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Control of Emulsion Polymerization Reactors

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The interest in emulsion polymerization is strong because it offers the possibility of producing products with special properties not easily produced by other types of polymerization processes. Because the main reaction medium is water, not an organic solvent, its importance is steadily increasing with efforts to design environmentally benign processes. The control of emulsion polymerization is a challenging problem due to major limitations encountered in its modeling and on-line monitoring. Although emulsion polymerization has been studied and used for several decades, progress has been slow. Industrial practice relies heavily on experience while several controversial issues are still being studied. The literature related to this issue is vast and sometimes contradictory, and most deals with experimental investigation of specific emulsion polymerization systems to improve the process understanding and develop a process model. However, universally accepted conclusions are scarce. This article reviews the major issues related to control of emulsion polymerization. The latest contributions in process understanding, mathematical modeling, sensor technology, and process control techniques for emulsion polymerization are discussed. Emphasis is on contributions, which are important in resolving the control of emulsion polymerization processes.

Introduction

Emulsion polymerization is a process of great industrial importance, offering profound advantages over other polymerization processes. Due to its multiphase and compartmentalized nature, an emulsion polymerization system provides the possibility to yield a product with unique properties and performance characteristics. Emulsion polymerization is widely used in industry to produce latexes for a variety of applications (such as latex paints, adhesives, coatings, binders in paper and textile products, and synthetic rubber). The quality control of polymer latexes is becoming of great industrial importance, as the production of more and more products involves emulsion polymerization processes. Environmental concerns and governmental regulations have initiated recently a major trend driving away from paint products with high solvent content and leading to the widespread use of water-based latexes (such as restrictions set forth on the automobile paints and finishes).

In spite of the economic importance of emulsion polymerization, the control of emulsion polymerization reactors is still a particularly difficult task. The slow progress in this area has been attributed mainly to the lack of on-line measurements for the important product properties. The product quality can be in general assessed by different off-line techniques and performance tests, which mainly provide information on the end-use properties of the latex (adhesive strength, viscosity, film forming, and opacity). These properties are hard, if possible, to predict. Although, it can be argued that, on a molecular scale, principles are well defined, this is by no means true for the macroscale, where the final product properties are identified. On-line measurements in emulsion polymerization systems present several difficulties ranging from latex sampling and handling to time delays introduced by long analysis times. Depending on the application, auxiliary measurements can be used to infer or estimate variables that are not available on-line. In this case, attention should be paid to observability issues which are not always easy to resolve.

There is an extensive literature dealing with different aspects of emulsion polymerization modeling based on "first principles." Most industrial applications, however, rely heavily on intuition, sound engineering judgment, past experience, and

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heuristic procedures. For the moment, it seems inevitable that heuristics are essential to carry out industrial-scale emulsion polymerizations. Existing models can be accurate in simulating some of the main molecular level properties, but they cannot predict the end-use properties, which are the key in determining the utility and value of the majority of emulsion polymerization products. Moreover, to obtain this type of simulation capability from "first principles," extremely sophisticated models based on several plausible but not proven assumptions are required. These models involve numerous parameters, which in most cases are not known *a priori*. If obtained after extensive experimentation and fitting of the model, their values are not very accurate. This is due to the large uncertainty involved in their determination or averaging procedures applicable only to the particular recipe or operating conditions used. However, relatively good process models are necessary to design both efficient control policies and reliable estimation schemes, and the major challenge is to select the model with the appropriate structure, level of detail, and number of parameters to be fitted to available experimental data.

Difficulties in modeling of emulsion polymerization reactors coupled with the lack of robust on-line measurements for critical product properties have forced the practitioners in the field to an evolutionary process improvement approach, which is carried out by repetitive experimentation and off-line product characterization until acceptable product quality is obtained. In most cases "quality control" is interpreted as proper recipe formulation, optimum initial conditions selection, and ad hoc operation based on experience. The most advanced control policies in effect are open-loop in nature derived either by experience or by the use of some sort of simplified models.

Industrial emulsion polymerization suffers from what can be generally described as "process variability." This term includes random disturbances to process operating conditions (such as temperature, feed rates, impurities in raw materials, agitation rate, reactor/sensor fouling or sensor degradation, dissolved oxygen), which have a direct, yet not clearly quantified, impact on the product quality. Even if such disturbances can be detected and compensated for, their effect on the product quality is usually irreversible and results in product quality variability. However, unlike the random effects at the microscopic molecular level, process variability can be in principle minimized by careful design and control.

While the general problem of predicting and "controlling" the end-use properties of the latex product is still a matter of accumulated experience and heuristic procedures, the control of other important process variables, which affect the final product quality, can be addressed rigorously. By reducing the variability of the most important process variables, one expects that a reduction in product quality variability can be achieved. Then, the next objective to be pursued would be clearly to identify (heuristically or rigorously) the direct effect of process variables to the end-use properties, and eventually control them directly.

Early Efforts to Current Developments in Emulsion Polymerization Modeling

One of the first attempts to describe the mechanism of emulsion polymerization was made by Harkins (Harkins, 1945, 1946). His qualitative theory explained consistently some experimental observations and for many years served as a basis for understanding the mechanism of emulsion polymerization. According to Harkins' scheme, initiator decomposes into free radicals in the aqueous phase and these radicals enter micelles to form polymer particles. These polymer particles grow absorbing monomer and emulsifier from the aqueous phase, thus causing monomer droplets and soap micelles to be depleted. After all uninitiated micelles disappear, particle nucleation stops, and the particles already formed grow until all the monomer is consumed. A particle grows while one radical is present in it. When a second radical enters the particle the reaction is terminated and only reinitiated when a third radical enters the particle, and so on. It is clear from this simple description that polymer particles must play an important role in segregating the radicals during the course of the polymerization and consequently influence the properties of the produced polymer.

Following Harkins' description, Smith and Ewart (1948) developed a quantitative theory for the first two stages of the batch emulsion polymerization process (intervals I and II).

Interval I. Smith and Ewart assumed that, when nucleation takes place, all free radicals are generated in the aqueous phase. They considered two possibilities: (1) all radicals enter the micelles and generate new polymer particles; (2) radicals enter both micelles and polymer particles in a proportion that depends on the external surface area of both types of particles. For these two cases, they developed the well-known expressions for the number of particles per unit volume. Hypotheses 1 and 2 represent two extreme situations establishing an upper and a lower limit to the actual number of particles.

Interval II. It starts after micelles have been depleted. Smith and Ewart considered a balance on the number of particles having i radicals. Using the steady-state assumption, they derived a recursive formula and considered three different limiting cases. A key assumption in the Smith-Ewart model was that all particles are of the same size and grow at a constant volume growth rate.

Interval III. It is the polymerization after monomer droplets have been completely depleted, which was not originally included in the Smith-Ewart theory. This interval that starts at about 50% monomer conversion was divided into three subintervals by Alexander and Napper (1971): (1) the period of monomer supply to the polymer particles by the dissolved monomer in the aqueous phase and by the monomer rich portion in the particles, (2) the period of increasing viscosity in the particle making monomer diffusion to the reaction sites rate determining, and (3) the period of approach to the glass transition.

Following the Smith-Ewart theory, many contributions (Table 1) to the understanding and modeling of emulsion polymerization systems have appeared in the literature. As new mechanisms were postulated to explain particular experimental occurrences, it was realized that a general theory for emulsion polymerization required a rather complex modeling framework. The most important issues in modeling emulsion polymerization are briefly discussed in the following.

Monomer partitioning

The monomer concentrations at the reaction site depend on the monomer partitioning among the different phases existing in the system. In addition to this, the monomer concentrations

Table 1. Semicontinuous Emulsion Polymerization Studies

System	Feed Policy	Reference
S	Constant Feed (Neat Monomer)	Wessling (1968)
S MA	Constant Feed (Neat Monomer, Monomer Emulsion)	Gerrens (1969)
VAc/BuA	Feed Programming (Neat Monomer)	Chujo et al. (1969)
BuM/BuA	Constant Feed (Monomer Emulsion)	Snuparek (1972)
S/BuA	Constant Feed (Monomer Emulsion)	Sunparek and Krska (1976)
VDC	Constant Feed (Neat Monomer)	Wessling and Gibbs (1973)
AN/BuA AN/S AN/BuA/S	Constant feed (Monomer Emulsion)	Snuparek and Krska (1977)
AN/MAc	Feed Programming	Pichot et al. (1978)
VAc	Constant Feed (Neat Monomer)	Bataille et al. (1978)
VAc/BuA	Constant Feed (Neat Monomer)	Misra et al. (1979)
EA/BuA	Constant Feed (Monomer Emulsion)	Snuparek and Kaspar (1981)
VAc/BuA	Constant Feed (Neat Monomer)	Pichot et al. (1981)
S/AN	Feedback Control	Guyot et al. (1981)
MMA/BuA/AA MMA/BuA S/EA S/EA/MAc	Constant Feeds but Variable Feed Concentration (Power Feed)	Bassett and Hoy (1981)
VAc/BuA	Constant Feed (Neat Monomer)	El-Aasser et al. (1983)
VAc/BuA	Constant Feed (Neat Monomer)	Misra et al. (1983)
S/B	Constant Feed and Model-Based Open-Loop Control	Broadhead et al. (1985)
S/AN	Headspace Analysis Model-Based Feedback Control	Oliveres et al. (1988)
VAc/BuA	Kalman Filter with Feedforward Feedback Control	Dimitratos et al. (1989a)
VAc/BuA	Kalman Filter with Feedforward Feedback Control	Dimitratos et al. (1989b)
MA/VAc	Semiempirical Open-Loop Control	Arzamendi and Asua (1990)
VAc/BuA	Constant Feed (Neat Monomer)	Dimitratos et al. (1990)
S/MA	Semiempirical Model-Based Open-Loop Control	van Doremaele (1990)
EA/MMA	Semiempirical Model-Based Open-Loop Control	Arzamendi et al. (1991)
VAc/BuA	Constant Feed Estimation with Kalman Filter	Dimitratos et al. (1991)
MA/VAc	Semiempirical Open-Loop Control Limited Heat Capacity	Arzamendi and Asua (1991)

Abbreviations: AA = Acrylic acid; AN = Acrylonitrile; BuA = Butyl acrylate; BuM = Butyl methacrylate; B = Butadiene; EA = Ethyl acrylate; MA = Methyl acrylate; MAc = Methacrylic acid; MMA = Methyl Methacrylate; S = Styrene; VAc = Vinyl acetate; VDC = Vinylidene Chloride.

in the latex particles depend on the assumed model for particle structure (monomer being located in a layer at the surface of the particle or diffusing everywhere in the particle volume). In the conventional batch or continuous emulsion polymerization process, monomer is distributed among three phases present in the system: aqueous phase, polymer particles, and monomer droplets. In a semibatch process, operating under monomer starved conditions, monomer is partitioned between the polymer particles and aqueous phase while no separate monomer phase is present. There are cases where all the monomer can be considered without large error to reside in the polymer particles. This is an assumption usually employed (Hamielec and Hoffman, 1985; Dougherty, 1986) in modeling interval III of a conventional batch emulsion polymerization process, which is quite similar to the monomer starved semibatch process. In the case that one of the participating monomers is soluble in water, then a considerable amount of that monomer will be present in the aqueous phase even under monomer starved conditions. Under these circumstances, a monomeric unit can only participate in the polymerization reactions within the particles if it diffuses through the aqueous phase, crosses the water/particle interface, and diffuses into the monomer-swollen polymer particles. Therefore, to obtain the monomer concentrations in the different phases involved, component balances must be developed for each phase, taking into account these transport processes. This requires knowledge of equilibrium concentrations, diffusion coefficients, and surface areas of the various phases (Brooks, 1970, 1971).

If the process is not diffusion controlled, we can consider the phases to be at equilibrium swelling conditions and, thus, greatly simplify the task of calculating monomer concentrations in the different phases. In fact, thermodynamic equilibrium is quickly reached and maintained in emulsion polymerization because of rapid diffusion of monomer through the aqueous phase (Oishi and Prausnitz, 1978). Thus, transport through the aqueous phase can be neglected as a rate determining step mainly because of the existence of agitation, which results in a convective mass-transfer process through the aqueous phase instead of a diffusive one. This is particularly applicable in a semibatch process or in interval III of the batch one. In this case, since there is no separate monomer phase in the system, diffusion across the monomer/aqueous interface cannot be the rate determining step as in the batch process. Diffusional resistance within the particles will show little discrimination between monomers. However, the magnitude of any resistance to monomer transfer that occurs at the water-particle interface will depend on the interactions between the surfactant and the monomers. If this resistance is not large enough to affect the monomer supply rate to the particles, the monomer partitioning in the different phases can be thought of as a quasi-static equilibrium process. The concentration of monomers in the polymer particles will then be determined by the balance between the gain in interfacial free energy caused by the increase in surface area on swelling and the loss in free energy caused by mixing monomer with polymer. Partial molar free energies are given by the Flory-Huggins lattice theory of polymer solutions (Flory, 1953), and at equilibrium conditions they have to be the same for any monomer in all phases. The quasi-static equilibrium established at any moment during the course of the semicontinuous polymerization is disturbed by subsequent polymerization in polymer particles and monomer addition to the reactor, moving the system away from equilibrium. Monomer flux between phases then takes place to reestablish equilibrium. Several works have dealt with the thermodynamics of emulsion polymer systems (Morton et al., 1954; Guillot, 1981; Ugelstad et al., 1980; Guillot, 1985; Delgado et al., 1988).

Average number of radicals per particle

Formation of free radicals may occur in the aqueous, monomer, or polymer phase, depending on the type of initiator (water or oil soluble). Radicals can also desorb from the polymer particles, monomer droplets, and micelles. Thus, in principle polymerization can take place in any phase of the system.

The average number of radicals per particle is one of the most difficult to predict variables in emulsion polymerization. It depends upon the rate of radical generation, the rate of radical termination in the aqueous phase, the rate of termination within a particle, the rate of radical desorption from the particles, and the rate of radical absorption into the particles. Many investigators presented solutions of the original or modified Smith-Ewart recursion equation for homopolymerization systems (Stockmayer, 1957; O'Toole, 1965; Ugelstad et al., 1967; Gardon, 1968b; Hawkett et al., 1975). Recursive formulas have also been derived for copolymerization systems, but their solution is extremely difficult (Ballard et al., 1981; Nomura et al., 1983). In any case a considerable number of rate coefficients and parameters related to the different phenomena taking place are involved.

The treatment of interval III has received less attention than it deserves, largely because the termination constant varies and the average number of radicals per particle in this region is extremely difficult to be predicted. The decrease in the termination constant at increasing conversion during interval III is the well-known gel-effect.

Effect of particle number and particle-size distribution

Particle number affects directly the reaction rate in emulsion polymerization and depends on the mechanism of particle formation (micellar initiation, precipitation from the aqueous phase, or polymerization in monomer droplets), as well as on coalescence processes. A discussion of particle formation is provided in the particle-size distribution control section of this article.

All the early attempts to quantify emulsion polymerization variables considered that the polymer particles were all of the same size. This assumption was first removed by making use of well-known distributions (for example, normal, log-normal, Poisson, binomial) to represent polymer particle-size distributions (PSD) with an analytic form. However, these approaches were too restrictive and prevented the development of the PSD along with conversion and molecular weight.

