CHALLENGES IN POLYMERIZATION REACTOR MODELING AND OPTIMIZATION: A POPULATION BALANCE PERSPECTIVE

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Abstract: In the present article, recent developments on modeling, monitoring, optimization and control of particulate polymerization processes are reviewed. A unified population balance approach is described to follow the time evolution of molecular and morphological polymer properties in batch and continuous polymerization reactors. Recent advances on the online monitoring of "polymer quality" are discussed in the context of available hardware and software sensors. The problem of real-time optimization of polymerization processes under parametric uncertainty is also examined along with its online implementation. Finally, new issues related with the modeling, numerical solution and control of multidimensional PBEs are conferred. *Copyright © 2004 IFAC*

Keywords: Polymerization, Particulate processing, Product quality, Distributions, Computational methods, Estimators, Optimization, Control

1. INTRODUCTION

Process modeling, optimization and control can have a significant impact on polymer plant operability and economics. Polymer manufacturers face increasing pressures for production cost reductions and more stringent quality requirements. However, product quality in polymer manufacturing is a much more complex issue than in more conventional simple chemical systems. Thus, a major objective of polymerization reactor modeling is to understand how the reaction mechanism, the physical transport phenomena (e.g., mass and heat transfer), mixing, reactor type and operating conditions affect the "polymer quality". The last term includes all the polymer molecular properties (e.g., molecular weight distribution (MWD), copolymer composition distribution (CCD), sequence length distribution (SLD), long and short chain branching distributions (SCB, LCB), stereoregularity, etc.) as well as the morphological properties of the product (e.g., particle size distribution, (PSD), pore size distribution, bulk density, etc.). One of the most difficult issues in polymer reactor optimization and control is to determine the quantitative relationships between the product physical, thermal, mechanical,

rheological, chemical properties and the molecular/morphological polymer properties. Table 1 summarizes both types of quality control measures.

Since the end-use properties of the produced polymers are directly linked with the molecular characteristics of the polymer chains, control of the polymer chain microstructure is of profound interest to the polymer manufacturing industry. This presupposes a thorough knowledge of the polymerization kinetics and the availability of advanced mathematical models to quantify the effects of process operating conditions on the molecular and morphological polymer properties. A great number of modeling studies on the prediction of MWD, CCD, PSD, etc. for linear and branched polymers have been published. Most of the models follow the general framework of population balances but having as internal coordinates the chain length, the chain composition, etc. of the polymer molecules or the particle volume.

Synthetic polymers are produced via a multitude of reaction mechanisms (e.g., free-radical, catalytic, ionic, etc.) and processes (e.g., bulk, solution, suspension, etc.). In general, polymerization

Table 1. Some Measures of Polymer Product Quality

MOLECULAR AND MORPHOLOGICAL PROPERTIES	END-USE PROPERTIES
- Average Molecular Weights and Molecular Weight Distribution (MWD) - Copolymer Composition Distribution (CCD) - Sequence Length Distribution (SLD) - Long-Chain Branching Distribution (LCBD) - Stereoregularity (Tacticity) - Particle Size Distribution (PSD) - Particle Porosity and Surface Area, etc.	- Physical and thermal properties (e.g., density, clarity, melting point, temperature stability, swellability, plasticizer uptake, etc.) - Chemical (e.g., corrosion resistance, etc.) - Mechanical properties (e.g., strength, toughness, stress crack resistance, abrasion resistance, impact resistance, etc.) - Rheological properties (e.g., flow properties, shear viscosity and elasticity, melt index, extensional viscosity, extrudate swell, etc.)

processes can be broadly classified into homogeneous and heterogeneous ones. The first class comprises polymerizations which are carried our in a single phase. The latter involves the presence of several phases (i.e., solid, liquid and gas). In heterogeneous polymerization, the final product is obtained in the form of a distribution of polymer particles in the sub-micron or micron size range. Table 2 presents the main characteristics of typical particulate polymerization processes employed for the production of some well-known commodity polymers (Kiparissides, 1996).

The analysis of particulate polymerization processes is a rather complex problem due to the highly coupled kinetics, thermodynamics, heat and mass transfer phenomena, taking place in a heterogeneous process. Furthermore, the physical properties (e.g., viscosity, density, transport coefficients, interfacial tension, etc.) of the various phases typically vary by several orders of magnitude in the course of polymerization. Thus, the framework of population balances is ideally suited to the description of the complex dynamics of a wide range of particulate polymerization processes.

Efficient polymer reactor process control requires correct information on the state of the polymerization process. Therefore, the availability of on-line measurements is an essential requirement for the implementation of high-level process and polymer quality optimization schemes. On-line monitoring devices have to be able to measure continuously (or at least semi-continuously) and often condition the

sampled material (and sometimes even chemically process it); they must have a satisfactory analysis and response time behaviour; and, finally, they have to supply correct results over long periods of time in environments that are often physically and chemically aggressive. In a review article (Kammona, et al., 1999), a comprehensive survey on recent advances on hardware and software sensors for on-line monitoring of polymer quality was presented.

The operating objectives in batch and continuous polymerization processes must satisfy complex molecular and morphological property requirements for the final product and simultaneously achieve the greatest economic potential for the plant. Basically, two types of optimization problems are encountered in polymerization processes. The first deals with the selection of the best (optimal) time invariant controls so that, in the absence of process disturbances, the final product attains some desired molecular and morphological properties. The second, the time optimal control problem, deals with the calculation of the time-optimal control trajectories to ensure the satisfaction of the "polymer quality" requirements and the operational process constraints. These optimal control policies can be calculated offline and implemented as set-point changes of the regulatory process controllers. However, the operation of a polymerization process is heavily affected by disturbances (e.g., process-related sources or inherent model parameter uncertainties) that cause the process to drift away from the offline

Table 2. Typical Particulate Polymerization Processes

Process:	Suspension	Emulsion	Precipitation	Liquid Slurry	Gas-Solid Polymerization
Particle Size (μm)	50-500	0.1-1.0	$100-10^4$	$10-10^4$	$10-10^4$
Reactor Type	Batch	Batch, CSTR	Batch, CSTR	Batch, Loop	Fluid Bed, Stirred Bed
Kinetic Mechanism	FR, I	FR, I	All	ZN	ZN
Polymers	PMMA PS, PVC	PS, PMMA, PVA, PTFE	PVC, PTFE	HDPE, PP, EP	HDPE, PP, LLDPE, EP

Kinetic Mechanisms: FR – Free Radical, I- Ionic, ZN- Ziegler-Natta
Polymers: PS – Polystyrene, PMMA – Poly(methyl methacrylate), PVA – Poly(vinyl acetate), PVC – Poly(vinyl cloride), HDPE – High density polyethylene, LLDPE – Linear low density polyethylene, PTFE – Poly(tetrafluorethylene), PP – Polypropylene, EP – Ethylene- Propylene copolymers

calculated optimal trajectories. To alleviate the above problems, an online estimation-optimization approach needs to be implemented (Kiparissides, *et al.*, 2002, Chatzidoukas, *et al.*, 2003). The updating of the time optimal control policies is carried out in two steps: in the first step, a state/parameter estimator utilizes the available process measurements to obtain reliable estimates of the state variables and the time-varying model parameters. In the optimization step, the time optimal trajectories are periodically reevaluated based on the most recent information about the process. The calculation of the time optimal control policy is obtained via dynamic programming techniques (including sequential and simultaneous discretization methods).

The present paper deals with the modeling and optimization of particulate polymerization processes using a population balance approach. In particular, the paper addresses the following topics. In section two, a unified population balance approach is presented to follow the molecular weight (e.g., MWD, LCB, etc.) and morphological (e.g., PSD) changes in a particulate polymerization process. The solution of the general PBE is reviewed in relation to available numerical methods (e.g., M-I and M-II approaches, finite differences, collocation, finite elements, wavelets, etc.). Subsequently, the general population balance approach is applied to typical polymerization processes to predict the dynamic evolution of MWD, PSD, etc. in batch and continuous systems. In section three, the calculation of the time optimal control policies under structural and parametric uncertainty is reviewed along with their on-line implementation to polymerization processes. Finally, in section four, future directions related to the modeling, monitoring, optimization and control of particulate polymerization reactors are conferred.

