Dynamic Modeling of Emulsion Polymerization Reactors

This paper is a survey of recent published works on the dynamic and steady state modeling of emulsion homo- and copolymerization in batch, semicontinuous, and continuous latex reactors. Contributions to our understanding of diffusion-controlled termination and propagation reactions, molecular weight, long chain branching and crosslinking development, polymer particle nucleation, and of the dynamics of continuous emulsion polymerization are critically reviewed.

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SCOPE

Emulsion polymerization, perhaps the least understood of the four principal types of polymerization processes (the other three being bulk, solution, and suspension), has of late become the most attractive technique for industrial production of polymeric materials. For the last three decades, enormous efforts have been made by researchers toward the elucidation of the complex physical and chemical phenomena (whose interpretation over the years led to many contradictory results) governing the various mechanisms which are operative in an emulsion system.

Considerable research in both academic and industrial circles on the optimization and control of polymer and/or latex quality has been performed in recent years. However, the success of all these efforts depends heavily upon having valid dynamic (or, in some cases, steady state) models of these complex polymerization systems. Therefore, a critical survey of the dynamic and steady state modeling of emulsion polymerization reactors would offer an initial stepping stone prior to any other effort to interfere in these systems, since, as is logically obvious, the effort to understand and interpret the rules which govern a process should precede any further attempt to monitor, extract information, or subsequently manipulate and control the process under study.

CONCLUSIONS AND SIGNIFICANCE

The use of comprehensive reactor models which incorporate detailed chemistry and physics of polymerization phenomena offers a deeper understanding of polymer production processes and permits the design of improved systems which otherwise might not be apparent.

The use of dynamic models to design polymer production systems has been shown to be very effective for processes involving continuous emulsion polymerization. Optimization attempts are greatly simplified and control problems are anticipated and largely eliminated at the design stage, giving control procedures which are relatively simple and highly effective.

INTRODUCTION

Research on the modeling, optimization, and control of emulsion polymerization reactors and processes has been expanding rapidly as the chemistry and physics of these systems become better understood and as the demand for new and improved latex products increases. The objectives are usually to optimize production rates and/or to control product quality variables such as polymer particle

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size distribution (PSD), particle morphology, copolymer composition, molecular weight, long chain branching and crosslinking frequency, and gel content.

Considerable research on the optimization of polymer (or latex) quality through the use of batch reactor temperature policies, semibatch (or semicontinuous) monomer feed policies, etc., has been performed in recent years. However, the success of these optimization efforts (or of any of the subsequent control efforts) depends heavily upon having valid dynamic (or, in some cases, steady state) models of the physical and chemical phenomena occurring in these complex polymerization systems. (A good overview of the several mechanisms, chemistry, and other physical and chemical phenomena underlying an emulsion polymerization system can be found in Fitch and Tsai (1971), Min and Ray (1974), Poehlein and Dougherty (1977), and Hansen and Ugelstad (1978). It is our intention in this paper to survey recent literature on the dynamic modeling of emulsion homo- and copolymerization in batch, semicontinuous, and continuous latex reactors. The paper is organized as follows. Models for various emulsion polymerization reactors are reviewed in the next section. Batch and semibatch reactors are then examined more specifically. Finally, literature on continuous latex reactors is discussed with respect to dynamic and steady state optimization, design of stable reactor systems, and the potential for on-line estimation and control of polymer and latex properties.

EMULSION POLYMERIZATION MODELS

Polymer production technology involves a diversity of products resulting from even a single monomer. Polymerizations are carried out in a variety of reactor types: batch, semibatch, and continuous flow stirred tank or tubular reactors. However, very few commercial or fundamental polymer or latex properties can be measured on-line. Therefore, if one aims to develop and apply control strategies to achieve desired polymer (or latex) property trajectories under such a variety of conditions, it is important to have a valid mechanistic model capable of predicting at least the major effects of the process variables.

Models for emulsion polymerization reactors vary greatly in their complexity. The level of sophistication needed depends upon the intended use of the model. One could distinguish two levels of complexity. The first type of model simply involves reactor material and energy balances, and is used to predict the temperature, pressure, and monomer concentrations in the reactor. Second-level models can not only predict the above quantities but also polymer properties such as particle size, molecular weight distribution (MWD), and branching frequency. In latex reactor systems, the level one balances are strongly coupled with the particle population balances, thereby making approximate level one models of limited value (Ray, 1980).

In recent years, considerable advances have been made in the modeling of emulsion polymerization reactors. In general, until 1974 models for these systems did not include the particle nucleation phenomena, nor did they consider population balances to account for the particle size distribution. Now, both homogeneous nucleation (Fitch and Tsai, 1971; Hansen and Ugelstad, 1978, 1982), and micellar nucleation mechanisms (collision or diffusion theory) are usually included in the models. Again, two levels of model are used to account for particle size. The "monodispersed approximation model" is based on modeling the development of the number of polymer particles and the total particle volume. Assuming monodispersed particles, the particle size is calculated as proportional to the cube root of the total volume of polymer phase divided by the number of particles. The surface area of polymer particles (needed to calculate the micelle area) is also obtained as proportional to the two-thirds power of the volume. The second level of emulsion polymerization model employs a population balance approach (or an age distribution analysis) to obtain the full PSD. By treating the moments of these population balance equations to get total or average properties, the set of equations that must be solved is greatly simplified. Since the method of characteristics gives the PSD as a function of (birth/growth) displaced back along the age axis, the moment equations may provide sufficient information to obtain the PSD.