The use of mass and energy balances is without doubt inadequate to model the development of the particle-size distribution or properties directly related to it. Population balances must be employed. Modeling within this framework is consistent with the qualitative understanding of PSD development, as being dependent on the size and age of particles. However, different approaches have been proposed particularly with respect to the selection of the "internal" coordinates of the population balances. Approaches using the particle size as the single internal coordinate have been criticized as introducing the hidden assumption that identically sized particles grow at the same rate (Kiparissides et al., 1979) and thus, they are inadequate to model the age-dependent PSD development. However, approaches relying on age distribution analysis ("birth time" is the internal coordinate) encounter severe difficulties in treating the coalescence mechanism. Although not without problems, modeling PSD within the population balance framework provides the most rigorous way of describing PSD development. Discussion on population balances can be found in Hulburt and Katz (1964), Randolph (1964), and Ramkrishna (1985). Population balances have been used in modeling the PSD in emulsion polymerization by several investigators (Nomura et al., 1971; Sundberg and Eliassen, 1971; Stevens and Funderburk, 1972; Min and Ray, 1974; Thompson and Stevens, 1977; Kirillov and Ray, 1978; Cauley et al., 1978; Min and Ray, 1978; Min and Gostin, 1979; Sundberg, 1979; Gilbert et al., 1984; Rawlings and Ray, 1988).

Effect of process operation

The type of process operation (batch, semibatch, continuous) has a strong impact on the course of emulsion polymerization. The three intervals of the batch process are not always clearly distinguished in semibatch or continuous operation. Depending on the feed streams, secondary nucleation can be induced at the same time that the particle population is growing. The thermodynamics of the system are affected by the incoming material and the distribution of both the radicals and the particle sizes is modified. As a result totally different products can be produced by the same recipe formulation.

Most of the early theories of emulsion polymerization were developed for batch reactors. However, semibatch as well as continuous reactors are also used in emulsion polymerization. Although extensive semibatch experimentation was conducted at the initial stages of research in emulsion polymerization, few fundamental insights were provided. However, in the case of continuous reactors, the use of the Smith-Ewart theory, uniform particle-size assumptions, residence time distribution analysis (DeGraff and Poehlein, 1971), and simple population balances (Nomura et al., 1971; Stevens and Funderburk, 1972) produced results in agreement with experimental data.

Although the importance of the issues discussed in the previous paragraphs has been recognized over the years after the Smith-Ewart theory, no comprehensive modeling framework for emulsion polymerization was presented until the work of Min and Ray (1974). Research on the understanding and modeling of the individual mechanisms involved has been conducted both before and after the work of Min and Ray. However, the framework of Min and Ray included all the mechanisms that have been postulated in the past and was flexible enough to permit the incorporation of new mechanisms. Their development took into consideration the formation of free radicals in all phases, the different nucleation mechanisms, the radical desorption from all sites, the particle stabilization both by emulsifer and polymer chain ends, the effect of coalescence, the impact of gel effect, the particle structure, the aqueous phase polymerization, and the particle-size distribution effect.

The mathematical description involved a set of overall material balances as well as subsystem balances. These include polymer particle population balances and individual particle balances, monomer droplet balances, micelle balances, and material balances in the aqueous phase. The model can predict the evolution of the PSD as well as the distribution of free radicals as a function of particle size. Possible interactions between particle size and the MWD can be seen from predictions of live and dead polymer distributions. Other variables of interest such as concentrations of monomer, initiator, and other components in the particles and in the aqueous phase are also available from the model.

After the work of Min and Ray, other authors concentrated in the practical solution of the model using different numerical techniques and tested its predictive capabilities with specific polymerizations. In the following sections we will describe some of these works and will discuss their contribution to the understanding of the effect of operational as well as design variables on PSD first and molecular properties later. In both cases we will discuss briefly the way in which the fundamental variables used in the mathematical models relate to the variables that define the quality of the final polymer.

Control of Particle-Size Distribution

Polymer latex emulsions are widely employed as paints. Essential properties, such as covering capacity, penetration, film-forming ability, "brushability," and stability are all critically influenced by the PSD of the polymer latex. Thus, when the latex is the final product of the polymerization, its PSD can be related to the end-use properties of the produced polymer. Under these circumstances, controlling the PSD of the latex may become a very important issue. In case that the final product is not in the form of a latex, as it often happens, the PSD is not directly related to the end-use properties of the polymer and then it becomes, from a control point of view, an intermediate variable. Controlling PSD in this situation may still help to indirectly control variables more closely related to end-use properties as are those that define the molecular architecture of the polymer.

Much insight has been obtained in recent years on the design of recipes and the feed policies of emulsifier and initiator components to yield a desired PSD in emulsion polymerization. The experience gained has been used in developing nonrigorous open-loop trajectories to obtain a desired PSD. This is currently achieved through seeding of the reactors or through controlling particle nucleation by manipulating the emulsifier and/or initiator feed rates. Closed-loop control of PSD has not yet been attempted.

A number of researchers have conducted experimental work in which they studied the influence of different variables on the emulsion polymerizations of a variety of monomers. In what follows, we will describe results from different authors who studied the influence of operational variables on the PSD of polymer latexes. However, we will restrict ourselves to discuss here only those works in which the experimental observations were used to validate models of the type commonly encountered in engineering applications such as process simulation, optimization, and control.

Mechanisms determining the PSD

The understanding of the development of PSD requires that the "state" of each particle is determined both by its size and age. In that respect, "new" particles are those for which a history of growth is absent. Thus, particle birth is accomplished not only by the nucleation mechanisms but also by coalescence or breakage processes. Nucleation is possible by micellar initiation (micellar nucleation), by monomer droplet initiation, by oligomer precipitation which follows the initiation in the aqueous phase (homogeneous nucleation), or by a combination of the above. Primary nucleation is responsible for establishing the first generation of small-sized particles. However, secondary nucleation may also occur (such as during interval III due to emulsifier release) or be induced (by emulsifier addition). In this case, nucleation enlarges the particle population and introduces small particle-size components in the existing PSD. Coalescence and breakage are particle birth and death processes at the same time. Particle-particle coalescence gives birth to young larger particles at the expense of older and smaller ones, decreasing in this way the particle population. Both types of coalescence have a two-fold effect on the PSD. They introduce larger particle-size components, while removing the "sacrificed" components of smaller particle size. Exactly the opposite holds for breakage. Of course, apart from the birth and death processes, the particle-size distribution development depends heavily on the particle growth process, which itself is determined by the size of each class of particles.

Considering the plethora of factors which affect each one of the mechanisms involved in the development of PSD, the complexity of its description is apparent. Severe difficulties are encountered particularly during the early stages of the emulsion polymerization process. The formation and the early growth of the latex particles is a result of many competing mechanisms. Initiated radicals can be captured into micelles, react with dissolved monomer, enter monomer droplets, terminate in the aqueous phase, or lose activity by transfer to other species. After the first latex particles appear they will compete for radical capture as well. These early born particles can also coalesce with each other. Initiation rate, emulsifier type and levels, and monomer solubility are key variables in determining the evolution of these early stages. The prerequisite for micellar initiation (Harkins, 1947; Smith and Ewart, 1948; Smith, 1948) is the existence of micelles; thus, the concentration of emulsifier must be above the critical micelle concentration (CMC). Homogeneous nucleation (Priest, 1952; Fitch and Tsai, 1970, 1971; Fitch, 1981; Hansen and Ugelstad, 1978, 1979a,b) can occur under any conditions, and it can be important when the emulsifier concentration is below CMC and monomers are fairly water soluble. Primary particles produced by homogeneous nucleation are likely to grow by coagulation between themselves until they become sufficiently stabilized by emulsifier. They can also be captured by existing latex particles. Monomer droplet nucleation (Ugelstad et al., 1973, 1974; Hansen and Ugelstad, 1979c) is more pronounced if the monomer droplets are made small enough, which can be the case when using mixed surfactants. High initiation rates combined within sufficient particle stabilization by emulsifier can induce particle coalescence at the nucleation step. Particles born at the nucleation step by different mechanisms will have different sizes and surface characteristics. Thus, their efficiency to capture radicals and their tendency to coalesce will vary. As a result, the growth of this early population will be a combined effect of different growth histories. A full-fledged discussion of particle formation in emulsion polymerization is beyond the scope of this text. The interested reader is referred to the excellent contributions by Hansen and Ugelstad (1982) and Song and Poehlein (1988).

Coalescence may occur throughout the emulsion polymerization process. Although coalescence has a direct impact on the development of PSD, its treatment in the literature has been limited (Min and Ray, 1974; Hansen and Ugelstad, 1978; Morbidelli et al., 1983) because of profound modeling difficulties. At very low surfactant concentrations the PSD may be completely determined by coalescence rather than nucleation, in which case agitation, ionic strength of the medium, particle size, and surface charge density become critical variables.

If compared to the rather involved particle birth and death processes, the particle growth development present less difficulties. The rate of particle growth depends on the number of radicals and the monomer concentration in the particle. As discussed earlier, the prediction of the number of radicals per particle is a central problem in emulsion polymerization, while the monomer concentration in the particle can be deduced by thermodynamic considerations. Both variables depend on the particle size.

Development of PSD in batch

In interval I of the batch process the PSD is expected to broaden with conversion because: (1) particles are nucleated at different times and thus experience different growth histories with the older ones being larger, and (2) radicals enter the particles at random. However, the polydispersity at the completion of the nucleation stage is very close to unity indicating that PSD at the end of interval I is quite narrow. Gardon (1968a,c) calculated the theoretical polydispersity to be 1.04, while the experimentally obtained value was 1.2. He attributed the difference to the effect of the random radical entry.

In interval II and following the Smith-Ewart case 2, the rate of volume growth of each particle is independent of its size. In that case the rate of increase in the particle radius is inversely proportional to the radius squared. The PSD will become narrower because small particles grow faster than big ones (in diameter). Competitive growth experiments (Bradford et al., 1956) showed that the volume growth is not independent of size, but is proportional to the diameter to the power of 2.5, instead of 0 in the Smith-Ewart model. In that case the smaller particles will grow with a relative rate that is higher than that of the larger particles and the PSD will become narrower as well. This means that the relative variance of the distribution will be a decreasing function of time, even though the absolute variance is an increasing function of time.

In interval III termination becomes diffusion controlled and termination rate decreases (gel effect). This leads to an accumulation of radicals in the particles and the distribution of the number of radicals per particle i broadens. Since each particle grows proportionally to i, this distribution defines also the distribution of growth rates. Therefore, the PSD is expected to broaden in interval III. It is also expected to become skewed towards larger particles. This is because as the distribution of radicals broadens, a decreasing number of particles would contain no radical (no growth), and a decreasing number of particles would contain few radicals (slow growth). More and more particles would contain many radicals (fast growth). Thus, most of the particles would become large and few will remain small. Thus, skewness will increase with conversion if 1 increases.

PSD studies and modeling efforts

The work of Sundberg and Eliassen (1971) presents an early effort to predict particle size and molecular weight distributions using population balances. The authors treated only micellar nucleation in a batch reactor assuming that radical entry into both the micelles and the particles is proportional to their surface area, that termination occurs either by chain transfer to monomer or by combination with a second radical entering the particle, and that all radicals produced in the aqueous phase are absorbed into the micelles or polymer particles. The authors compared their predictions with Gerrens' (1959b) experimental results on particle size. They found that their predictions agreed with the experiments and were also well represented by the Smith-Ewart theory. They also concluded from these results that PSD has little effect on conversion and MW for the polymerization of styrene. This last conclusion is in agreement with the validity of Smith-Ewart theory, based on the monodispersity assumption, for polystyrene.

In a subsequent publication Sundberg (1979) discusses in more detail this attempt including additional information and conclusions. The author reports that both the mean and standard deviation of the PSD decrease as the initiator increases and that all curves obtained are skewed toward the smallest particle size. Variations in surfactant level demonstrated that while the average particle size and standard deviation decrease with increased surfactant charge, the distributions become significantly broader when viewed relative to the mean. This is unlike the effect of increased initiator level and underscores the independent control of each variable during the particle formation period. The decrease of both average particle size

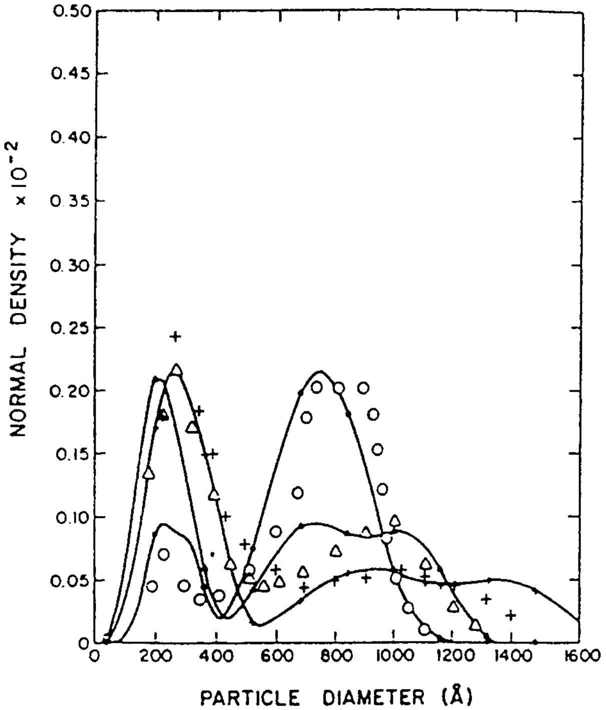


Figure 1. Particle-size distributions for various initial initiator concentrations (Min and Ray, 1978).

and standard deviation with temperature increase was also confirmed. The study of the effect of the monomer to water ratio concluded that increasing solids content results in a distribution narrower relative to the mean but broader on an absolute basis.

One of the first attempts to systematically study the influence of operational variables on latex characteristics was conducted by Min and Ray (1978) who simulated the batch polymerization of methyl methacrylate (MMA). Based on observations made by other authors when trying to explain experimental data of MMA, Min and Ray concluded that in order to explain the observed behavior that the classical models were not able to represent, mechanisms such as water polymerization and gel effect should be included. They compared their model predictions with data of Gerrens (1963, 1964). Figure 1 shows how well the model predicts the PSD at different initiator concentrations. In all cases the experimentally observed data agreed quite well with the predictions. Having tested the model with experimental data, the authors used this "validated" model to make predictions about the influence of operating conditions on this polymerization. Based on these predictions they concluded that: (1) a small initiator concentration causes slow and protracted particle formation, resulting in a much broader particle PSD with relatively small number of larger particles, (2) a large initiator concentration causes rapid particle formation so that all the particles are formed almost simultaneously and grow to a relatively narrow PSD, (3) very small emulsifier concentrations cause a small number of particles to be formed quickly, and these grow together to form almost monodisperse-size distributions, (4) a very large emulsifier concentration allows particle formation over a longer period of time and produces a very broad-size distribution and a large number of particles, and (5) the ionic strength of the polymerizing medium (affected by the concentrations of initiator, emulsifier, chain transfer agents, among others) has a strong influence on the rate of particle coalescence, thus broadening the PSD.