2. THE POPULATION BALANCE EQUATION

The development of the general population balance equation (PBE) follows the works of Hulburt and Katz (1964) and Ramkrishna (1985). Let us consider a distribution of countable entities (e.g., polymer chains, monomer droplets, polymer particles, etc.) $n(x, y, z, p_1, p_2, ... p_k, t)$ where x, y and z represent ordinary spatial coordinates, t is the time, and p_i represents the ith property of the entity. For example, p_i could denote the degree of polymerization, or the comonomer composition or the volume of a polymer particle. Actually, the term $n\, dxdydzdp_1...dp_k$ represents the fraction of entities in the geometric volume element $\delta V = \delta x \delta y \delta z$, with property values in the range $\delta p_1, \delta p_2, ... \delta p_k$. Note that the distribution function n will satisfy the following condition:

$$\int n(x, y, z, p_1, p_2, ... p_k) dxdydz\, dp_1 dp_2 ... dp_k = 1 \quad (1)$$

In the above formulation, there are $(3 + k)$ independent variables plus time involved that can be viewed as a $(3 + k)$ dimensional space. Thus, for an ordinary small volume element in this space, Ω, the general population balance becomes (Himmelblau and Bischoff, 1968):

$$\frac{d}{dt} \int_{\Omega} n d\Omega = \int_{\Omega} (B - D) d\Omega \quad (2)$$

where

$$d\Omega = dxdydzdp_1 dp_2 ... dp_k \;\; ; \;\; \int_{\Omega} = \int \int \int_{x\,y\,z\,p_1} ... \int_{p_k} \quad (3)$$

B and D represent the corresponding rate of "birth" and "death" of entities per unit time, unit geometric volume and unit property change. The left-hand side of eq (2) can be modified by using the general form of Leibnitz's rule for differentiating definite integrals. Thus, following the general developments of Himmelblau and Bischoff, the differential form of eq (2) can be obtained:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x}(u_x n) + \frac{\partial}{\partial y}(u_y n) + \frac{\partial}{\partial z}(u_z n) +$$
$$+ \sum_{i=1}^{k} \frac{\partial}{\partial p_i}(u_i n) + D - B = 0 \quad (4)$$

where $u_x = dx/dt$, $u_y = dy/dt$ and $u_z = dz/dt$ denote the usual geometric velocities in the x, y and z spatial coordinates, respectively. $u_i = dp_i/dt$ is the rate of change of the property p_i. Very often, the average values of the properties in the entire reactor volume, V, are only required. Accordingly, one can define the following geometrically averaged distribution function, $\bar{n}$.

$$\bar{n} = \frac{1}{V} \int_{V} n dV \quad (5)$$

By integrating eq (4) over the geometric volume, V, and using the Gauss' divergence theorem, the following macroscopic population balance equation is obtained:
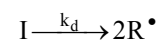
$$\frac{1}{V} \frac{\partial}{\partial t}(V\bar{n}) + \sum_{i=1}^{k} \frac{\partial}{\partial p_i}(u_i \bar{n}) + \bar{D} - \bar{B} =$$
$$= \frac{1}{V}(q_{in}\bar{n}_{in} - q_{out}\bar{n}_{out}) \quad (6)$$

where q_{in} and q_{out} are the inlet and outlet volumetric flow rates, respectively.
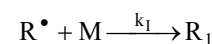
2.1 Calculation of Molecular Weight Distribution

Let us assume that the kinetic mechanism of the chemically initiated free-radical polymerization of a vinyl monomer comprises the following elementary reactions:
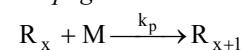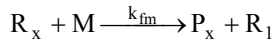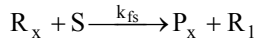
Initiator decomposition:
$$I \xrightarrow{k_d} 2R^{\bullet}$$

Chain initiation:
$$R^{\bullet} + M \xrightarrow{k_I} R_1$$

Propagation:
$$R_x + M \xrightarrow{k_p} R_{x+1}$$

Chain transfer to monomer:

$$R_x + M \xrightarrow{\ k_{fm}\ } P_x + R_1$$

Chain transfer to solvent (CTA):

$$R_x + S \xrightarrow{\ k_{fs}\ } P_x + R_1$$

Termination by disproportionation:

$$R_x + R_y \xrightarrow{\ k_{td}\ } P_x + P_y$$

Termination by combination:

$$R_x + R_y \xrightarrow{\ k_{tc}\ } P_{x+y}$$
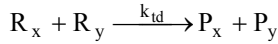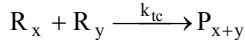
Chain transfer to polymer:

$$R_x + P_y \xrightarrow{\ k_{fp}\ } R_y + P_x$$

Reaction with terminal double bond:

$$R_x + P_y^{=} \xrightarrow{\ k_{db}\ } R_{x+y}$$
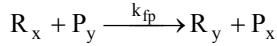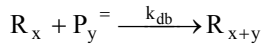
The subscripts x and y denote the number of monomer units in a polymer chain. The above kinetic mechanism includes propagation and termination reactions by both disproportionation and combination, molecular weight control reactions via transfer to monomer and to chain transfer agent, long-chain branching formation by transfer to polymer and reaction with terminal double bonds.

Based on the above kinetic mechanism, we can derive the following population balance equations for the "live", $R(x,t)$, and "dead", $P(x,t)$, polymer chains of length x. Assuming that the degree of polymerization, x, can only take discrete values $(x : 1,2,...\, N_f)$, the inlet and outlet terms in eq (6) are equal to zero (i.e., batch reactor) and the rate of change of property x is equal to zero, one can easily derive the following macroscopic population balances for the entities $R(x,t)$ and $P(x,t)$.

$$\frac{1}{V}\frac{d}{dt}(VR) = \left\{ k_I [R^\bullet][M] + \left(k_{fm}[M] + k_{fs}[S] \right) \sum_{y=1}^{\infty} R(x,t) \right\} \delta_{x,1} +$$

$$+ k_p \{ R(x-1,t) - R(x,t) \} [M] - \{ k_{fm}[M] + k_{fs}[S] \} R(x,t) +$$

$$+ k_{fp} \{ x D(x,t) \} \sum_{y=1}^{\infty} R(y,t) - k_{fp} R(x,t) \sum_{y=2}^{\infty} y D(x-y,t) -$$

$$- k_{td} R(x,t) \sum_{y=1}^{\infty} R(y,t) - k_{tc} R(x,t) \sum_{y=1}^{\infty} R(y,t) - \qquad (7)$$

$$- k_{db} R(x,t) \sum_{y=2}^{\infty} D(x-y,t) + k_{db} \sum_{y=1}^{x-1} \{ R(x-y,t) D(x-y,t) \}$$

$$\frac{1}{V}\frac{d}{dt}(VP) = \{ k_{fm}[M] + k_{fs}[S] \} R(x,t) -$$

$$- k_{fp} \{ x D(x,t) \} \sum_{y=1}^{\infty} R(y,t) + k_{fp} R(x,t) \sum_{y=2}^{\infty} \{ y D(x-y,t) \} +$$

$$+ k_{td} R(x,t) \sum_{y=1}^{\infty} R(y,t) + \frac{1}{2} k_{tc} \sum_{y=1}^{x-1} \{ R(y,t) R(x-y,t) \} -$$

$$- k_{db} D(x,t) \sum_{y=1}^{\infty} R(y,t) \qquad (8)$$

where $\delta_{x,1}$ is the Kronecker's delta function (i.e., $\delta_{x,1} = 1$ if $x = 1$ and $\delta_{x,1} = 0$ if $x \neq 1$).
Note that the right-hand side terms in eqs (7-8) represent the net production rates of "live" and

"dead" polymer chains. The actual number of rate equations for the "live" and "dead" polymer chains will depend on the total degree of polymerization, N_f, that may be of the order of hundreds or/and thousands monomer units. Consequently, the computational effort associated with the solution of the complete set of differential equations becomes prohibitively high for most cases of interest and makes the on-line application of such a model unrealistic. To deal with the above high-dimensionality problem, several methods have been proposed to reduce the infinite system of differential equations into a low-order system of DAEs. These can be broadly classified into kinetic lumping methods, continuous variable approximations, z-transforms, method of moments, discrete weighted Galerking, orthogonal collocation on finite elements and so forth.

In the kinetic lumping methods (Crowley and Choi, 1997a,b, 1998), the polymer chains population is divided into a specified number of "chain lump" domains and the resulting population balance equations are solved numerically. A uniform concentration is assumed for all polymer chains that are members of a "chain lump" domain. However, the calculation of MWD for branched polymers (e.g., systems involving transfer to polymer and terminal double bond reactors) suffers from significant inaccuracies. Continuous variable approximation and z-transform methods, besides their elegant mathematical formulation, lack the ability to handle complex polymerization systems efficiently. Polynomial expansion methods of the MWD require the calculation of high-order moments and may lead to slow convergence (Tobita and Ito, 1993). Pladis and Kiparissides (1998) proposed a polymer chain fractionation approach and used the method of moments to reconstruct the joint molecular weight – long-chain branching distribution for branched polymers. The total population of the polymer chains was divided into a number of classes with respect to the number of long-chain branches. However, in addition to the well-known problem of closure of the "higher-order" moments, the reconstruction of the overall MWD at high monomer conversions and high LCB content requires a very large number of classes to reduce the approximation errors for high molecular weight fractions. Monte-Carlo simulations (Tobita, 1993, 1995) are straightforward techniques that can generally handle complex kinetic mechanisms but usually require significant computational effort for the determination of the MWD. Discrete weighted Galerkin formulation (Deuflhard and Wulkow, 1989, Wulkow, 1992), even though are computationally demanding, provide a powerful tool for the prediction of the MWD in complex polymerization systems (Iedema et al., 2000). However, the approximation of the infinite summation terms (e.g., resulting from termination by combination reactions) requires special treatment.

