

Optimisation of Emulsion Co-polymerization of Styrene and MMA in Semi-batch Reactor

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For emulsion co-polymerization of styrene and MMA in semi-batch reactor, two dynamic optimization problems are formulated here and solved for different pre-batch time for the seed formation. In the first one, the number average molecular weight (M_n) was maximized while in the second one, the monomer conversion (X_n) was maximized for a given total monomer feed over the batch time. A process model involving the equations for mass and energy balance, population balance describing the particle evolution in the reactor and diffusion controlled kinetics is incorporated into the optimization framework. The results of the first optimization problem show that, the value of M_n increases slightly by about 3% for the same total batch time as the pre batch time decreases. Reduction of the pre-batch time, allows the polymer chain in the particles to grow with the continuous addition of monomers into the reactor. The results of the second problem shows that similar conversions can be achieved for a given value of M_n with about 5 % lower batch time and with lower pre-batch time.

1. Introduction

Emulsion polymerization is widely used in industry especially for water based paints or adhesives where the emulsified product can be used directly which is one of the advantages among others. The radical polymerization starts with emulsion of initiator, monomer and surfactant in a continuous phase of water (Gilbert, 1995). Emulsion copolymerization is a heterogeneous reaction of two monomers with very complex mechanisms (Saldivar and Ray, 1997) which makes the desired copolymer properties difficult to achieve.

In an *ab initio* emulsion polymerization, pre-batch time is needed for the seed formation and to eliminate any dissolved oxygen from the system (Gilbert, 1995; Coen et al., 1998; Zeaiter et al., 2002). Various properties of polymers that are important in terms of their processability and their end-uses are directly related to specific molecular weight averages. Maximizing X_n is very important to reduce downstream separation. For a given total amount of monomer ($N_{m,T} = 8.0$ mol) and a given pre-batch time (1500 s) Alhamad (2005) and Alhamad et al. (2005) considered maximization of M_n for emulsion copolymerization of styrene and Methyl Methacrylate (MMA).

In this work the dynamic optimization for emulsion copolymerization of Styrene and Methyl Methacrylate (MMA) in a semi batch reactor is carried out. Two dynamic optimisation problems with different pre-batch time are considered. In the first one, the Mn was maximized while in the second one, the monomer conversion (Xn) was maximized for a given Mn. In both problems monomer flow rates (FmA and FmB), initiator flow rates (FI), surfactant flow rates (FS) and reactor jacket temperature (Tj0) were optimised using gPROMS software. Control Vector Parameterisation (CVP) technique has been used to discretise the reactor temperature. This converts the dynamic optimisation problem into a Nonlinear Programming (NLP) problem which is solved by standard SQP method available in gPROMS.

2. Kinetics And Dynamics Model

A system with zero-one kinetics for emulsion copolymerization of Styrene and MMA was employed here based on Alhamad et al. (2005). The process begins with the decomposition of initiator molecule to form free radicals which then propagate with the monomer to produce oligomeric radicals. The propagation occurs in aqueous phase until it reaches the degree of polymerization (z) resulting the species to become a micelle. This happens either by entering the pre-existing micelle or by forming a micelle by aggregation with surfactant molecules in the aqueous phase. However, some of the oligomeric radicals which propagate with another radical species in aqueous phase may undergo termination. The oligomeric radical propagates rapidly in the micelles to produce polymer particle. Monomer is consumed and the weight fraction of polymer in the particles increases as the propagation is taking place. Transfer to monomeric radicals takes place within the particle phase. The monomeric radical can either continue propagation in the particle or escape into the aqueous phase by diffusion. Then the termination of the radicals in the particles is taking place. Some of the process model equations are presented in Figure 1 in compact form and the rest can be found in Alhamad et al. (2005).

