

Recent Advances in Polymer Reaction Engineering: Modeling and Control of Polymer Properties

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Abstract—Complex reaction kinetics and mechanisms, physical changes and transport effects, non-ideal mixing, and strong process nonlinearity characterize polymerization processes. Polymer reaction engineering is a discipline that deals with various problems concerning the fundamental nature of chemical and physical phenomena in polymerization processes. Mathematical modeling is a powerful tool for the development of process understanding and advanced reactor technology in the polymer industry. This review discusses recent developments in modeling techniques for the calculation of polymer properties including molecular weight distribution, copolymer composition distribution, sequence length distribution and long chain branching. The application of process models to the design of model-based reactor optimizations and controls is also discussed with some examples.

Key words: Polymer Reaction Engineering, Mathematical Modeling, Polymerization Kinetics, Polymer Reactor Optimization, Polymer Reactor Control, Parameter Estimation

INTRODUCTION

The polymer industry is facing many challenges to meet a rapidly changing and diversifying market environment and the pressure for cost reductions and new product developments. Product quality specifications are becoming tighter, and timely introduction of new products to customers is becoming critical to staying in business.

Many problems encountered in industrial polymerization reactors or processes are associated with inherent complexities in polymerization kinetics and mechanisms, physical changes and transport effects (e.g., viscosity increase, particle formation, precipitation, interfacial mass and heat transfer limitations), non-ideal mixing and conveying, and strong process nonlinearity (potential thermal runaway, limit cycles, multiple steady states). Moreover, many of the process variables that affect important product quality indices are difficult, if not impossible, to measure on-line or they can be measured only at low sampling frequencies with time delays, making product quality monitoring and control difficult. The actual customer specifications for end-use applications are often represented by non-molecular parameters (e.g., tensile strength, impact strength, color, crack resistance, thermal stability, melt index, density, etc.) that must be somehow related to fundamental polymer properties such as molecular weight distribution (MWD), composition, composition distribution, branching, crosslinking, stereoregularity, etc. Unfortunately, more than one reaction or process variable affects these properties, and quantifying the exact relationships

between the process variables and end-use properties is generally very difficult and not well established. Polymer reaction engineering is a discipline that deals with various issues concerning these problems. Table 1 illustrates some examples of major topics discussed in recent international conferences on polymer reaction engineering attended by academic and industrial researchers. Notice that fundamental studies on polymerization kinetics and polymerization process modeling continue to be the main topics of discussion.

Modeling of polymerization processes, especially modeling of polymer architectural properties, is of enormous industrial importance because it plays a key role in achieving the industry's goal of speedy introduction of new products into markets. Many polymer manufacturers find that a better understanding of their existing polymerization reactions and process behaviors would enable them to design more efficient polymerization technology and to develop improved or new products. In general, polymerization models are derived from the fundamental chemistry and physics of the polymerization processes to calculate reaction rates and polymer architectural parameters. Such models are called the first principles models. For certain polymerization systems, complex molecular structures are not appropriate for first-principles modeling and hence empirical or semi-empirical models such as neural network models are the practical alternatives [Chum and Oswald, 2003].

Polymerization process modeling was started in the 1970s by academic and industrial researchers, and now it is widely used in the polymer industry for a broad range of applications such as process design, product development, process control, and optimization. Several commercial process simulation packages utilizing computer-aided design (CAD) tools are also available for the modeling of a variety of industrial polymerization processes. For example, POLYRED developed at the University of Wisconsin is an open-

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‡This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

Table 1. Topics in recent conferences on polymer reaction engineering

Polymer Reaction Engineering Conference IV (Palm Cost, USA, 2000)	DECHEMA Workshop on Polymer Reaction Engineering (Hamburg, Germany, 2001)	Polymer Reaction Engineering Conference V (Quebec, Canada, 2003)
<ul style="list-style-type: none"> - Recent developments in polymerization kinetics - Approaches for developing process understanding - Commercial viability of processes and products - Scale-up of polymerization processes - Process modeling - Control and monitoring of polymerization processes 	<ul style="list-style-type: none"> - Emulsion and dispersion polymerization - Catalytic olefin polymerization - New reactor concepts - Molecular simulation of polymers - Modeling and simulation of polymerization kinetics and reactors - Polymer modification and reactive processing - Heterogeneous polymerization in various reaction media 	<ul style="list-style-type: none"> - New mathematical modeling techniques - Structure property relationships - New polymerization systems - Polymer fundamentals - Industrial applications of polymer reaction engineering - Process monitoring and control