A few years later, Min and Gostin (1979) studied the semibatch polymerization of vinyl chloride (VC). They used a seeded reactor in which emulsifier and initiator were fed at a constant flow rate. These authors modeled this polymerization considering the formation of new particles from micelles during the reaction, the stabilization of particles both by emulsifier and by polymer chain ends on the particle surface, the agglomeration of polymer particles, and the presence of the "gel effect" even at the very early stages of the reaction, among others. The predictive capabilities of the model were successfully validated with pilot-plant data. Excellent agreement was obtained for conversion, volume fraction of small particles, and size of large particles. Subsequently, the model was used to study the effects of the following variables on PSD: solids content of seed, quantity of seed, initial amount of initiator, and seed particle size. It is well understood that the emulsifier added to the reactor plays two main roles; one is to provide surface coverage to the growing polymer particles, and in case that is not needed for particle coverage, the other role is to form micelles which will nucleate new particles. The proposed model was used to confirm this intuitive notion in a quantitative way by analyzing two cases. First the percent of solids of the seed latex was reduced with respect to that of a base case. The model predicts that fewer particles grow into large particles. However, the large particles are larger than in the base case because of the higher radical flux due to less total surface area for all particles. The smaller number of particles growing to large sizes is simply explained because by having kept the remaining variables as in the base case, the total polymer mass at the end of the reaction is less than in the base case. The model also predicted that more and larger second generation particles are formed. This is because with less seed a smaller coverage area is required, thus leaving the emulsifier free to generate earlier a larger number of micelles. A second study was done in which the amount of seed was increased with respect to that of the base case. The effect is opposite to the effect of reducing the solids content of the seed to the extent it causes a reduction in the percentage of small particles. However with more seed, the large particle volume fraction is greater than in the base case. The effect of increasing initial initiator concentration with respect to that of the base case results in an increase in the size of the large particles and a delay in the birth of second generation particles. These two effects predicted by the model can be qualitatively explained by the increase in radical flux into the seed particles. Finally, the effect of seed particle size on the final PSD of the latex was investigated. The model predicts a slower growth rate of large particles and a smaller fraction of the small particles. These differences with respect to the base case can be explained by a lower micelle concentration and a lower radical flux due to the increase in the surface area of the seed.

A model similar to Min and Ray's was used by Thompson and Stevens (1977) to study continuous stirred tank reactors (CSTRs). These authors cast their model in dimensionless variable form and solved the population balance equations at steady state. Some of the model predictions were compared with experimental data from Stevens and Funderbuck (1972). The result of this comparison was a reasonable agreement between theory and experiments. The model was used subsequently to analyze the effects of two key operational variables on the PSD of the latex. The authors found that: (1) an increase in the ratio of feed concentrations of initiator and emulsifier narrows the PSD, whereas a decrease in the same variable broadens the PSD and produces more large particles; (2) in their particular study, variations in the average residence time produce little variation in the overall PSD. However, they pointed out that for different model parameters the conclusion may well not be the same. In general, a longer residence time should produce a broader PSD.

More recently, Kanetakis et al. (1984) investigated procedures for modifying the PSD in CSTR trains used in the manufacture of cold styrene butadiene rubber (SBR). Under normal operation a CSTR train produces PSDs that become narrower along the train. Using steady-state models these authors proposed two modifications to the normal operation in order to broaden the PSD of the final latex. One is to feed excess emulsifier to an intermediate reactor in the train and thus produce a second particle generation. The second is to divert some of the latex leaving the first reactor to an intermediate reactor in the train. The same steady-state models were used by these authors to optimize with respect to residence time the number of particles generated in the first reactor of a train.

Sustained oscillations is an important phenomenon in continuous emulsion polymerization reactors. This undesired behavior can lead to emulsifier levels that are too small to adequately cover polymer particles with the result that excessive agglomeration and fouling can occur. Furthermore, polymers with excessive branching and poor processability can result when monomer systems where long chain branching occurs are subject to excursions to high polymer concentrations due to the cycling behavior of conversion. When oscillations are present, all variables in the reactor will have an oscillatory behavior due to the interrelations among them. However, in order to attack the problem of suppressing these oscillations, the physical phenomena that originates them must be clearly identified. According to the age distribution model of Kiparissides et al. (1979) and Pollock et al. (1981), oscillations in systems following Case I kinetics ($\bar{i} \ll 1$) are due to the periodic formation and depletion of emulsifier micelles, which lead to short periods of particle generation followed by long periods where no nucleation occurs. This periodic nucleation leads to the formation of discrete particle populations with concomitant oscillations in polymerization rates and conversion. Oscillations in Case II systems ($\bar{i} = 1/2$), when present, are likely due to the consequence of strong diffusion-controlled termination. When particle nucleation phenomena, as is normally the case, are responsible for sustained oscillations, the elimination of such oscillations becomes a problem of particle-size control. However, although the use of advanced control schemes can damp these oscillations, it cannot eliminate them using levels of soap that do not violate economic constrains and latex contamination limits. For these reasons, the key to solve this problem is in the redesign of the process, as suggested by several authors. In all cases the inclusion of a small preliminary seeding reactor was the proposed solution. For example, Greene et al. (1976), Omi et al. (1969), Ueda et al. (1970), and Nomura and Harada (1981) based their redesigns on the inclusion of a tubular reactor to seed the CSTR train. A CSTR train with a CSTR seeder was designed by Pollock et al. (1981) using a comprehensive dynamic model of the train. The novel configuration consists of a very small seeding CSTR to which only a portion of the monomer and water is fed, and the remainder is being fed to a second or subsequent large reactor in the train. The idea of a configuration like this is to make the nucleation step totally take place in the first very small reactor in which the concentrations of initiator and emulsifier are kept high. In this way the large volume reactors in the train are just used for particle growth. Under this new configuration, the flexibility to control particle size as well as all the important variables that influence the quality of the latex is greatly increased. This 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.

Controlling PSD

The work of Gordon and Weidner (1981) represents a very interesting attempt to control PSD. Using calorimetric principles the authors followed the extent of PVC emulsion polymerization by calculating conversion. Initiator and emulsifier were continuously fed in the reactor. An algorithm (not presented in the publication) quantifying the effect of emulsifier on the PSD was used to control PSD. Although this work seems to be the only existing attempt to control the PSD in a closed-loop fashion, our opinion is that conversion was used as a reference base to detect the formation of new particles and accordingly manipulate the emulsifier addition so that further addition is avoided.

Another interesting development is the recent work of Tang et al. (1991). The authors studied the effects of different monomer addition policies in a seeded polymerization of n-Butyl Acrylate using conventional emulsion and miniemulsion polymerizations. The seeded semicontinuous emulsion polymerization in which the feed stream was a miniemulsion produced a large number of new particles as compared to a small amount formed when a neat monomer and an aqueous solution of surfactant were added over a period of time. The development of the PSD in the two cases was totally different. Provided that polymerization in monomer droplets (the underlying process in miniemulsion polymerization) is quantified and incorporated in the existing modeling framework of emulsion polymerization, miniemulsions can be used to affect and eventually control the PSD.

The problem of PSD control in the feedback sense presents a formidable task. Total control of all the mechanisms determining the PSD development has not been demonstrated. Particle breakage and particle coalescence are extremely difficult to model. Homogeneous nucleation and nucleation in droplets are still under investigation. The only processes that can be used to influence PSD in a controlled fashion are the micellar nucleation and particle growth. Thus, PSD control at the moment seems to be feasible in systems where micellar nucleation is the predominant particle formation mechanism. Successful control in this case would require proper recipe formulation and design, so that the effect of the "uncontrolled" processes is minimized. While the effect of changing the duration of the nucleation stage has been studied to some extent, the impact of controlling particle growth on PSD is not yet very clear.

Micellar particle nucleation can be controlled by manipulation of the emulsifier and/or initiator feeds. Delaying the addition of these ingredients will extend the duration of the nucleation stage and will lead to broader or multimodal PSDs (secondary nucleation). However, since the problem is a distributed control problem (control of number of particles distributed over size) care must be exercised in the formulation of the control objective. With an infinite-dimensional problem, the issue of controllability is raised. Even in the case that on-line measurement of the entire PSD is available, it seems more reasonable to attempt the control of the leading moments of the distribution instead of its entire shape. Alternative control objectives could be to control the absolute or relative breadth of the PSD, the polydispersity index (a function of the 1st, 3rd, and 4th moment), or some of the leading moments independently. In typical distributed parameter systems the manipulated variables are either distributed themselves or applied at the boundary. In the case of PSD, the "boundary" is the smallest possible particle size or the newly initiated micelle. In this context only the emulsifier feed can be considered as a manipulation applied at the boundary. The other available manipulations cannot really be considered either distributed or at the boundary.

Control of Molecular Properties: Molecular Weight

Apart from a safe and economic operation, the objective of the reactor control is to attain acceptable product quality. Except when the final polymer product remains as a latex, as was explained in the previous section, quality is just related to the molecular architecture of the polymer, and it is mainly determined at the synthesis stage. Unlike other simple products, such architecture cannot normally be modified in post polymerization finishing. This is because operations such as fractionation or blending are impossible or costly. Some of the important molecular properties that define the molecular architecture responsible for polymer quality are the chemical nature of repeating units, the MWD in linear homopolymers, the multivariate distribution of molecular weight, the composition and sequence length in copolymers, the degree of chain branching, and the stereo regularity.

The quality of a polymer is normally quantified by variables that measure the properties of the polymer related to its end-use application. Some of these end-use properties are mechanical strength, elastomer relaxation, adhesive tack, melt viscosity, brittleness, flex life, impact strength, drawability, elastic modulus, hardness, softening temperature, tear strength, stress-crack resistance, and adhesive strength. If it is desired to control on-line the quality of the polymer produced, several on-line measurements are needed as well as a mathematical model that relates the product quality variables to the measured variables. Mathematical models presently available often relate the operating and measured variables of the process to the fundamental molecular variables (such as composition, molecular weight, particle size) of the polymer and not directly to its end-use properties. In most cases on-line measurements directly related to end-use properties are not available. Thus, the on-line control problem becomes one of specifying as set points one or a set of molecular properties that correspond to the desired set of end-use properties.

Even this indirect solution is not a trivial problem, by specifying a group of molecular properties that hopefully will give the desired end-use variables. In many cases a relationship between molecular and end-use properties is simply not available. Normally qualitative correlations are easier to find. For example, it is known that the loss modulus curve of a homopolymer reflects the shape of its MWD. This was quantitatively analyzed by Misra et al. (1983) by comparing the MWDs and the dynamic mechanical spectra of poly-butyl acrylate latex films. The results were consistent with the qualitative knowledge. For polymer with larger amounts of low-molecular-weight molecules (semicontinuous polymerization of butyl acrylate (BuA)) the loss modulus curve showed a small shoulder at low temperatures. Furthermore, the loss modulus curve was broader for polymers produced semicontinuously than for those produced in batch, in the same way that the MWD of the semicontinuous polymer was broader than that of the batch polymer.

The molecular weight of polymers is directly related to the polymer chain length and thus associated with all those elementary processes by which a chain is created, grows, or ceases to grow. From the general kinetic scheme for free-radical polymerization, termination and transfer reactions play an important role in the determination of the molecular weight distribution. Both termination or transfer suspend the growth of a particular polymer chain, but the two types of reactions have a different impact on the system's kinetic behavior. Transfer reactions do not change the total number of radicals in the system, and therefore usually do not influence the rate of polymerization. As a result, with the exception of transfer to dead polymer, they cause a shift in the MWD of the polymer to lower molecular weights. On the other hand, transfer to dead polymer can lead to branching causing a shift to higher molecular weights. The type of termination reaction is also significant. Termination by combination results in the production of a long chain at the expense of two shorter ones. Termination by disproportionation produces one shorter and one longer chain. The relative importance of termination mechanisms and transfer reactions determines to a large extent the MWD development.

MWD control has been attempted for several free radical homogeneous polymerization systems (Hoffman et al., 1964; Beste and Hall, 1966; Hicks et al., 1969; Sacks et al., 1972; Chen and Jeng, 1978, 1991; Schmidt and Ray, 1981; Tanner et al., 1987; Peterson et al., 1992; Soroush and Kravaris, 1992).

In emulsion polymerization the MWD development becomes far more complicated by the compartmentalized nature of the system. In addition to the processes considered up to now, one should include the radical entry to the particles and the radical exit from them. The latter one presents another chain growth suspension process. If termination reactions are the controlling steps of the kinetic mechanism, then the number of particles and their PSD influences the development of the MWD, as they directly influence the radical entry rate per particle. Even if the PSD is known, the specific radical entry mechanism into the particles is required. The modeling of the MWD in this case is particularly complicated, and population balance methods must be employed to calculate the polymer PSD, and to determine its effect on the polymerization (Min and Ray, 1974). However, it is generally accepted that the effect of compartmentalization is to broaden significantly the PSD if termination is dominant (Katz et al., 1969; Napper et al., 1981) and, with termination as controlling step, a broader PSD always leads to a broader MWD.

The MWD is decoupled from the PSD, if transfer reactions take place with much higher frequency than termination reactions. MW development is controlled by transfer reactions and is independent of particle size, number, and distribution. Clearly, if transfer reactions occur much more frequently than termination reactions, the rates at which radicals enter and exit the particles (that depend strongly on the PSD) become unimportant for the development of the MWD because of the availability of radicals in the particle. These radicals instead of being terminated are being transferred to other molecules where they will continue growing. The modeling of MWD is much simpler in the case of transfer to monomer or transfer agents, and compartmentalization has no major effect on the breadth of the MWD (Gerrens, 1959; Sundberg and Eliassen, 1971; Napper et al., 1981). Fortunately, for most commercial recipes, chain transfer agents are used extensively for MW control. However, when chain transfer to polymer is important, long chain branching occurs and the modeling of MWD is very involved. MWD is relatively broad when significant long chain branching is present and the breadth increases with conversion.

As mentioned before, PSD is not of interest to specify end-use properties of the polymer when the final product is not the polymer latex. However, PSD may have an important influence in determining MW, as was investigated by Min and Ray (1978). These authors found through a simulated study, that for the batch polymerization of MMA without chain transfer control, the MW of the polymer produced depends strongly on the particle size and is thus expected to be influenced by the shape of the PSD. The model used in this simulation had been tested in its ability to predict the MW using data of Gerrens (1963, 1964). The detailed simulation showed that at low conversions the MW is more dependent on particle size than at high conversions. This result is not valid for all monomers, as shown by Abdel-Alim and Hamielec (1972) for the polyvinyl chloride system. In this case, since the rate of chain transfer from growing polymer radicals to VC monomer is very fast compared with the rate of termination, the MWD is independent of the latex PSD. Another case in which particle size does not influence MW is in the polymerization of styrene. Sundberg and Eliassen (1971) predicted a MWD of the Flory type with a polydispersity of 2 for the polymerization of styrene in a well mixed batch reactor. These authors considered that termination takes place by chain transfer to monomer or instantaneous recombination. They concluded that their results were the same whether or not the PSD had been considered, and that the value of the chain transfer to monomer rate constant has a significant effect upon both the average MW and the MWD. Under the influence of the experimentally confirmed chain transfer to monomer mechanism, a dependence of about the 1/5 power of the emulsifier concentration and of $<1/5$ power of the reciprocal of the initator concentration were predicted.

One of the first to study the MWDs of emulsion polymers produced in CSTRs were DeGraff and Poehlein (1971). In their work they extended the results of Katz et al. (1969) to include the polydisperse latex product of a CSTR. This polydispersity in particle sizes, as well as the stochastic process for the entry of free radicals into particles of the same size inherent to the residence time distribution that develops in CSTRs, contribute to the formation of a distinctive distribution of molecular weights in this type of reactor. The model developed in this work predicts the influence of initiation rate, surfactant concentration, and mean residence time on MW. The linear decrease of the number average MW with rate of initiation predicted by the model is in agreement with the experimental data of styrene obtained by the same authors. The model also predicts the experimentally observed increase of the number and weight average MWs with surfactant concentration. The agreement between experiment and theory for the two average MWs at different mean residence times is only good at high values of this parameter. Poor predictions at low residence times could not be completely explained by the authors.