$\frac{d[I]}{dt} = -2k_d[I] + \frac{F_I}{V_w}; f = \left(\frac{(k_d[I]k_{t,aq})^{0.5}}{k_{p,aq}C_w} + 1 \right);$ $IM_1 = \frac{2k_d[I]}{k_{p,aq}C_w + k_{t,aq}T}; IM_i = \frac{k_{p,aq}^{i-1}IM_{i-1}C_w}{k_{p,aq}C_w + k_{t,aq}T} \text{ for } i = 2 \text{ to } (z-1);$ $IM_i = \frac{k_{p,aq}^{i-1}IM_{i-1}C_w}{k_{p,aq}C_w + \sum (k_e^n) \Delta r + k_{e,micelle} C_{micelle} + k_{t,aq}T} \text{ for } i = z \text{ to } (j_{rit} - 1);$ $IM_{jcrit} = \frac{k_{p,aq}^{jcrit-1}IM_{jcrit-1}C_w}{k_{t,aq}T}; k_{p,aq}^i = k_{p,aq,A}^i \bullet f_A \bullet \phi_A + k_{p,aq,B}^i \bullet f_B \bullet \phi_B;$ $k_p = k_{p,AA}P_A^2 + k_{p,AB}P_AP_B + k_{p,BA}P_BP_A + k_{p,BB}P_B^2;$ $k_t = k_{t,AA}P_A^2 + 2k_{t,AB}P_AP_B + k_{t,BB}P_B^2;$ $Mn = \frac{\sum M \bullet P(M)}{\sum P(M)}; Mw = \frac{\sum M^2 \bullet P(M)}{\sum M \bullet P(M)};$	$k_d = 8 \times 10^{15} e^{-\frac{135000}{RT}};$ $k_{po,A} = 10^{7.63} e^{-\frac{32500}{RT}};$ $k_{po,B} = 10^{6.4} e^{-\frac{22200}{RT}};$ $k_{tr,A} = k_{p,A} 10^{-0.658} e^{-\frac{23400}{RT}};$ $k_{tr,B} = 4 \times 10^{5.3} e^{-\frac{45900}{RT}};$ $\frac{dN_{m,A}^{fed}}{dt} = F_{mA,in}; \frac{dN_{m,B}^{fed}}{dt} = F_{mB,in};$ $x_A = 1 - \frac{N_{m,A}}{N_{m,A}^{fed}}; x_B = 1 - \frac{N_{m,B}}{N_{m,B}^{fed}};$ $x = \frac{x_A Mw_A + x_B Mw_B}{Mw_A + Mw_B};$
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Figure 1: Process model

The data used for the simulation in this work are: Styrene monomer (410.40 g); MMA monomer (410.40 g); Water (2.5 L); Initiator (1.875 g); and Surfactant (5.39 g). 17.1% of total monomers were charged at the beginning of the process for the seed formation while the remaining 82.9% is charged in continuous mode over the batch time.

The initiator used in this work is Persulfate $K_2S_2O_8$ and the surfactant is Sodium Decoeyl Sulfate (SDS) which has been widely used in the conventional emulsion polymerization of styrene (Luo et al., 2011). The surfactant forms micelles in the water which is then swollen with the monomer added to the reactor to form polydisperse droplets of emulsion. Monomer added to the reactor must be control at low rate in order to remove heat of polymerization process from the reactor. The flow rate of surfactant added along the process has to be controlled so that it will act to stabilize the particles and not to form any secondary nucleation that would reduce the molecular weight. The flow rate of initiator also have to be controlled to ensure that whether new oligomeric radical are needed or not for the process to achieve the desired product properties.

3. Dynamic Optimization Problem Formulation

The dynamic optimization formulation can be described as:

$$\begin{aligned}
 & \text{Max} && \text{Mn or Xn} \\
 & FmA(t) ; FmB(t) ; FS(t) ; FI(t) ; T_{j0} \\
 \text{s.t.} & && f(t, x'(t), x(t), u(t), v) = 0, [t_0, t_f] \quad [\text{model equations}] \\
 & && 0.0 \text{ g/s} < FmA < 0.2 \text{ g/s} \quad ; \quad 0.0 \text{ g/s} < FmB < 0.2 \text{ g/s} ; \\
 & && 0.0 \text{ g/s} < FS < 0.2 \text{ g/s} \quad ; \quad 0.0 \text{ g/s} < FI < 0.2 \text{ g/s} ; \\
 & && 343.00 \text{ K} < T_{react} < 358.00 \text{ K} \quad ; \\
 & && 0.4 \times 10^{-7} \text{ m} < dmm < 9.0 \times 10^{-7} \text{ m} \quad ; \\
 & && N_{m,T} = 8 \text{ mol};
 \end{aligned}$$

