictions show relatively lower number average molecular weight with lower flow rate as shown in figures 4.17b and 4.17d. The rate of polymerisation increases with monomer concentration, which is due to the increasing of monomer feed rate, and consequently molecular weight increases. The trends for weight average molecular weight (Mw) are similar to those for Mn.

The model predictions, as shown in figure 4.18, reveal that the MWPI, which is a measure of the homogeneity of the MWD, decreases with the increase of MA ratio in the feed composition, slightly decreases with temperature and very slightly increases with monomer feed rate. This is due to the fact that the concentration of MA in the aqueous phase is about 100 times to that of styrene, so the rate of polymerisation in aqueous phase increases, thus the average number of radicals in the polymer particles increases which leads to a decrease in Mn and MWPI.

Figure 4.18 Experimental [●] and simulated [—] results of MWPI in emulsion terpolymerisation with 5/3/2 styrene/MMA/MA for operation in the following modes: a) Batch at 75°C; b) Semibatch at 75°C and 0.034g/sec feed rate; c)
Semibatch at 65°C and 0.034g/sec feed rate; d) Semibatch at 75°C and 0.0173g/sec feed rate.

The shape and broadness of MWD, as shown in figure 4.19, are related to MWPI. A relatively broader MWD is obtained with the relatively lower monomer feed rate as shown in figures 4.19b and 4.19d. With a lower feed rate, some degree of secondary nucleation and a slower polymerisation rate induces a relatively broader MWD. Also a relatively broader MWD is obtained with lower polymerisation temperature as shown in figures 4.19b and 4.19c.

Those results indicate that, in addition to initiator and surfactant feed rates, both MWD and its averages could be controlled to a certain degree by temperature, feed rate and monomer feed composition. Therefore semibatch emulsion terpolymerisation has six manipulated variables that could be used to control the key polymer properties. These manipulated variables are: temperature, surfactant flow rate, initiator flow rate and three different monomers flow rates.

Figure 4.19 Experimental [●] and simulated [—] results of MWD in emulsion terpolymerisation with 5/3/2 styrene/MMA/MA for operation in the following modes: a) Batch at 75°C; b) Semibatch at 75°C and 0.034g/sec feed rate; c) Semibatch at 65°C and 0.034g/sec feed rate; d) Semibatch at 75°C and 0.0173g/sec feed rate.
4.4.4 Terpolymer Composition

The model predictions were validated against cumulative terpolymer composition obtained from NMR measurements. Figure 4.20 and 4.21 show good agreement between the simulations and experimental data. The figures show that the terpolymer composition of semibatch process is more fixed than that of the batch one. The cumulative composition of Styrene in figure 4.20 decreases with time while that of MA increases. This is due to the fact that the rate of polymerisation of styrene is the highest one in the present monomers. Thus, the free monomer of styrene in the reactor decreases rapidly which results in a decrease of its rate of polymerisation. While MA has the lowest rate of polymerisation which results in its accumulation inside the reactor, this leads to an increase in its rate.

The trend of MMA is approximately straight because MMA has the moderate rate and its composition is 3/10 of the total monomers in the reactor which is close to its starved condition. However in the semibatch, figure 4.21, the trend of all the monomers is approximately straight, since the flow rate is close to starved condition. Therefore the terpolymer composition can be controlled via semibatch processes under starved condition by manipulating the monomer feed rate, composition and temperature of the system.

![Figure 4.20 Experimental [●, ■, ▲] and simulated [—] results of the cumulative terpolymer composition of batch system at 75°C and 5/3/2 monomers mixture ratio.](image)

Figure 4.20 Experimental [●, ■, ▲] and simulated [—] results of the cumulative terpolymer composition of batch system at 75°C and 5/3/2 monomers mixture ratio.
Figure 4.21 Experimental [●, ■, ▲] and simulated [—] results of the cumulative terpolymer composition of batch system at 75°C and 5/3/2 monomers mixture ratio with 0.034g/sec feed rate.

### 4.4.5 Glass Transition Temperature

Table 4.4 shows good agreement between the measured and simulated values of the glass transition temperature, \( T_g \), for experiments carried out at 75°C, 0.034g/sec and 50/30/20, 30/30/30, 30/20/50 feed composition rate of sty/MMA/MA. As expected, an increase in the fraction of MA in the terpolymer composition leads to a decrease in \( T_g \).

