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Polymerization Reactor Modeling in Industry – An Overview of Concepts and Tools

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Summary: The description of polymerization reactors by means of fundamental mathematical models is a challenging problem. At the same time, these models offer a very powerful tool for process control, monitoring, optimization, scale-up, and operator training and often allow for a better understanding of underlying mechanisms. Some approaches and tools used in industry to meet these challenges are illustrated. The scope and complexity of polymerization models developed and applied to industrial processes are shown. In addition to kinetic aspects of the model development some emphasis is given to the thermodynamic description of phase behavior and phase partitioning in polymerization reactors. Also, the important task of a careful and thorough parameter evaluation is briefly discussed as this is a prerequisite of predictive modeling. Finally, some typical model predictions are illustrated with experimental data.

Keywords: kinetics, mathematical modeling, polymerization, structure-property relations, thermodynamics

Introduction

Polymers can be classified in various ways. For example, depending on the source, they are natural polymers (e.g. protein, rubber) or synthetic polymers (plastics). Depending on number and arrangement of monomers they can be classified into homopolymers, copolymers (e.g. random, block, graft), terpolymers etc. Amorphous, semicrystalline, and crystalline polymers differ with respect to their chain order (cf. Figure 1).

Synthetic polymers can be classified with respect to their synthesis. In condensation or step-growth polymerization monomers can react with other monomers and also with polymer chains of any length to build up molecular weight. Typical condensation polymers are polyesters like polyethylene terephthalate (PET), and polyamides like nylon 6,6. In addition or chain-growth polymerization growing chains add on monomers to build up molecular weight and there are live and dead polymer chains. Subtypes can be identified with respect to the active site (free-radical, cationic, anionic or coordination polymerization). Typical addition polymers are polyethylene, polystyrene or polymethylmethacrylate (PMMA).

Classifying a given polymerization system is usually the first step in polymerization modeling, and will help to decide how to attack the problem. In this work, we show some concepts and tools that are used in industry to solve polymer reaction engineering (PRE) problems using mathematical modeling. Rather than elaborating on an example of a specific polymerization system we will review some typical kinetic, thermodynamic and mass transfer models that we use to analyze and solve our commercial polymerization processes which are oftentimes complex in nature.

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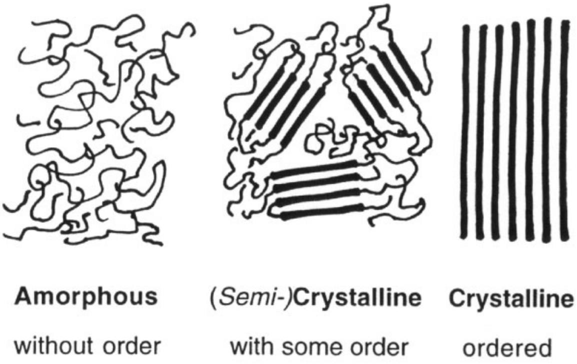

Figure 1.
Classification of polymers with respect to their chain order.

Elements of Polymerization Models

During the model development stage usually multiple submodels or elements are treated and eventually combined to yield the final global polymerization models. Figure 2 shows typical elements of a polymerization model. It is worth noting that not every model needs all of these elements. Conversely, Figure 2 may not be complete as there can be other elements important such as mixing for example.

The Reaction Kinetics submodel consists of mass and population balance equations, which are derived based on elementary reactions proposed in the reaction mechanism [1]. This usually yields a system of differential and/or algebraic equations that can be solved using various numerical methods (e.g. method of moments or numerical discretization).

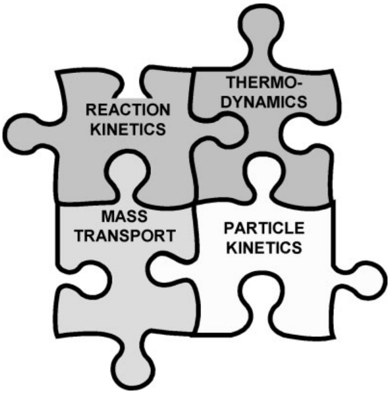

Figure 2.
Elements (submodels) of polymerization models.

