A method is described to scale-up polymerization processes using the METTLER TOLEDO RC1 reaction calorimeter. The method consists in combining a series of specific polymerizations in the METTLER TOLEDO RC1 reaction calorimeter with a simple mathematical treatment. The kinetic behavior is thus quickly predicted without the need of elaborate mechanistic details. The combination of experimentation and the mathematical treatment allows one ultimately to predict the thermal response of different size reactors. The method is demonstrated for a suspension and an emulsion polymerization process.

Keywords: Polymerization, scale-up, emulsion, suspension, radical, Arrhenius, modeling, kinetics, validation, heat generation.

Introduction

One of the limitations in the scale-up of chemical processes is the need for a kinetic model to predict the thermal response of the process in a large reactor. Even though the kinetics of free radical polymerization are in general well understood, the values for the rate constants of the different physical events that determine the rate of polymerization and thus the rate of heat generation are difficult to obtain.

As a result, a large scattering of values for propagation and termination rate constants is found in the literature for any particular monomer system [1].

In cases like emulsion polymerization the kind of physical events that determine the kinetics of the systems such as particle generation, particle disappearance, radical entry, radical desorption and chain termination may change as the temperature changes, making the development of mathematical models to predict all these events complicated [2].

This paper presents an approach to circumvent some of these difficulties by combining a protocol of experiments in a calorimeter such as the METTLER TOLEDO RC1 a mathematical treatment of the data and the solution of the heat balance equation for the reactor under consideration. The process is illustrated for two polymerization processes with substantial differences in kinetics: suspension polymerization and emulsion polymerization.

Experimental

All polymerizations were carried out in a METTLER TOLEDO RC1 reaction calorimeter. The reactor used in the calorimeter was Mettler-Toledo’s MP10 reactor equipped with metal inserts.

Description of the method

In order to predict the behavior of a particular reactor the following heat balance equation needs to be solved (equation 1), where dQ_r/dt is the rate of heat generation during the polymerization, U is the overall heat transfer coefficient, A is the area over

\[-dQ_r/dt + UA(T_r - T_j) + m C_p dT_r/dt + Q_{loss} = 0\]

(1)
which heat transfer takes place between the jacket and the reactor, \( m \) is the mass in the reactor, \( C_p \) is the heat capacity of the mass in the reactor, \( T_j \) is the temperature of the reactor, \( T_r \) is the temperature of the jacket of the reactor and \( Q_{\text{loss}} \) is the rate of heat losses in the system.

The change of \( dQ_r/dt \) as a function of time and temperature is the key parameter that needs to be predicted to solve equation 1.

The method proposed here consists of carrying out a series of isothermal reactions in the RC1 at different temperatures that cover the range of temperatures expected during the exotherm in the reactor under consideration for scale-up. With these reactions, curves of the rate of heat generation due to polymerization \( dQ_r/dt \) versus the calorimetric conversion are constructed for each temperature. Calorimetric conversion is defined as:

\[
x = \int_0^{t'} (dQ_r/dt) \, dt / \int_0^{t'} (dQ_r/dt) \, dt
\]

or

\[
x = \int_0^{t'} (dQ_r/dt) \, dt / (M \Delta H_p)
\]

where \( x \) is the conversion, \( M \) is the monomer mass and \( \Delta H_p \) is the enthalpy of polymerization.

The curves of \( dQ_r/dt \) versus conversion are fit to a mathematical equation. The same mathematical function is used for all temperatures. In this manner, the values of the coefficients of the equation are generated as a function of the polymerization temperature (reactor temperature) and a general equation expressing the value of \( dQ_r/dt \) as a function of conversion and reactor temperature \( (T_r) \) is obtained. This function will be called \( dQ_r/dt(x, T_r) \).

Once \( dQ_r/dt(x, T_r) \) is known, the heat balance (equation 1) is solved for the RC1 calorimeter using a constant value of \( T_j \) and the evolution of \( T_r \) as a function of time in the RC1 calorimeter is predicted.