Two of the most comprehensive discussions of these models were presented by Min and Ray (1974) and Poehlein and Dougherty (1977). Min and Ray gave a very general model framework which should be capable of modeling most emulsion polymerization systems. Of course, decisions must be made on the relative importance of the various phenomena occurring in a particular system. Other, more recent efforts on the modeling of emulsion reactors include: the dynamic modeling of a continuous stirred tank reactor (CSTR) for a general polymer system using a population balance approach (Thompson and Stevens, 1977); the dynamic and steady state modeling of a methyl methacrylate (MMA) CSTR using a population balance (Kirillov and Ray, 1978); the study of a general continuous emulsion system using population balances (Cauley et al., 1978); the modeling of a batch MMA reactor (Min and Ray, 1978); the population balance approach to a general continuous polymer system (Sundberg, 1979); the age distribution analysis approach to a continuous vinyl acetate (VAc) system (Kiparissides et al., 1979; Chiang and Thompson, 1979); the population balance modeling of a semibatch poly(vinyl chloride) (PVC) reactor (Min and Gostin, 1979); the dynamic modeling of a MMA CSTR using monodispersed approximation models (Schork et al., 1980); the simulation of a batch styrene (STY) reactor (Kiparissides and Ponnuswamy, 1981), and of a STY and a MMA reactor (Cauley and Thompson, 1982), and the discussion of PSD evolution (Lichti et al., 1981, 1983; Gilbert and Napper, 1983; Gilbert et al., 1984); the description of a typical emulsion copolymerization system (Ballard et al., 1981); the study of batch and continuous VAc latex reactors (Penlidis et al., 1984; Pollock et al., 1981, respectively); the simulation of a STY emulsion reactor (Bataille et al., 1982); the dynamic modeling of the batch and continuous emulsion polymerization of vinyl chloride (Penlidis et al., 1984); and the steady state and dynamic modeling of both batch and continuous reactors for styrene-butadiene rubber (SBR) using both "monodispersed approximation" and population balance models (Hoffman, 1981; Hamielec et al., 1983; Broadhead, 1984; Broadhead et al., 1984).

A problem in modeling emulsion systems is that of accounting for the equilibrium partitioning or the dynamic transport of monomers, modifiers, etc., between the several phases involved. The simplest approach employs constant partition coefficients, but more recent work on using thermodynamics (e.g., UNIFAC programs, Morton equations) has shown promise in accounting for nonideal solution behavior (Guyot et al., 1981).

As in most free radical polymerizations, another phenomenon, the "gel effect" or "Trommsdorf effect," which results in an autoacceleration of the polymerization rate, may have to be accounted for. It results from diffusion-controlled termination reactions involving large polymer radicals. At very high conversions, the propagation rates may also become diffusion-controlled if the polymerization temperature is below the glass transition temperature of the polymer being synthesized. These effects have often been accounted for by empirical correlations of the rate constants and conversion. Recently, more fundamental approaches using free volume theory or de Gennes reptation theory have been used quite successfully to model these effects for homopolymers (Marten and Hamielec, 1979, 1982; Chiu et al., 1982; Tulig and Tirrell, 1981; Hamielec et al., 1982; Tirrell and Tulig, 1983; Soh and Sundberg, 1982a–d), and for copolymers (Hamielec and MacGregor, 1983), It is this "gel effect" that is often responsible for multiple steady states with a CSTR. These multiple steady states, and the very interesting behavior that they lead to, have been investigated in several papers (Jaisinghani and Ray, 1977; Hamer et al., 1981; Schmidt et al., 1982, 1984).

A summary of recent studies of diffusion-controlled termination and propagation reactions in free radical polymerization which are pertinent to emulsion polymerization kinetics is given in Harris et al. (1981) and in Hamielec (1983). Also included are discussions of the effects of diffusion-controlled termination and propagation on molecular weight and branching development, with particular reference to the synthesis of PVC at high conversions and to the significant reduction of thermal stability of PVC which occurs.

Uses of Models

Future advances in latex production technology will be achieved largely through the efficient use of these comprehensive emulsion polymerization reactor models. Obvious uses of the models include the simulation and design of batch and continuous reactor systems. Novel operating strategies or recipe modifications which give higher productivity or improved quality can be identified. Control policies can be developed through simulation of various schemes of operation, or by using the model directly to develop advanced multivariable control algorithms for a production system in place. Reactor venting systems can be designed which will reduce the risk of vessel rupture during a runaway polymerization. Operators can be trained using iterative graphics terminals along with the stimulation model. Analysis of the consequences of system failures or upsets, which is an important safety consideration, can be greatly simplified. Finally, a less obvious use of the models is to offer guidance in the selection and development of on- or off-line sensors for reaction monitoring or product characterization (Duijfjes, 1975; Pollock, 1984).