Method of Moments. The method of moments is based on the statistical representation of the average molecular properties of the polymer (e.g., number average, M_n, and weight average, M_w, molecular weights) in terms of the leading moments of the

number chain length distributions (NCLDs) of "live" and "dead" polymer chains, defined by the following equations:

$$\lambda_k = \sum_{x=1}^{\infty} x^k R_x \ , \ \mu_k = \sum_{x=1}^{\infty} x^k P_x \ , \ k = 0, 1, 2 \quad (9)$$

The relevant rate functions for the moments of the NCLDs of the "live" and "dead" polymer chains can be obtained by multiplying each term of eqs (7-8) by x^k and summing the resulting expressions over the total degree of polymerization, N_∞. The resulting rate equations for the leading moments are (Pladis and Kiparissides, 1998):

$$\frac{d\lambda_k}{dt} = k_I[R^\bullet][M] + k_{fm}[M]\lambda_0 + k_{fs}[S]\lambda_0 +$$

$$+ k_p[M]\sum_{i=0}^{k}\binom{k}{i}\lambda_i - k_p[M]\lambda_k - k_{fm}[M]\lambda_k -$$

$$- k_{fs}[S]\lambda_k - k_{fp}\lambda_k\mu_1 + k_{fp}\lambda_0\mu_{k+1} - k_{db}\lambda_k\mu_0 +$$

$$+ k_{db}\sum_{i=0}^{k}\lambda_i\mu_{k-i} - k_t\lambda_0\lambda_k \quad (10)$$

$$\frac{d\mu_k}{dt} = k_{fm}[M]\lambda_k + k_{fs}[S]\lambda_k + k_{fp}\lambda_k\mu_1 - \quad (11)$$

$$- k_{fp}\lambda_0\mu_{k+1} - k_{db}\lambda_0\mu_k + \frac{1}{2}k_{tc}\sum_{i=0}^{k}\binom{k}{i}\lambda_i\lambda_{k-i} + k_{td}\lambda_0\lambda_k$$

where $[R^\bullet]$, $[M]$ and $[S]$ denote the concentrations of "live" radicals, monomer and chain transfer agent, respectively. Usually, one needs to know the leading moments (i.e., λ_0, λ_1, λ_2 and μ_0, μ_1, μ_2 of the "live" and "dead" polymer distributions) to calculate the values of the number-average, M_n, and weight-average, M_w, molecular weights.

Orthogonal Collocation on Finite Elements. A key characteristic of the OCFE method is the treatment of the discrete polymer chain length domain as a continuous one. Hence, the concentrations of "live" and "dead" polymer chains are handled as continuous variables. Accordingly, the chain length domain is divided into a number of finite elements, NE, with element boundaries at the points: $\zeta_0 = 1$, ζ_1, $\zeta_2,\ldots, \zeta_{NE-1}$, $\zeta_{NE} = N_f$, where N_f is the final degree of polymerization. For each element, a number of n interior collocation points, $[s_1, s_2,\ldots, s_n]$ are specified. The concentrations of the "live" and "dead" polymer chains are then approximated by continuous low-order polynomial functions within each finite element. In the present study, Lagrange interpolation polynomials were used to approximate the concentrations of the "live" and "dead" polymer chains:

$$\widetilde{R}(s) = \sum_{i=0}^{n} W_{i,j}^R(s)\widetilde{R}(s_{i,j}) \quad \zeta_{j-1} \le s \le \zeta_j \quad j = 1,\ldots, NE \quad (12)$$

$$\widetilde{P}(s) = \sum_{i=1}^{n} W_{i,j}^P(s)\widetilde{P}(s_{i,j}) \quad \zeta_{j-1} \le s \le \zeta_j \quad j = 1,\ldots, NE \quad (13)$$

The tilde denotes approximation variables. The functions, $W_{i,j}^R(s)$ and $W_{i,j}^P(s)$ are Lagrange

interpolation polynomials of order n+1 and n, respectively, given by the expressions:

$$W_{i,j}^R(s) = \prod_{\substack{k=0 \\ k\neq i}}^{n} \frac{s - s_{k,j}}{s_{i,j} - s_{k,j}} \quad \zeta_{j-1} \le s \le \zeta_j \quad (14)$$

$$i = 0,\ldots, n \quad j = 1,\ldots, NE$$

$$W_{i,j}^P(s) = \prod_{\substack{k=1 \\ k\neq i}}^{n} \frac{s - s_{k,j}}{s_{i,j} - s_{k,j}} \quad \zeta_{j-1} \le s \le \zeta_j \quad (15)$$

$$i = 1,\ldots, n \quad j = 1,\ldots, NE$$

The Lagrange polynomials $W_{i,j}^R(s)$ and $W_{i,j}^P(s)$ are equal to zero at the collocation points $s_{i,j}$, for $k\neq i$ and equal to unity for $k=i$. To take into account the concentration of "live" polymer chains at chain length x=1, the left boundary point of the first element was included as an interpolation point.

A set of residual equations are then derived by substituting eqs (12-13) into eqs (7-8). The main requirement of the OCFE formulation forces the residual balances to vanish at the selected collocation points, $s_{i,j}$. The number of the finite element controls the density of the collocation points in the overall chain length domain. In general, a high density of collocation points is required in chain length regions where steep changes in the concentrations of "live" and "dead" polymer chains are foreseen. Extensive simulations showed that low-order interpolation polynomials predict the overall MWD more accurately, compared to high-order polynomials for the same total number of collocation points. This was attributed to the oscillatory behavior of the high-order Langrange polynomials.

Fixed Pivot Method. The inherent limitations of the discretized PBE approach, resulting from the discretization of the chain length domain, can be avoided in the more general formulations (i.e., fixed and moving pivot techniques) of Kumar and Ramkrishna (1996a,b) and (1997). The last methods guarantee the correct calculation of any two moments of the distribution and are applicable to any type of discretization of the chain length domain.
The fixed pivot technique is a very efficient method for the calculation of the number chain length distribution (NCLD). It assumes that the overall polymer chain population can be assigned to selected discrete chain lengths. Specific reaction steps (e.g., termination, propagation, etc.) leading to the formation of polymer chains other than the selected ones, are incorporated in the set of discrete equations in such a way that specified properties of the NCLD (i.e., total number, mass of polymer chains, etc., corresponding to any two moments of the NCLD) are exactly preserved.

Simulation results. The outlined methods (Moments, OCFE and FPM) were applied to the free-radical batch polymerization of methyl-methacrylate (MMA). The values of the kinetic rate constants as well as the gel and glass effect models were taken from the original paper of Chiu, *et al.,* (1983). The polymerization was carried out isothermally at 60°C. For the fixed pivot method, the chain length domain
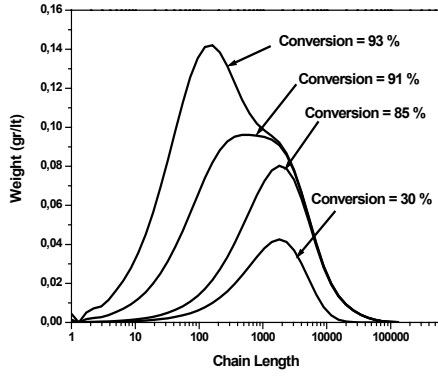
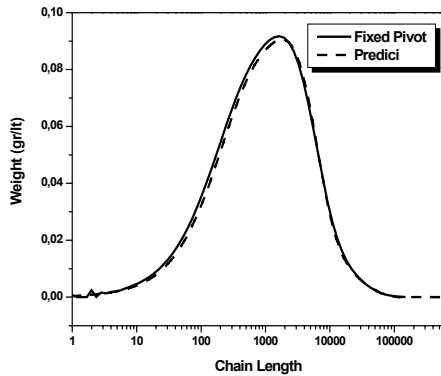Fig. 1. Time evolution of the MWD calculated by the FP method.

Fig. 2. Comparison of MWDs calculated by the FP and discrete Galerkin methods.

was partitioned into 70 finite elements leading to a number of $2 \times NE+2 = 142$ residual differential equations.

Figure 1 depicts the time evolution of the molecular weight distribution of PMMA as calculated by the fixed pivot method. As can be seen, as the monomer conversion increases the MWD becomes broader. At very high monomer conversions (e.g., > 90%), a bimodal distribution is obtained. In Figure 2, a comparison of the MWDs calculated by the FP method and the discrete Galerkin h-p method (PREDICI simulation package) is shown at 90% monomer conversion. It is evident that the calculated distributions are in excellent agreement, verifying the ability of the FP method to accurately predict the MWD.