Regarding the thermodynamics of a polymerization system, there are several approaches with different levels of complexity to describe phase behavior and phase partitioning of a polymerization mixture, ranging from simple partition coefficients to complex equations of state and activity coefficient models. Typical equations of state are Peng-Robinson (for small molecules), Sanchez-Lacombe [2,3] or PC-SAFT [4,5]. The Thermodynamic submodel usually consists of a set of non-linear algebraic equations that is solved simultaneously with the differential mass balances.

Many polymerization systems are characterized by the existence of a separate polymer-rich phase which often appears in the form of polymer particles. In these systems, a submodel describing the Particle Kinetics needs to be developed. It usually contains the description of particle formation (nucleation), particle coagulation and sometimes also particle breakage. There are various approaches to describe the particle kinetics in a polymerization system. Simple ones, for example, assume instantaneous nucleation (seeded polymerization) yielding equal-sized spherical particles of constant number (no coagulation). More detailed ones include particle formation by homogeneous and heterogeneous nucleation followed by particle coagulation where particles can be described as equal-sized spheres or as a distribution of a range of sizes. Particle coagulation is promoted by Brownian motion (perikinetic), shear (orthokinetic) or sedimentation. There are also models that account for the role of surfactants or stabilizer such as the DLVO theory [6].

Finally, mass transport effects are important in many polymerization systems. Diffusion limitations usually affect both chemical rate constant and interphase mass transport. The latter can be described by film theory with the help of correlations for mass transfer coefficients. Typical diffusion limitations on polymerization reactions are cage, glass and gel effect. The cage effect describes the decrease of initiator efficiency whereas glass and gel (or Trommsdorff) effects denote the reduction of propagation and termination reaction coefficients, respectively. Models to evaluate diffusion coefficients of monomers and polymer chains are usually needed to accurately describe mass transport effects.

Parameter Evaluation

The estimation of the large number of model parameters is a critical task when developing fundamental mathematical models. For most reliable model predictions and highest predictability the number of adjustable or ‘‘free’’ parameters should be kept to a minimum. Parameters can be obtained from literature sources or by fitting to experimental data.

Figure 3 shows cost functions of the effort to independently evaluate model parameters and the effort to fit model results to system behavior as a function of model complexity. It can be seen that there is an optimum of model complexity that minimizes the combination of these two efforts. Improvements in experimental capabilities may shift the minimum towards more complex models. The following subsections show some examples of typical types of parameters and how they can be estimated by fitting independent experimental data.

For example, reactivity ratios used to evaluate cross-propagation rate constants in free-radical copolymerization can be estimated from copolymerization composition data as shown in Figure 4. The composition of a copolymer can be calculated as a function of monomer mixture composition by using the Mayo-Lewis equation [1]:

$$F_1 = \frac{(r_1x_1 + x_2)x_1}{(r_1x_1 + x_2)x_1 + (r_2x_2 + x_1)x_2}$$

where F_i is the mole fraction of monomer i in the polymer, x_i monomer i's mole fraction in the monomer mixture and r_1 and r_2 are the reactivity ratios defines

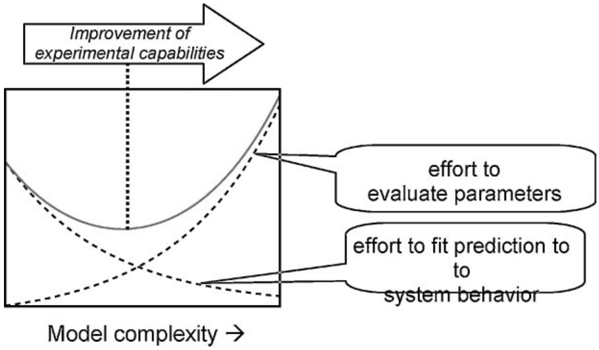

Figure 3.
Cost function showing effort to independently evaluate model parameters and effort to fit model results to system behavior as a function of model complexity.