The algorithm used to solve the heat balance equation with the function \( dQ_r/dt(x, T_r) \) will be explained in the next section. The model prediction is compared with the experimental values obtained in an actual run in the RC1 when the temperature of the jacket is held constant at a given \( T_j \) value. Comparing the predicted values and the experimental values for the constant \( T_j \) run, one can assess the accuracy of the empirical model and do adjustments to \( dQ_r/dt(x, T_r) \). This step allows the validation of the model without the need of using a different size reactor. When reasonable agreement is obtained, the value of the parameters for the large reactor (mass, overall heat transfer coefficient, transfer area, and temperature control algorithm) can be inserted in equation 1 and predictions of the feasibility of the scale-up in the reactor under consideration can be obtained. For a different size reactor the heat generated due to polymerization will be given by the expression:

\[
dQ_r/dt = (M_r/M_{rc1}) \cdot dQ_r/dt(x, T_j)
\]

where \( M_r \) is the monomer mass in the reactor under consideration and \( M_{rc1} \) is the monomer mass used in the experiments in the METTLER TOLEDO RC1 calorimeter.

**Mathematical Algorithm**

It is important to explain why to use curves of \( dQ_r/dt \) versus conversion to generate a function \( dQ_r/dt(x, T_r) \), instead of using curves of \( dQ_r/dt \) versus time to generate a function \( dQ_r/dt(t, T_r) \), which depends on time and reactor temperature. At a first glance it seems more obvious to use \( dQ_r/dt(t, T_r) \) to solve the differential equation, since the ultimate goal is to determine the evolution of the reactor temperature as a function of time and not conversion.

The heat produced during the polymerization is the result of the conversion of monomer to polymer. Regardless of the thermal history followed to convert the monomer to polymer, the mass and energy conservation principles have to be satisfied.

The total amount of energy released is given by the enthalpy of polymerization multiplied by the amount of mass converted from monomer to polymer. The total amount of energy produced during the polymerization is thus independent of the thermal path taken to convert the monomer to the polymer.

Mathematically, the polymerization process in a non-isothermal reactor can be visualized as a continuum of curves of \( dQ_r/dt \) versus time for each polymerization temperature. As the temperature of the reactor changes we move from one curve to another. Let us consider using absolute time continuum as the only criteria to switch from curve to curve. As time increases and the temperature of the reactor
increases, we would move to points in curves where the polymerization rate would correspond to a conversion higher than the true conversion. On the other hand, as time continues and the temperature of the reactor decreases we would move to curves corresponding to lower temperatures, but because the criteria used to move from curve to curve was a time continuum criteria only, we would move to points in curves with values of dQ_r/dt that would correspond to points where the conversion is lower than that in the time interval before. Thus, the mass conservation principle would not hold. Another consequence is that the value of the integral of dQ_r/dt over the time that the polymerization takes place would have different values depending on the thermal path taken.

A boundary condition to take into account the mass balance must be used. This condition states that for each time interval under consideration, the value of dQ_r/dt at the beginning of that interval is given by the curve of dQ_r/dt corresponding to the particular value of T_r at the point where the conversion has a value similar to the conversion at the end of the previous time interval.

There are two ways to mathematically apply this boundary condition. In the first approach, for each integration step used to solve the differential equation, the function dQ_r/dt(t,T_r) is solved with the value of T_r obtained during the solution of the differential equation to determine the time t for which the integral of the function dQ_r/dt(t,T_r) between t=0 and t=t is equal to the amount of heat produced up to the end of the previous time interval. The value for the time thus obtained is substituted in the function dQ_r/dt(t,T_r) and the value of dQ_r/dt is calculated and inserted in the heat balance equation being solved in the interval under consideration. The process is iterated until convergence is obtained for the time interval. This method is cumbersome and computationally intensive.

The second approach is simpler and is the one used in this paper. For each time interval used to solve the differential equation it is considered that the conversion at the beginning of the interval is that at the end of the previous time interval. The conversion is defined as the integral (summation) of the calculated values of dQ_r/dt up to that time divided by the product of the monomer mass times the enthalpy of polymerization. The value of dQ_r/dt is obtained from the fitted function dQ_r/dt(x,T_r) for the value of T_r estimated by the differential equation solving algorithm (Runge-Kutta-Fehlberg) and the value of the conversion at the end of the previous time interval. The value of dQ_r/dt is inserted in the differential equation to calculate the time derivative. A new estimate of T_r is obtained for the corresponding value of dQ_r/dt. The new conversion is calculated at that point and used for the next iteration until convergence occurs.

The following sections describe the process applied to suspension and emulsion polymerization.

**Application of the Method to Suspension Polymerization**

In suspension polymerization the polymerization kinetics are similar to those occurring in a bulk process. The type of physical events taking place during the polymerization do not change with temperature, only their magnitude changes. The series of physical events that occur are radical generation (initiation), radical propagation (chain growth) and radical termination (chain termination). The rate of polymerization (Rp) is given by [3].

\[ Rp = k_p [M] (f k_d [I]/k_t)^{0.5} \]  

where \( k_p \) is the propagation rate constant, \([M]\) is the monomer concentration, \( k_d \) is the initiator decomposition rate constant, \( f \) is the initiator efficiency, \([I]\) is the initiator concentration and \( k_t \) is the termination rate constant. As the polymerization temperature changes only the values of the rate constant coefficients change.