ended package for the analysis and design of polymerization systems with a highly modular structure. It allows for performing steady state and dynamic simulations, stability analysis, and parameter estimation with an extensive library of kinetic models for polymerization process systems. PREDICI® is also a CAD simulation package that enables the modeling and dynamic simulation of industrial polymerization processes with detailed kinetic models including rigorous computation of molecular weight distributions, and composition and branching analysis. Advanced features such as parameter estimation, treatment of cascades and their recipes, as well as an interfacing to other applications are supporting this task [Wulkow, 1996, 2003]. Polymers Plus® (Aspentech) is another commercial simulation package for the design of industrial polymerization processes.

In this paper, we discuss some recent trends in polymer reaction engineering, but this review is not intended to provide a comprehensive review of all the advances in polymer reaction engineering; rather, we will focus on recent advances in modeling and controlling the polymer's molecular properties that impact the polymer's end-use properties. For a review of general modeling techniques for polymerization kinetics and reactors, see recent reviews published elsewhere [Ray, 1972; Choi, 1993; Kiparissides, 1996; Dubé et al., 1997].

MODELING OF ARCHITECTURAL PARAMETERS OF POLYMERS

The two most representative objectives in modeling polymerization reactions are to compute (1) polymerization rate and (2) polymer properties (molecular level and microscopic level) for various reaction conditions. Quite often, these two types of model outputs are not separate, but are very closely related to each other. For example, an increase in reaction temperature in free radical polymerization results in increasing polymerization rate but decreasing polymer molecular weight; an increase in catalyst concentration raises polymerization rate but lowers polymer molecular weight. Therefore, there is a need for detailed understanding of the polymerization kinetics to devise a scheme to simultaneously achieve high productivity and desired polymer properties.

Here, for process modeling purposes, we define the polymer properties as those that represent the polymer architecture: e.g., molecu-

lar weight distribution (MWD), molecular weight averages, copolymer composition (CC), copolymer composition distribution (CCD), monomer sequence length distribution, short-chain and long-chain branching, crosslinking, and stereoregularity. Polymer particle size, particle size distribution (PSD), and polymer morphology, etc., are not molecular properties but meso-scale properties that influence a polymer's physical, chemical, thermal, mechanical, and rheological properties. The macro-scale modeling that deals with the overall reactor behaviors through macroscopic mass and energy balances is not discussed in this paper.

1. Modeling of Molecular Weight Distribution

Polymer molecular weight and MWD, along with other properties such as short chain branching (SCB) and long chain branching (LCB), affect a polymer's mechanical, rheological, and physical properties. Besides polymer MWD, the rheological behavior of a polymer also depends on many other factors, such as the types of flow field, the intensity of the rate of deformation, temperature, and thermal histories. For example, for a given polymer, one type of rheological response (e.g., shear viscosity) is not as sensitive to a slight change in molecular parameters as others (e.g., normal stress effects) [Han and Kwack, 1983]. Therefore, it is important to understand that controlling the MWD in a polymerization process does not necessarily implicate the control of rheological properties during polymer process operations. Nevertheless, the MWD is regarded as one of the most important polymer architectural parameters to be controlled in any industrial polymerization processes. Table 2 illustrates the qualitative effects of polymer density, melt index (MI), and MWD on some end-use properties of polyolefins.