BATCH EMULSION REACTORS

A batch reactor is one which is charged initially with a given recipe of ingredients which are then reacted to a desired degree of conversion. Batch reactors are used extensively for homopolymerizations but, in general, they are not ideal for polymerizations involving more than one monomer because of the composition drift that can result when the reactivities of the various monomers differ. By operating the reactor in a semibatch mode with respect to monomer feed this composition drift can theoretically be eliminated. However, the properties and characteristics of the polymer produced can be very different for different monomer feed policies. Another potential problem with batch polymerizations is that one has little or no control over the polymer PSD. Inaccuracies in the charging step or the presence of impurities can adversely influence the final PSD.

Penlidis et al. (1984) presented a general model based on a particle age distribution analysis and applied it to the batch emulsion polymerization of vinyl acetate. The ability of the model to provide accurate reactor simulations was demonstrated by the excellent agreement of predicted with experimental data from the literature (data on conversion-time histories) and measured in their laboratories (data on particle size and molecular weights, as well as conversion-time histories). The model has few adjustable parameters and is sufficiently flexible to be applied to more complex reactor configurations.

SEMICONTINUOUS LATEX REACTORS

Generally, semibatch (or semicontinuous) polymerization involves the addition of monomer (or any other ingredient) to the batch during the reaction with a time-varying or constant feedrate. The addition of precooled monomer during polymerization has the beneficial effect of providing extra cooling of the reaction mixture, thus permitting better temperature control and higher productivity. The monomer concentration in polymer particles can be controlled at levels where the gel effect is operative; this yields higher polymerization rates and also easier control of the reaction temperature (monomer feedrate can be used to control temperature). Additionally, semibatch polymerization offers the potential of better PSD control.

As mentioned in the previous section, by operating a batch reactor in a semibatch mode whereby one continuously or intermittently feeds the more reactive monomers, the composition drift can be minimized. Alternatively, by running the reactor at very high conversions and feeding the monomers in the exact ratio that one desires in the polymer, one can accomplish the same effect. Of course, the molecular weight, branching frequency, and crosslinking of the final polymer produced at low monomer concentrations can be substantially higher. For example, in the emulsion copolymerization of styrene and butadiene the frequency of long chain branching and the amount of gel formation is strongly dependent upon the feed policy used. The batch time, the heat release due to reaction, and the potential for reactor runaway also differ substantially for the different feed policies. On the other hand, controlled composition drift can often be advantageous in producing latexes with core-shell type morphologies (Bassett and Hoy, 1979).

There are many semibatch feed policies that can be used to maintain constant copolymer composition during polymerization. For example, all of the slowest monomer and some of the fastest monomers are added to the reactor at time zero to provide the desired monomer ratios (and the desired polymer composition). The faster monomers are then fed in over time at feed rates which maintain the monomer molar ratios constant. In general, for constant polymer composition these feed rates will differ and vary with time. For practical considerations it is of interest to know whether polymers with small composition drift can be made when the two monomers are premixed and fed to the reactor (this would eliminate the need for two pumps), and also when the premixed monomers are fed at a constant flowrate (this simplifies the reactor operation). The same questions could be asked for initiator feed rates (and components of a redox couple, if one is used). Another feed policy is to maintain monomer concentrations in the reacting mixture constant during polymerization. In the previous policy, monomer concentrations are constantly decreasing with time. With this latter policy, when monomer concentrations are maintained at a low level in the reactor the composition of the polymer produced is the same as the composition of the monomers being fed. With such a feed policy the monomers can be premixed and fed at any convenient rate including a constant feed rate. The choice of the feed rate would be based on the heat removal capacity of the reactor to maximize productivity. The choice of monomer concentration levels would also be dictated by the requirements for long chain branching (LCB) and crosslinking.

The feed policy in which molar ratios of monomers in the reactor are kept constant and the calculation of the optimal feed rates of monomers required to produce a polymer of constant composition are very well illustrated in Hamielec and MacGregor (1983). Of course, each policy for controlling composition drift will have different effects on molecular weight and LCB development, and will give a different production rate.

Guyot et al. (1981) and Guyot (1983) investigated some of these policies experimentally for the emulsion polymerization of styrene/acrylonitrile (STY/AN) in a CSTR. An on-line gas chromatograph was used to measure the monomer composition ratio in the liquid phase, and then a feedback scheme was used to adjust the feedrate of monomers to maintain this ratio constant (first policy). A subsequent analysis of the copolymers showed that rather than obtaining a desired constant composition polymer, the polymer composition drifted toward compositions too rich in styrene. They showed that this was clearly due to not accounting for the partitioning of the monomers between the three phases. A high solubility of AN in water coupled with its low solubility in the polymer leads to a much higher styrene/AN ratio in the polymer particles than in the total system. This partitioning would have to be accounted for in any control scheme for emulsion systems using monomers with greatly different solubilities.

Branching often affects polymer processability; therefore it is of interest to devise feed policies which would minimize frequency without significant loss in productivity. To minimize long chain branching, one normally uses a semibatch reactor and the policy of starting the polymerization with all of the slowest monomer in the reactor, and then feeding in the faster monomers over time to maintain constant monomer molar ratios. This policy should produce polymer with low levels of LCB (and crosslinking), and in general produce polymer with a molecular weight distribution which is similar to that obtained in a batch reactor.