The total batch time is discretized into 5 control intervals within which FmA, FmB, FI, Fs and T_{j0} are assumed to be piecewise constant and are optimised. The jacket temperature (T_{j0}) is parameterized using Control Vector Parameterization so that the dynamic optimization problem can be posed as Nonlinear Programming (NLP). The total amount of monomer ($N_{m,T}$) added into the reactor is set as end point equality constraint at 8 mol (maximum limit for the monomer added to the reactor). For a zero-one model, the particle diameters (dmm) are small (~100 nm). Polymerization within a relatively large particle is known as pseudo-bulk kinetics where the cross over diameter of styrene for zero-one to pseudo-bulk is reported between 100 nm – 120 nm (Gomes et al., 2009). This process was design to produce latex with maximum diameter of 90 nm. The total batch time including pre-batch time is set to 5500 s and Xn more than 94 % when Mn is maximized. Alhamad et al. (2005) has maximized the Mn with 5 intervals and 1500 s pre batch time for the seeds formation. Here we considered 5 different pre-batch time set at 1500 s, 1200 s, 900 s, 600 s and 300 s. For different values of given Mn (=Mn*), Xn is maximized for two different pre-batch time (1200 s and 1500 s) but the total batch time is optimised.

4. Result And Discussion

4.1 Case study 1: maximization of Mn

Results using different pre-batch time are summarized in Table 1. As the pre batch time decreases, the average number molecular weights (Mn) is increased with slight decrease in overall conversions (Xn). The results show that the maximum molecular weight 258654.4 g/mol can be achieved with 300 s pre-batch time with an overall conversion of 94.13%. This result clearly shows that pre-batch time for the seeds formation is needed but can be reduced to maximize the molecular weight (although by 3% only in this case study). During the pre-batch time, a seed population with a smaller particle and larger size particles are produced (Zeaiter et al., 2002). In this work, an average particle size of 87.7 nm was produced for different pre-batch time.

Table 1: Summary of the results for different pre-batch time

Run	Mn	Xn %	dmm (nm)	Pre-batch time
1	251199.0	94.29	87.7	1800
2	253041.0	94.25	87.7	1500
3	254816.0	94.20	87.7	1200
4	256371.6	94.18	87.7	900
5	257717.6	94.16	87.7	600
6	258654.4	94.13	87.6	300

Figure 2 shows the optimization results with the optimal profile of monomer feed rate (Fig. 2b) and reactor temperature (Fig. 2d) for Run 2. During 1500 s pre batch time (Run 2), no further feed of monomer was added to the reactor. It can be seen that the temperature will remain constant at 358 K until 4200 s before it goes down to 343 K when the reaction stop. At high temperature, the radical transfer in the polymerization process will increase (Fig. 2d) which will lead to shorter chains of polymer (low Mn) as shown in Figure 2a. When the temperature is decreased the molecular weight will increase to achieve the maximum molecular weight. When the transfer coefficient is increased, the monomeric radicals are increased resulting in an increase in termination reaction. Besides that, the entry of radicals to the particles also will result in instantaneous termination. The transfer and termination reaction will stop the increase of molecular weight. The jacket temperature profile (Fig. 2c) was constant at 358 K until 4200 s to ensure that the reactor temperature is high for the radical transfer to happen in the process. Then it was decrease to 343 K to ensure that Mn was increase to its maximum value with the lower reactor temperature. On the other hand, lowering the reaction temperature, will lead to decrease in the transfer event resulting in longer polymer chains meaning higher molecular weight. Alhamad (2005) made similar observation. However, the maximum Mn in his work for 1500 s feed batch time was 235758 g/mol which is lower than that obtain in this work due to lower batch time of 4998 s.