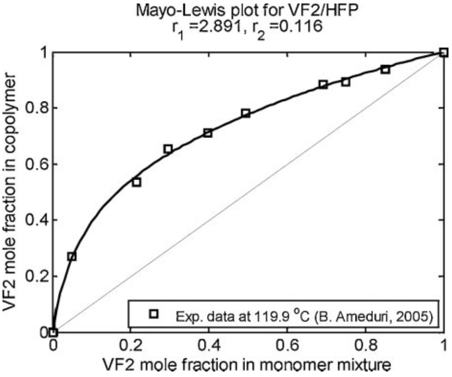

Figure 4.
Calculated (line) and experimental [7] (symbols) VF2 mole fraction in VF2/HFP copolymer as a function of VF2 mole fraction in monomer mixture; fitted values of reactivity ratios are given in the figure title.

as follows:

$$r_1 = \frac{k_{p,11}}{k_{p,12}}$$

$$r_2 = \frac{k_{p,22}}{k_{p,21}}$$

with $k_{p,ij}$ being the propagation rate coefficient of the addition of monomer of type j on a growing chain ending with a radical of type i. Figure 4 shows the results of the fitting and the obtained values of the reactivity ratios for the example of vinylidene fluoride (VF2) and hexafluoropropylene (HFP) copolymerization.

If available, additional experimental data about the sequence information can be used to obtain even better estimates of the reactivity ratios. Figure 5 shows an example of a copolymerization of monomers A and B where in addition to composition data triad information obtained from Nuclear Magnetic Resonance (NMR) spectroscopy is used. The triads for the monomer sequences shown in Figure 5, F_{ABA}, F_{BBA} and F_{BBB} are obtained from the following expressions [1]:

$$F_{ABA} = \frac{x_1^2}{(r_2 x_2 + x_1)^2}$$

$$F_{BBA} = \frac{2 r_2 x_1 x_2}{(r_2 x_2 + x_1)^2}$$

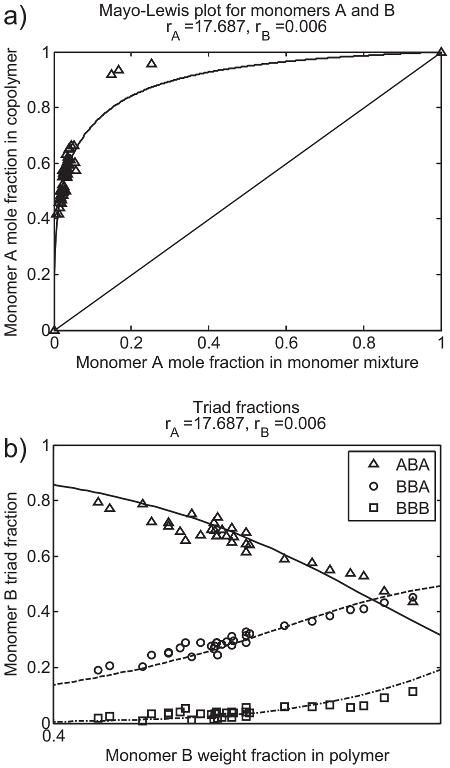

Figure 5.
(a) Calculated (line) and experimental (symbols) mole fraction of monomer A in A/B copolymer as a function of A mole fraction in monomer mixture; (b) calculated (lines) and experimental (symbols) triad fractions as a function of monomer B weight fraction in A/B copolymer; fitted values of reactivity ratios are given in the figure title.

$$F_{BBB} = \frac{(r_2 x_2)^2}{(r_2 x_2 + x_1)^2}$$

Another class of parameters is thermodynamic parameters. Thermodynamic models usually ask for a number of pure component or molecular parameters and depending on the mixing rules used one or more binary interaction parameters. For example, the Sanchez-Lacombe equation of state uses three temperature independent molecular parameters per component. Figure 6 shows the result of estimating such parameters for ethane using experimental data of density as a function of temperature and pressure and saturated vapor pressure