Another policy (Hamielec and MacGregor, 1983) would be to feed in all the monomers over time and do so at feed rates which maintain constant monomer concentrations in the reacting mixture. The levels of LCB and crosslinking with this policy (which might be very high) will of course depend on the monomer concentration levels which are being kept constant during the addition of monomers. A common commercial practice is to maintain low monomer concentrations so that the composition of the polymer produced is the same as the monomer composition in the feed. An advantage of this feed policy is that premixed feed can be fed in at a constant rate.

The problem of lack of control over PSD in batch reactors can be overcome through seeding of the reactors (the use of seed particles improves batch-to-batch reproducibility of particle size), or through controlling particle nucleation by manipulating the emulsifier and/or initiator feedrates. Some policies using both of these methods have been investigated. Min and Gostin (1979) used initial seeding of the reactor followed by a controlled emulsifier feedrate to produce a secondary particle generation. The bimodal PSD's obtained in a pilot plant reactor for PVC emulsion polymerization were well predicted by their population balance model. The effects of the following variables on the final latex PSD were investigated: seed particle size, quantity of seed, solid content of the seed, and the initial amount of initiator.

Gordon and Weidner (1981) used the ideas of Min and Gostin (1979) to control the PSD in the emulsion polymerization of vinyl chloride by manipulating the emulsifier feedrate as a function of conversion. An on-line measure of conversion was obtained from an unsteady-state heat balance and then used as the feedback variable to control the emulsifier feedrate. Emulsifier feedrate policies which produce multiple particle generations, or extend the period of particle nucleation, have been studied by Penlidis (1982) for VAc emulsion polymerization. These policies significantly broaden the resulting PSD over that of a batch reactor operation.

CONTINUOUS LATEX REACTOR TRAINS

Where production volume warrants it, continuous reactors can offer many advantages, including lower operating and capital costs, improved heat removal capabilities, low levels of long chain branching and crosslinking in CSTR trains, and potentially more consistent product quality. The use of a theoretical, empirical, or semiempirical model to investigate alternative operating procedures for a reactor system could be very helpful in an attempt to devise techniques and policies with the ultimate aim of increasing productivity and improving quality. Such optimization studies using both steady state and dynamic models could also offer a better in-depth understanding of the process itself and therefore be the basis of developing feasible on-line control strategies.

In this section we survey some of the recent literature on continuous emulsion reactors from the following viewpoints: steady state and dynamic optimization efforts, reactor design optimization, and the potential for on-line estimation and control. As with batch and semibatch reactors, good process models play a dominant role.

Steady State Optimization

Steady state models of continuous polymerization reactors are very useful for simulating the behavior of these systems for various changes in the recipes and/or operating conditions. Conditions which yield higher productivity or quality can be investigated prior to implementing changes in the plant.

The steady state computer modeling of latex reactor trains used in the manufacture of cold SBR is treated in Hamielec et al. (1983) and Kanetakis et al. (1984). Their models predict copolymer composition, molecular weight averages, and long chain branching frequencies as measures of polymer quality, plus the particle size distributions through the train. Several modified operating procedures which give higher production rates and/or SBR quality are identified. Procedures for modifying the PSD are also investigated. Some of their results are summarized below.

Improved Productivity. When simulating the cold SBR train under normal operation it was observed that the monomer droplets disappeared in reactor 5. The presence of a large excess of monomers in the form of droplets in the first five reactors does nothing to affect the properties of the polymer produced. Rather, it simply consumes reactor volume which might otherwise be used in a productive manner. Therefore, by diverting a fraction (around 20%) of the styrene and butadiene from the feedstream of reactor 1 to reactor 4, the simulation showed that productivity could be increased by 6% while still monitoring essentially the same conversion, the same molecular weight averages, and the same LCB frequency (Kanetakis et al., 1984).

Modified Particle Size Distribution. The number and weight average particle size distributions predicted for the various reactors along the six-reactor train operating under normal conditions are shown in Figure 1. As expected, the PSD's become narrower as one progresses along the train (approaching plug flow). There are a number of ways to broaden these PSD's. By feeding excess soap to reactor 5 as illustrated in Figure 2, a second particle generation is promoted thereby giving a broad and bimodal PSD in reactors 5 and 6. A similar result can be obtained in a more practical manner by simply diverting some of the particles leaving reactor 1 to reactor 5 (Kanetakis, 1984).

Optimizing the Number of Particles Generated in Reactor 1. It is well known that the number of particles formed in a single CSTR for a fixed flow of initiator and soap varies with the reactor mean residence time, giving a maximum number of particles at some optimal value of the residence time. Model predictions (Figure 3) are consistent with these observations.

Stability of the Reactor Train. The dynamic model has clearly shown that under normal operation of a cold SBR train, sustained oscillations in conversion and particle number do not occur (Broadhead, 1984). Furthermore, any overshoot in properties due to the initial burst of particle generation upon start-up is quickly damped out.