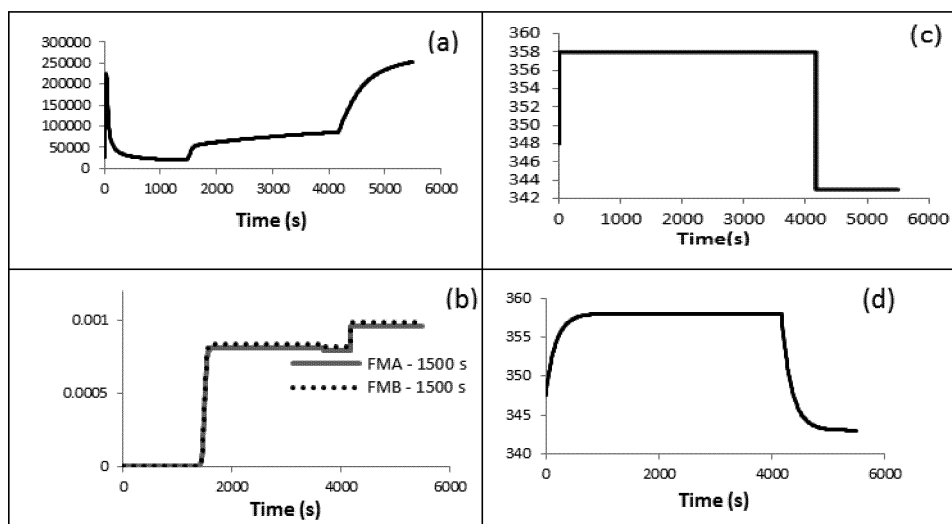


Figure 2: Run 2- Optimization result, (a) average number molecular weight (M_n), (b) optimal profile of monomer flow rate [A-styrene; B-MMA], (c) jacket temperature, (d) reaction temperature

The surfactant was added at very low flow rate when the temperature was decrease to ensure that the added surfactant will stabilize the particles, not to form any secondary nucleation that will reduce the M_n . Meanwhile, the initiator flow rate was zero all the time to prevent any new particles to occur since it also can reduce the molecular weight.

4.2 Case study 2: maximization of X_n

Results are shown in Table 2 and Table 3 below. The maximum overall conversion for specified molecular weight of 100000 g/mol, 150000 g/mol and 200000 g/mol is compared with different pre-batch time of 1200 s and 1500 s.

Table 2: Summary of the results with pre-batch time 1200 s

X_n %	M_n	M_n^*	Time
96.24	100002	100000	4895.48
97.10	150004	150000	5170.87
95.79	200012	200000	5293.15

Table 3: Summary of the results with pre-batch time 1500 s

X_n	M_n	M_n^*	Time
96.16	100047	100000	5079.93
96.96	150039	150000	5214.09
95.67	200013	200000	5546.68

The results show that by reducing the pre-batch time, the desired molecular weight can be achieved in shorter time and with higher overall conversion. For example, for a given $M_n^* = 200000$ g/mol, the total batch time is 4.57 % shorter with pre-batch time of 1200s compared to the pre-batch time of 1500 s. This is because the shorter the pre-batch time, the sooner the monomer are added to the reactor which leads to increasing polymer chain length.

5. Conclusion

Two dynamic optimization problems are formulated to maximize the number average molecular weight and the overall conversion for different pre-batch time for emulsion co-polymerization of MMA and styrene in a semi batch reactor. The results show that (M_n) can be increased by decreasing the pre-batch time. However, the maximum molecular weight was achieved at pre-batch time 300 s. Also the desired molecular weight can be achieved in shorter time and with higher overall conversion by reducing the pre-batch time. This is because with shorter pre-batch time, the monomer can be added earlier in the reactor which can led to the increasing polymer chain length (i.e higher M_n).

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