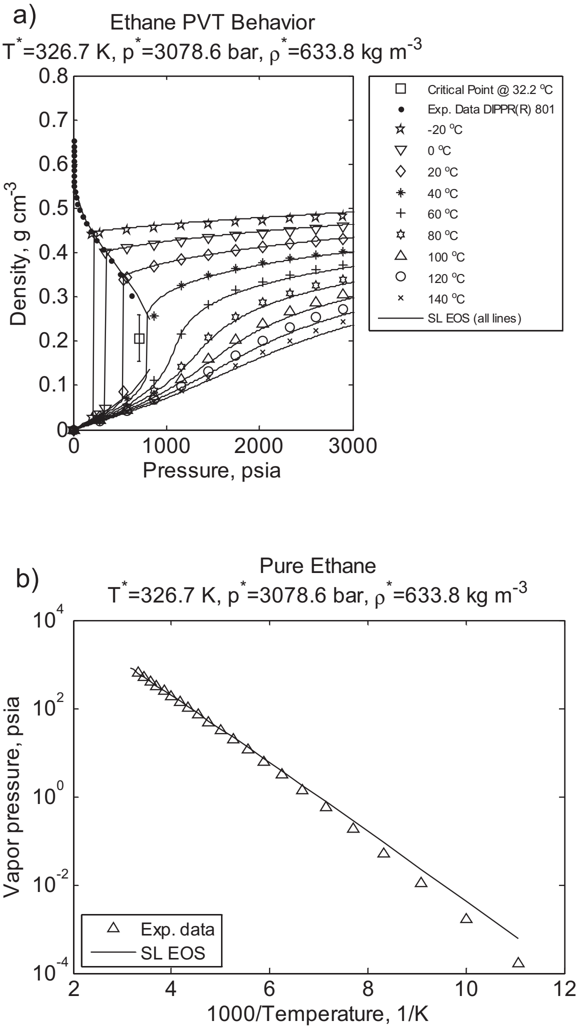

Figure 6.

(a) Calculated (lines) and experimental (symbols) *PVT*-data for ethane; (b) calculated (line) and experimental (symbols) ethane vapor pressure as a function of temperature; fitted values of Sanchez-Lacombe molecular parameters are given in the figure title; experimental data is from DIPPR® database (saturated liquid density and vapor pressure [8], critical point [9]) and from NIST Chemistry WebBook (density vs. pressure) [10].

as a function of temperature. It is worth noting that the method used to obtain the parameter values shown in Figure 6 uses both types of experimental data simultaneously.

Mixing rules are used to relate pure component properties with mixture behavior. Usually, for a given equation of state many different mixing rules are available in the literature, some asking for one, others for more than one binary interaction parameter per component pair. The results of the evaluation of binary interaction parameter between components A and B using binary VLE data is shown in Figure 7 for the Sanchez-Lacombe equation of state as well as for PC-SAFT. Unlike the pure component parameters for some equations of state, the binary interaction parameters are usually temperature dependent.