2.2 Calculation of Particle Size Distribution

To follow the dynamic evolution of the PSD in a particulate process, a population balance approach is commonly employed. The distribution of the particulates (e.g., solid particles, liquid droplets, etc.) is considered to be continuous over the volume variable and is commonly described by a number density function. Thus, the term $n(V,t)dV$ represents the number of particles per unit volume in the differential volume size range (V to V+dV). For a dynamic particulate system undergoing simultaneous particle nucleation, growth and aggregation, the rate of change of the number density function with respect to time and volume is given by the following

nonlinear integro-differential population balance equation:

$$\frac{\partial n(V,t)}{\partial t} + \frac{\partial (G_V(V) n(V,t))}{\partial V} = \frac{q_{in} n_{in}(V,t) - q_{out} n(V,t)}{V} -$$

$$- \frac{n(V,t)}{V}\frac{\partial V}{\partial t} + \int_{V_{min}}^{V/2} \beta(U,V-U) n(U,t) n(V-U,t)\, dU -$$

$$- n(V,t) \int_{V_{min}}^{V_{max}} \beta(V,U) n(U,t)\, dU + S_v(V,t) \qquad (16)$$

where q_{in} and q_{out} are the inlet and outlet volumetric flow rates, respectively. $n_{in}(V,t)$ is the inflow number density function, V the total volume of the reactor, G_V is a particle volume growth rate function and $\beta(V,U)$ is a particle aggregation rate kernel for particles of volumes V and U. V_{min} and V_{max} denote the corresponding minimum and maximum size of particles present in the system. Finally, $S_v(V,t)$ is the particle nucleation rate. In general, eq 16 will satisfy the following initial condition:

$$n(V,0) = n_0(V) \ , \ \text{at} \ \ t = 0 \qquad (17)$$

The numerical solution of the dynamic PBE for a particulate system, especially for a reactive one, is a notably difficult problem due to both numerical complexities and model uncertainties regarding the particle nucleation, growth, aggregation and breakage mechanisms that are often poorly understood. Usually, the numerical solution of the PBE requires the discretization of the particle volume domain into a number of discrete elements that results in a system of stiff, nonlinear differential or algebraic/differential equations that is solved numerically. In the open literature, several numerical methods have been developed for solving the steady-state or dynamic PBE. These include the full discrete method (Hidy, 1965), the method of classes (Marchal, *et al.*, 1988; Chatzi and Kiparissides, 1992), the discretized PBE (Batterham, *et al.*, 1981; Hounslow, *et al.*, 1988), the fixed and moving pivot discretized PBE methods (Kumar and Ramkrishna, 1996a,b), the high order discretized PBE methods (Landgrebe and Pratsinis, 1990; Bleck, 1970; Gelbard and Seinfeld, 1980), the orthogonal collocation on finite elements (Gelbard and Seinfeld, 1979), the Galerkin method (Nicmanis and Hounslow, 1998), and the wavelet-Galerkin method (Chen, *et al.*,1996). In the reviews of Ramkrishna (1985), Dafniotis (1996), and Kumar and Ramkrishna (1996a,b), the various numerical methods available for solving the PBE are described in detail. Moreover, in three publications by Kostoglou and Karabelas (1994, 1995), and Nicmanis and Hounslow (1996), comparative studies on the different numerical methods are presented. Based on the conclusions of these studies, the discretized PBE method of Litster, *et al.*, (1995) the pivot methods of Kumar and Ramkrishna (1996a,b), the Galerkin and the orthogonal collocation on finite element methods were found to be the most accurate and stable numerical techniques.

In Table 3, selective publications on the numerical solution of the general PBE are reported.

Table 3. Numerical Methods for the Solution of the PBE

Methods	Author	Test Cases	Comments
M-I	Hiddy (1965)	➤ Aggregation	● Full discrete method.
	Batterham et al. (1981)	➤ Aggregation	● Geometric discretization of the form $V_{i+1}=2V_i$.
	Marchal et al. (1988)	➤ Aggregation / Growth	● Method of classes.
	Hounslow et al. (1988)	➤ Aggregation / Growth / Nucleation	● Fixed discretization of the form $V_{i+1}=2V_i$.
	Litster et al. (1995)	➤ Aggregation / Growth (Batch) ➤ Aggregation / Growth / Nucleation (CSTR)	● Discretization based on the rule $V_{i+1}=2V_i^{1/q}, q \geq 2$
	Kumar and Ramkrishna (1996[a,b]; 1997)	➤ Aggregation / Growth / Nucleation	● Arbitrary discretization.
	Vanni (2000)	➤ Aggregation /Breakage	● Comparison of DPBE methods based on a very coarse discretization
M-II	Bleck (1970)	➤ Aggregation	● Use of two different types of discretization. (i.e . $V_{i+1}=2^{1/2} V_i$ and $V_{i+1}=2^{1/3} V_i$).
	Gelbard et al (1980)	➤ Aggregation	● Generalization for the multi-component PBE case (Gelbard and Seinfeld, 1980).
	Satry and Gaschignard (1981)	➤ Aggregation	● Different set of equations for every moment of the distribution.
	Landgrebe and Pratsinis (1990)	➤ Aggregation	● Comparison of the numerical results only with respect to the moments of the distribution.
WR	Sigh and Ramkrishna (1975)	➤ Aggregation	● Employment of problem-specific polynomials as basis functions.
	Sampson and Ramkrishna (1985)	➤ Aggregation	● Employment of root-shifted problem-specific polynomials as basis functions. Improved accuracy based on the correct choice of the collocation points
FE	Gelbard and Seinfeld (1978)	➤ Aggregation / Growth / Nucleation	● Comparison of two collocation methods (i.e., spline collocation and orthogonal collocation on finite elements).
	Pillinis (1990)	➤ Aggregation / Growth	● Galerkin on finite elements method. Simulations of multi-component particulate systems.
	Erasmus et al. (1994)	➤ Aggregation / Growth	● Galerkin on finite elements method with b-splines.
	Nicmanis and Hounslow (1996 and 1998)	➤ Aggregation / Growth /Nucleation / Breakage (CSTR)	● Steady state formulation of the PBE. Collocation and Galerkin techniques with quadratic basis functions.
	Mahoney and Ramkrishna (2002)	➤ Aggregation / Growth / Nucleation	● Galerkin on finite elements with linear basis functions. Special treatment of moving discontinuities that arise in problems with particle growth.
	Rigopoulos and Jones (2003)	➤ Aggregation / Growth /Nucleation / Breakage (Batch, CSTR)	● Galerkin on finite elements with linear basis functions.
	Sandu and Borden (2003)	➤ Aggregation / Growth	● General framework for the solution of PBE with finite element techniques. Several formulations are considered with respect to the choice of basis functions, co-ordinates etc.

Common problems related to the numerical solution of the PBE include the inaccurate calculation of the PSD for highly aggregating processes, numerical instabilities for growth-dominated processes, increased stiffness of the system of DAEs for processes involving rapid particle nucleation, and domain errors for high-order aggregation kernels (Kumar and Ramkrishna, 1996a,b ; Dafniotis, 1996). In two recent publications (Alexopoulos, et al., 2004; Alexopoulos and Kiparissides, 2004), a comprehensive investigation on the solution of the dynamic population balance equation, in the presence of particle growth, aggregation and nucleation, is presented and the numerical difficulties and limitations of two very commonly employed methods (i.e., the orthogonal collocation on finite elements and the discretized PBE approach) are critically examined.

The Discretized Population Balance Equation. In the discretized PBE approach, it is assumed that the number density function, n(V,t), remains constant in the discrete volume interval (V_i to V_{i+1}).

Accordingly, a particle number distribution, $N_i(t)$, corresponding to the "i" element is defined:

$$N_i(t) = \int_{V_i}^{V_{i+1}} n(V,t)\, dV = \overline{n}_i(t)\left(V_{i+1} - V_i\right) \quad (18)$$

where $\overline{n}_i(t)$ is the average value of n(V,t) in the element "i".

Following the original developments of Litster, *et al.*, (1995) the total volume domain (V_{min} to V_{max}) is divided into a number of elements using the fractional geometric discretization rule, $V_{i+1} = 2^{1/q}\, V_i$,

where q is an integer, positive number. As the value of q increases the total number of volume elements increases (i.e., a finer grid is generated) and so does the computational effort for the calculation of the PSD. Accordingly, the discretized PBE for a batch particulate system undergoing simultaneous growth, aggregation and nucleation becomes:

$$\frac{dN_i(t)}{dt} = S_0(t)\sum_{j=1}^{3}\delta(i-j)f_i + \frac{2G_V}{3(1+r)V_i}\left\{\frac{r\,N_{i-1}}{r^2-1} + N_i - \frac{N_{i+1}}{r^2-r}\right\}+$$
$$+\sum_{k=2}^{q}\sum_{j=i-S(q-k+2)-k+1}^{i-S(q-k+1)-k}\beta_{i-k,j}N_{i-k}N_j\frac{2^{(j-i+1)/q}-1+2^{-(k-1)/q}}{2^{1/q}-1} +$$
$$+\frac{1}{2}\beta_{i-q,i-q}N_{i-q}^2 - \sum_{j=1}^{i-S(q)}\beta_{i,j}N_iN_j\frac{2^{(j-i)/q}}{2^{1/q}-1} + \qquad (19)$$
$$+\sum_{k=2}^{q}\sum_{j=i-S(q-k+2)-k+2}^{i-S(q-k+1)-k+1}\beta_{i-k+1,j}N_{i-k+1}N_j\frac{2^{1/q}-2^{(j-i)/q}-2^{-(k-1)/q}}{2^{1/q}-1} -$$
$$-\sum_{j=i-S(q)+1}^{\infty}\beta_{i,j}N_iN_j + \sum_{j=1}^{i-S(q)-1}\frac{2^{(j-i+1)/q}}{2^{1/q}-1}\beta_{i-1,j}N_{i-1}N_j$$

where $S(q) = q(q+1)/2$. "ne" is the total number of elements, $\beta_{i,j} = \beta(V_i,V_j)$ is the equivalent discrete kernel for particle aggregation and r is equal to the ratio D_{i+1}/D_i.