A mathematical formulation describing the evolution of the number distribution of the MW was given by Lichti et al. (1980). They considered the microscopic events of free radical entry, exit, chain annihilation, bimolecular termination (by both combination and disproportionation), and chain transfer. The authors point out the possibility of using their approach to prescribe experimental conditions to grow a desired MWD. Also, a study of the sensitivity of the MWD to different kinetic mechanisms was performed with the following results:

- If the polymer chains stopped growing because of the transfer of their free radical activity (either to monomer or some chain transfer agent), the MWD will be monotonically decreasing.
- If in contrast the dominant mechanism is bimolecular termination by combination, the MWD will exhibit a single maximum.
- If disproportionation is dominant, the MWD of the shorter of the two chains involved will differ significantly from that of the longer, although the overall MWD will still be monotonically decreasing.
- The polydispersity of the MWD is found to be significantly increased in emulsion polymerization compared to that in bulk systems irrespective of whether bimolecular termination occurs by combination or disproportionation. Only if chain transfer is a dominant chain stopping mechanism, the polydispersity is relatively unaffected by the compartmentalized nature of emulsion polymerization.

Although only interval II of the polymerization was taken into account, the authors consider that an extension to interval III offers no insurmountable difficulties.

The control of the MW and branching frequency in CSTR trains can be achieved by manipulating the feed rates of the chain transfer agent and the split of monomer feeds between the first and subsequent reactors. Control policies based on these approaches have been investigated through computer simulation of the steady-state model of a latex reactor train used in the manufacture of cold SBR (Hamielec et al., 1983; Kanetakis et al., 1984). These simulations showed that, for instance, changing the split from 40% of the monomer/water entering the seeding reactor to only 10%, the MW and branching frequency are increased.

Control of Molecular Properties: Copolymer Composition

Early investigations of the course of batch free-radical copolymerization systems pointed out the problem of compositional drift encountered, particularly when the participating monomers presented a wide difference in their reactivity ratios. This occurs in response to the fact that the relative supply of the more reactive monomer becomes depleted as the reaction proceeds. The resulting drift gives rise to a copolymer composition distribution (CCD) ranging from the copolymer composition formed by the initial mixture to the composition formed in the final stages of the reaction. Homogeneous polymerization (bulk or solution) is used to produce many of the common polymers and presents certainly less modeling problems than those encountered in heterogeneous polymerization. Thus, it is not surprising that early efforts, as well as many recent investigations, addressed the copolymer composition control problem in homogeneous polymerization, and particularly in solution (Hanna, 1957; Ray and Gall, 1969; Tsoukas, 1980; Tirrell and Gromley, 1981; Pittman-Bejger, 1982; Johnson et al., 1982; Hamielec and MacGregor, 1983). Emulsion copolymerization processes, while being commercially very important, are by far more difficult to model. In fact, several modeling problems in emulsion polymerization are still pending for solution.

Kinetics in semicontinuous emulsion polymerization: reaction rate "steady state" under starved conditions

The problem of compositional drift in emulsion copolymerization systems received less attention in the academic community, mainly because of the complex kinetics and numerous phenomena involved during the course of these processes. The delayed addition of the most reactive monomer has been recognized as a common denominator, upon which all the efforts to control composition were based. Thus, semicontinuous operation has been almost the underlying principle in all approaches presented.

Early kinetic studies of semicontinuous emulsion homopolymerization processes with constant monomer feed rates concluded with the observation that, under certain conditions, the rate of polymerization assumes a constant value (Wessling, 1968; Gerrens, 1969; Wessling and Gibbs, 1973; Bataille et al., 1978). If the monomer addition flow rate is large enough to maintain the saturation value of monomer concentration in the latex particles, then the rate of polymerization is independent of the addition rate (flooded region). If this concentration falls below the saturation value, then the polymerization rate approaches a constant value which depends on the monomer addition rate (starved region). Wessling's treatment (1968) predicted that at the steady-state conditions the rate of polymerization R (mol/s) and the monomer feed rate F (mol/s) will follow the relationship $1/R = G + 1/F$, where G is a constant. In the case of fixed-radical concentration, Wessling's analysis predicted $R = F$. Gerrens' results (1969) indicated in general that $R = sF$ with $s = 1$. In a followup work, Wessling and Gibbs (1973) reported the same results with $s = 0.91$. Bataille et al. (1978) confirmed the reciprocal relationship proposed by Wessling.

On the other hand, the same behavior was reported for emulsion copolymer systems (Snuparek, 1972; Snuparek and Krska, 1976, 1977; Snuparek and Kaspar, 1981). The conducted studies confirmed the appearance of the steady-state for copolymer systems and verified the relationship $R = F$ with $s = 1$. They also reported that at a sufficiently low feeding rate, the copolymer composition equals the ratio of monomers in the emulsion feed. Their analysis showed that this result may be applicable to ternary systems as well (Snuparek and Krska, 1977). Recently (Dimitratos et al., 1990), a theoretical analysis with experimental support of the appearance of the steady state in emulsion copolymer systems was presented. The authors concluded that the individual consumption rates of both monomers participating in the copolymerization process assume a constant value if the monomer addition rate is kept constant. These consumption rates depend linearly on the monomer addition rate with a slope of unity. The analysis presented arguments for a universal applicability of the relationship $R = F$ under different experimental conditions.

Impact of monomer addition to composition and product homogeneity in emulsion copolymerization: early approaches to "control" composition and homogeneity

The above mentioned observations resulted in empirical approaches for composition control in emulsion copolymerization, which consisted of the precursor of the contemporary attempts to address the issue. Namely, since a particular correlation between constant monomer feed rates and resulting constant monomer consumption rates can be derived, compositionally uniform copolymers can be obtained by prespecified constant feed policies. Moreover, it was recognized that the issue of composition control, and thus the method of monomer addition, was directly linked to copolymer homogeneity and product performance. An early attempt to address the issue of copolymer homogeneity in emulsion copolymerization was presented by Chujo et al. (1969). Their work was mostly oriented to examining the effects of various feed policies on the product quality rather than investigating the kinetics of the process. The authors concluded that homogeneous copolymers (chain-chain homogeneity) were obtained by continuous monomer addition methods and heterogeneous products by the initial addition of total monomers or stepwise monomer addition methods. The heterogeneity was deduced from characterization and dynamic viscoelasticity. The first reported attempt to produce constant composition emulsion copolymers was made by Pichot et al. (1978). The authors, using the reactivity ratios, calculated a program for the addition of both monomers, so that the initial feed of monomers was kept constant. The monomer addition was carried out in a stepwise mode, fixed but different for the two monomers intervals. The constancy of composition was checked by gas chromatography and acidimetric determination. The compositions were actually found to be constant with a maximum deviation of about 5%. No systematic drift in composition was observed. Examination of the microstructure (composition and sequence distribution) of copolymers prepared with constant monomer feed rates (Pichot et al., 1981) confirmed the homogeneity of the products obtained. Similar conclusions were reached by Misra et al. (1979, 1983) and El-Aasser et al. (1983), who investigated a broad spectrum of bulk, surface, colloidal, morphological, and mechanical properties and found that the comonomer composition and the method of monomer addition have a remarkable effect on many properties of the final product.

The experience gained by studying the kinetic effects and the impact on the product quality of various monomer addition methods in semicontinuous emulsion copolymerization of many binary systems prepared the ground for addressing the issue of actually controlling composition and related properties of copolymer systems. However, several unresolved problems are still presenting major difficulties in achieving such a goal.

Issues in controlling composition in emulsion copolymerization

Despite the plethora of existing studies and the advances in emulsion polymerization modeling, the problem of composition control was rigorously addressed only during the last decade. The advent of computer and sensor technology made possible the implementation of elaborate algorithms and the on-line determination of important process variables. On the other hand, it was greatly understood that the solution to the problem requires the merging of expertise from different fields. The control engineer for an emulsion polymerization process requires a deep understanding of the process itself and expertise in the existing specialized sensor technology. The engineer must work closely with the chemist and the emulsion polymers expert to take into account the idiosyncrasies of the particular system and its recipe.

In general the composition control problem (when treated as a single objective) can be formulated as a trajectory tracking problem. In homogeneous copolymerization and when the control goal reduces to maintain a constant instantaneous composition, the problem is disjoint (Denn, 1969), and the optimal monomer feed profile admits an analysis solution, which can be derived from the material balances and the reaction rate expressions. The situation is by far more complicated in emulsion polymerization because of the compartmentalized nature of the system.

Assuming isothermal operation, the control objective is to follow a function of two of the states of the system, and as a result only one manipulated variable is necessary. If both monomer feed rates are used, then the system will be overdetermined. One way of addressing this problem is to fix the feed rate for one of the monomers, using heat removal considerations to meet the cooling requirements of the reactor. This is very important in industrial-scale polymerizations, where the highly exothermic reactions and the size of the reactors call for the use of the inlet monomer streams as means for temperature control. Otherwise, one of the monomer feed rates can be fixed to a specific value (design parameter) using production rate considerations. A third option is to charge initially into the reactor the entire amount of one of the monomers and part of the other, which accordingly is used for manipulation. A thorough investigation of the controllability in every scheme will result in the conclusion that the faster (more reactive) monomer should be used for manipulation. In principle, it is possible to use initially for manipulation the less reactive monomer. However, switching to the manipulation of the more reactive one will be necessary during the final stages of the process. Caution should be exercised in systems with azeotropic behavior, where the apparently more reactive monomer is not the same above and below the azeotrope.

The initial charge of the reactor and the monomer amount intended to be fed during the entire course of the reaction may have an important impact on the compositional drift. Calculation of the appropriate proportions involves knowledge of the partition coefficients of the monomers or the system's thermodynamic behavior. In general the initial charge should provide a monomer molar ratio at the reaction site capable of producing the desired copolymer composition. The total monomer amounts for addition (if both monomers are fed) will not be in the same proportion as the one derived from the desired copolymer composition. If, for example, the desired copolymer composition is 80:20, the proportion of the monomer amounts for addition will not be the same.

While the above mentioned considerations can be taken into account, the rigorous design of a composition control system in emulsion copolymerization faces several problems, as discussed in the following.

Particle Growth and the Control Objective. In emulsion copolymerization, copolymer composition, chain sequence, and particle morphology have a strong influence on the performance of the polymer product. All three properties are closely related, and this sometimes introduces confusion in defining the control objectives and verifying the claims made for the efficiency of a control scheme.

Chain sequence refers to the arrangement of monomer units bounded as polymer in a polymer chain. Thus, one distinguishes between block copolymers A-A-A-A-. . .-A-B-B-B-. . .-B from purely alternating copolymers of the form A-B-A-B-. . .B-A-B-A. Chains of different monomer unit sequences can still contain same overall chemical composition. In this way copolymer composition is defined at the polymer chain level, and a copolymer made of chains having the same chemical composition is considered a homogeneous copolymer (chain-chain homogeneity). The way a chain grows determines both the chain sequence and the copolymer composition. Of course in reality, one has to deal with an entire distribution of copolymer compositions and chain sequences, which are affected by the inherently random nature of the polymerization reaction in the microscopic scale. While this effect is beyond any control, for the copolymer composition distribution it is small enough and can be ignored for long polymer chains (Bamford et al., 1958).

In emulsion polymerization, where the main loci of the reaction is in the latex particles, there are some additional factors to be considered besides the way a chain grows. The conformational properties of the polymer chains and their interactions with the particle-water interphase are the primary factors controlling the particle morphology. Largely block copolymer chains of the same chemical composition can be arranged in a latex particle in such a way that distinct domains appear. These domains are made of polymer segments composed of a single type of monomer unit. This introduces structure to a polymer particle and depending on the structure a particular morphology is assumed. Thus, compositionally homogeneous copolymers in emulsion copolymerization can be found in heterogeneous latex particle (structured latexes).

Structure formation can occur either due to the specific mechanism of polymerization, for instance, the shell polymer forms on the surface of the core particle, or it forms during or after polymerization as a result of phase separation. Technologically, the most significant structured latex is the core-shell type with a rubbery core and a glassy shell. This type generally represents high impact strength polymers.

In most cases the control objective is the minimization of the breadth of the copolymer composition distribution. Compositional uniformity or homogeneity refers to chain-chain homogeneity and is usually achieved by maintaining the instantaneous copolymer composition constant. This corresponds to keeping constant the ratio of the individual monomer consumption rates. There are several ways to formulate such an objective. Minimization of the instantaneous copolymer composition deviation or the amount of polymer that deviates from the desired instantaneous copolymer composition are some of the candidate formulations.

On-line Measurement of Important Process Variables. The issue of composition control in emulsion copolymerization becomes more complicated by the fact that most of the variables required to resolve problems of the type presented previously cannot be measured on-line. The composition of the monomer resident in the polymer particles can only be determined off-line by a multistage method requiring sample centrifugation, phase separation, and chromatographic analysis of the aqueous phase. In this indirect way the average monomer concentration in the polymer particles can be calculated, provided that the total particle volume is known and a model for monomer distribution within the particle volume is assumed. The average number of radicals per particle, again, can be measured only off-line by electron paramagnetic or electron spin resonance spectroscopy. Otherwise, it can be inferred by solving the reaction rate expression, provided that the involved process variables and the reaction rate are known. The number of particles in the system can be calculated via measurement of an average particle size obtained by light scattering methods or electron microscopy. This calculation requires again the total volume of the particle phase.

The instantaneous chemical composition of the copolymer can be calculated via the cumulative chemical composition obtained by infrared or nuclear magnetic resonance spectroscopy. Other properties such as chain sequence or particle homogeneity are deduced similarly by expensive, tedious, and time-consuming off-line techniques. The lack of on-line measurement of the controlled variable is a severe limitation to the design of an effective control system. Open-loop policies suffer from modeling limitations and require prior model identification or iterative off-line optimization before they become satisfactory. A solution to this problem can be sought through on-line estimation. Observability of copolymer composition or other ways to be inferred on-line are discussed in the section of on-line measurements in emulsion polymerization.

Mixing Effects. As mentioned earlier, mixing is very important in semicontinuous operation, because it directly influences the distribution of copolymerization compositions. Homogeneity of the continuous phase is generally required to avoid unexpected deviations from the anticipated monomer mixture composition in the latex particles. This is particularly important for the relatively water insoluble monomers. Agitation rate should not only provide enough mixing to promote the necessary mass transfer and ensure the homogeneity of the continuous phase but also avoid shear coagulation by inducing velocity gradients in the reactor. This might be a problem when fast addition rates of neat monomer are used because they might often cause bulk or droplet polymerization in commercial reactors.

Recent advances in copolymer composition control in emulsion copolymerization

Monomer Partitioning, Thermodynamic Modeling, and Feedback Control. Guyot et al. (1981) implemented a feedback scheme based on residual monomer analysis by gas chromatography to produce constant-composition copolymers in emulsion polymerization. The strategy keeps the molar ratio of the monomers in the reactor constant by manipulating the addition rate of one of the monomers. The method was applied to the styrene-acrylonitrile emulsion copolymerization system, but the results showed a continuous drift of the copolymer composition instead of the expected constant copolymer composition. The authors attributed this to a large acrylonitrile amount, which remained dissolved in the water phase, and proposed the use of thermodynamic modeling to predict the monomer distribution among the different phases. Provided that information on the monomer partitioning are available, the compositional drift can be eliminated by a similar feedback scheme, which keeps the molar ratio of the monomers in the latex particles constant.

Variable Composition via the Power Feed Method. The so called "power feed" method was reported as an approach for continuously changing the composition of the monomer mix fed into a reactor to produce copolymers whose instantaneous compositions vary as the polymerization proceeds. Bassett and Hoy (1981) stressed the advantages of using variable composition operations to achieve desired product properties. They found that nonuniform copolymers exhibit broad transitions in dynamic mechanical and stress relaxation measurements and claimed that their method can be used to control particle morphology, viscosity, functional group location, and molecular weight.