Controlling the MWD is a key operational objective in many industrial polymerization processes. In the polymer industry, MI is frequently used as a measure of viscosity, or indirect polymer molecular weight, but the limitations in using MI as a property measure should be understood. The MI is the measurement of the flow rate in g/10 min of polymer flowing through a die at a given temperature under the action of a weight loaded onto a piston. Typical MI test conditions are 190/2.16, i.e., 190 °C temperature and 2.16 kg weight. Many different conditions exist for performing the MI test which require different weight loadings and different temperatures. However, MI does not represent the true rheological characteristics of the resin under high shear processing conditions because MI is, at best, a single value of viscosity at the particular shear rate

Table 2. Effect of density, melt index and molecular weight distribution of polyolefins on end-use properties

Property	As density increases, property	As MI increases, property	As MWD broadens, property
Tensile strength (at yield)	Increases	Decreases	
Stiffness	Increases	Decreases slightly	Decreases slightly
Impact strength	Decreases	Decreases	Decreases
Low temperature brittleness	Increases	Increases	Decreases
Abrasion resistance	Increases	Decreases	
Hardness	Increases	Decreases slightly	
Softening point	Increases		Increases
Stress crack resistance	Decreases	Decreases	
Permeability	Decreases	Increases slightly	
Chemical resistance	Increases	Decreases	
Melt strength		Decreases	Increases
Gloss	Increases		Decreases
Haze	Decreases	Decreases	
Shrinkage	Decreases	Decreases	Increases

and temperature employed in the test [Han et al., 1983a, b]. Nevertheless, MI is still used in the industry, and quite often MI is correlated with molecular weight averages (e.g., $MI = a\bar{M}_w^b$).

To calculate MWD in a polymerization process, a kinetic model is needed. A typical polymerization process model consists of material balances (component rate equations), energy balances, and an additional set of equations to calculate polymer chain length distribution. The kinetic equations for a linear addition polymerization process include initiation or catalytic site activation, chain propagation, chain termination, and chain transfer reactions. Table 3 illustrates the reactions that occur in homogeneous free radical polymerization of vinyl monomers and coordination polymerization of olefins catalyzed by transition metal catalysts.

In general, MWD is not represented by a simple distribution function because many reactions and polymerization conditions contribute to the growth and termination of polymer chains. When quasi-steady state assumption is applied to live polymers or propagating active centers, the MWD of live polymers is often represented by the Schulz-Flory most probable distribution. For example, in free radical polymerization the concentration of live polymers of chain

length n is expressed as $P_n = (1 - \alpha)\alpha^{n-1}P$ where P is the total live polymer concentration and α is the probability of propagation. In α -olefin polymerization with single site metallocene catalysts, it is easy to show that the polymer MWD also follows the Flory's most probable distribution expressed in continuous form as

$$w(n) = \tau^n \exp(-\tau n) \quad (1)$$

where $w(n)$ is the weight fraction of polymers with chain length n and τ is the ratio of chain transfer rates to propagation rate. The chain length distribution function is often combined with a reactor residence time distribution function to calculate the overall molecular weight distribution in a continuous process.

We can calculate MWD by solving the population balance equations (rate equations) for the polymers of different chain lengths. However, it is often impractical to solve a large system of polymer population balance equations represented by an infinite number of differential equations. Hence, molecular weight averages are frequently used as a measure of molecular weight properties. The molecular weight averages can be calculated by solving the molecular weight moment equations derived from the polymer population balance equations. Only the first few leading moments are sufficient to calculate the molecular weight averages.

For homopolymerizations, the polymer molecular weight moment is defined as follows:

$$\lambda_k \equiv \sum_{n=1}^{\infty} n^k M_n \quad (2)$$

where λ_k is the k -th molecular weight moment, n is the number of monomer units, and M_n is the concentration of polymers with n repeat units (monomer units). Notice that the zero-th moment represents the total concentration of polymer molecules and the first moment represents the total weight of polymer. The number average and weight average molecular weights are defined as: $\bar{M}_n = \lambda_1/\lambda_0$, $\bar{M}_w = \lambda_2/\lambda_1$. Z-average molecular weight is defined as $\bar{M}_z = \lambda_3/\lambda_2$. The ratio of the two molecular weight averages, \bar{M}_w/\bar{M}_n , is a measure of MWD broadening and it is called the polydispersity (PD). The variances of number average and weight average molecular weights can also be calculated as follows:

Table 3. Reaction schemes for addition polymerizations

Free radical polymerization	Coordination polymerization
Initiation	Site activation
$I \xrightarrow{k_d} 2R$	$C_0^* + A \xrightarrow{k_a} C^*$
$R + \xrightarrow{k_i} P_1$	Initiation
Propagation	$C^* + M \xrightarrow{k_i} P_1$
$P_1 + M \xrightarrow{k_p} P_2$	Propagation
$P_n + M \xrightarrow{k_p} P_{n+1} (n \geq 2)$	$P_1 + M \xrightarrow{k_p} P_2$
Chain transfer	$P_n + M \xrightarrow{k_p} P_{n+1} (n \geq 2)$
$P_n + M \xrightarrow{k_{tm}} M_n + P_1$	Chain transfer
$P_n + X \xrightarrow{k_{tx}} M_n + X$	$P_n + M \xrightarrow{k_{tm}} M_n + P_1$
Chain termination	$P_n + X \xrightarrow{k_{tx}} M_n + C^*$
$P_n + P_m \xrightarrow{k_{tm}} M_{n+m}$	$P_n \xrightarrow{k_{\beta}} M_n + C^*$
$P_n + P_m \xrightarrow{k_{fm}} M_n + M_m$	

Table 4. Kinetic equations in free radical polymerization

Mass balance equations	MW moment equations
$\frac{dI}{dt} = -k_d I$	$\lambda_0^1 = P$
$\frac{dR}{dt} = 2f_i k_d I - k_i R M$	$\frac{d\lambda_1^1}{dt} = k_i R M + (k_{fm} M + k_{fs} S)(P - \lambda_1^1)$ $+ k_p M P - (k_{tc} + k_{td}) P \lambda_1^1 \approx 0$
$\frac{dM}{dt} = -k_i R M - k_p M \sum_{n=1}^{\infty} P_n - k_{fm} M \sum_{n=1}^{\infty} P_n$	$\frac{d\lambda_2^1}{dt} = k_i R M + (k_{fm} M + k_{fs} S)(P - \lambda_2^1)$ $+ k_p M (2\lambda_1^1 + P) - (k_{tc} + k_{td}) P \lambda_2^1 \approx 0$
$\frac{dP_1}{dt} = k_i R M - k_p M P_1 + (k_{fm} M + k_{fs} S) \sum_{n=2}^{\infty} P_n - (k_{tc} + k_{td}) P_1 \sum_{n=2}^{\infty} P_n$	$\frac{d\lambda_0^d}{dt} = \frac{1}{2} k_{tc} P^2 + k_{td} P (P - P_1) + (k_{fm} M + k_{fs} S)(P - P_1)$ $= \frac{1}{2} k_{tc} P^2 + (k_{fm} M + k_{fs} S + k_{td} P) \alpha P$
$\frac{dP_n}{dt} = k_p M (P_{n-1} - P_n) - (k_{fm} M + k_{fs} S) P_n - (k_{tc} + k_{td}) P_n \sum_{n=1}^{\infty} P_n (n \geq 2)$	$\frac{d\lambda_1^d}{dt} = \frac{1}{2} k_{tc} P^2 (1 - \alpha)^2 \sum_{n=2}^{\infty} n(n-1) \alpha^{n-2} + k_{td} P^2 (1 - \alpha) \sum_{n=2}^{\infty} n \alpha^{n-1}$ $+ (k_{fm} M + k_{fs} S) P (1 - \alpha) \sum_{n=2}^{\infty} n \alpha^{n-1}$ $= \frac{1}{1 - \alpha} [k_{tc} P^2 + (k_{fm} M + k_{fs} S + k_{td} P) P (2\alpha - \alpha^2)]$
$\frac{dM_n}{dt} = (k_{fm} M + k_{fs} S) P_n + k_{td} P_n \sum_{n=1}^{\infty} P_n + \frac{1}{2} k_{tc} \sum_{m=1}^{n-1} P_m P_{n-m} (n \geq 2)$	$\frac{d\lambda_2^d}{dt} = \frac{P}{(1 - \alpha)^2} [(k_{fm} M + k_{fs} S + k_{td} P)(\alpha^3 - 3\alpha^2 + 4\alpha) + k_{tc} P(\alpha + 2)]$ where $\alpha = \frac{k_p M}{k_p M + k_{fm} M + k_{fs} S + (k_{tc} + k_{td}) P}$