As mentioned previously, diffusion limitations are not only affecting the mass

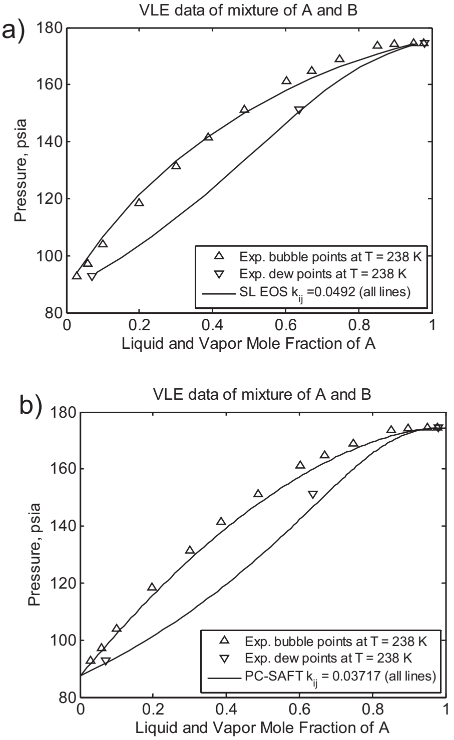

Figure 7.
Calculated (lines) and experimental (symbols) bubble and dew point pressures as a function of composition for a mixture of A and B; (a) Sanchez-Lacombe; (b) PC-SAFT; fitted values of binary interaction parameters are given in the figure legends.

transport of molecules between adjacent phases in a polymerization mixture, but may also influence the apparent kinetics of the reactions. For example, the following expression can be used to predict the termination rate coefficient of the bimolecular termination between radical chains of length x and y [11]:

$$k_t(x,y) = \left[\frac{1}{k_{t0}} + \frac{1}{4\pi r_{xy}\left(D_{x,com} + D_{y,com} + k_p[M]\frac{a^2}{3}\right)N_A}\right]^{-1}$$

Here, k_{t0} denotes the intrinsic chemical termination rate constant, r_{xy} the reaction radius (i.e. the distance at which two chains of length x and y react instantaneously), $D_{x,com}$ the center-of-mass diffusion coefficient of a chain of length x, k_p the propagation rate constant, $[M]$ the monomer concentration, a the root mean square end-to-end distance divided by the square root of the number of monomer units in the chain and N_A the Avogadro constant. Figure 8 shows a typical behavior of the termination rate constant as a function of chain length and polymer weight fraction evaluated from the expression above.

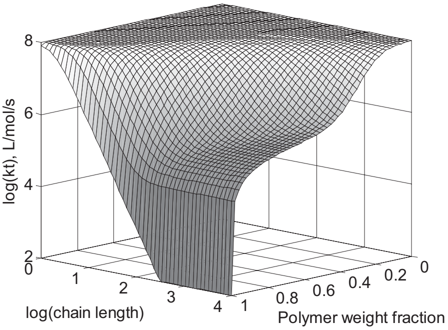

Figure 8.
Bimolecular termination rate constant as a function of chain length and polymer weight fraction in the reaction mixture.

Similar expressions can be used to calculate propagation rate coefficient k_p and initiator efficiency f_d [11]:

$$k_p = \left[\frac{1}{k_{p0}} + \frac{1}{4\pi\sigma_M D_M N_A}\right]^{-1}$$

$$f_d = \left[1 - \frac{D_{I,0}}{D_I}\left(1 - \frac{1}{f_{d,0}}\right)\right]^{-1}$$

Here, k_{p0} denotes the intrinsic chemical propagation rate coefficient, σ_M the Lennard-Jones diameter of the monomer, D_M the self-diffusion coefficient of the monomer in the reaction mixture, $D_{I,0}$ and D_I the initiator diffusion coefficients at zero and actual monomer conversion, respectively, and $f_{d,0}$ initiator efficiency at zero conversion. A large number of models for the evaluation of diffusion coefficients in gases and liquids are available in the literature. Diffusion coefficients in polymer-rich phases can be estimated from the free-volume theory by Vrentas and Duda [12–14].

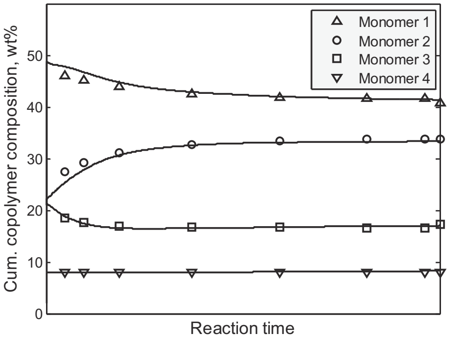

Figure 9.
Calculated (lines) and experimental (symbols) cumulative copolymer composition as a function of reaction time for an emulsion polymerization with four monomers.