The method employs a number of feed tanks (at least two) in series which contain proper monomer mixtures. The feed from one tank to the next and from the last to the polymerization reactor are kept constant but at different rates. However, the intermediate monomer concentrations vary with time. As a result, the polymerization reactor is fed with a stream of variable monomer concentration. Since the variation is a power function of time, the process is named power feed.

Utilizing Reliable Models for Model-Based Control Policies. Broadhead et al. (1985) developed a dynamic model for the emulsion copolymerization of styrene with butadiene in batch, semibatch, and continuous processes. Only micellar nucleation was considered with nucleation rates calculated using the collision theory and an empirical capture efficiency factor. The average number of radicals per particle is calculated using the Stockmayer-O'Toole solution of the Smith-Ewart recursion equations. The Marten-Hamielec free-volume theory is employed to model the gel effect. The model developed was validated and used to obtain constant or time-varying open-loop feed policies to obtain copolymers with uniform composition. The authors considered two basic policies and the third one was a combination of the first two. According to the first policy all of the slower monomer and part of the faster monomer are added to the reactor, and the faster is then fed in with a controlled/time-varying feed rate. The control law requires that the molar ratio of the monomers in the polymerizing medium is kept constant. The second policy employs time-varying feed rates for both monomers, and in the initial charge of the reactor parts of both monomers are added. The condition imposed in this case was that the concentrations of both monomers are kept constant during the course of the run. The combined policy consists of two stages. The first stage is essentially according to the first policy, and the second is a variation of the second policy using constant feed rate for one of the monomers.

A different approach based again on an identified kinetic model was presented by Oliveres et al. (1988). The authors presented a feedback scheme to minimize the copolymer composition drift in the emulsion copolymerization of styrene with acrylonitrile based on headspace analysis. In an earlier work, Alonso et al. (1987) had related vapor compositions to copolymer compositions by identifying the parameters that define the multiple-phase equilibria (liquid-liquid-vapor). The control strategy consists of a model-based predictive (open-loop) and corrective (feedback) part.

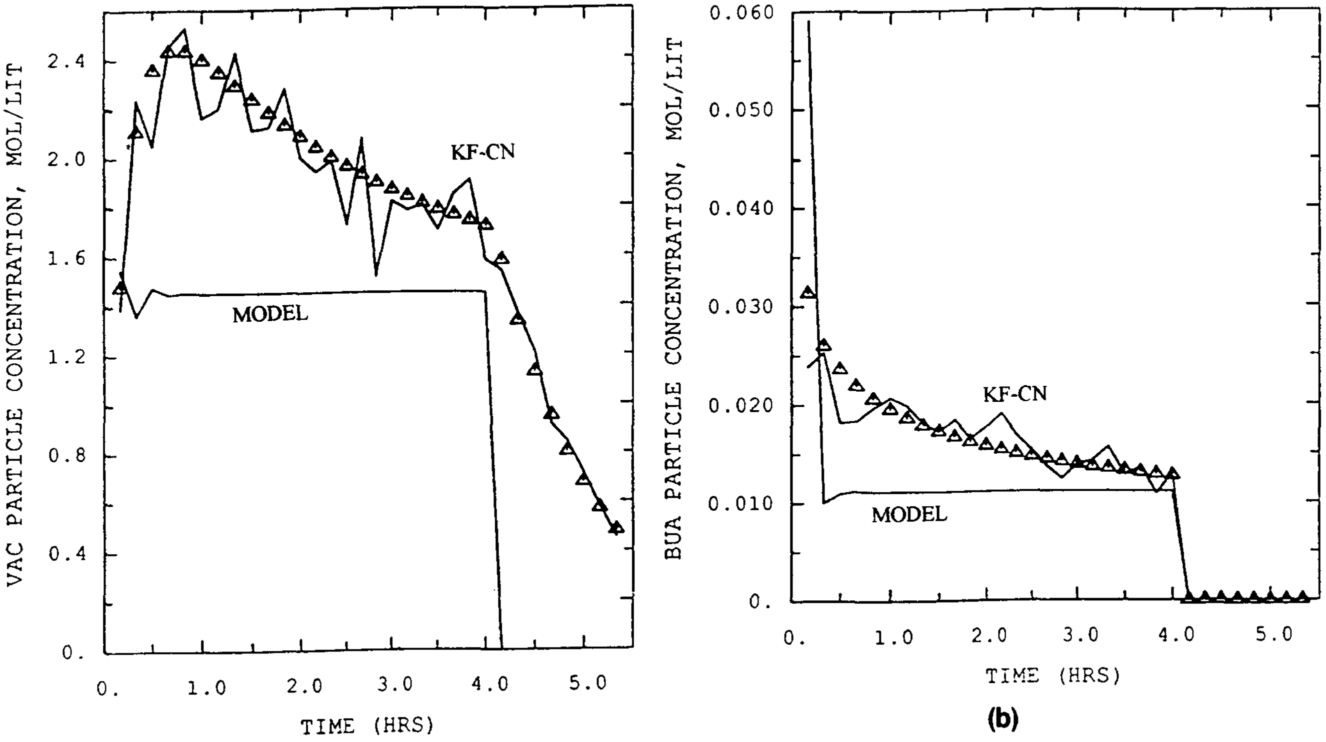
On-Line Kalman Filtering and Feedforward/Feedback Control with Inaccurate Models and Limited Measurements. Although few works have been published for emulsion copolymerization systems, Kalman filtering has been efficiently used in the past for state estimation in polymerization reactors. Choquette et al. (1970) used an extended Kalman filter for state estimation and an optimal control policy derived from dynamic programming methods. Their control strategy was developed for an industrial (Polysar's Butyl-Rubber Plant, Sarnia, Ontario, Canada) polymerization multireactor system, but no further details about the nature of the process were reported. Jo and Bankoff (1976) studied the problem of digital monitoring and estimation of polymerization reactors. They investigated both theoretically and experimentally the performance of various Kalman filters on the free-radical solution polymerization of vinyl acetate. Their conclusions were similar to those of previous studies, indicating that poor initial estimates of the state variables or of the state covariance matrix could easily be tolerated, but too small estimates of the process noise covariance matrix caused the filter to diverge. Ahlberg and Cheyne (1979) developed and implemented an adaptive control strategy for an industrial (Polysar Butyl-Rubber Plant) continuous solution polymerization reactor for producing butyl synthetic rubber. The quality control goal was to minimize the standard deviation of finished product quality (rubber viscosity). Control action was calculated by dynamic programming, primarily because measurements were periodic. The state of the process was described by a process model updated by an extended Kalman filter. Kalman filtering was employed because of the anticipated time-varying nature of the model parameters, which were treated as state variables in the filter. Several benefits and process improvements were reported from this application. Kiparissides et al. (1981) developed a suboptimal stochastic control scheme for a continuous latex reactor to minimize the effects of process disturbances and possible sustained oscillations. An extended Kalman filter was used to estimate the reactor states, and a quadratic objective functional was used to derive the suboptimal feedback control law. MacGregor et al. (1986) discussed the problem of state estimation for polymerization reactors and employed an extended Kalman filter using on-line density measurements to track conversion and particle growth states for the emulsion polymerization of styrene in batch and continuous reactors.

Dimitratos et al. (1989a,b, 1991) developed and tested experimentally different Kalman filter designs with the purpose of compensating for modeling errors and few and corrupted measurements in the semicontinuous emulsion copolymerization of vinyl acetate and butyl acrylate. The modeling limitations mainly due to using constant partition coefficients, and an average number of radicals per particle were in this way overcome. The Kalman filters estimated directly the monomer concentrations in the polymer particles (see Figure 2), variables that cannot be directly measured but are important for composition control. Essentially, the scheme provided an estimate of the individual monomer consumption rates, so that the feeds can be controlled to achieve constant instantaneous copolymer composition and thus compositionally uniform particles. A simple nonlinear feedforward/feedback controller operating in a deterministic way on the available state estimates was experimentally tested and proven capable of drastically minimizing the compositional drift. The control policy involved the manipulation of the faster monomer and the constant feed of the slower one. The superiority of the method to open-loop methods (with the same model) was demonstrated. On the other hand, an open-loop controller based on the best model developed was able to almost eliminate the drift, but such a model is not usually available for a typical polymerization system. The authors concluded that a control strategy utilizing an existing process model and a standard estimation scheme can drastically improve the product quality. The advantage of this approach is that it mimimizes the modeling effort and the extensive experimentation, which might be necessary to obtain numerous parameters involved in a highly sophisticated modeling framework. As a result, a less detailed process model might be used along with an estimation scheme to provide the process monitoring necessary for improved quality control or process safety.

A similar approach involving a reiterated extended Kalman filter, an open-loop controller, and a feedback controller was proposed by Kozub and MacGregor (1992a). The authors reported successful results in the control of instantaneous copolymer composition, total conversion, and instanteous weight average molecular weight of a simulated styrene/butadiene semibatch emulsion polymerization reactor. In a second article (Kozub and MacGregor, 1992b), the authors presented a comparison of different Kalman filter approaches for tracking semibatch emulsion polymerizations. Their simulation studies with the same emulsion system (styrene/butadiene) demonstrated the importance of including nonstationary disturbance states.

Predicting the Average Number of Radicals per Particle by Batch-to-Batch Optimization. To overcome the difficulty of predicting $\bar{i}$ for copolymer composition control purposes, the application of an iterative approach has been proposed (Arzamendi and Asua, 1990; Arzamendi et al., 1991). According to this method, each one of a series of semicontinuous runs is used to correlate $\bar{i}$ with the volume fraction of polymer in the latex particles. The time dependency of $\bar{i}(t)$ obtained from each run is subsequently used to calculate the monomer feed control policy for the next run. The method converges in two or three iterations and a satisfactory open-loop control policy is thus obtained. This semiempirical approach to obtain an "optimal" open-loop monomer feed policy has been successfully employed to the emulsion copolymer systems of methyl acrylate-vinyl acetate (Arzamendi and Asua, 1990) and ethyl acrylate-methyl methacrylate (Arzamendi et al., 1991). Along the same lines is the work of van Doremaele (1990) with the styrene-methyl acrylate copolymer system.

In a followup work Arzamendi and Asua (1991) considered the problem of copolymer composition control in reactors with



(a)

(b)

Figure 2. On-line estimation of monomer concentrations in the polymer particles of the latex system VAc/BuA by extended Kalman filtering.

Comparison between off-line data (triangles), the model used (MODEL), and the filter performance (KF-CN) (Dimitratos et al., 1991).

limited capacity of heat removal for the emulsion system vinyl acetate and methyl acrylate.

Control of Operational Variables

Reactor stability and dynamics

As control of the end-use properties of the fundamental molecular properties of the produced polymer is an important but challenging task limited by the lack of accurate models and the availability of on-line measurements of the most critical variables, one often resorts in controlling the operational variables. Such variables predominately include the reactor pressure, a measurement related to the conversion of the reacting mixture, and in some cases the reactor pressure. Controlling these operational variables is convenient, because these are easily measurable. Of course, the hope is that their control will minimize the variations in the molecular and the end-use properties of the product. Even though the control of the operational variables is less difficult than the control of the molecular properties, it is by no means a trivial task. As in other exothermic reactors, the interplay between temperature and conversion is a nonlinear one. It can yield a plethora of phenomena that the plant operator will characterize as troublesome or unwanted and will try to avoid them. On the other hand, the university investigator will label them as interesting or peculiar, if not exciting. These phenomena are often linked to the existence of multiple steady states and the associated stability characteristics of the reactor to which we turn our attention at this moment.

Multiple steady states and sustained periodic oscillations under isothermal conditions are present in a variety of emulsion polymerizations when they are carried out in CSTRs. The oscillating behavior particularly has prevented the use of this type of reactor for the production of a broader range of polymer products. A uniform product quality is incompatible with a sustained and sometimes erratic oscillating behavior of the key variables describing the polymerization.

In a previous section we have analyzed reactor oscillations from the point of view of particle-size control. Qualitative explanations of this phenomena, as well as ad hoc solutions to prevent it, were analyzed. Now oscillations and steady-state multiplicity will be studied as a reactor stability problem.

Steady-state multiplicity has been observed in monomers such as styrene and MMA, and has been explained as a consequence of the gel effect. Even quite simple models of the polymerization including the gel effect kinetics have been able to predict multiple steady states (Gerrens et al., 1971; Ley and Gerrens, 1974; Kirillov and Ray, 1978). Kirillov and Ray (1978) developed a mathematical model for the continuous methylacrylate polymerization process to predict multiple steady states, as well as sustained oscillations, for certain operating conditions. The authors managed to simulate the sustained oscillations despite the simplifications introduced in their model. Particle-particle coalescence was neglected and the PSD was handled through the use of moments. Only the zeroth and first moments of each peak were considered. A more comprehensive study, with emphasis on the continuous reactor dynamics and, particularly, the appearance of sustained oscillations, multiple steady states, ignition, and extinction phe-

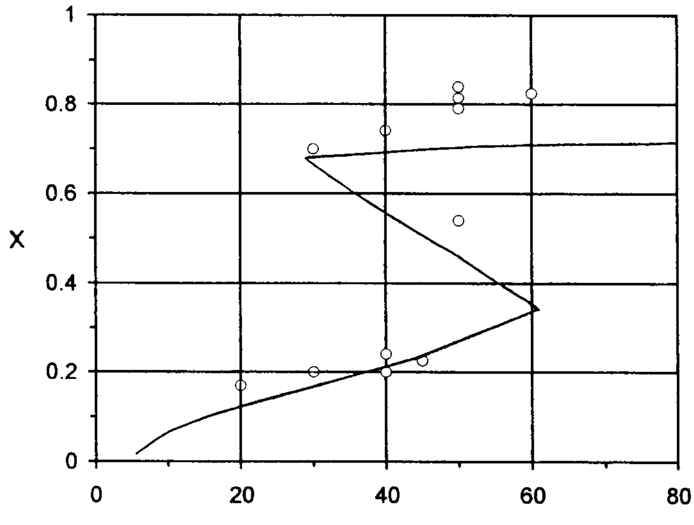


Figure 3. Comparison of model simulation with data of Schork (1981) and Rawlings and Ray (1988).

nomena, was presented recently (Rawlings and Ray, 1988). The authors developed a population balance model for batch and continuous emulsion polymerization reactors accounting explicitly for the PSD. A numerical method for its solution based on orthogonal collocation on finite elements was employed. The birth time of the particles was found to be computationally more attractive as an internal coordinate than the particle size. The authors compared data of Schork (1981) for the polymerization of MMA with predictions obtained with a very detailed model of the polymerization (Rawlings, 1985). Their results are shown in Figure 3. The S-shaped curve predicted by the model using just parameters of MMA from the literature, represents quite well the experimental data. When the reactor is operated isothermally at 40°C, three steady states for polymer conversion are observed in the range of residence times that lies between 50 to 60 min. The locations of the ignition and extinction points are also in agreement with the experiments. In the same work Rawlings and Ray examined the sensitivity of the model to different parameters. Their results corroborated that when the gel effect is not considered (propagation and termination rate parameters are constant), the conversion curve continues to increase monotonically with residence time and no multiplicity can be predicted.

The oscillating behavior observed for most monomers is a more complex phenomenon. Rawlings and Ray (1987a,b) studied the dynamic behavior of emulsion polymerization CSTRs using the structure of the model developed in Rawlings (1985). Two versions of this model were considered. A simplified version retains the essential mechanistic features and the full population balance equation. This version allows an analytical calculation of the main dynamic characteristics of the model and provides insight into the mechanism of the instabilities. A detailed version of the model, which includes all the nonlinear complexities and fine details, was required for quantitative comparison with the experimental data. This detailed model is an excellent tool for the understanding of the stability transitions and bifurcation structures of specific polymer systems.