Finite Element Techniques. The continuous form of the PBE (eq 16) can be solved using the finite element method (FEM). Recently, Nicmanis and Hounslow, (1998), employed a collocation and Galerkin FEM to determine the steady state PSD for a continuous particulate process undergoing combined particle growth and aggregation.

In the OCFE, the particle volume domain is first divided into "ne" elements based on an appropriately selected volume discretization rule. Then, "nc"

internal collocation points are specified within each element. Accordingly, the unknown number density function is approximated at the internal and boundary collocation points of each element, "e", in terms of Lagrange basis functions, φ_j:

$$n(V,t) = \sum_{j=0}^{nc+1} n_j^e(t)\, \varphi_j(V) \qquad (20)$$

where n_j^e denotes the value of $n(V, t)$ at the "j" internal or boundary collocation point. The above approximation, results in a total number of (ne(nc+1)+1) unknown values of the number density function, n_j^e.

Following the general developments of Finlayson (1980), eq 16, for a batch process, can be recast into a system of (ne•nc) residual equations, corresponding to all the internal points of the "ne" volume elements.

$$\dot{n}_i^e(t) = -\sum_{j=0}^{nc+1}\left(\frac{d\varphi_j}{d\xi}\right)_i n_j^e(t)\,|J|^e\, G_V(V_i) - \left(\frac{dG_V}{dV}\right)_i n_i^e(t) -$$

$$- n_i^e(t)\sum_{f=1}^{ne}\sum_{k=1}^{nc} w_k^G\,|J|^f\, \beta\!\left(V_i^e, V_k^f\right) n_k^f(t) +$$

$$+ \sum_{f=1}^{g-1}\sum_{j=1}^{nc}\left[w_j^G\,|J|^f\, \beta(V_i^e - V_j^f, V_j^f)\, n_i^e n(V_i^e - V_j^f)\right] +$$

$$+ \int_{V_l^g}^{V_i^e/2} \beta(V_i^e - V, V)\, n(V)\, n(V_i^e - V)\,dV \qquad (21)$$

According to the standard finite element formulation, the global volume domain of each element "e" is linearly transformed into a local domain [-1,1]. The index "g" denotes the element containing the ($V_i^e/2$) discrete point. $|J|^f$ is the Jacobean of the volume transformation and w_k^G are the weights of the Gauss-Legendre quadrature integration rule. More details regarding the derivation of eq 21 can be found in Alexopoulos, *et al.*, (2004).

At the boundary points between the various elements, the number density function and its first derivative are forced to be continuous. Thus, the following (ne-1) continuity conditions between all the adjacent pair of elements (e and e+1) are written:

$$\sum_{j=1}^{nc}\left(\frac{d\varphi_j}{d\xi}\right)_{\xi_{nc+1}} n_j^e(t)\,|J|^e = \sum_{j=1}^{nc}\left(\frac{d\varphi_j}{d\xi}\right)_{\xi_0} n_j^{e+1}(t)\,|J|^{e+1} \quad (22)$$

Since the total number of unknown nodal values of n_j^e (i.e., ne (nc + 1) + 1), is more than the total number of residual equations and continuity conditions (i.e., ne (nc + 1) – 1), two additional equations are needed to produce a closed system of DAEs. These equations correspond to the values of n_j^e at the minimum V_{min} (e = 1, j = 0) and maximum V_{max} (e = ne, j = nc+1) value of the volume integration domain. At $V = V_{max}$, a residual equation similar to eq 21 can be written. On the other hand, at $V = V_{min}$ the zero boundary condition, $n(V_{min},t) = 0$, can be employed.

2.3 Application of PBE to Particulate Polymerizations

The Suspension Polymerization Process. In suspension polymerization, the monomer is initially dispersed in the continuous aqueous phase by the combined action of surface active agents (e.g., inorganic or/and water-soluble polymers) and agitation. All the reactants (i.e., monomer, initiator(s), etc.) reside in the organic or "oil" phase. The polymerization occurs in the monomer droplets that are progressively transformed into sticky, viscous monomer-polymer particles and finally into rigid, spherical polymer particles of size 50-500 μm. The polymer solids content in the fully converted suspension is typically 30-50% w/w. Large quantities of polymers, including poly(vinyl chloride) and polystyrene, are produced by the suspension polymerization process.

One of the most important issues in the operation of a suspension polymerization reactor is the control of the final particle size distribution (Yuan, *et al.*, 1991). The initial monomer droplet size distribution as well as the final polymer particle size distribution in general depend on the type and concentration of the surface active agents, the quality of agitation and the physical properties (e.g., density, viscosity and interfacial tension) of the continuous and dispersed phases. The transient droplet / particle size distribution is controlled by two dynamic processes, namely, the drop breakage and drop coalescence rates. The former mainly occurs in regions of high shear stresses (i.e., near the agitator blades). The latter is either increased or decreased with the intensity of the turbulent flow field and can be assumed to be negligible for dilute dispersions at sufficiently high concentrations of surface active agents (Chatzi, *et al.*, 1989).

The dynamic behavior of a liquid-liquid dispersion in a stirred vessel and, therefore, the drop-size distribution are determined by the droplet breakage and coalescence rates. In general, the drop-size distribution in a batch system can be predicted by the solution of the following population balance equation:

$$\frac{\partial\left(n(V,t)\right)}{\partial t} = \int_V^{V_{max}} k(U,V)\, u(U)\, g(U)\, n(U,t)\,dU +$$

$$+ \int_{V_{min}}^{V/2} \beta(V-U,U)\, n(V-U,t)\, n(U,t)dU - \qquad (23)$$

$$- n(V,t)\, g(V) - n(V,t)\int_{V_{min}}^{V_{max}} \beta(V,U)\, n(U,t)\,dU$$

The left-hand side term in eq 23 represents the rate of change of the number density function, n(V,t). The first term on the right-hand side of eq 23 represents the generation of droplets in the size range (V , V+dV) due to drop breakage. k(U,V) is a daughter drop probability function, accounting for the probability that a drop of volume V to be formed by the breakage of a drop of volume U. u(U) is the number of droplets formed by the breakage of a drop of volume U and g(U) is the breakage rate of a droplet of volume U. The second term represents the
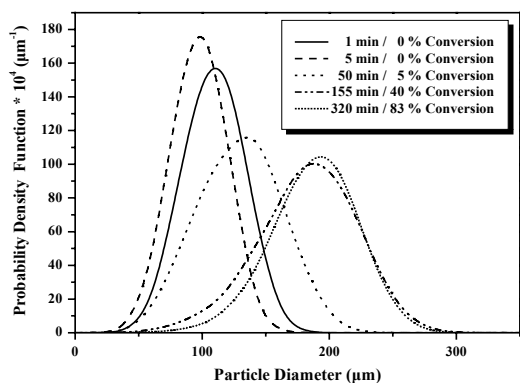
Fig. 3. Dynamic evolution of the volume probability density function with respect to polymerization time for the VCM suspension polymerization (Polymerization temperature: 56.5 $^{\circ}$C, impeller speed: 330 rpm, dispersed phase volume fraction: 40%).
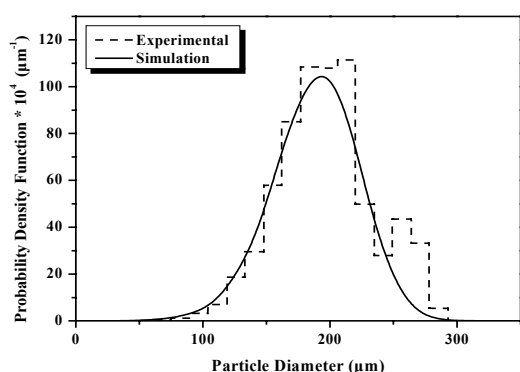

Fig. 4. Predicted and experimental PSDs for the VCM suspension polymerization

generation of drops in the size range (V , V+dV) due to the coalescence of two smaller droplets. $\beta(V, U)$ is the coalescence rate between two drops of volume V and U. Finally, the third and fourth terms represent the disappearance rates of drops of volume V due to breakage and coalescence, respectively.

The predicting capabilities of the present model were demonstrated by a direct comparison of model predictions with experimental data on the drop/particle size distribution for a VCM suspension polymerization system. The experiments were carried out in a 30 lt batch reactor, using 40 % v/v VCM in water. The polymerization temperature was set equal to 56.5 $^{\circ}$C while the agitation speed remained constant at 330 rpm. Detailed experimental measurements on polymerization rate, monomer conversion and PSD were provided by ATOFINA.