Table 4.4 Experimental and simulated glass transition temperatures, \( T_g \) (°C), of terpolymers resulting from polymerisations carried at 75°C with variable monomer composition.

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Sty (wt %)</th>
<th>MMA (wt %)</th>
<th>MA (wt %)</th>
<th>( T_g ) (°C) Exp.</th>
<th>( T_g ) (°C) Simul.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.540</td>
<td>0.270</td>
<td>0.190</td>
<td>92.5</td>
<td>95.2</td>
</tr>
<tr>
<td>2</td>
<td>0.501</td>
<td>0.250</td>
<td>0.250</td>
<td>85.5</td>
<td>87.9</td>
</tr>
<tr>
<td>3</td>
<td>0.340</td>
<td>0.240</td>
<td>0.420</td>
<td>70.5</td>
<td>68.7</td>
</tr>
<tr>
<td>4</td>
<td>0.297</td>
<td>0.215</td>
<td>0.488</td>
<td>64.0</td>
<td>61.1</td>
</tr>
<tr>
<td>5</td>
<td>0.550</td>
<td>0.201</td>
<td>0.250</td>
<td>85.2</td>
<td>84.7</td>
</tr>
<tr>
<td>6</td>
<td>0.417</td>
<td>0.226</td>
<td>0.357</td>
<td>76.1</td>
<td>76.1</td>
</tr>
</tbody>
</table>
4.5 MICROCALORIMETRY SOFT SENSOR VALIDATION

Batch and semibatch emulsion terpolymerisation reactions of styrene, MMA and MA were carried out in a jacketed 1L stainless steel reactor equipped with an agitation speed controller and three RTD sensors which is discussed in section 4.2. A computer-controlled system was used for data information recording and manipulation. The temperature within the reactor, inlet and outlet of the jacket and also monomer feed rate, which corresponded to the electronic balance and time, are all recorded in a database system, and so for calculating the heat. The reactor details are given in Table 4.5. The cumulative composition of polymer samples was determined off-line by $^1$H NMR.

Table 4.5 Reactor dimensions and operating parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor height (m)</td>
<td>0.18</td>
</tr>
<tr>
<td>Reactor diameter (m)</td>
<td>0.085</td>
</tr>
<tr>
<td>Jacket height (m)</td>
<td>0.13</td>
</tr>
<tr>
<td>Jacket volume (ml)</td>
<td>350</td>
</tr>
<tr>
<td>Water flow rate through jacket (l/min)</td>
<td>20</td>
</tr>
<tr>
<td>Agitation speed (rpm)</td>
<td>300</td>
</tr>
</tbody>
</table>

Polymerisations were carried out with the addition of monomers, water and surfactant to the reactor and the contents were brought to the desired reaction temperature (steady state). Temperature readings were taken during the heating process i.e. the reactor contents were being heated to the operation temperature, to allow determination of $U$. The average heat transfer coefficient $U$ for emulsion terpolymerisation was estimated as 86W/m$^2$.K.
Once heat transfer coefficient had been determined, the heat losses parameters $\alpha$ and $\beta$ were estimated based on temperature measurements with the reactor operating at 65-83°C, and monomer molar feed rates set for variable monomer ratios. The heat losses parameters $\alpha$ and $\beta$, were estimated by solving Eq. 3.95 at the steady state while maintaining the reactor temperature constant just before adding the initiator solution. Then heat loss was determined with respect to the difference between the reactor and ambient temperatures (Eq. 3.101). Since $Q_l$ depends on the geometry of the reactor, the temperature difference between the reaction mixture and the surroundings, the values of parameters $\alpha$ and $\beta$ were varied with variable process conditions especially with the reaction temperature and ambient temperature. Therefore, the parameters $\alpha$ and $\beta$ were estimated for each experiment and consequently led to good agreement with the experimental results and model estimation. Table 4.6 shows the values of $\alpha$ and $\beta$ that were obtained at different experimental conditions.

After completing the heat transfer analysis, monomer conversion was calculated using the calorimetric model with constant values of $U$, $\alpha$ and $\beta$ that were previously estimated. As mentioned earlier, this assumption is reasonable because of the low solids content and high shear rate inside the reactor.

Table 4.6 Estimated values of $\alpha$ and $\beta$ parameters over the range of experimental conditions.

