Macromol. Symp. ***150,*** *109–114 (2000)*

Evaluation of Emulsion Polymerisation Kinetics Using a Non-Linear State Estimator

N. Othman[1], A.M. Santos[2], G. Févotte[3], T. McKenna[1]

[1] LCPP-CNRS/ESCPE and [3] LAGEP-Université de Lyon I, Villeurbanne, France

[2] FAENQUIL, Rodovia Itajuba-Lorena, km 74.5, 12600000 Lorena/SP, Brazil.

SUMMARY: The use of adaptive calorimetric state estimators allows one to accurately follow the evolution of monomer composition in an emulsion co- and ter-polymerisation reactor. In addition, the non-linear estimator tested in the current work can provide useful information on the evolution of a lumped kinetic parameter $\bar{n}N_p$. This information can be used on-line to detect particle nucleation, or combined with off-line measurements of N_p to study the evolution of $\bar{n}$.

Introduction

It is quite well known that the monitoring and control of polymerisation reactors is a difficult task for several reasons, one of which is that it is very difficult to identify with precision all of the kinetic parameters needed to implement model-based control schemes. In emulsion polymerisation, radical entry and exit rates depend on the monomer in question, chain transfer to small molecules, conversion, particle size, surface coverage... This situation is even more complex once we begin to consider systems involving the simultaneous polymerisation of several different monomers. Thus well-designed state estimators provide a convenient way of extracting on-line information from a reacting system, and providing accurate, important information on kinetic parameters.

State Estimation Approach

In previous papers from this research group [1,2] we introduced a combined hardware-software approach to the state estimation of both solution and emulsion copolymerisations. This approach relies on occasional on-line gravimetric measurements and an on-line energy balance. The data is used in a model-based non-linear state estimator to obtain composition and conversion data, as well as information on kinetic constants.

CCC 1022-1360/00/$ 17.50+.50/0

For a copolymerization of water insoluble monomers (which is the case for styrene and butyl acrylate), the basic dynamics of the evolution of monomer conversion and initiator consumption are given by the material balances for the monomer 1 (monomer 2 is the same with change of subscripts):

$$\frac{dN_1}{dt} = \mu[M_i]^P\left(k_{p11}\phi_1 - k_{p21}\left(1-\phi_1\right)\right) \qquad (1)$$

where N_1 refers to the number of moles of monomer i in the reactor, k_{p11} and k_{p21} are rate constants, $[M_1^P]$ is the concentration of monomer 1 in the particles, and ϕ_1 is the fraction of radicals of type 1. The variable $\mu(t)$ is proportional to the total number of radicals per particle and the number of particles in the reactor:

$$\mu = \frac{\bar{n}N_p^T}{N_A} \qquad (2)$$

In this work, we present the results of the experimental evaluation of an up-dated version of this technique in the semi-batch copolymerisation of styrene and BuA. In this case, the state estimator provides us with an estimate of a lumped kinetic parameter μ, residual monomer composition, and an indication of the amount of energy evacuated from the reactor (and the overall heat transfer coefficient) as a function of time. We tested the capability of the estimator to respond to sudden variations in reactor conditions, and looked at the types of problems one can hope to solve with state estimators in the area of polymerisation reactions.

Results and Discussion

The on-line estimator was tested under dynamic experimental conditions in order to follow the individual monomer conversions and $\bar{n}$ during butyl acrylate-styrene (BuA/Sty) emulsion copolymerisations.

The heat generation rate for a seeded batch copolymerisation, during which a second population of particles was renucleated is shown in Figure 1. The original charge (90 g PS latex with d_p = 82 nm, 143.7 g Sty, 117 g BuA, 7.6 g sodium lauryl sulphate, 1.3 g KPS and 2620 g water) was allowed to polymerise in the 7-litre jacketted calorimeter at an initial temperature of 60°C. A shot containing 148.8 g BuA, 162 g Sty, 1.52 g KPS, 24 g SLS, and

30 g of water were injected at 50 minutes. This on-line estimator allows us to "see" events such as the sudden increase in reaction rates (similar heat release is also characteristic of batch polymerisations of MMA-Vac) due to particle re-saturation and particle nucleation. The value of μ obtained on-line can be used with off-line measurements of N_p (e.g. from light scattering) to find values of $\bar{n}$ (see Figure 2).

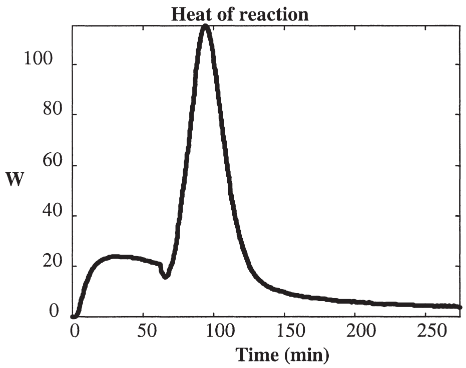

Figure 1. Heat generation rate in a batch polymerisation with massive renucleation of particles.