Figure 3 illustrates the dynamic evolution of the calculated PSD at different monomer conversions. More specifically, the volume probability density function (defined as $d_v^3 n/V_{tot}$) is plotted with respect to the particle diameter. One can easily distinguish the three stages that the suspension polymerization undergoes (Maggioris, *et al.*, 2000). During the initial low-viscosity period (e.g., up to 5% monomer conversion), drop breakage is the dominant mechanism and the distribution shifts to smaller sizes. Afterwards, during the sticky stage of the polymerization (e.g., 5-75 % monomer conversion), the drop breakage rate decreases while the drop coalescence becomes the dominant mechanism. In Figure 4, the predicted final PSD (continuous line) is compared with the experimental one (discrete line). As can be seen, the simulation results are in very good agreement with the experimental measurements.

Emulsion Polymerization. In emulsion polymerization, an aqueous dispersion of monomer(s) is converted by free-radical polymerization into a stable dispersion of polymer particles of 0.1-1 μm in diameter. A typical emulsion recipe comprises the dispersing medium (e.g., water), monomer(s), a water soluble initiator and an emulsifying agent (e.g., sodium and potassium salts of saturated long-chain acids). The excess of surfactant forms micelles (ca. 5-10 nm in diameter). A very small part of the monomer can be found in solution, some is solubilized by the micelles but most stays in the monomer droplets (ca. l0μm in diameter). Usually, the concentrations of micelles and monomer droplets are 10^{18} micelles/cm^3 and 10^{10}-10^{11} droplets/cm^3, respectively. Polymerization occurs either in the interior of the micelles (micellar nucleation) or in the continuous phase (homogeneous nucleation) when the monomer is at least slightly soluble. Typical emulsion processes include copolymerization of styrene and butadiene (SBR rubber) and polymerization of chloroprene (neoprene rubber). Also vinyl acetate and several acrylic monomers are polymerized in emulsion in the manufacture of latex paints.

The mathematical modeling of emulsion polymerization reactors has been the subject of a great number of publications (Saldivar and Ray, 1997a,b; Richards, *et al.*, 1989; Storti, *et al.*, 1989; Napper and Gilbert, 1989; Dougherty, 1986). Nevertheless, the development of a comprehensive mathematical model, capable of predicting the molecular (e.g., molecular weight distribution, copolymer composition, etc.) and morphological (e.g., particle size distribution) properties of the latex is not a trivial task, for there is a number of physical and chemical phenomena, which cannot be experimentally assessed and, thus, be easily modelled.

In a recent study by Kammona, *et al.*, (2003), a detailed experimental and theoretical study on the Styrene / 2-Ethylhexyl Acrylate emulsion copolymerization was reported. Kinetic experiments were carried out in a laboratory batch reactor to assess the effect of key process variables (e.g., concentrations of initiator and nonionic surfactant, temperature and initial monomer molar ratio) on the polymerization rate, monomer conversion, copolymer composition and particle size distribution (PSD). To predict the evolution of molecular and morphological properties, a comprehensive mathematical model was developed in terms of a detailed emulsion copolymerization kinetic mechanism, the dynamic molar species balances in the aqueous and polymer phases and a population balance equation (PBE) describing the time evolution of PSD in the reactor. A generalized model
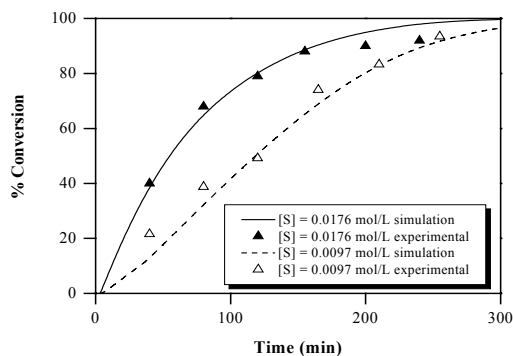
Fig. 5. Comparison of model predictions and experimental measurements on overall monomer conversion. Effect of surfactant concentration on the overall monomer conversion.
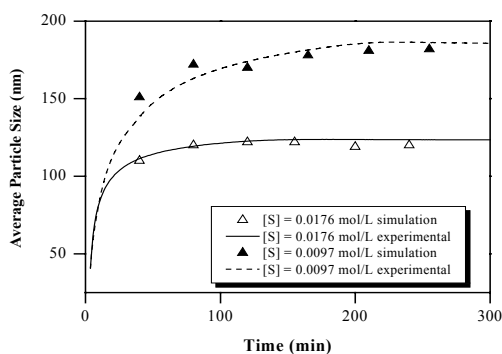

Fig. 6. Comparison of model predictions and experimental measurements on average particle size. Effect of surfactant concentration on the average particle size.
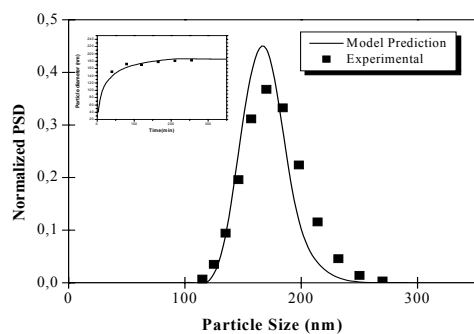

Fig. 7. Predicted and experimental PSDs (f_{10} = 0.81, [APS]= 0.0095 mol/L and [NP-30] = 0.0097 mol/L).

(Lazaridis, *et al.*, 1999) was employed for the calculation of the total interaction potential of sterically stabilized particles, in order to describe particle stability during the polymerization process. The predictive capabilities of the proposed model were thoroughly assessed by a direct comparison of theoretical predictions with experimental data on monomer conversion, average particle size and PSD.

In Figures 5 and 6, model predictions are compared with experimental measurements on overall monomer conversion and average particle diameter, respectively, for an initial styrene mol fraction of f_{10} = 0.81 at two different concentrations of the nonionic surfactant (NP-30) (e.g., 0.0097, 0.0176 mol/L). As

can be seen, model predictions are in very good agreement with experimental measurements. As expected, an increase in emulsifier concentration results in an increase of the number of generated particles which leads to a decrease of the average particle size (see Figure 6) and to a respective increase of the polymerization rate (see Figure 5). In Figure 7, the predicted final PSD is compared with the experimentally measured one. As can be seen, model predictions are in very good agreement with the experimentally measured PSD. The small inserted graph shows the time evolution of the average diameter.

3. REAL-TIME OPTIMIZATION AND CONTROL

Process optimization and control can have a significant strategic impact on polymer plant operability and economics. The main goals in operating a polymer reactor (e.g., high yield, better product quality and safe operation) are very difficult, if not impossible, to achieve without efficient and reliable polymer characterization techniques. Although the weakest link in polymer reactor control is undoubtedly the on-line instrumentation, lack of understanding of the process dynamics, the highly sensitive and nonlinear behavior of polymer reactors and the lack of well structured control strategies all contribute to the impairment of competitiveness. Thus, the main problems to be addressed in the development of an optimization/control policy for a polymer process are:

- Better understanding of process dynamics (via mechanistic/data-based modelling and experimentation).

- Ability to measure and characterize a whole range of polymer quality variables (via on-line sensors and nonlinear estimation algorithms).

- Development of nonlinear model-based predictive controllers with emphasis on achieving superior performance and constraint handling.

The key to building a reliable model is to mathematically describe the chemical and physical phenomena involved in a process and to derive the necessary material, energy and momentum balances. These mathematical descriptions involve nonlinear algebraic and differential equations. Needless to say that the rigour and accuracy of a simulation model are strongly affected by the prediction of the thermophysical properties of the polymerization system.

Hardware and Software Sensors. In Table 4, selective references on the online monitoring of "polymer quality" are reported. In several occasions, the measurements become available with delay and poor signal to noise ratio. On the other hand, mathematical models based on fundamental material, energy and population balances are capable of calculating the process states accurately. However, the predictions from mathematical models frequently diverge from the real process output variables due to the presence of time varying model parameters and unknown process disturbances or/and the inherent model-plant mismatch. The first problem to be addressed

Table 4. On-line Hardware Sensors for the
Monitoring of Polymer Quality

Measured Property	Sensing Technique
Monomer Conversion Zeaiter et al.(2002), Mikes et al.(2002), Rudschuck et al.(1999), Van Den Brink et al. (2001), Sasic et al.(2002)	*Densimetry, Gas Chromatography, Calorimetry/Reactor Energy Balances, Ultrasound, Raman Spectroscopy, Near Infrared Spectroscopy, Mid-range Infrared Spectroscopy, UV reflection spectroscopy, Refractive Index Measurements*
Copolymer Composition Stavropoulos et al.(2001), Chatzi et al. (1997), Asua et al.(1995), Gugliotta et al.(1995)	*Gas Chromatography, Near Infrared Spectroscopy, Mid-range Infrared Spectroscopy, Calorimetry/ Reactor Energy Balances*
Molecular Weight and MWD Vega et al. (2001), Vicente et al.(2001), Cherfi et al. (2002)	*Viscometry, Gel Permeation Chromatography, Calorimetry, Near-Infrared Spectroscopy*
Particle Size Distribution Thomas and Dimonie (1990), Gossen et al. (1993), Brandolin and Garcia-Rubio (1991), DosRamos and Silebi (1991)	*Dynamic Light Scattering, Turbidimetry, Near-Infrared Spectroscopy, Packed Column Chromatography, Capillary Hydrodynamic Chromatography*

in a real-time optimization or/and control application is the design of an efficient nonlinear state estimator to establish an information feedback from the process to the model that enables the correction of modelling errors. Apart from the nonlinear control applications, estimators can play a key role in process monitoring for an early detection of undesired reactor conditions (e.g., violation of safety regulations, environmental standards, operating constraints and product quality specifications).