<table>
<thead>
<tr>
<th></th>
<th>$3.564 \times 10^{-5}$</th>
<th>$1.172 \times 10^{-3}$</th>
<th>$8.051 \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>3.460</td>
<td>2.478</td>
<td>1.353</td>
</tr>
<tr>
<td>Reaction temp. (°C)</td>
<td>65</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Ambient temp. (°C)</td>
<td>21</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>Monomer ratio (Sty/MMA/MA)</td>
<td>5/3/2</td>
<td>5/3/2</td>
<td>5/3/2</td>
</tr>
<tr>
<td>Flow rate (g/s)</td>
<td>0.044</td>
<td>0</td>
<td>0.044</td>
</tr>
</tbody>
</table>
4.5.1 Polymerisation Rate

The rate of polymerisation, which is directly proportional to the heat of reaction $Q_r$, was high at the beginning of the reaction. This is because the small amount of the monomer (17.78%) fed initially during the seed formation stage was consumed rapidly leading to an increase in the reaction rate. Subsequently, the rate of polymerisation stabilizes and later decreases for a batch operation as depicted in figure 4.22. When additional monomer is fed during semibatch operation, the unreacted monomer concentration increased in the aqueous phase, which induced an increase in the monomer concentration inside the particles. Consequently, $Q_r$ and the rate of polymerisation increases with time and reached a plateau (Figure 4.22a).

Figure 4.22a shows that the batch operation exhibits greater exothermic heat evolution in the first period of reaction (0-2000s) where the process conversion within this period reaches about 80% (Figure 4.23a). This is due to the greater quantity of monomer reacting during this stage of the process. Subsequently, the heat evolution decays with time as the monomer concentration decreases, reaching low values at high conversion. The semibatch operation exhibited less heat evolution since 17.78% of the total monomer was charged initially. However, the heat production increases with addition of monomer, because the propagation reaction is maintained within the particles with the gradual addition of monomers. The percentage of average heat losses ($Q_l$) with batch process is much less than that in semi-batch process (Fig. 4.23b).
Figure 4.22 (a) heat production and (b) percentage ratio of average heat losses (Ql) to heat generation (Qr) respectively estimated by calorimetric model: [--] batch at 75°C and [---] semibatch at 75°C, 0.072g/sec feed rate with (5/3/2) ratio of styrene/MMA/MA.

4.5.2 Conversion

The accuracy of the on-line calorimetric model was validated by comparing monomer conversion estimated by the model with the experimental data obtained via off-line gravimetry for the styrene/MMA/MA system (Figure 4.23 & 4.24). The experiments were run at variable monomer flow rates, monomer feed composition and reactor temperatures. Good agreement was obtained between the on-line calorimetric measurements and the off-line gravimetric results.
Figure 4.23 shows the time evolution of the overall conversion profiles during batch emulsion terpolymerisation of Sty/MMA/MA, while figures 4.24(a, b, c) are for semibatch operations with variable temperatures. The initial segments of the conversion profiles for semibatch operations (Figure 4.24) are similar to that for the batch process (Figure 4.23), since the semibatch process comprises a batch operation for the first 1500 seconds.

![Graph](image)

Figure 4.23 Experimental [*] and simulated [—] results of the conversion of batch emulsion terpolymerisation of styrene, MMA and MA (5/3/2) mixture at 75°C.

On adding monomers to the reactor thereafter, the overall conversion decreased slightly. This was because of the sudden increase in monomer flow rate, resulting in an accumulation of monomer volume within the reactor. The responses show that the highest conversion drop occurs with the highest monomer flow rate. However, this decrease is short-lived as the species concentration inside the particles starts to increase with monomer diffusing from the aqueous phase. As a result, the reaction rate and the monomer conversion increase.
Figure 4.24 Experimental [•] and simulated [-] results of the conversion of emulsion terpolymerisation of styrene, MMA and MA (5/3/2) mixture at a) 75°C and 0.044g/sec feed rate; b) 65°C and 0.044g/sec feed rate; c) 75°C and 0.072g/sec feed rate.

The conversion is greater at higher temperature, as shown in figures 4.24a and 4.24b. This is because the rate of polymerisation is greater at a higher temperature.
Thus, these results show that with a semibatch process, one can control the conversion better than with a batch process. Temperature is the only manipulating variable available to control conversion for a fixed-time batch operation after start up, while with semibatch operation, one may use monomer feed rate, feed composition and temperature as manipulation variables for achieving the desired objectives.