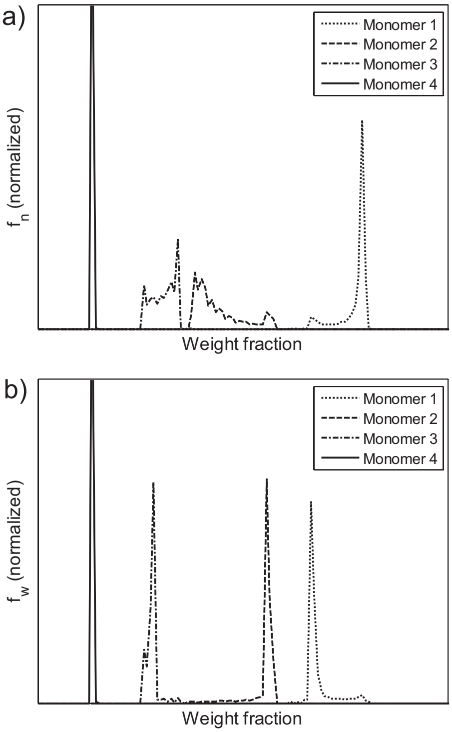

Figure 10.
Calculated normalized composition distribution for the same emulsion polymerization as shown in Figure 9; (a) number distribution; (b) weight distribution.

Model Implementation

After formulating the model in terms of a set of equations, which could in principle include algebraic, integral, difference, partial and ordinary differential equations, various numerical methods are used to solve the entire model as they are typically too complex for analytical solution. Software platforms used to numerically solve model equations include Fortran, Matlab®, Aspen Custom Modeler™, gPROMS™, Predici™, DuPont TMODS™. The latter is an in-house proprietary dynamic simulator that can be used to transfer a validated model to plant sites for example. In the following subsection some examples are shown of typical output of polymerization models.

Figure 9 shows the cumulative copolymer composition average as a function of reaction time for a free radical emulsion

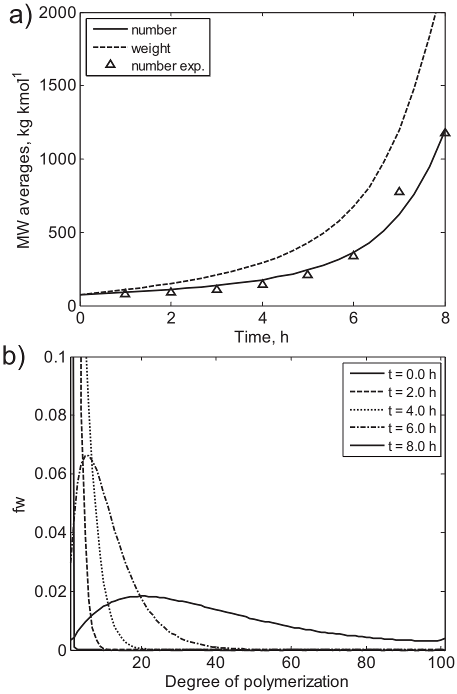

Figure 11.
Calculated (lines) and experimental molecular weight distribution as a function of reaction time for a condensation polymerization; (a) number (solid) and weight (dashed) averages; (b) molecular weight distribution at various reaction times.

polymerization with four monomers. Composition number and weight distributions for the same polymerization are given in Figure 10. The shown composition distribution has been obtained by counting the number (or mass) of polymer chains of a given instantaneous composition. The integration over reaction time yields the total number (or mass) of chains with that composition. The entire distribution is obtained by repeating the counting and integration for all possible compositions.

Another example of model output is the molecular weight distribution as shown in Figure 11 as a function of reaction time for a condensation polymerization. It is seen that the molecular weight averages exhibit the typical behavior observed in condensation polymerization, i.e. a significant increase in molecular weight late in the polymerization.