A dynamic study of the polymerization of MMA was performed using the detailed version of the model (Rawlings and Ray, 1987b) to demonstrate the method proposed to study the stability of the reactor. The example process is the same that produced the S-shaped curve shown in Figure 3. The main feature of the dynamic behavior is the bifurcation to periodic solutions at about 5 min residence time. As a result, most of the lower branches and all of the upper branches of the steady-state curve are unstable. However, because the solutions are bounded, unstable steady states and stable periodic solutions are anticipated for any resident time greater than 5 min. These stable periodic solutions were examined for the lower and upper branches of the steady states (the middle branch is an unstable saddle and has no periodic solutions). For the lower branch, it was found that the model predicts oscillations of very small amplitude in conversion, while the experimental data has ripples of comparable size but not clear oscillations. For the upper branch, although the model predicts an oscillatory behavior, the amplitude of these oscillations is so small that they cannot be verified experimentally by measuring conversion or surfactant level. However, the authors suggest that perhaps an oscillatory behavior in particle size could be seen experimentally in that situation. From their observations, the authors concluded that at least two physical factors determine the stability transition to sustained oscillations. The first factor is the growth rate of the newly formed particles. The smaller this growth rate is, the smaller the residence time at which the transition to sustained oscillations occurs. Growth rate is strongly affected by chain transfer to monomer, chain transfer agents, and impurities. The second factor is the ability of the particles to significantly affect the particle initiation rate before they are washed out of the reactor. For large residence times, the particles have more possibilities to affect the particle initiation rate, increasing the chances of observing oscillatory behaviors.

When the stability analysis is performed with the simplified version of the complete model the same authors (Rawlings and Ray, 1987a) found similar qualitative results. However and because of the simplicity of the model, analytical solutions for the evolution of the main variables could be obtained. These solutions allow one to draw more general conclusions on the behavior of emulsion polymerization reactors. For example, it was theoretically demonstrated that under no circumstances, reactors with Smith-Ewart case II kinetics can oscillate.

Temperature control

Reaction temperature has a direct effect on most of the product properties in emulsion polymerization. Minimization of temperature excursions from the set point (in both isothermal or trajectory-tracking operation) improves product quality and reduces batch to batch variability. However, effective temperature control in large-scale industrial polymerization reactors usually requires large heat-transfer areas. Heat removal is achieved through jacket cooling, internal cooling coils and water cooled baffles, external heat exchangers, and reflux condensers. Provided that a substantial temperature gradient is feasible, jacket cooling may be sufficient for small reactors, where the ratio of the reactor wall heat-transfer area to reaction volume is large enough. As reactors are scaled up in size, the heat generation rate increases proportionally to the volume, but the heat-transfer area through an annular jacket increases to the 0.67 power of the volume ratio.

When a reactor jacket is used for heat removal, the overall heat-transfer coefficient can also fall sharply because of increasing medium viscosity as polymerization proceeds. Polymer buildup (scale) on the heat-transfer surfaces reduces further the heat-transfer coefficient during the course of the reaction and sets a practical and important constraint on the amount of heat that can be removed. This causes the temperature on the reactor wall to decrease. Such temperature decrease might result in polymer "freezing" on the walls and complete loss of convective heat transfer. To account for the changes in the overall heat-transfer coefficient, a base value is obtained (from on-line energy balance) in a clean reactor. Empirical correlations of viscosity as a function of temperature and solids content, and of the film heat-transfer coefficient as a function of medium viscosity at the wall, are derived from experimental data. The overall heat-transfer coefficient is then a function of the film coefficient and a fouling factor.

The use of a cooling coil within the reaction volume increases substantially the heat-transfer area, but it also affects the system hydrodynamics. It can possibly induce coagulation and cause additional scale formation because of poor mixing in the dead spots created around the coil. External heat exchangers are frequently used in emulsion processes when the latex presents good mechanical stability. If foaming is not a problem, reflux condensers can be effective in processes where monomers have large vapor pressure at the reaction temperature.

Batch reactors present the most demanding conditions for heat removal. In semibatch reactors by delaying the addition of the reaction limiting component, the rate of heat generation can be maintained within the cooling capacity of the system. When the feed is cold the effective heat-removal capacity is further increased. Respectively, in continuous reactors a large fraction of the heat generated is removed in the exit stream. However, nonminimum phase behavior can be experienced in when the cold feed is stopped or reduced.

The transient nature of the batch and semibatch processes results in a continuously changing reactor heat load. Minimizing the duration of initial heating and the overshoot to the subsequent constant temperature phase should be one of the control design objectives. This objective is justified not only for the sake of minimizing batch time but also for avoiding the production of higher molecular weight polymer during the heat-up period. Bang-bang policies are employed in this case with an initial heating rate. When temperature reaches a value within the target range a maximum cooling rate policy is applied.

Reactive impurities and changes in heat-transfer coefficient result in batch-to-batch variation of the heat load curves and thus, jacket temperature scheduling is impractical in most cases. In addition to this, the large activation energies in polymer reactions make the heat generation very sensitive to small temperature perturbations. This can be extremely important at high conversions where the cooling capacity of the reactor is reduced because of increased viscosity and scale formation. Peak heat generation is usually several times larger than average, and since the heat-transfer system must be capable of removing heat at the maximum heat generation rate, the heat-transfer system is underutilized for much of the polymerization time. Optimum operation or minimum batch time requires that heat generation rate is always equal to heat removal capacity with some allowance for safety. Thus, temperature trajectories that aim to produce a constant reaction rate with time, or, equivalently, a linear variation of conversion with time, can increase productivity or reduce batch time. However, the resulting nonisothermal operation might be unacceptable due to product quality deterioration or due to difficulties in implementing the appropriate policies. Open-loop policies present uncertainties, and closed-loop policies require a measurement or estimate of the reaction rate.

Most recipes in emulsion polymerization are developed under the assumption of isothermal batch operation. Thus, given the importance of product quality and in most cases the difficulty to quantify the effect of temperature on product quality variables, isothermal operation is frequently the desired operation in the production scale. Given the considerations presented earlier in the section, the problem is that of temperature control in exothermic batch reactors and has been discussed in the literature (such as Marroquin and Luyben, 1972; Hopkins and Alford, 1973; Keyes and Kennedy, 1974; Lake, 1977; Amrehn, 1977; Kiparissides and Shah, 1983; Jutan and Uppal, 1984).

Conversion control

Conversion control or its equivalent, reaction rate control, cannot be analyzed independently of the effects that these variables have on almost all other operational variables, and on the final properties of the produced polymer.

In batch or semibatch polymerization the final conversion at the end of the reaction is just an indicator of how much monomer was depleted and in principle will tell us little about what was produced during the polymerization. This final conversion when related to the total reaction time will determine the reactor's productivity. However, the importance of this last variable only becomes apparent when it is associated with the parameters that determine the quality of the produced polymer, and with safety considerations. Clearly, what is more important in conversion or reaction rate control in batch or semibatch reactors are the trajectories in time of these controlled variables rather than their final values. An example of this is the effect of the conversion profile on the operation of the heat removal system of the reactor. In order to have an efficient operation the heat generation rate at any time should be equal to the heat removal capacity of the system with some allowances for safety. It is, therefore, required that the conversion of monomer vary linearly with time at a rate consistent with the heat removal capacity of the system. Another typical example of the effect of conversion is when two or more monomers participate in the polymerization. In this case as explained in previous sections, one of the typical product specifications is that of a polymer with an homogeneous composition. This can be achieved by operating the reactor semicontinuously using very low flow rates in the monomer feeds. As explained before, this operation will result in reaction rates of the individual monomers that will coincide with their corresponding flow rates, or equivalently in individual conversions that will vary linearly with time. These are just two examples of the effects of overall and individual conversions on important variables related to the polymerization. In a later section we will elaborate more on aspects related to the closed-loop control of conversion and reaction rate as an indirect way of affecting other variables more clearly related to the properties of the final product.

Unlike in discontinuous polymerizations, conversion or reaction rate control in continuous reactors is mostly a regulatory control problem. The conversion at which a reactor or train of reactors is operated has an important effect on almost all the properties of the produced polymer.

Once a conversion value is selected based on operational as well as product quality considerations, the control objective is either to keep this value at set point or to provide a way of changing the desired conversion value to a new prespecified one as quickly as possible with minimum effect on the remaining variables of the process. If appropriate on-line sensors of conversion are available, the on-line conversion measurements can be used to implement a closed-loop control scheme to perform the tasks of disturbance rejection and set point tracking. To manipulate monomer conversion, the feed rate of initiator or catalyst is typically adjusted.

The set point tracking problem was addressed by Leffew and Deshpande (1981) in the control of a train of reactors for the emulsion polymerization of vinyl acetate. More precisely, they focused on the problem generated by a period of no response (dead time) between the time of increase in the flow of initiator and the response of monomer conversion. In order to compensate for this dead time the authors used a model of the polymerization to develop an analytical predictor of the conversion of the monomer at some point in the future based on the current measured conversion. This prediction was then used to specify the control action. When intermittent particle nucleation did not occur (high surfactant concentrations), the control scheme proposed by Leffew and Deshpande provided tighter control than a standard PID control algorithm. However, at low surfactant concentration, where oscillations may be observed, the implementation of the analytical predictor was unable to control monomer conversion by manipulation of either initiator flow rate or reactor temperature. It should be noted that manipulation of reactor temperature to control monomer conversion should be avoided due to the possible detrimental effect it may have on MWD.

Kiparissides et al. (1981) applied suboptimal control to the continuous emulsion polymerization of vinyl acetate to control, among other variables, monomer conversion. The authors simulated the closed-loop control of monomer conversion via manipulation of both surfactant and initiator flow rate. They showed that with low and high surfactant levels the controller was able to rapidly take monomer conversion to steady state with moderate overshoot. Oscillations due to low emulsifier concentrations were properly eliminated by the proposed control scheme. However, the success of the control scheme seems to be more related to the choice of the manipulated variable rather than to the control algorithm. In fact, manipulation of surfactant flow rate will have a direct influence on particle nucleation and then will be capable of counteracting the oscillatory behavior. The same reasoning applies for the scheme of Leffew and Deshpande. The manipulation of initiator feed rate has only a slight effect on particle generation and then any control scheme using that manipulated variable will fail in eliminating oscillations.

A more recent example of control of conversion in continuous emulsion polymerizations is the work of Temeng and Schork (1989). The authors used the concepts of the plug-flow seeder reactor and water bypass, already introduced in other sections of this article, to control monomer conversion and particle size. A multivariable adaptive controller was used to compensate for the system nonlinearities. Simulations showed that when one of the set points of the two controlled variables is changed, the variable whose set point remained unchanged is minimally disturbed. The authors attributed this behavior to the multivariable nature of the controller. The elimination of oscillations is in this case due to the presence of the seeding reactor.

On-Line Measurements in Emulsion Polymerization

It is well known that even the off-line analysis and characterization of polymers involves laborious procedures. Thus, it is not surprising that the field of polymerization reactor control severely suffers from the lack of polymer property on-line measurements. The problems, usually encountered in the analysis of other polymer systems, are more pronounced in the case of emulsion polymerization, because of the multiphase nature of a latex system. Most of the latex properties cannot be analyzed by either a noninvasive technique or a simple sensor attached to a probe as is the case for pH or conductivity.

The majority of the existing off-line methods for latex characterization are sample-destructive techniques since they usually require a number of operations on the sample before it is analyzed (such as extraction, dilution, dissolution, evaporation, drying, phase separation). As a result, the on-line implementation of these techniques (when possible) requires the attachment of an automatic accessory to perform the latex sampling and the necessary operations on the sample before the final analysis. Even if this sample "pre-processor" is available, the prior to the analysis sample treatment will prolong even more the total analysis time, introducing undesirable time delays. On the other hand, the on-line adaptation of the nondestructive techniques (such as oscillating tube density meter) involves the use of a flow-through cell, which is placed in-line with a latex stream. In batch or semibatch operations the accommodation of the flow-through cell calls for a circulation loop, which recycles the reaction mixture from and then back to the reactor. In this case the old-up in the circulation loop should be minimized, but the stability of the latex returning to the reactor must be preserved as well. Thus, reasonable circulation rates are used and as a result time delays are also observed in this case.

In addition to the time delays, the on-line version of both the destructive and nondestructive techniques for emulsion polymerization suffers from other problems, related to the latex transfer involved (sampling and pumping). Polymer emulsions are sensitive to mechanical work. The latex is normally subjected to a much higher shear rate in the pump than it is in the agitated reactor and shear coagulation may be induced. The suspended solids in the latex might also clog and damage the pump or the sampling device. In general the sampling device must be simple in construction and easily disassembled for periodic cleaning. Reproducibility of the sampled latex volume is necessary in many cases. The most appropriate pumps (not though without problems) to be used for handling a latex stream are of either the peristaltic or the diaphragm type. When using peristaltic pumps the tubing fails due to either monomer swelling or mechanical fatigue after a certain period of time, depending on the monomer and tubing type. The diaphragm pumps might fail because of polymer plaque formed on the check valves.

In conclusion, the use of any type of on-line measurement in emulsion polymerization requires dealing with time delays (with consequences to the applied feedback control) and requires at least one auxiliary latex transfer system (sampling device, transfer or circulation pumps, sampling loop, flow-through cells). Periodic switching from the main to the auxiliary one should be automated, so that cleaning and service of the backup system is possible without interrupting the process monitoring and before failure of the operational one is experienced. If the service operations (such as flushing, removal of early polymer film deposits by solvents) can be automated too and the time required can be tolerated between samples, then the lifetime of the latex transfer system will be prolonged and switching to the auxiliary system will be necessarily less frequently.

In the following we review techniques for the on-line measurement of the most important process and property variables in emulsion polymerization. Although the emphasis of this work is in emulsion systems, we feel that there is a considerable amount of information in applications of the same techniques to other polymer systems (particularly solution polymerization). Thus, some of these applications are reported here, as well. The reader is also referred to the review of Chien and Penlidis (1990).

Conversion and reaction rate

Information on conversion and reaction rate can be used in a closed-loop fashion to account for inhibition and induction periods or errors in the amount of materials charged in the reactor. Thus, feeding policies in semibatch operation can be accordingly delayed or adjusted. Conversion data are necessary to detect the formation of new particles, since the slope of the conversion curve changes at that point due to an increase in the number of polymer particles in the latex. This type of information can be useful in applications where control of particle-size distribution is attempted. On-line measurements of conversion can be used directly for reaction rate and conversion control. In a simulation study of a batch PVC suspension process, Kiparissides and Shah (1983) developed a self-tuning regulator and an adaptive controller on the basis of on-line conversion measurements. Conversion can also be used to estimate the number of latex particles and the volume average particle diameter, as well as to control other polymer quality variables, which cannot be directly measured. In this latter case process models are necessary to determine the evolution of other properties (such as particle-size distribution) using conversion as the basis of reference between the actual process and its model. Other reported applications of on-line measurement of conversion are mentioned under the respective technique used in the following paragraphs.

On-line monomer to polymer conversion in emulsion polymerization can be inferred from on-line total heat release, density, refractive index, and residual monomer measurements. The residual monomer in the latex system (unreacted monomer) is obviously a direct measure of conversion and is discussed later on. Depending on the process and process model used, conversion is usually observable (that is, it can be estimated) from particle size, molecular weight, viscosity, and copolymer composition measurements.