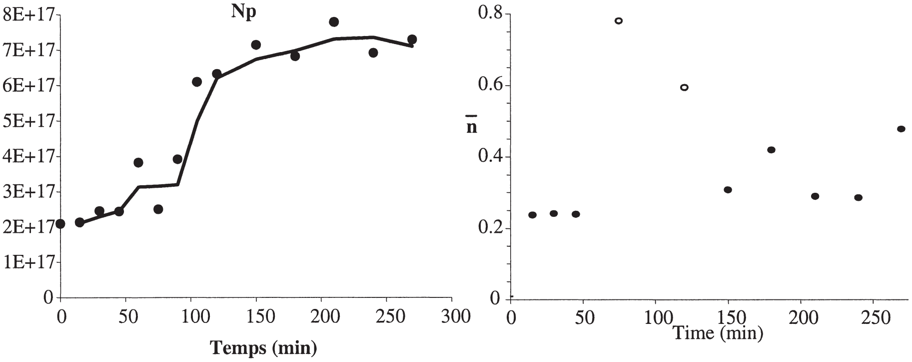

Figure 2. Number particles per liter of emulsion and number of radicals per particle ($\bar{n}$).

It is a bit difficult to estimate $\bar{n}$ during the renucleation phase, thus the open circles in Figure 2b are values of $\bar{n}$ in which we have little confidence. Nevertheless, even if $\bar{n}$ is somewhat sensitive to measurements of N_p (highly scattered during renucleation), Figure 3 shows that we can follow the number of moles of residual monomer in the reactor quite well.

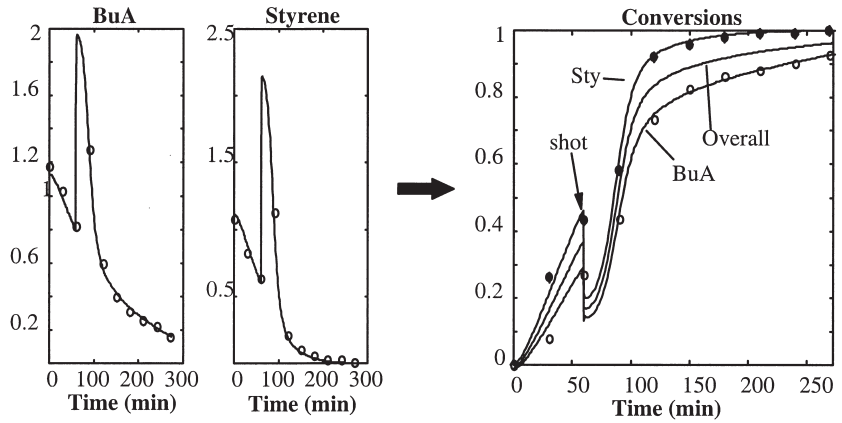

Figure 3. Moles of residual monomer for renucleation experiment (left) and conversions (right). Points represent off-line verification by gas chromatography, lines represent values returned by state estimator using on-line calorimetric data.

This approach has been extended to terpolymerisation systems, and the estimator has been tested experimentally. mass balance of emulsion terpolymerisation has the following form for monomer 'i':

$$\frac{dN_i(t)}{dt} = Q_i(t) - R_{pi}(t)\,V_e(t) = Q_i(t) - \mu(t)[M_i^p(t)].\left[\sum_{j=1}^{3} k_{p_{ji}} P_j\right] \qquad (3)$$

Figure 4 shows the validation of this observer structure for two different emulsion batch terpolymerisations of MMA/BuA/VAc with different initial conditions, performed in the laboratory-scale reactor described in [1,2]. It is clear that, even for systems with monomers that have very different reactivities (the MMA reacts before the BuA, which reacts before the VAc), the estimator provides us with excellent values of the states (moles of residual monomer) of the system. One of the more process-oriented applications of the state estimator is composition control. The output from the calorimetric estimator yields values of the overall conversion, which is then used to estimate compositions such as those shown in Figure 4, as well as a value for μ. This information can be used not only to obtain a fixed copolymer composition in a batch reactor, but can also be used to do so in such a way as to keep the rate