Reactor Train Start-up and Switching Reactors. The dynamic model has been used to investigate start-up policies for the reactor train which will minimize the amount of off-spec material produced and yet avoid excessive overshoot in the conversion and the number of particles, something which could lead to excessive heat generation in the first reactor. Policies for switching reactors into

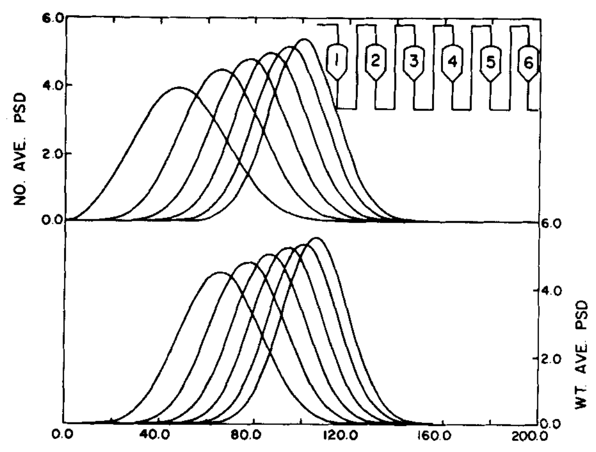

Figure 1. Number (upper plot) and weight (lower plot) average PSD for each reactor in the base case configuration. The abscissa is in a coded variable, proportional to diameter (nm).

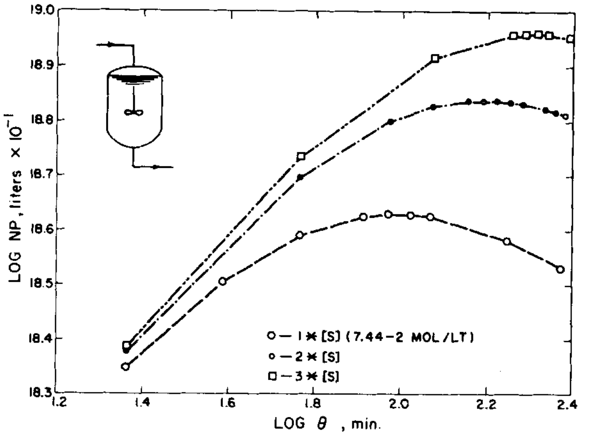

Figure 3. Number of particles per dm^3 of water as a function of mean residence time for varying emulsifier levels.

and out of the train for cleaning, etc. have also been studied.

Reactor Control. Control of molecular weight, branching frequency, and conversion can be achieved by manipulating the feedrates of chain transfer agent and the split of monomer feeds between the first and subsequent reactors. Since the reaction kinetics follow Case II behavior ($\bar{n}$ = ½ radical per particle) changes in the initiator feedrate to any reactor except reactor 1 will be ineffective in controlling conversion. Changes in initiator feedrate to reactor 1 will affect conversion indirectly by changing the number of particles generated. This change will be directly proportional to the change in initiator feedrate to the first reactor.

Copolymer composition drift down the reactor train, although slight in the normal case (18% to 20% styrene in the total polymer), can easily be controlled by feeding smaller amounts of butadiene down the train. Alternatively, by step feeding both styrene and butadiene in the desired proportion to all reactors down the train so that one maintains only small excess of monomer as droplets in each reactor, one will produce constant composition polymer and achieve a higher production rate, as stated earlier.

The above discussion has been very general but serves to illustrate the potential use of comprehensive models for optimizing the operating conditions of continuous emulsion polymerization reactor trains.

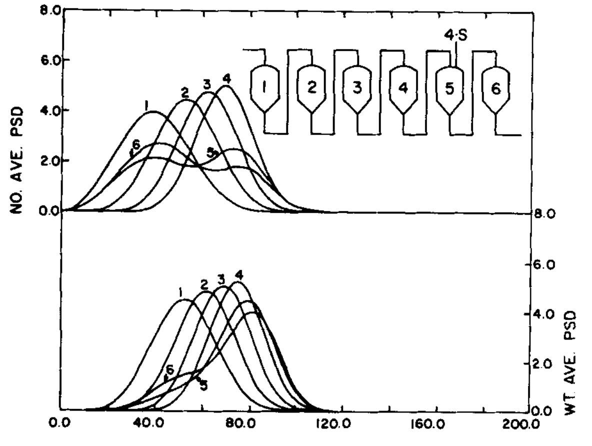

Figure 2. Effect on number (upper plot) and weight (lower plot) average PSD of the injection of additional emulsifier into the fifth reactor.

In a similar work the simulation and optimal design of reactors for a seeded continuous emulsion polymerization was studied by Lin and Chiu (1982). They found that, in general, an increase in the number of stages inside the seeder can reduce the volume of a CSTR for a required production rate. Finally, Lin et al. (1980) studied the performance of an emulsion CSTR for styrene comparing continuous flow operations with and without recycling.

Dynamic Optimization

Dynamic models for continuous reactors allow one to investigate their transient behavior and stability under various conditions such as start-up, forced oscillations, or upsets due to equipment failures, impurity variations, etc.