Soroush (1998) categorized the design methods for nonlinear estimators into three classes. The first class includes methods that are based on the extension of the Luenberger observer and Kalman filter estimation using a linearized process model. The second class refers to methods that incorporate the estimation problem within an optimization framework, utilizing the full nonlinear process model. The estimated values for the state variables result from the minimization of the difference beween the measured and predicted responses over a specified time horizon. The third class is based on model linearization through coordinate transformation derived from results in nonlinear control theory.

MacGregor, *et al.*, (1986) illustrated the successful application of an Extended Kalman Filter (EKF) to batch and continuous styrene emulsion polymerization reactors for the online tracking of conversion and latex particle size. De Valliere and Bonvin, (1989), Gagnon and MacGregor, (1991) and Kozub and MacGregor (1992) demonstrated through simulation examples the need to augment the state vector with additional stochastic states to account for the non-stationary variations and eliminate the bias from the state estimates. Ellis, *et al.*, (1994) formulated a multi-rate sampled data EKF incorporating infrequently online GPC measurements of the "dead" polymer concentrations along with temperature and conversion that successfully traced the evolution of the molecular weight distribution in a methyl methacrylate polymerization batch reactor. Muhta, *et al.*, (1997) proposed an algorithm that can handle several measurements with different time delays. Dimitratos, *et al.*, (1989) and (1991) developed several different nonlinear EKFs and experimentally applied them to a semi-batch vinyl acetate/butyl acrylate copolymerization reactor with

excellent state and parameter tracking performance. Crowley and Choi (1998) and Ahn, *et al.*, (1999) implemented EKF algorithms for the optimal control of the molecular weight distribution.

Jang and coworkers (1987) implemented an optimization-based estimator to obtain estimates of the unknown initial state vector. Such an approach was shown to outperform the EKF with increased robustness with respect to measurement noise. Later, Jang, *et al.*, (1987) used similar ideas to identify unmeasured disturbances and to estimate the states and the model parameters for control purposes of a simple CSTR. Muske, *et al.*, (1995) studied the convergence properties and the performance of the receding horizon state estimation technique. Vos, *et al.*, (1997) suggested a receding horizon parameter estimation technique for process monitoring that uses past information for the model parameter behavior in order to enhance the robustness of the procedure. Nonlinear state observers based on coordinate transformations (Soroush, 1997 ; Fevotte, *et al.*, 1998a,b) is another alternative for reconstructuring the state vector of dynamic systems from process measurements but suffers in practical implementation when complex process models are involved.

In Table 5, recent publications on monitoring, estimation, optimization and control of particulate polymerization processes are reported.

3.1 Optimization under Parametric Uncertainty

The real-time optimization of a polymerization process, compared to its off-line counterpart, has as a distinctive merit the inherent capability of exploiting the information springing continually from the process. As a result, it can more easily cope with the process variability and redefine in context the optimal operating conditions. In a recent paper by Kiparissides, *et al.*, (2002), an on-line, multi-level estimation/optimization procedure was described to control the MWD in batch polymerization reactors. The proposed estimation/optimization scheme combined a state/parameter estimator with an on-line optimizer that calculated periodically the time optimal control policies based on the most recent information about the process. The state/parameter estimator included an extended Kalman filter (EKF) for estimating the state variables and the time-varying kinetic rate constants. Subsequently, the time optimal trajectories that drive the process to the desired final property specifications were determined using a dynamic programming approach.

Figure 8 shows the schematic of the information flowsheet for the on-line optimizing controller. The measured output variables, $\mathbf{Y_{meas}}$, are compared to the model predictions, $\mathbf{Y_m}$. The anticipated error incorporates the unmeasured process disturbances, $\mathbf{d}$, the measurement noise and the process-model mismatch. The state/parameter estimation block uses the error term to retrieve the entire state vector of the system, $\mathbf{Y_{est}}$, as well as the values for the stochastic time varying model parameters. Subsequently, the updated values for the state variables and the model

parameters, Y_{est}, enter the optimizer block. A set of target values associated with the molecular weight properties, $Y_{q,sp}$, and a performance index that specifies the overall process control objectives in a hierarchical order conclude the input stream to the optimization block. The optimizer computes a series of optimal set-point changes for the controlled variables that would ensure the satisfaction of the overall control objectives in an optimal sense. The time optimal sequence of set-point changes, $Y_{opt,sp}$, are then passed to the regulatory controller that forces the process to follow the optimal trajectory as close as possible. The execution of the optimization task is performed periodically, depending on the rate of change of the model parameters, the frequency of the process disturbances and the dynamic behavior of the process in tracking the optimal control trajectory.

Optimizing Control of a Batch Polymerization Reactor. The control scheme outlined in Figure 8 was applied to a simulated model of a free-radical methyl-methacrylate (MMA) batch polymerization reactor. The polymerization temperature was controlled by a cascade control system consisting of a primary PID and two secondary PI controllers. The polymerization exhibits a strong acceleration in reaction rate due to gel-effect (e.g., the termination rate constant decreases with conversion). Usually,
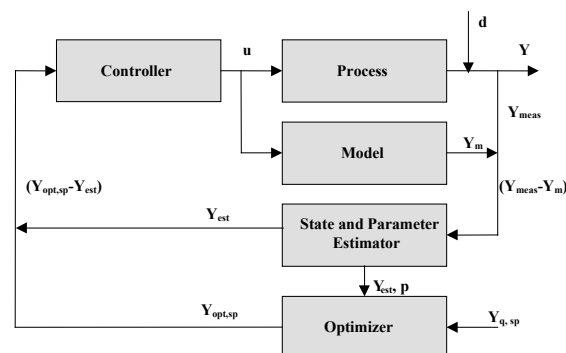

Fig. 8. Schematic representation of the control loop

the gel-effect contribution on the termination rate constant can be expressed in terms of an intrinsic chemical rate constant, k_{t0}, and a diffusion-controlled gel-effect function g_t, accounting for the observed decrease of k_t with monomer conversion. Because of the uncertainty in determining the value of g_t, a correction term, $g_{t,corr}$, was employed to account for the imprecise knowledge of g_t.

$$k_t = k_{t0} \, g_t \, g_{t,corr} \qquad (24)$$

An EKF was employed to provide estimates for the process state variables and the time varying parameter $g_{t,corr}$ that was assumed to follow a random walk model:

$$g_{t,corr}^s = w^s \qquad (25)$$

where w^s is a zero mean, white Gaussian noise.

At the optimization level, the time optimal sequence of temperature set-point changes was calculated by minimizing the following performance index:

$$J = w_1 \left(\frac{X_f}{X_d} - 1.0 \right)^2 + w_2 \left(\frac{t_f}{t_d} \right)^2 + w_3 \left(\frac{M_{n,f}}{M_{n,d}} - 1.0 \right)^2 + $$
$$w_4 \left(\frac{M_{w,f}}{M_{w,d}} - 1.0 \right)^2 + w_5 \sum_{i=1}^{NC} \left(\frac{WCLD_i}{WCLD_{i,d}} - 1.0 \right)^2 \qquad (26)$$

where X_f, t_f, $M_{n,f}$, $M_{w,f}$, and $WCLD_{i,f}$ are the monomer conversion, batch time, number and weight average molecular weights and the values of the WCLD (evaluated at N_C collocation points), respectively. X_d, t_d, $M_{n,d}$, $M_{w,d}$, and $WCLD_{i,d}$ are the corresponding desired values of the variables. The weighting factors, w_1-w_5 in eq 26 specify the relative importance of the corresponding competing terms.

The polymerization temperature was selected as the control variable because of its apparent effect on the reaction kinetics and consequently, on the final molecular weight properties and monomer conversion. The minimization of the performance index in eq 26 subject to the polymerization model equations was carried out using a simultaneous discretization approach. An OCFE technique was employed to discretize the set of model differential equations.

The time optimal polymerization temperature that minimized the objective function (eq 26) was calculated for a desired polymer grade ($M_{n,d}$=4.0·10^5 kg/kmol, $M_{w,d}$=2.0·10^6 kg/kmol, X_d=0.85). The state variables and the time varying gel-effect parameter, $g_{t,corr}^s$, were estimated every two minutes. A new optimal temperature trajectory was evaluated every 20 minutes using the most recent value of the termination rate constant. In the simulated process-model mismatch case, the value of $g_{t,corr}$ term in eq 24 was assumed to increase linearly with time (i.e., $g_{t,corr}$=1+ct).