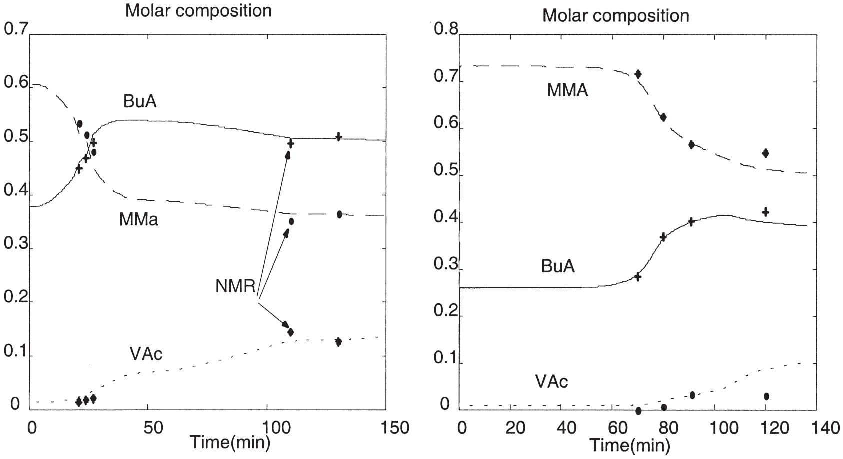

Figure 4. Estimated (line) and measured values of copolymer composition for 2 batch terpolymerisations of MMA, BuA and VAc. Experimental values are obtained by NMR. Initial batch compositions: 515 g BuA, 290 g MMA, 110 g VAc (left) and 300 g of MMA and of BuA, 60 g VAc (right).

of reaction as high as possible. Here, a proportional-Integral controller is used to obtain a specified terpolymer composition. The controller uses the flow rates of the more reactive monomers (MMA and BuA) to minimise the error between the estimated value of the terpolymer composition and the set point. The instantaneous fraction of polymer i in the terpolymer is the fraction of its rate of polymerisation with respect to the total rate:

$$F_i = \frac{R_{pi}}{R_{p1} + R_{p2} + R_{p3}}$$

To fix the terpolymer composition the fraction of monomers 1 and 2 must be constant with respect to monomer 3. So F_1 / F_3 and F_2 / F_3 must stay constant during the reaction. Then it can be seen that it is enough to fix the fractions N_1 / N_3 and N_2 / N_3 to fix the instantaneous terpolymer composition.

$$\frac{F_1}{F_3} = \frac{R_{p1}}{R_{p3}} = \frac{N_1\left(k_{p11}\alpha' + k_{p21}\beta' + k_{p31}\gamma'\right)}{N_3\left(k_{p13}\alpha' + k_{p23}\beta' + k_{p33}\gamma'\right)}.$$

The desired fraction of rate of polymerisation of monomers 1 and 2 with respect to that of monomer 3, the set point, is then determined: $F_{1d} = \frac{N_1}{N3}$, $F_{2d} = \frac{N_2}{N3}$, and $Q_j = R_{Pj} + K_{Cj}\left(F_{jd} * N_3 - N_j\right) + \frac{1}{\tau_{ij}}\int_0^t \left(F_{jd} * N_3 - N_j\right)dt$, $j = 1,2$. Here K_{Cj} are proportional constants and τ_{ij} are integral constants to eliminate the static error of the model.

Figure 5 shows the excellent convergence of the controller proposed here for a semi-batch emulsion terpolymerisation of MMA/BuA/VAc. The initial composition is slightly different from the setpoint composition in order to demonstrate the robustness of the controller.

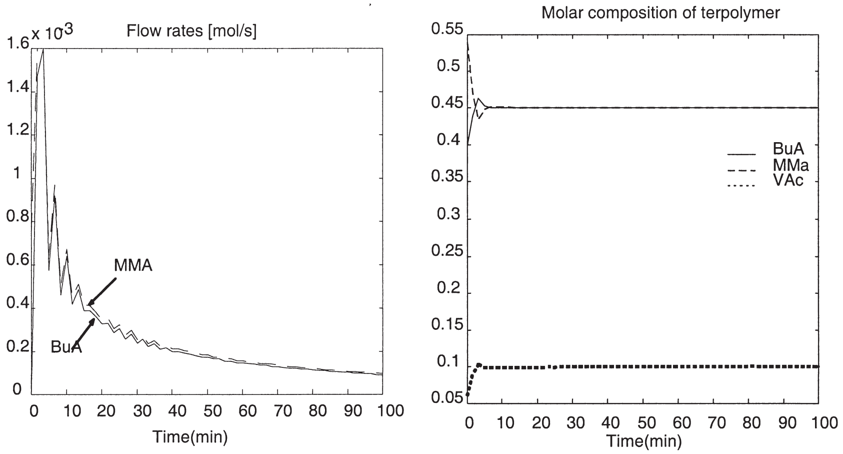

Figure 5. Manipulating the feed rates of Mma and BuA, at left, to control the terpolymer instantaneous composition, at right. The desired composition is 45% MMA, 45% BuA and 10 % VAc. Initial conditions in reactor: 50 g BuA and of VAc, 25 g MMA.

Conclusions

It should be clear by now that state estimators can be extremely useful tools in the reaction engineering of emulsion systems. Not only do they provide accurate on-line measurements of composition, which is obviously useful for modelling and for property estimation, but they also can be used with off-line information to help understand reaction kinetics.

References

1. Févotte, G., H. Hammouri, T. McKenna, S. Othman, *Chem Eng. Sci.* **53**, 773 (1998)
2. Othman, S., I. Barudio, G. Févotte, T. McKenna, *Polym. React. Eng.* **7,** 1 (1999)