Calorimetry. The application of calorimetric principles is a very well established practice in industrial polymerization reactor control. Bench-scale calorimeters for the investigation of polymerization dynamics, determination of kinetic constants and heat-transfer coefficients, and validation and selection of models are widely used. Solution of the dynamic energy balance of a stirred tank reactor can be used to monitor conversion on-line. In general, the heat flux generated by the exothermic reaction and the heat input due to agitation are compared with the heat accumulation and heat removal by convection, conduction, and loss to the surroundings. In contrast with laboratory-scale reaction vessels, the energy balance of large industrial-scale reactors is not very sensitive to the heat loss to the environment, because of the large volume-to-surface area ratio. This minor effect can be usually accounted for by some simple calibration procedure. Thus, the use of on-line calorimetry can be easily justified in commercial polymerization, while it presents several difficulties in the laboratory. However, even with large reactors the accurate evaluation of the involved derivative terms from noisy measurements might be a problem. Isothermal operation offers many advantages in that respect. If the reactor operates non-isothermally, then estimation of the derivative terms is appropriate in the context of optimal estimation theory. Calorimetry is a particularly convenient method for inferring conversion, since almost every reactor is or can be well equipped with flow and temperature measurements. On the other hand, instrumentation capable for dynamically closing the enthalpy balance around large-scale polymerization reactors is also useful for optimization of reactor performance and selectivity, safe operation, and reactor control. An excellent review of calorimetric principles with application to polymerization, different designs of bench-scale calorimeters and a comparative assessment of their capabilities has been published by Moritz (1989). The author also discusses an experimental application of feedback conversion control in the semibatch emulsion polymerization of vinyl acetate.

Gran et al. (1974) used the energy balance for the optimal control of PVC autoclaves. Amrehn (1977) discusses temperature control strategies for batch polymerization based on the reaction heat balance. In a similar way Gordon and Weidner (1981) obtained conversion data during the emulsion polymerization of PVC to control the particle-size distribution. Calorimetric principles have been used in many pilot- and industrial-scale reactors for a variety of applications (Pierru and Alexandre, 1973; Bailey, 1977; Harris and Rushing, 1982; Schuler, 1986a,b; Wu, 1985; Choo and Plaumann, 1985; MacGregor, 1986).

Densitometry. Monomer to polymer conversion in emulsion polymerization can be also inferred through the volume additivity rule using the density of the polymer latex, the densities of the different species in the reactor and appropriate mass balances applicable to the type of operation and chemical formulation. Thus, if polymer latex density can be monitored on-line, monomer conversion can be readily obtained. Three different types of on-line densitometers have been reported in the literature. The first of them is the oscillating-tube density meter, an instrument that in principle can be used for off-line determinations of the density of any fluid, and, if equipped with a flow-through cell, can continuously monitor the density of a process stream (Schork and Ray, 1981). This instrument has a U-shaped sample tube which is rigidly supported at its open ends. The tube is electronically excited to vibrate at its natural frequency. The frequency of oscillation, which is continuously monitored electronically, is directly related to the density of the test fluid, providing an almost continuous density measurement (the period of oscillation is updated every two seconds). The instrument is normally calibrated with water and air, and recalibration is only necessary if the tube is replaced. In order to obtain accurate converesion results, a highly accurate density measurement must be utilized. Fortunately, models of this instrument are available with four, five and six decimal points precision and results with a dispersion of $\pm 1.5\%$ in conversion were obtained with an accuracy of $\pm 3.0 \times 10^{-4}$ g/cm^3 in the density determinations (Canegallo et al., 1993). However, the measurements might be extremely noisy, particularly at low conversions. Nitrogen bubbles and monomer droplet coalescence can produce significant variability in the measurement. The introduction of a phase separator can substantially improve the sensor performance. Other problems usually encountered with emulsion systems are related to the latex transfer, as discussed earlier.

The oscillating tube density meter has been used by Rentsch and Schultz (1978) with cationic polymerization. Abbey (1981) discusses the application of the instrument to the bulk and solution polymerization of styrene, a multicomponent acrylic semibatch solution polymerization, as well as the semibatch emulsion polymerizations of styrene and methyl methacrylate and the batch emulsion copolymerization of butyl acrylate with methyl methacrylate. MacGregor et al. (1986) used the on-line density measurements to estimate residual monomer, number of latex particles, particle phase volume, average particle diameter, as well as the impurity levels in the emulsion polymerization of styrene. Ellis et al. (1988) used the on-line densitometer along with size exclusion chromatography to follow the course of methyl methacrylate solution polymerization in batch. Penlidis et al. (1989) obtained conversion data using on-line densitometry to study the oscillatory behavior of the continuous emulsion polymerization of vinyl acetate and evaluate the dynamic performance of a new reactor train design. Recently, Gagnon and MacGregor (1991) presented a simulation study of state estimation in the styrene-butadiene (SBR) process. The authors assumed on-line measurements of density and volume-average particle diameter to obtain estimates of total number of particles, particles containing one radical, reacted moles of the two monomers, and amount of impurities.

A second instrument suitable for on-line operation is the so-called bubble densitometer (Schork and Ray, 1983). It involves the use of two orifices of equal radii mounted at unequal depths below the liquid surface. A sensitive differential pressure transducer is connected to pressure taps on the orifices. Compressed nitrogen is bubbled from each orifice at a slow rate. The pressure needed to form each bubble is the sum of the pressure due to liquid head and that necessary to generate the interfacial surface. The differential pressure sensed by the transducer will be only due to the difference in depth of the two orifices and the liquid density, because the surface tension effects will cancel out if the radii of both orifices are the same. By placing the orifices in a flow cell, the instrument can be used to monitor flowing streams. A prototype of this device was used to monitor monomer to polymer conversion in emulsion polymerization up to a precision of 6%. Although less precise than the vibrating densitometer, it may be more appropriate in applications in which durability is a critical factor. In the case of laboratory-scale batch or semibatch reactors, the flow cell must be in-line with a recycling stream and the required holdup might cause problems.

Finally, density can be measured by a noninvasive method based on γ-ray radiation. Different types of instruments based on this principle exist. The only application to emulsion polymerization of such a unit was reported by Poehlein and Dougherty (1977) without elaboration. Density meters based on γ-ray radiation are in use for the determination of the density of liquid streams flowing through pipes. The sensor, including source housing and detector, is mounted to an existing pipe or vessel with a two-piece pipe saddle. Low-level gamma energy emitted from the gamma source is beamed in a precise shape through the walls of the pipe and is measured on the other side. The detector is an ionization chamber. It is filled with a gas under pressure, which ionizes in the presence of gamma energy. When the gas is ionized, a low current is emitted from the detector. The current output is inversely proportional to the liquid density or % solids by weight or volume.

Copolymer composition

On-line information about copolymer composition in the polymer reactor can be used for reaction rate, conversion, and copolymer composition control. Copolymer composition can be either determined directly or inferred from the composition analysis of the residual monomer using the material balances for the system. In copolymer systems, conversion reflects the individual contributions of each monomer in the copolymer. Thus, copolymer composition can be obtained either by two independent on-line measurements of conversion or by one of them supplemented with an estimation technique. Copolymer composition is in principle observable from molecular weight or particle-size measurements. However, its estimation would require extremely detailed modeling, which cannot be justified (for the sole purpose of composition estimation) considering that the on-line measurements of molecular weight or particle size are time consuming and by far more complicated than those available for copolymer composition.

Direct Determination. Direct determination of average copolymer composition is possible by melt viscometry, chemical analysis, pyrolysis gas chromatography, nuclear magnetic resonance spectroscopy, and infrared spectroscopy. Melt viscometry and chemical analysis are typical off-line techniques that can be applied to almost any polymer. Pyrolysis gas chromatography (GC) can be implemented on standard chromatographic equipment with moderate cost and interfaced to a data acquisition system but the problems associated with its robustness and reliability are usually prohibitive. Establishing the composition of a polymer from its thermal degradation products has not been yet solved theoretically. Constructing a calibration graph on the basis of peaks that reflect the composition of the polymer requires samples of known composition and with the same structure as the system under investigation because pyrolysis GC is very sensitive not only to the composition of the copolymer, but also to its structure. When passing from two- to multicomponent systems, the problems become very complicated. The equipment for nuclear magnetic resonance is complicated and expensive, and its use is justified only in special cases. At the moment only infrared spectroscopy holds some promise as an on-line robust measurement for emulsion polymerization. Spectroscopic techniques can be used on-line (with polymer solutions) to obtain copolymer composition distributions (CCD). This can be achieved by employing a size fractionation technique. However, in size exclusion chromatography (of a polymer solution not latex) the separation is carried out on the basis of molecular size instead of composition. Thus, the CCD obtained is the variation of the average polymer composition with molecular size and not the concentration vs. molecular composition.

Infrared spectroscopy (IR) can be used as an on-line measurement employing a flow-through cell. As any analysis of spectroscopic information, IR is based on the combined Beer-Lambert law. There is an immense literature concerning the theory and interpretation of vibrational data. While the available literature deals with off-line IR measurements (Hummel, 1966; Henniker, 1967), IR is currently used for on-line monitoring and control of pilot-plant and industrial-scale solution polymerization. Calibration of the instrument is required using solutions of copolymers with known compositions. Separate IR bands are monitored for each monomer. An internal standard with constant concentration can be also employed. While not impossible in principle, the on-line use of infrared spectroscopy in emulsion polymerization presents several problems related to the transfer and handling of the sample. Multistage analysis methods to obtain a polymer solution might be necessary for the acceptable performance of the instrument.

Residual Monomer Analysis. Gas chromatography, gas-liquid chromatography, and high-pressure liquid chromatography are standard techniques for analyzing residual monomer. As mentioned before, this information is useful to obtain conversion, reaction rates, and copolymer composition. Gas chromatography has been traditionally used in polymer characterization and can be easily integrated in a data acquisition system for on-line operation.

Volatile monomers can be identified on-line by gas chromatography (GC) and quantitative results can be obtained by GC analysis of a latex sample. However, on-line GC of latex samples presents some difficulties, which require some modifications of the standard instrumentation. A packed glass liner is usually inserted in the preheater. The liner contains packing material characterized by low retention with respect to the test compounds (monomers). The deposition of the sample onto a layer of inert material promotes the distribution of the polymer as a thin layer on the packing, and hence encourages rapid diffusion of the volatile compounds from the polymer. At the same time it retains polymers and high boiling point compounds, preventing them from being carried into and contaminating the analytical column. The liner has to be regularly checked and cleaned to avoid clogging of the preheater. A "guard" column is usually installed before the analytical column for additional safety. Proper selection of the preheater temperature is required, so that cracking of polymer at the rather high temperatures necessary is avoided. A possibility, which does not suffer from the problems involved in analyzing a latex sample, is the GC analysis of the reactor head space. However, this approach requires an adequate thermodynamic equilibrium model of the involved liquid and vapor phases. A very comprehensive source of information and techniques related to gas chromatography of polymers is the work of Berezkin et al. (1977).

Using GC, there might be cases, in which one of the monomers is almost impossible to be detected. If the other participating monomers can be analyzed, then an independent measurement of conversion (such as by densitometry) can provide information on the impossible to detect monomer. If the GC response is heavily influenced by the nature of the sample, the calibration of the instrument should be conducted with samples not only of known composition but also of the same nature as those to be analyzed in reality (similar concentrations and same ingredients as in the actual recipe). In the case of semibatch or continuous operation the monomer feed streams should be precisely known to be able to close the material balance. Finally, the injection in the GC sample volume must be reproducible, and the volume of the latex in the reactor at any time is required. An internal standard will always improve the quality of the measurements, but it should be present as a nonreactive agent in the actual recipe, which might be difficult to achieve. Estimation techniques and knowledge of the monomer partitioning among the different phases are of great help in analyzing the residual monomer in emulsion polymerization.

The GC techniques used traditionally for the determination of volatile compounds in polymer systems have been recently proven to be a powerful tool for polymerization control. Ahlberg and Cheyne (1979) used GC to obtain the discharge compositions of the outlet streams of a butyl synthetic rubber copolymerization process. Estimation techniques were used (Kalman filter) in an adaptive strategy to control rubber viscosity. Guyot et al. (1981) used GC with the semicontinuous emulsion copolymerization of styrene/acrylonitrile for copolymer composition control. Alonso et al. (1987) and Oliveres et al. (1988) used the vapor-phase composition by GC in the emulsion copolymerization of styrene and acrylonitrile to control copolymer composition. Dimitratos et al. (1989a,b; 1991) investigated several estimation techniques based on GC analysis of latex samples to control composition in the emulsion copolymerization of vinyl acetate/butyl acrylate.

Surface tension

Surface tension is a very important variable in blending processes involving surfactants, as well as in emulsion polymerization processes. The surface tension of a reacting latex system can be related to the concentration of emulsifier dissolved in the aqueous phase. This "free emulsifier" concentration, as opposed to the emulsifier units adsorbed on polymer particles, monomer droplets, or bound in micelles, is critical to the system dynamics. Early in an emulsion polymerization process, the latex surface tension is at its crucial micelle concentration (CMC) value. After initiation, the newly formed growing polymer particles require additional emulsifier to be stabilized. As the necessary emulsifier molecules are adsorbed on the surface of the polymer particles, the free emulsifier concentration is kept constant by micellar breakage and the latex surface tension is maintained at its CMC value, as long as micelles exist. When the micelles disappear (either because of nucleation or dissociation), the required emulsifier for particle stabilization is supplied by the free emulsifier units and thus, the latex surface tension increases above the CMC value. The dependence of particle generation rate on the free emulsifier concentration has been the conclusion of several modeling efforts in emulsion polymerization systems (such as Nomura et al., 1971).

Monitoring of surface tension provides information on the presence or absence of micelles especially in the case of emulsifier addition to the reactor. Secondary nucleation due to new formation of micelles and periods of homogeneous nucleation can be detected. The free emulsifier concentration can be monitored and used for particle-size distribution control. This can be accomplished by increasing the emulsifier concentration above CMC and thus inducing a secondary nucleation, which will result in a second particle generation of smaller size (Min and Gostin, 1979). This information coupled with conversion data can be used to control the particle-size distribution of the second generation of particles by emulsifier feed manipulation.

Accordingly the emulsifier addition can be manipulated so that the introduced emulsifier is barely enough to stabilize the growing particles (old and new) and does not induce further nucleation (Gordon and Weidner, 1981). Another potential application is the preparation of heterogeneous latex particles by two or more stages. After a seed preparation, more monomer(s) are added at a different composition to continue the growth of the seed particles in an attempt to produce composite layered or core/shell particles. In this case the amount of surfactant in the seed latex must be below the CMC, before and during the semibatch step, if complete seed growth is to occur (Bradford et al., 1956; Vandergaer, 1965). Maintaining a desired surfactant concentration (or a desired particle surfactant surface coverage) can be achieved by monitoring surface tension.

Surface tension measurements have been traditionally carried out through the Whilhelmy plate technique, which measures the force exercised on a plate by the liquid surface as the plate is removed out of the liquid. The method, while being accurate, cannot be used for on-line monitoring of surface tension. A surface tensiometer, suitable for on-line applications, has been developed by Schork and Ray (1981, 1983) and is commercially available in a variety of automated units compatible with computer data acquisition systems. The method is based on the maximum bubble pressure principle. Two orifices of different diameters are submerged in the liquid contained in a sample or flow-through cell, and gas bubbles are introduced through them in the liquid. The differential back pressure between the two orifices is measured and the output signal is directly proportional to the surface tension of the sample. Calibration of the instrument accounts for the effect of the orifice radii on the differential back pressure and density correction improves the accuracy of the measurement (0.5–2.0%). The free emulsifier concentration can be determined directly from the latex surface tension measurements (Schork and Ray, 1981, 1983).