A theoretical investigation of the optimal start-up problem for styrene emulsion polymerization reactor trains was carried out by Dickinson (1976). He developed numerical algorithms and applied them to the problem of achieving steady state conversion in the shortest possible time. Simulation results showed that a considerable reduction in start-up time without extended transient oscillatory behavior of excessively large steady state conversion overshoots can be attained by application of an optimal soap start-up program. A similar start-up problem for a simulated vinyl acetate emulsion polymerization CSTR was treated by Kiparissides et al. (1981), using suboptimal control algorithms. Hamielec et al. (1983) used a simulation model to study the stability of an SBR reactor train during start-up and under various upset conditions, and they investigated ways of adding and removing a reactor from the train.

Problems encountered with the development of continuous reactor systems and some of the ways of dealing with these problems are extensively discussed in Poehlein (1979), Poehlein et al. (1983), and Ray (1983). A stochastic approach was employed by Nassar et al. (1981) to analyze and model, in a uniform fashion, both emulsion polymerization and dispersive mixing in a CSTR. Tsai et al. (1983) presented a model for continuous emulsion polymerization of styrene to predict the particle size and conversion for various operating conditions, accounting for the effects of residence time and initiator and surfactant level. Finally, Lynch and Kiparissides (1981) and Nigam and Nigam (1983) were concerned with the mathematical modeling of a tubular emulsion polymerization reactor and the simulation of its performance under various operating conditions.

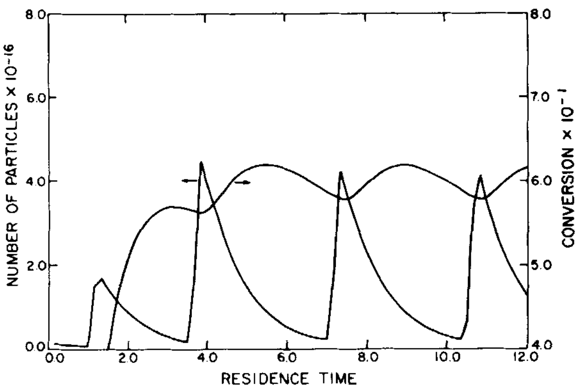

Figure 4a. Conversion and number of particles vs. residence time for a single CSTR. Conditions: θ = 1,800 s, I = 0.01 mol/L, S = 0.01 mol/L.

Reactor Design Optimization

Unlike the stable behavior of Case II SBR emulsion polymerization when carried out in a CSTR train, Case I kinetics systems (e.g., PVC, PVAc) exhibit large and sustained oscillations in conversion and all the polymer and latex properties (Greene et al., 1976; Kiparissides et al., 1980). Gerrens et al. (1971) and Brooks et al. (1978) showed similar smaller amplitude oscillations for styrene, and Greene et al. (1976) also showed sustained oscillations for MMA emulsion polymerization (oscillations in Case II systems, when present, are likely a consequence of strong diffusion-controlled termination).

According to the age distribution model of Kiparissides et al. (1979) and Pollock et al. (1981), Case I oscillations are due to the periodic formation and depletion of soap micelles, which lead to short periods of rapid particle generation followed by long periods where no nucleation occurs. These oscillations can lead to particle agglomeration during the periods of rapid particle nucleation because of inadequate coverage of the polymer particles by soap, and to excessive long chain branching during the high conversion portion of the oscillations.

Large quantities of soap could possibly damp or eliminate these oscillations, but this is undesirable from a standpoint of both economics and product contamination. The use of advanced control schemes can also damp these oscillations but not eliminate them at reasonable soap levels (Kiparissides et al., 1980; Pollock, 1984), because they are inherent in the fundamental particle nucleation phenomenon. The major control problem of eliminating the oscillations must therefore be solved at the design stage. This has been theoretically accomplished (Pollock et al., 1981) by using a comprehensive dynamic model to redesign the stirred tank reactor train. The new design consists of a conventional CSTR train but with a very small preliminary seeding reactor to which only a portion of the monomer and water is fed, the remainder being fed to the second or subsequent large reactor in the train.

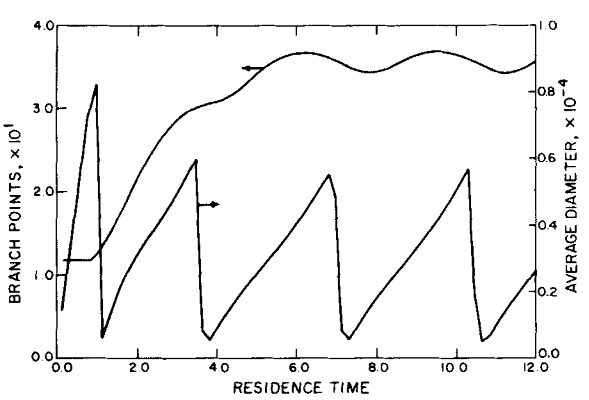

Figure 4b. Average number of branch points and number average particle diameter vs. residence time for a single CSTR; conditions as in Figure 4a.

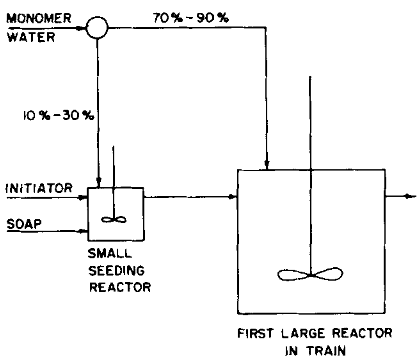

Figure 5. New reactor configuration with a small seeding reactor preceding the first large CSTR of the train.