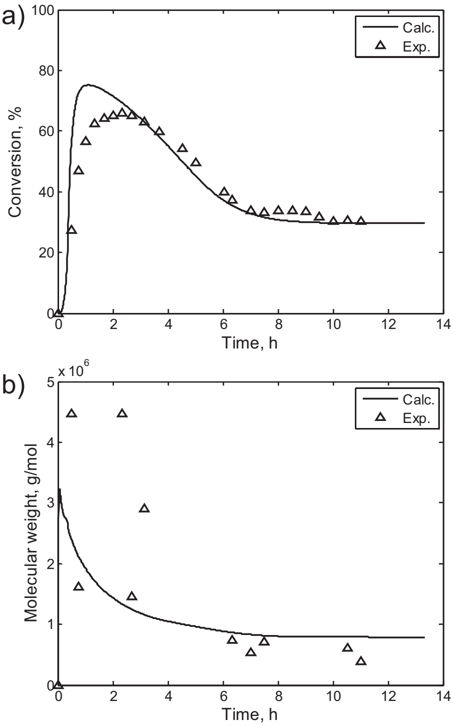

Figure 12.
Comparison of model outputs (lines) and experimental data (symbols) for a continuous styrene emulsion polymerization as a function of reaction time [6]; (a) monomer conversion; (b) number average molecular weight.

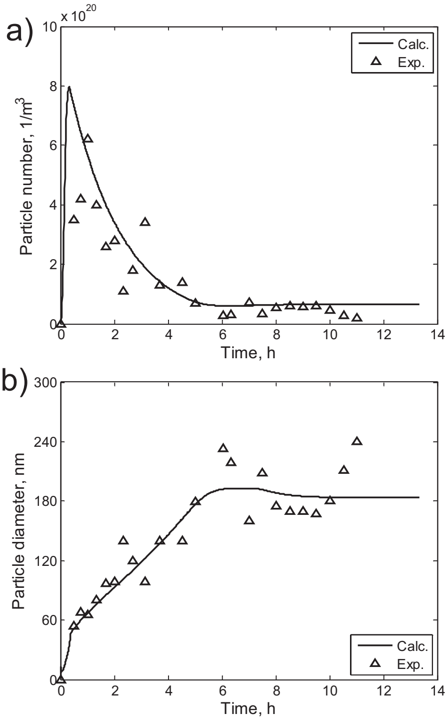

Figure 13.
Comparison of model outputs (lines) and experimental data (symbols) for a continuous styrene emulsion polymerization as a function of reaction time [6]; (a) particle number; (b) particle diameter.

The same behavior is of course reflected in the molecular weight distribution.

Various model outputs for a heterogeneous polymerization are given in Figures 12 and 13. In particular, conversion, molecular weight average, particle number and particle diameter are shown as a function of process time for the dynamic startup of a styrene emulsion polymerization in a CSTR [6]. This model uses a lumped particle balance to describe the particle size distribution (PSD). Full particle size distributions may also, with considerably more effort, be computed and compared to this lumped particle balance approach [15].

Conclusions

With the tools and concepts available today, some of which have been briefly discussed in the present article, detailed polymerization models can be developed and used to address PRE problems in industry. Polymerization models may be applied to different stages of process and product development. The support of early lab investigations focuses mainly on getting an improved understanding of underlying mechanisms and also model-guided optimization of product quality. At an intermediate scale, process and product development in pilot plants are supported by models. An optimization of recipe and conditions can be achieved by combining modeling and experimental efforts. Finally, for existing processes, models can be developed and implemented at plant sites where they can be used for operator training, process optimization, monitoring and control. In some cases, models are even used in real time in parallel with the process to aid in troubleshooting and process control.

Even though the development of fundamental polymerization models can be very laborious and time consuming, we have found that, just like well planned experiments, the model building activity can be very profitable. In fact, it is preferable that the model development is done based on and in combination with good experiments. Using models and experiments together in combination offers a very powerful tool and is a recommended alternative to empirical methods and experimentation alone.

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