4.5.3 Polymer Composition

The model predictions were validated against cumulative terpolymer composition obtained from NMR measurements. The composition of the terpolymer was determined using the Proton Nuclear Magnetic Resonance (\(^1\)H-NMR) spectroscopy (Bruker AM 400 MHz) at 35\(^\circ\)C with CDCl\(_3\) as a solvent. The details of terpolymer composition calculations via NMR technique were discussed in section 4.3.4.

Figures 4.25 and 4.26 show reasonable agreement between our calorimetric model estimations and the experimental data for the terpolymer compositions with batch and semibatch operations. In a few cases, the model predictions show slight overestimation compared to the experimental results, however, the trends are similar and the agreement is within the experimental error. The terpolymer composition obtained for the semibatch process (Figure 4.26) exhibit somewhat greater stability than that for the batch process (Figure 4.25). This implies that the terpolymer composition can be better controlled via semibatch processes under starved conditions by manipulating the monomer feed rate, feed composition and temperature of the system.

The cumulative composition of styrene in a batch process, as inferred from figure 4.25, decreases while that of MA increases. This is because the rate of polymerisation is the highest for styrene among the three monomers employed. Thus, the free monomer of styrene in the reactor decreases rapidly, and this results in a decrease in its polymerisation rate. MA has the lowest rate of polymerisation among
the three monomers which results in its accumulation within the reactor and the consequent increase in its rate. For MMA, the trend is approximately unchanging, since MMA has a moderate reactivity and its composition is about 3/10 of the total monomers in the reactor which is close to its starved condition. However, for the semibatch operation (Figure 4.26), the polymerisation rate profiles for the monomers approximately reach their plateaus rapidly, since the flow rate is close to starved condition.

Figure 4.25 Experimental [●, ■, ▲] and simulated [—] results of the cumulative terpolymer composition of batch system of styrene/MMA/MA (5/3/2) mixture at 75°C.

Figure 4.26 Experimental [●, ■, ▲] and simulated [—] results of the cumulative terpolymer composition of semibatch system of styrene/MMA/MA (5/3/2) mixture at 75°C and 0.044g/sec feed rate.

Based on these and additional results obtained with our simulations and measurements, we conclude that our calorimetric model is capable of tracking
monomer conversions and terpolymer compositions with prediction errors (within 3-5%), that are reasonably acceptable. Thus, calorimetry is suitable as a soft-sensor for estimating conversion and polymer composition for on-line monitoring and control applications and can online validate the predictions of our developed dynamic model.

4.6 CONCLUSION

The dynamic model, developed in chapter three, for the emulsion terpolymerisation of styrene, MMA and MA in batch and semibatch operating modes is validated experimentally in this chapter. A detailed description of the design and installation of the different components in the facility was presented first. Then, the experimental model validation was carefully conducted for the emulsion terpolymerisation of styrene MMA and MA in batch and semibatch operations. It has been found that the model prediction of the key polymer properties, average particle size, conversion, PSD, MWD, $M_n$, $M_w$, $T_g$, and terpolymer composition are in good agreement with the experimental results.

From the experimental results and model validation, it can be concluded that the polymer products of the emulsion polymerisation process are highly affected by its operational conditions. The particle size of the polymer formed in batch process was greater than that in semibatch one. Different PSDs were obtained at different monomer and surfactant flow rates. Terpolymer composition was mainly affected by the flow rates of the three monomers. Moreover, process temperature, monomers flow rates and initiator flow rate have a significant effect on the MWD and $M_n$. MWD was increased with a decrease in the temperature and an increase in the initiator flow rate.

We conclude that the dynamic model can be used for optimising the process and developing optimal trajectories to produce terpolymers with specific composition, PSD, MWD, $M_n$ and $T_g$ characteristics. This will be conducted in the following chapter.
The microcalorimetric soft sensor was also validated for the emulsion terpolymerisation of Sty, MMA and MA monomer systems. The results show good agreement between the conversion profiles and the cumulative terpolymer compositions estimated from calorimetric data and those measured by gravimetric and NMR analysis. The approach was found to be suitable for the advanced control of polymerisation reactors, especially to implement closed-loop control of conversion and composition, which are crucial in establishing terpolymer product properties.

**BIBLIOGRAPHY**