The logic behind the new design is that all the generation of particles can be entirely accomplished in the first very small reactor by running under conditions of high soap and initiator concentrations, and the subsequent reactors used only for particle growth. In this way one achieves either a steady state generation of particles in the first reactor, or else a very rapid periodic generation which has no destabilizing effect on the much larger downstream reactors. In effect, the small early reactor becomes a continuous seeding reactor.

A comparison is shown in Figure 6 between the single CSTR of Figure 4 and the same reactor with a seeding reactor, Figure 5. With the seeding reactor present, all property oscillations are effectively eliminated while maintaining essentially the same polymer product in terms of conversion and particle size. In addition, the new configuration yields approximately 80% particle coverage by soap at all times, while in the single reactor case the coverage dropped to only 50% or even less immediately after each particle generation.

Under the new reactor configuration the oscillations have been eliminated at the design stage by using a dynamic model to design the "seeding" reactor and to optimally split the feeds among the reactors. One can therefore concentrate on the simpler but fundamental control problem of producing a latex with a specified conversion, particle size, molecular weight, etc. In the proposed reactor system one has much greater flexibility in controlling latex or polymer properties over a very wide range. This greatly increased flexibility comes from the ability to manipulate a new physical variable, namely the flow split of the monomer/water stream between the first and second reactors. Small changes in this feed split greatly affect the number of particles generated in the "seeding" reactor, thereby allowing for fine control over particle size. Small changes in initiator flow can then be used to maintain or change the conversion.

Some steady state effects of changing the split and initiator feedrate are shown in Table 1. The effect of changing only the feed split is illustrated in the upper four rows in the table. By changing the split from 40% of the monomer/water entering the seeding reactor to only 10%, the average particle diameter can be reduced from 1,150 Å to 610 Å. However, by changing the split alone, the

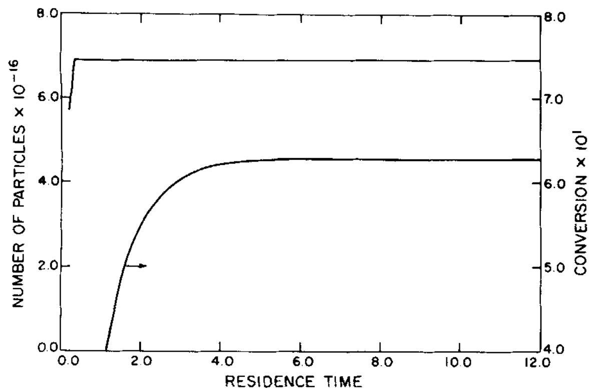

Figure 6a. Conversion and number of particles vs. residence time for the new configuration. Conditions: θ_2 = 1,800 s, v_1 = 75 mL, split = 0.4, I = 0.01 mol/L, S = 0.01 mol/L in the product.

conversion, $\overline{M}_W$ and $\overline{B}_N$ are seen to increase. The bottom four rows of Table 1 illustrate that, by changing the initiator feedrate $[I]$ as well (to give the concentrations shown in the second reactor), essentially the same range of particle diameters can be achieved while, maintaining conversion constant. Manipulation of $\overline{M}_W$ and $\overline{B}_N$ is most easily accomplished through the use of a chain transfer agent. The simulated dynamic behavior of the new reactor system was stable and nonoscillatory during all of these changes.

Obviously, any control scheme must be centered around the control of the "seeding" reactor, and the only control necessary on subsequent reactors in the chain is to insure that the emulsifier concentration is maintained both below the CMC to insure that no secondary generation of particles will occur and yet is high enough to maintain a stable latex. This can be checked by using an on-line measure of surface tension (Schork and Ray, 1981) in the downstream reactors and adding additional emulsifier if necessary. However, if proper control is maintained over the number of particles generated in reactor 1, there should be no difficulty in satisfying this constraint in the later reactors.

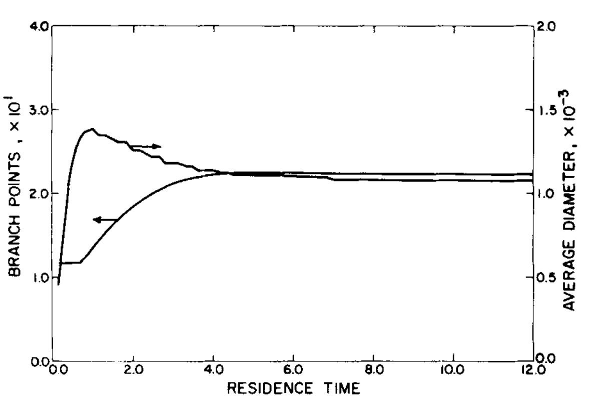

Figure 6b. Average number of branch points and number average particle diameter vs. residence time for the new configuration; conditions as in Figure 6a.

Experimental confirmation of these simulations is now under way in our stainless steel pilot plant reactor train. In addition to the surface tension measurements mentioned above, conversion is being followed with an on-line densitometer and particle diameter with an on-line UV spectrophotometer (Kiparissides et al., 1980). Off-line measurements of particle diameter using liquid exclusion chromatography (LEC) (Singh and Hamielec, 1978), and measurements of $\overline{M}_W$ using low-angle laser light scattering (LALLS) are also being made.