$$\sigma_n^2 = \frac{\sum_{i=1}^{\infty} (M_i - \bar{M}_n)^2 n_i}{\sum_{i=1}^{\infty} n_i} = \left[\frac{\lambda_2}{\lambda_0} - \left(\frac{\lambda_1}{\lambda_0} \right)^2 \right] M_0^2 \quad (3)$$

$$\sigma_w^2 = \frac{\sum_{i=1}^{\infty} (M_i - \bar{M}_w)^2 n_i M_i}{\sum_{i=1}^{\infty} n_i M_i} = \left[\frac{\lambda_3}{\lambda_1} - \left(\frac{\lambda_2}{\lambda_1} \right)^2 \right] M_0^2 \quad (4)$$

where M_0 is the molecular weight of a repeating unit. To calculate the molecular weight moments, dynamic molecular weight moment equations must be derived for the first three leading moments. Then, they are solved together with the rate equations for monomer, initiator (catalyst), and polymers. Table 4 illustrates the kinetic equations for initiator, monomer, live polymers and dead polymers, and the molecular weight moment equations for live and dead polymers in free radical polymerization. The molecular weight moment equations for other addition polymerization processes such as transition metal catalyzed olefin polymerization can also be derived similarly. The mathematical techniques to derive the molecular weight moment equations can be found elsewhere [Ray, 1972; Schork et al., 1993; Dotson et al., 1996].

For a homopolymer, number and weight average degrees of polymerization are often used: i.e., $\bar{X}_n = \bar{M}_n / M_0$, $\bar{X}_w = \bar{M}_w / M_0$. But for a copolymer, the degree of polymerization is not defined except for alternating copolymers. The k -th molecular weight moment of a binary copolymer is defined as

$$\lambda_k = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} (n w_1 + m w_2)^k \quad (5)$$

where w_1 is the molecular weight of comonomer 1 (M_1) and w_2 is the

molecular weight of comonomer 2 (M_2). The derivation of molecular weight moment equations for a copolymerization system is much more complicated than for a homopolymerization system. Table 5 shows the copolymer molecular weight moment equations for a free radical binary copolymerization of vinyl monomers [Butala et al., 1988].

For a linear binary copolymerization system, the instantaneous chain length and composition distribution can be calculated by using the modified Stockmayer bivariate distribution function [Dubé et al., 1997]:

$$w(r, y) dr dy = (1 + y \delta) \tau^2 \exp(-\tau r) \frac{1}{\sqrt{2\pi\beta\tau}} \exp\left(-\frac{y^2}{2\beta}\right) dy \quad (6)$$

where $w(r, y)$ is the instantaneous chain length and composition distribution of polymer, $\beta = \bar{F}_1(1 - \bar{F}_1)[1 + 4\bar{F}_1(1 - \bar{F}_1)(r_1 r_2 - 1)]^{1/2}$, $\delta = \frac{1 - w_2/w_1}{w_2/w_1 + \bar{F}_1(1 - w_2/w_1)}$; \bar{F}_1 = average mole fraction of monomer 1; r = chain length, y = deviation from average copolymer composition, τ = ratio of chain transfer rates to propagation rate, and r_1, r_2 = reactivity ratios. The instantaneous chain length distribution is obtained by integrating Eq. (6) with respect to y :

$$w(r) = \int_{-\infty}^{\infty} w(r, y) dy = \tau^2 \exp(-\tau r) \quad (6.1)$$

Note that Eq. (6.1) is the Schulz distribution. Also, the composition distribution over all chain lengths is given by:

$$w(y) = \int_0^{\infty} w(r, y) dr = \frac{3}{4} \frac{(1 + y \delta)}{\sqrt{2\pi\beta\tau} \left(1 + \frac{y^2}{2\beta\tau}\right)^{5/2}} \quad (6.2)$$

Although molecular weight averages are a convenient measure

Table 5. Free radical copolymerization model and molecular weight moment equations [Butala et al., 1988]