![Figure 1: Evolution of dQ_r/dt as a function of time for suspension polymerization at three different temperatures: 60°C, 65°C and 70°C.](image)
Equation 11 above was solved for two cases: one where the temperature of the jacket \( T_j \) in the RC1 was kept constant at 60°C and another one where the temperature of the jacket was kept constant at 65°C. The value determined for \( UA \) in the RC1 was 4.22 W/°K. The value of \( Q_{\text{loss}} \) as a function of \( T_r \) was determined experimentally for the reactor from a plot of \( UA(T_r-T_j) \) versus \( T_r \) at isothermal values of \( T_j \) (from 60°C to 75°C) in the absence of any reaction. The relationship found was:

\[
Q_{\text{loss}} = 136.87 - 0.418 T_r
\]  

(12)

where \( Q_{\text{loss}} \) has units of watts and \( T_r \) is in degrees Kelvin.

Figures 3 and 4 show the prediction of the model and the actual experimental curves obtained in the RC1 by running polymerizations under isothermal jacket control at 60°C and 65°C respectively. The agreement is very good, with a small deviation at peak temperature.

**Application of the Method to Emulsion Polymerization.**

The method presented in this paper was applied to an emulsion polymerization process. The kinetics of free radical emulsion polymerization are significantly different that those of solution, bulk or suspension free radical polymerization because of the different physical events that take place. Without getting into mechanistic details, the rate of polymerization in an emulsion polymerization process is given by [4]:

\[
R_p = k_p [M]_p \bar{n} N_p / N_A
\]  

(13)

where \( k_p \) is the propagation rate constant, \([M]_p\) is the monomer concentration in the polymer particles, \( \bar{n} \) is the average number of radicals per polymer particle, \( N_p \) is the concentration of polymer particles and \( N_A \) is the Avogadro number. The number of polymer particles is determined by the particle nucleation mechanism and stability of the particles. The average number of radicals per particle is determined by events such as radical entry, radical desorption and radical termination.

The heat balance for the MP10 reactor of the RC1 calorimeter is given by a rearranged form of equation 1, shown in equation 11.

\[
dQ_r/dt = dQ_r/dt(x,T_r)/(mC_p) - UA_r/(mC_p) + UA_j/(mC_p) + Q_{\text{loss}}/(mC_p)
\]  

(11)
Because of the direct dependence of the rate of polymerization and therefore the rate of heat generation on the number of particles, the approach described before needs to be modified slightly. In emulsion polymerization, particle nucleation takes place over a very short conversion interval (less than 5% conversion). The number of particles is strongly dependent on the temperature over which the nucleation takes place. In systems where the number of particles is constant after the nucleation period is finished, it is safe to assume that the number of particles in a non-isothermal reactor is determined by the temperature at which the polymerization is started. Using this approximation, the only modification that needs to be done is the use of the function:

\[
\frac{1}{N_p(T_r)} \frac{dQ}{dt(x,T_r)}
\]

instead of \( \frac{dQ}{dt(x,T_r)} \), where \( N_p(T_r) \) is the number of particles generated at the temperature \( T_r \).

The heat balance for the MP10 reactor of the RC1 will be given as in equation 15, where \( N_p(T_{r0}) \) is the number of particles generated at the initial temperature \( T_{r0} \).

![Figure 3](image1.png)

**Figure 3:** Comparison between the experimental results (symbols) and model predictions (continuous thin line) for the evolution of the reactor temperature \( (T_r) \) in a suspension polymerization conducted under constant \( T_j \) value of 60°C.

![Figure 4](image2.png)

**Figure 4:** Comparison between the experimental results (symbols) and model predictions (continuous thin line) for the evolution of the reactor temperature \( (T_r) \) in a suspension polymerization conducted under constant \( T_j \) value of 65°C.

![Figure 5](image3.png)

**Figure 5:** Evolution of \( \frac{dQ}{dt} \) as a function of time for emulsion polymerization at three different temperatures, 60°C, 65°C and 70°C.

Figure 5 shows the rate of heat generation (\( \frac{dQ}{dt} \)) during the emulsion polymerization for three different emulsion polymerizations carried in isothermal (\( T_r \) control) conditions at 60°C, 65°C and 70°C.