Similar redesigned continuous emulsion polymerization reactor systems have been proposed by other authors. Greene et al. (1976) showed results for methyl methacrylate emulsion polymerization where a plug flow reactor (no feed splitting) was used to seed a CSTR train, yielding stable operation and constant conversion. Omi et al. (1969), Ueda et al. (1971), and Nomura and Harada (1981) used steady state models to maximize the number of particles formed in the emulsion polymerization of styrene by using optimally sized tabular seeding reactors. The latter authors also considered a CSTR seeder with the possible splitting of the monomer feed stream.

On-Line State Estimation and Control

Realistically, one could never hope to have on-line measurements of all the major polymer or latex properties of interest, but perhaps one could achieve adequate control with one or two. Herein lies the utility of a good dynamic model for the process, in that, by using the measurements that are available, the remaining properties (or states) of the system can be inferred from the on-line solution of the model equations. Such state estimation can be accomplished by using Kalman filters or observers, which essentially combine the model equations with the measurements to yield a set of recursive equations providing estimates of all the states. The state measurements that are made serve to keep the model tracking those particular states closely, thereby forcing reasonable estimates of the other states, provided the model is valid.

An extended Kalman filter was investigated by Kiparissides et al. (1981) to estimate some of the PSD states in the emulsion polymerization of VAc from turbidity measurements. Pollock (1984) studied the optimal selection and development of sensors, the choice of which optimized the generalized variance of the state estimates of interest obtained from the Kalman filter.

Finally, there are very few reported applications of on-line control over the properties of the polymers being produced in

TABLE 1. COMPARISON OF POLYMER LATEX PROPERTIES FROM REACTOR 2 WHEN USING DIFFERENT BYPASS PERCENTAGES AS CONTROL VARIABLE*

Split	$[I]$ mol/L	x	D_p Å	N_p $\times 10^{-18}$	$\overline{M}_N$ $\times 10^{-5}$	$\overline{M}_W$ $\times 10^{-6}$	$\overline{B}_N$
0.4	0.01	0.616	1,150	0.069	5.06	2.40	0.250
0.3	0.01	0.637	1,050	0.075	5.33	3.29	0.920
0.2	0.01	0.666	980	0.17	5.77	6.22	1.20
0.1	0.01	0.702	610	0.62	6.32	—	1.67
0.4	0.01	0.616	1,150	0.69	5.06	2.04	0.250
0.3	0.0085	0.616	1,070	0.078	5.21	2.75	0.833
0.2	0.0069	0.617	1,000	0.16	5.49	3.73	0.993
0.1	0.005	0.618	640	0.58	5.79	8.06	1.20

*Conditions: θ_2 = 1,800, v_1 = 75 mL, [S] = 0.01 mol/L.

continuous latex reactors. Amrehn (1977) reported on conversion control in a SBR reactor train. Leffew and Deshpande (1981) applied PI controllers with dead-time compensation to the simulation model of Kiparissides et al. (1979) in an effort to eliminate or damp the oscillations in the continuous emulsion polymerization of VAc, but their results indicated no success. Of course, from an understanding of the particle nucleation phenomena involved, it is obvious that unless one uses large amounts of soap it is impossible to eliminate oscillations in this manner. Kiparissides et al. (1981) and Pollock (1984) investigated the possibility of damping down the oscillations by using optimal control and extended Kalman filtering. Very little improvement was obtained. A much more effective way of eliminating these oscillations was theoretically discussed by Pollock et al.(1981). A dynamic model was used to redesign the continuous reactor system to that shown in Figure 5, which uses a small seeding reactor and splits the monomer and water feeds between it and the large reactor. This will eliminate the oscillations and thereby allow one to concentrate on the problem of controlling the states of interest. The conversion and particle size can easily be controlled in this system by manipulating the split of the monomer/water feed streams between the reactors together with the initiator feedrate to the seed reactor. The soap flow can be left constant at the value required for stability of the latex.

Concluding, we would like to leave the reader with some thoughts from Aris (1983): "Chemical reaction engineering has been notable for the balance between experiment and theory that has marked it from the beginning. . . . A further characteristic of chemical reaction engineering is its facility in refining concepts. . . . As a branch of practical engineering [polymer] reactors may be tolerably well understood without all the refinements of their intricate behavior. As an object of intellectual study their apparently esoteric features are of great moment; they show that the vein, rich as it has proved to be, is not mined out yet."

NOTATION

$\bar{B}_N$ = average number of branch points, gmol/L
D_p = polymer particle diameter, Å
$[I]$ = concentration of initiator, gmol/L
$\bar{M}_N$ = number average molecular weight, gr/gmol
$\bar{M}_W$ = weight average molecular weight, gr/gmol
$\bar{n}$ = average number of radicals per polymer particle
N_p = total number of polymer particles per liter of latex
$[S]$ = concentration of emulsifier, gmol/L
v_1 = volume of seeding reactor
x = conversion

Greek Letters

θ_2 = reactor residence time, s

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