Figure 9 depicts the time optimal temperature profiles at different time instances, calculated through successive state/parameter estimation and optimization steps. Notice that the updated time optimal temperature profiles differ from the polymerization temperature profile calculated at the

beginning of the batch both in shape and duration due to the process-model mismatch caused by the variation in the termination rate constant. In Figure 10 the average molecular weights corresponding to the uncorrected and updated temperature profiles are plotted with respect to batch time. Finally, Figure 11 shows the time evolution of the WCLD. It can be seen that the final WCLD coincides with the desired one. The results of Figures 10 and 11 indicate that the updated temperature trajectories result in a definite improvement of the final product properties and successfully compensate for the effect of the time varying termination rate constant, k_t.
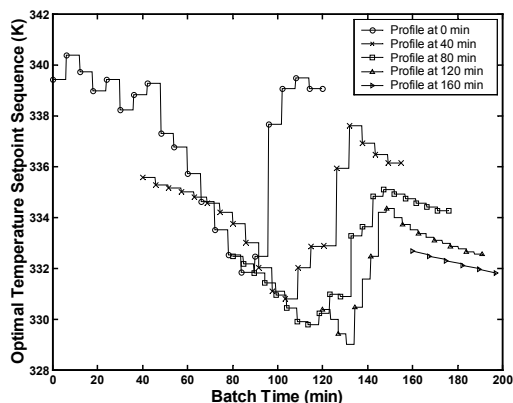

Fig. 9. Updated time optimal temperature trajectories for a positive disturbance scenario in k_t ($g_{t,corr}=1+8.0\times10^{-3}$ t).

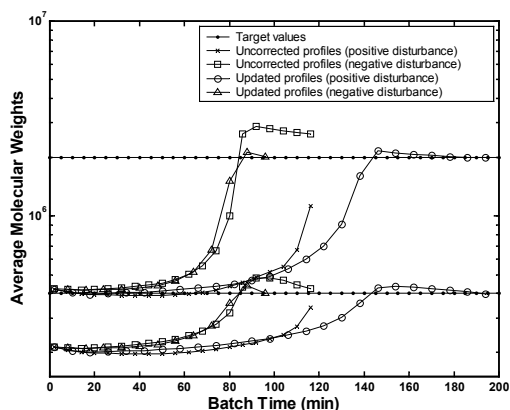

Fig. 10. Uncorrected and updated number and weight average molecular weight profiles.

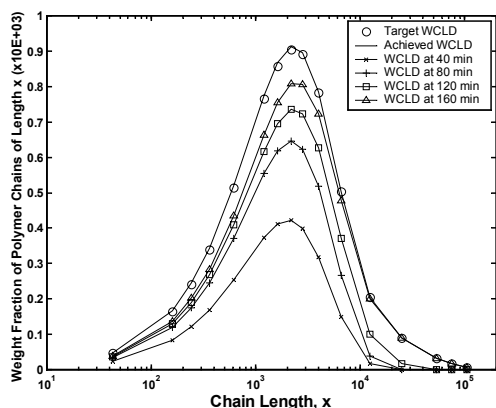
Fig. 11. Time evolution of WCLD.

4. FUTURE DIRECTIONS

New Issues on Population Balance Models. In the general form of PBE (eq. 4), it is recognized that the distribution function $n(x,y,z,p_1,...,p_k,t)$ has some "external" and some "internal" coordinates. The external coordinates (x,y,z) express the change in the population in a particular volume element due to the particle velocity, $\underset{\sim}{u}$. The summation term expresses the change in the population due to the particle properties, p_i. This term always includes the particle size as an internal coordinate but the summation sign recognizes the fact that there may be more than one property of interest. As discussed in the recent paper of Verkoeijen, *et al.* (2002), the internal particle parameter that determines changes in the population should be the particle volume. As a result, the basic PBE should be expressed in terms of the mass distribution, or the volume distribution if the density is constant, so the mass in the system is automatically conserved.

Traditionally, one-dimensional PBEs have been employed to describe the evolution of a population. However, in many cases this assumption does not hold true. Thus, to follow the molecular and compositional developments in a copolymerization reactor one needs, for example, to introduce tri-variate distributions for the "live" and "dead" polymer chains. Accordingly, the notation P(n,m,b,t) denotes the concentration of "dead" polymer chains having n units of monomer M_1, m units of monomer M_2, and b long chain branches (LCB) per molecule. The general rate functions for such a polymerization system are given in Achilias and Kiparissides (1992). It should be pointed out that the calculation of the tri-variate molecular weight – copolymer composition – long chain branching distribution is an extremely difficult problem. Moreover, in many particulate polymerization processes, 2-D or 3-D population balances are required to describe the evolution of the PSD in the reactor. Thus, in addition to the standard particle volume property one needs to include the particle age or catalyst activity to follow the evolution of PSD in a gas-solid Ziegler-Natta olefin polymerization reactor. On the other hand, in emulsion polymerization, it is often necessary to introduce a bivariate distribution n(V,i,t) to describe the time-evolution of PSD with respect to the particle volume, V, and the number of radicals, i, in the particle. The numerical solution of the resulting 2-D or 3-D dynamic PBE in batch and continuous polymerization reactors is a very demanding numerical problem. In the review article of Ramkrishna and Mahoney (2002), present challenges and requirements regarding the formulation and numerical solution of multi-dimensional PBEs are discussed. Needless to say that the identification of the functional forms of particle nucleation, growth, "death" and "birth" rate terms appearing in a multi-dimensional PBE is by no means a trivial task.

In most publications on the modeling of particulate polymerization processes, it is assumed that the multiphase reaction system can be approximated by a pseudo-homogeneous medium, (i.e., the population does not vary with respect to the external (spatial)

coordinates. However, this is rarely the case in industrial polymerization processes. For example, in industrial semi-batch emulsion polymerization, the mixing of the monomer feed stream with the reactor content and, thus, the transfer of monomer to the particulate polymer phase may vary with respect to the spatial coordinates. Moreover, particulate polymerization processes are characterized by a particle volume increase during polymerization that strongly influences the rheological properties and, thus, mixing of the dispersion. Consequently, a range of different problems can arise during the course of a particulate polymerization, including the appearance of a secondary particle size distribution, catastrophic particle agglomeration, particle settling, hot spots, etc. In gas-solid polyolefin fluidized bed reactors, the distribution of solids along the bed-height can be far from uniform. Thus, particle segregation in the bed should be accounted for in any relevant PSD modeling study. In a recent publication by Alexopoulos, *et al.* (2002), a computational fluid dynamic (CFD) approach is described for calculating the spatial distribution of energy dissipation rate in a batch suspension polymerization reactor. A two-compartment model is derived to calculate the time evolution of the monomer droplet size distribution by taking into account the large spatial variations of the turbulent kinetic energy in the reactor.

Such complex multiphase polymerization processes face challenges both on issues of model formulation as well as computation. In fact, the mutual coupling of the particulate and continuous fluid phases in regard to the transport of momentum, mass and energy as well as the quantification of particle nucleation, growth and aggregation mechanisms in terms of spatial coordinates increase significantly the modeling and computational efforts for calculating the time evolution of PSD.

New Issues on Optimization and Control. Despite the rich literature on the dynamics of population balance systems, there are limited industrial applications on the dynamic optimization and control of particulate polymerization processes. There are several valid reasons for the lack in closed-loop "quality" control applications for particulate polymerization processes. More specifically,

1. Particulate polymerization processes are highly nonlinear, containing a large number of time-varying kinetic and transport parameters.
2. Modeling of particulate polymerization systems typically leads to nonlinear integro-differential equations. Their infinite-dimensional nature does not allow their direct use for the design of nonlinear controllers that can be easily implemented in real-time.
3. On-line measurement of MWD, CCD, LCB, PSD, etc. is very difficult and the available secondary measurements are often insufficient for the accurate inference of the entire molecular weight or/and particle size distribution.
4. Formulation of a meaningful objective function in terms of distributed molecular and morphological properties (e.g., MWD, PSD, etc.) is not easy, especially when the end-use properties of the product need to be controlled.

Furthermore, the controlled variables react in opposite directions to changes in the manipulated variables.

However, recent advances in online measurements (Kammona, et al. 1999) and in control theory (Christofides, 2001 ; Chiu and Christofides, 1999 ; Crowley, *et al.* 2000 ; Valappil and Georgakis 2002 and 2003) have made possible the nonlinear optimization and control of molecular weight and particle size distributions in particulate polymerization processes. Key to the successful application of optimal control to a particulate polymerization processes is the availability of appropriate mathematical models that need to range from detailed fundamental mechanistic forms to database forms such as those provided by statistical (Yabuki, *et al.* 2002) and neural network approaches.

Needless to say that the diverse requirements imposed by various particulate polymerization processes require equally diverse control strategies to address the specific process goals. In particular, for semi-batch processes different control strategies, including batch-to-batch, on-line model-based control and mid-course correction, have been proposed by Lee, *et al.* (2002), Pringle and MacGregor (1998), Yabuki and MacGregor (1997) and Doyle, *et al.* (2003) to control the MWD and PSD developments in a polymerization reactor. On the other hand, for continuous particulate polymerization processes, on-line "polymer quality" soft-sensing, optimal grade changeover and scheduling are some of the issues to be addressed for maximizing productivity, improving product quality while keeping safety regulations (Chatzidoukas, *et al.* 2003 ; BenAmor, *et al.* 2004).

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