![Figure 6](image4.png)

**Figure 6:** Comparison between the experimental results (symbols) and model predictions (continuous thin line) for the evolution of the reactor temperature (\( T_r \)) in a suspension polymerization conducted under constant \( T_j \) value of 65°C.

The experimental curves for \( \frac{dQ}{dt} \) as a function of conversion for the three temperatures and the fitted curves using the equation:

\[
\frac{dQ}{dt}(x,T_r) = -a + bx - cx^3 + dx^{0.5} + fe^{-x}
\]

Notice the different experimental profiles of \( \frac{dQ}{dt} \) obtained for the emulsion polymerization compared to those obtained in the suspension polymerization process, this is a reflection of the different physical events taking place.

\[
\frac{dQ}{dt} = \frac{N_p(T_{r0})}{N_p(T_r)} \frac{dQ}{dt}(x,T_r)/(mC_p) - \frac{UA}{mC_p}T_r + \frac{UA}{mC_p}T_j + \frac{Q_{loss}}{mC_p}
\]
The dependence of the coefficients on the polymerization temperature is obtained, as in the case for the suspension polymerization process, from Arhenius plots of the values of each coefficients versus the temperature. The results are:

\[
\begin{align*}
\ln a &= -74.13 + 53754/T_r - 885197/T_r^2 \\
\ln b &= 1.757 + 1743.2/T_r \\
\ln c &= 248.95 - 161063.88/T_r + 26675041.13/T_r^2 \\
\ln d &= 16.743 - 3612.37/T_r \\
\ln f &= -58.021 + 42965.39/T_r - 7045340.96/T_r^2
\end{align*}
\]

(17) \hspace{1cm} (18) \hspace{1cm} (19) \hspace{1cm} (20) \hspace{1cm} (21)

Figure 7 shows the number of particles generated as a function of the polymerization temperature. From this information an expression for the dependence of the number of particles generated as a function of temperature can be obtained:

\[
N_p(T_r) = 4.86 \cdot 10^{18} - (1.48 \cdot 10^{21}/T_r) \quad (22)
\]

Figure 8 shows the predictions obtained when equation 15 was solved compared with the experimental values for an emulsion polymerization carried in the RC1 calorimeter under constant T_j condition. In the experiment as well as in the simulation the temperature of the jacket was maintained at 60°C.

Conclusions
A method has been presented to evaluate polymerization processes for scale-up purposes. The method circumvents the need of an accurate kinetic model to describe the polymerization process and the experimental determination of rate constants.

The method relies on experimental kinetic information obtained in a reaction calorimeter. The method consists of the following steps:

1. Experimental determination of kinetics
A series of isothermal polymerizations are run at different temperatures in a reaction calorimeter such a Mettler-Toledo’s RC1 reaction calorimeter.

2. Curve fitting
From the experimental results, curves of dQ_r/dt versus conversion are built and fit to a mathematical function. By using the same mathematical function for all the temperatures, the values of the coefficients of the mathematical function can be obtained as a function of temperature. At the end of this step a function \(dQ_r/dt(x,T_r)\) is obtained which provides values of \(dQ_r/dt\) for any value of conversion and temperature.

3. Model validation
3a) The heat balance differential equation for the reactor of the calorimeter, is solved numerically for a constant value of T_j, using the function \(dQ_r/dt(x,T_r)\) to obtain the value of the rate of heat generation due to polymerization at any given conversion and reactor temperature. Predictions of the temperature of the RC1 reactor as a function of time are obtained.

3b) The model is validated by running polymerizations in the reaction calorimeter polymerizations under constant T_j control mode. The experimental values of the evolution of the reactor temperature as a function of time are compared with the predictions of step 3a.

4. Model correction
Adjustments are made to \(dQ_r/dt(x,T_r)\) until agreement is obtained between the predictions for the polymerization under constant T_j in the calorimeter and the experimental results.

5. Predictions
The heat balance equation for the reactor under consideration is solved using the function \((M_r/M_{rc1})dQ_r/dt(x,T_r)\), where \(M_{rc1}\) is the mass of
monomer in the calorimeter run and $M_r$ is the mass of monomer in the reactor under consideration.

The method has been applied to suspension polymerization showing good agreement with experimental results. For emulsion polymerization the dependence of the number of polymer particles generated during the polymerization with the temperature is needed to estimate correctly the rate of heat generation.

\[ [1] \text{Polymer Handbook, 3rd edition, Brandrup and Immergut editors.} \]


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