Particle concentration, particle size and particle-size distribution

Particle concentration and particle size are key variables in emulsion polymerization because they play an important role in affecting the system dynamics and defining the physical properties of the latex product. The determination of particle concentration involves more errors than any other variable in emulsion polymerization. It usually employs the measurement of some average of the particle size, from which particle concentration is calculated by comparison with the total volume of polymer, usually obtained by conversion. The calculated value strongly depends on the type of the average used if the particle-size distribution is broad. Since particle concentration refers to the subdivision of the total polymer volume present in a unit volume of water, it cannot be related to the number average radius, but to the number average volume. Thus, the correct radius average to use is the root-mean cube average. As a result, any errors in measuring particle diameter are cubed in the calculation of the particle concentration. A direct way to determine particle concentration is by flow ultramicroscopy (Derjaquin and Vlasenko, 1962; Davidson et al., 1967). A latex sample is accurately diluted and pumped at a constant rate through a cell observed in the ultramicroscope, so that the number of particles in a given volume can be counted.

Average particle size and particle-size distributions in latexes can be in principle determined using a variety of methods. These methods can be classified in three major categories: (1) microscopy, which includes optical, transmission, scanning, scanning transmission, and tunnel microscopy, (2) light scattering, both classical and quasi-elastic, and (3) fractionation which includes sedimentation (both gravity and centrifugation), size exclusion chromatography (which includes liquid exclusion chromatography, hydrodynamic chromatography, and capillary hydrodynamic fractionation), sedimentation field flow fractionation, and electrozone sensing. Specific details of particular techniques, their ranges of application and other details, can be found extensively in the literature (Barth, 1984; Provder, 1987; Craver and Provder, 1990). In what follows, those techniques that can currently be used as an on-line instrument or hold some promise of being adapted as such will be described in more detail. Average particle size and particle number are observable from conversion measurements, while particle growth states are observable from MWD moments provided that termination reactions control the molecular weight development.

Turbidimetry. Turbidimetry is a classical light scattering method. In general, the optical spectral extinction or turbidity observed when a sample of suspended particles is illuminated with some kind of electromagnetic radiation, provides information about the size and number of those particles. If the particles are considered to be hard spheres and if enough dilution prevents multiple scattering, turbidity at various wavelengths can be related to concentration and size by Mie theory (Kerker, 1969). The information content of a turbidity spectrum may not be enough to obtain the particle-size distribution of the latex when such a distribution is not unimodal. However, multiwavelength detection, as obtained with a photodiode array UV/VIS spectrophotometer, coupled with careful data handling may improve the resolution of the technique and provide quite satisfactory results even with strongly bimodal latexes (Eliçabe and Garcia-Rubio, 1989, 1990). Although the use of an instrument of this kind has not yet been reported in an on-line application, it appears to be a logical choice when one desires simplicity in sample preparation and a reasonably short analysis time. However, care must be exercised so that the required dilution is quantitative and very precise. In addition to particle-size distribution, other process variables can be obtained from on-line turbidity measurements. Kiparissides et al. (1980) demonstrates how on-line turbidity measurement at seven wavelengths can be used to provide estimates of polymer volume and conversion in the continuous emulsion polymerization of vinyl acetate.

Angular Light Scattering. Angular light scattering is another classical light scattering method in which information on particle size and number can be obtained by measuring light scattered by a sample of suspended particles at different angles. For instance, turbidimetry is a particular case of angular light scattering in which light is detected on a line forming an angle of 180° with the incident beam. Because turbidimetry is restricted to a single angle, different wavelengths must be used to increase the information content of the recorded signal. The number of wavelengths depends on the number of parameters needed to characterize the particles in terms of size. On the contrary, general angular light scattering relies on increasing the number of angles at which measurements are taken in order to provide an increased information content according with the complexity of the sample to be analyzed.

Other particular but pure angular light scattering methods are:

(1) *Dissymmetry.* In this technique the intensity of scattered light at 45° and 135° is measured, and only an average diameter is obtained.

(2) *Maximum-minimum.* In this technique scattered light intensity is measured at different angles and the angles of maximum and minimum intensity are noted. Again an average diameter is calculated.

(3) *Forward Angle Ratio.* Here intensities at several angles are measured and the ratio of those intensities at five degree intervals is computed.

(4) *Polarization Ratio.* The sample is illuminated with unpolarized monochromatic light and the horizontal and vertical components of the scattered intensity at 90° are measured. In this way there is no need of having an absolute measure of intensity, because only the ratio of the two components (polarization ratio) is of interest.

In all cases the values obtained using light scattering techniques are influenced by the large particles in the system and are close to a light scattering or weight average size. When more than one average is sought these techniques can be modified by increasing the number of instruments at different angles and/or the number of wavelengths detected. Thus, new pieces of information will be incorporated, and after proper handling they will provide an increasing number of moments of the distribution of particle sizes. In principle, and if enough meaningful measurements are taken, it is possible to invert the experimental results using Mie theory and obtain the entire distribution (Glatter et al., 1985; Glatter and Hofer, 1988a,b; Hofer et al., 1989).

On-line determination of PSD using angular light scattering has not yet been reported. However, instruments in which measurements at a number of different angles are available in a single step have some promise for on-line analysis of latexes (Muly and Frock, 1980).

Dynamic Light Scattering. Dynamic light scattering (also called quasi-electric light scattering and photon correlation spectroscopy) is concerned with the time behavior of the scattered intensity obtained from a sample of suspended particles. This approach contrasts with classical light scattering techniques that measure an average scattered intensity. Suspensions of particles below 1 nm in size exhibit significant random motion due to collisions with molecules of the surrounding liquid medium. As a result, when a particulate sample of such characteristics is illuminated by a light source, the phases of each of the scattered electromagnetic waves (arriving at the detector located at a fixed angle) fluctuate randomly in time because of the fluctuations in the positions of particles that scatter the waves. Since these waves mutually interfere, the net intensity of the scattered light fluctuates randomly in time around a mean value. The dynamic light scattering technique makes use of the fact that the time dependence of the intensity fluctuations as measured by the autocorrelation function of the scattered intensity can be related to translational diffusion coefficient of the particles, which in turn is related to the particle size through the Stokes-Einstein equation. Details on theoretical as well as practical aspects of the dynamic light scattering technique can be found in a number of sources (Chu, 1974; Beme and Pecora, 1976; Pecora, 1985; Stock and Ray, 1985).

As with all light scattering methods, the calculations necessary to analyze a bimodal particle-size distribution from quasi-elastic light scattering data are very sensitive to noise. This technique has been adapted to on-line use and tested in a pilot-plant emulsion polymerization reactor by Kourti et al. (1990). The authors report the design and implementation of a system for automatic sample acquisition and dilution before PSD analysis.

Size Exclusion Chromatography. In recent years new methods of fractionation on the basis of particle size have been applied for the determination of particle sizes in a polymer latex. In liquid exclusion chromatography a dilute polymer latex is eluted from a column packed with porous spheres. As in gel permeation chromatography, the smaller particles have a larger accessible bed volume due to their ability to diffuse into the pore structure of the packing. As a result they elute more slowly than the larger particles, which bypass a larger number of pores. The fractionated sample is detected at the outlet of the column, using some method of light scattering. The signal from the detector is a function of the size of the particles currently being eluted from the column and can be related to the particle-size distribution of the original latex sample (Singh and Hamielec, 1978).

When nonporous packing is used the chromatographic technique is referred to as hydrodynamic chromatography. This technique was pioneered by Small (1974) who used it to measure particle-size distributions of polystyrene latexes. In principle the method has its basis in separation forces derived exclusively from factors operating in the interstitial volume of the packed bed. Even in the absence of pores, large particles are prevented by their size from reaching regions near the surface of the packing where the axial velocities are small, and hence experience a higher average velocity. As a result, shorter retention times, as compared to those of the small particles, evidence the desired fractionation.

Early attempts to replace packed columns by single open bore capillary tubes were made first by Sadao et al. (1974). Noel et al. (1978) are credited as the first to obtain separation of particles by size in a capillary tube with an internal diameter of 250 mm, coining the term capillary hydrodynamic chromatography. In order to overcome the serious resolution problem that arises in hydrodynamic chromatography due to radial dispersion, Silebi and coworkers (Silebi and Dos Ramos, 1989; Dos Ramos and Silebi, 1990) developed a technique called capillary hydrodynamic fractionation, because the separation mechanism results from the parabolic velocity profile rather than the partitioning of the species to be fractionated between two phases. The technique uses capillary columns with diameters as small as 4 mm and eliminates the possibility of radial dispersion producing chromatograms of much higher resolution. The on-line implementation of the technique requires automatic predilution of the concentrated latex sample drawn from the reactor.

Molecular weight and chain length distribution

The molecular weight distribution (MWD) determines to a large extent the bulk properties of the polymer (elongation, strength, toughness, and so on). In emulsion polymerization of linear polymers MWD also reflects the types of molecular events contributing to the polymer growth. The states involved in material balances are generally observable from molecular weight moments. If termination reactions control the molecular weight development, then MWD depends on particle-size distribution and particle growth states are observable from MWD moments. However, molecular weight is in general difficult to be inferred or estimated from other on-line measurements. Molecular weight moments are unobservable from material balance and particle growth states in most cases. In specific applications, molecular weight averages can be estimated from on-line measurements, which are known to depend on molecular weight.

Polymer molecular weight averages can be obtained by a variety of techniques. Number average molecular weight (MW_n) can be determined by end-group analysis, membrane and vapor pressure osmometry. None of these techniques can be used in an on-line manner. Weight average molecular weight (MW_w) of homopolymers is determined by light scattering. On-line determination is possible by a low angle light scattering measurement (Hamielec et al., 1978; Green, 1983) combined again with a refractometer to provide the polymer concentration. The technique presents several difficulties if used with copolymers.

The entire MWD can be obtained only by a fractionation technique such as turbidimetric titration or gel permeation chromatography (GPC). Turbidimetric titration is a fractionation technique based on the gradual precipitation of polymer from its solution. The technique has very limited applicability and requires extensive preliminary tests. GPC has become almost the standard technique for the off-line determination of polymer molecular weight and chain length distribution (CLD).

GPC is a particular form of liquid chromatography employing a fractionation technique based on differences in molecular size. It is basically a size exclusion chromatography technique like those applied for PSD determination with the difference being the basis of fractionation (molecular size vs. particle size). Molecules are separated according to their hydrodynamic volume as this property affects their permeability of the pore structure of microporous gel particles. In fact, the interpretation of molecular-size separation in terms of molecular weight introduces the limitations of the technique. Absolute calibration presents difficulties with linear homopolymers, complete interpretation of analysis of branched polymers is not possible and copolymer analysis depends on copolymer composition.

On-line determination of MWD or CLD has become possible with the introduction of a microprocessor controlled GPC. The instrument performs automatic sampling, dilution, injection, elution, detection and analysis, much like an on-line gas chromatograph. Deconvolution is automatic, as is recalibration from a mixture of standards. At the moment, no report has been published on the use of this instrument in emulsion polymerization.

The estimation of MWD and CLD has been attempted in solution polymerization systems (Jo and Bankoff, 1976; Schuler and Suzhen, 1985; Schuler and Papadopoulou, 1986; Papadopoulou, 1987; Ellis et al., 1988; Adebekun and Schork, 1989) and some of the proposed schemes can be promising for emulsion systems as well.

Conclusions

Even though emulsion polymerization is one of several types of polymerization processes, the research articles referenced here on the modeling and control of the process are quite numerous. They attest to the great interest and activity that the subject has attracted especially during the last decade. Of the list of approximately 200 references mentioned here more than half are dated in the 1980s and 1990s. The interest is not expected to decrease in the future but rather to increase. This will probably be motivated by the increased desire for polymer products with tailor-made properties that can be produced in batch or continuous reactors. An important environmental factor will also increase the importance of emulsion polymerization. This relates to the efforts to reduce the emission of organic solvents in the atmosphere which is inevitable with products produced by solution polymerization and the desire to convert such processes to emulsion polymerization. Furthermore, the present interest in statistical process control (SPC) and/or statistical quality control (SQC) will increase the need for operating emulsion polymerization processes in such a manner so that they produce products with very small variation in their properties. Provided that control engineers and applied statisticians understand and accept each other's objectives and approaches and combine them in a comprehensive overall approach, substantial progress can be stimulated. For substantial progress to be achieved we need to bring to the problem at hand an effective interdisciplinary approach. The components that need to be interphased and coordinated consist of: (1) the understanding of the process and its quantitative documentation in the form of a model, (2) the accurate measurement of several process variables, and (3) the design of effective operating procedures and feedback control strategies that make the most use of the available model and process measurements. To elucidate the need for such an interplay we would like to briefly examine the following two idealized situations.

One of the idealized situations is the perfect model condition (PMC). Under the PMC, we possess a perfectly accurate and sufficiently detailed model with *all* the appropriate thermodynamic or kinetic parameter values to accurately simulate *every* emulsion polymerization system of practical interest. Min and Ray (1974) postulated such a framework in a seminal article 20 years ago. Since that time substantial progress has taken place and many of, but not all, the parameters of this detailed model are now known for some, but not all, of the emulsion polymerization processes. If one assumes that the PMC becomes reality tomorrow, we can argue that we will almost have no need to measure and feed back any process measurements. Such a perfect model enables us to preprogram the whole process operation. What is the use of measuring, for example, the molecular weight of the polymer produced if such a *perfect* model is available? Such a perfect model should be able to model all process variability, anticipate and account for the effect of all disturbances, and in general provide us with all the information needed about the process. If it appears that all such conditions are not possible to be met, this means that the perfect model condition is difficult to realize.

The second of the idealized situations is the comprehensive instrumentation condition (CIC). Under the CIC all state variables of the process can be measured on-line with sufficient frequency and accuracy. We here denote as state variables all those needed to describe fully and in sufficient detail the state (or condition) of the emulsion polymerization reactor at each time instance. Such state variables include the reactor temperature, the monomer concentrations in the water phase and in the polymer phase, the corresponding concentrations of the initiator and emulsifier, the number of radicals per particle of a given size, those involved in the description of the particle-size distribution and the molecular-size distribution, and as many other variables of this type as necessary to fully describe the state of the process. In other words the CIC assumes that we can measure *everything* that matters. Under such an idealized assumption, we can argue that the need of a detailed quantitative model is drastically lessened. If we can measure everything then we know everything and can operate the process to produce the desired products.

The point with respect to emulsion polymerization is the realistic target is somewhere between the above two extreme idealized situations. First, we should always try to incorporate our process knowledge in the form of the most accurate model possible. If our knowledge is incomplete, as is often the case, we should not discard the use and value of an imperfect model. The model can be substantially complemented with each online measurement that is available. The question that it is important, but cannot be answered abstractly for all cases, is whether we have an accurate enough model and a sufficient number of measurements for the process of interest. If the answer is positive, then modern model-based feedback control techniques can effectively utilize both the model and the available measurements for an effective operation of the process. However, we should not forget that the answer to the above question depends on the tightness of our standards for product quality and our process productivity objectives. There is no doubt that there is a large number of industrial processes that operate very profitably with a minimal quantitative process model at hand and with the help of few on-line measurements. At the same time, we have no doubt that such a process will require a more accurate model and additional measurements as the product specifications become tighter, as the desire to increase the process productivity increases, as the price of the raw materials increases, as the selling price of the product reduces, as more competitors enter the market, or as customers demand the production of products that are tailor-made for certain applications.

Concerning the modeling and control of emulsion polymerization that we reviewed here, we feel that the available models are accurate enough for a few model processes but not for many of the more complex ones of industrial interest. Furthermore, the available on-line measurements are sufficient enough for a few laboratory applications, but the majority of industrial processes will greatly benefit from additional reliable on-line measurements. Consequently, many important questions remain unanswered, and additional research efforts need to be undertaken. We hope that this survey article helps in understanding the present state of the art that is always an essential first step for any further progress.

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