Kinetic scheme	Molecular weight moment equations
Initiation $I \xrightarrow{k_d} 2R$ $R + M_1 \xrightarrow{k_{i1}} P_{1,0}$ $R + M_2 \xrightarrow{k_{i2}} Q_{0,1}$	$\frac{d\lambda_0}{dt} = \frac{1}{2}k_{ic11}P^2 + k_{ic12}PQ + \frac{1}{2}k_{ic22}Q^2 + k_{id11}P^2$ $+ 2k_{id12}PQ + k_{id22}Q^2$ $+ (k_{f11}M_1 + k_{f12}M_2)P + (k_{f21}M_1 + k_{f22}M_2)Q$
Propagation $P_{n,m} + M_1 \xrightarrow{k_{p11}} P_{n+1,m}$ $P_{n,m} + M_2 \xrightarrow{k_{p12}} Q_{n,m+1}$ $Q_{n,m} + M_1 \xrightarrow{k_{p21}} P_{n+1,m}$ $Q_{n,m} + M_2 \xrightarrow{k_{p22}} Q_{n,m+1}$	$\frac{d\lambda_1}{dt} = k_{ic11}P_1P + k_{ic12}(P_1Q + PQ_1) + k_{ic22}Q_1Q$ $+ k_{id11}PP_1 + k_{id12}(P_1Q + Q_1P)$ $+ k_{id22}QQ_1 + (k_{f11}M_1 + k_{f12}M_2)P_1$ $+ (k_{f21}M_1 + k_{f22}M_2)Q_1$
Combination termination $P_{n,m} + P_{r,q} \xrightarrow{k_{tc11}} M_{n+r,m+q}$ $P_{n,m} + Q_{r,q} \xrightarrow{k_{tc12}} M_{n+r,m+q}$ $Q_{n,m} + Q_{r,q} \xrightarrow{k_{tc22}} M_{n+r,m+q}$	$\frac{d\lambda_2}{dt} = k_{ic11}(P_2P + P_1^2) + k_{ic12}(P_2Q + PQ_2 + 2P_1Q_1)$ $+ k_{ic22}(Q_2Q + Q_1^2) + k_{id11}PP_2$ $+ k_{id12}(P_2Q + Q_2P) + k_{id22}QQ_2$ $+ (k_{f11}M_1 + k_{f12}M_2)P_2 + (k_{f21}M_1 + k_{f22}M_2)Q_2$
Disproportionation termination $P_{n,m} + P_{r,q} \xrightarrow{k_{td11}} M_{n,m} + M_{r,q}$ $P_{n,m} + Q_{r,q} \xrightarrow{k_{td12}} M_{n,m} + M_{r,q}$ $Q_{n,m} + Q_{r,q} \xrightarrow{k_{td22}} M_{n,m} + M_{r,q}$	<p>where</p> $P_1 = \frac{w_1 C_1 \alpha_1 + \left(\frac{\alpha_1 \gamma}{r_1}\right) Q_1 + w_1 \alpha_1 \left(P + \frac{\gamma Q}{r_1}\right)}{1 - \alpha_1}$ $P_2 = \frac{w_1 C_1 \alpha_1 + \left(\frac{\alpha_1 \gamma}{r_1}\right) Q_2 + 2w_1 \alpha_1 \left(P_1 + \frac{\gamma Q_1}{r_1}\right) + w_1^2 \alpha_1 \left(P_1 + \frac{\gamma Q_1}{r_1}\right)}{1 - \alpha_1}$ $Q_1 = \frac{w_2 C_2 \alpha_2 + \left(\frac{\alpha_2}{r_2 \gamma}\right) P_1 + w_2 \alpha_2 \left(Q + \frac{1}{r_2 \gamma} P\right)}{1 - \alpha_2}$ $Q_2 = \frac{w_2^2 C_2 \alpha_2 + \frac{\alpha_2}{r_2 \gamma} P_2 + 2w_2 \alpha_2 \left(\frac{1}{r_2 \gamma} P_1 + Q_1\right) + w_2^2 \alpha_2 \left(\frac{1}{r_2 \gamma} P + Q\right)}{1 - \alpha_2}$
Chain transfer to monomer $P_{n,m} + M_1 \xrightarrow{k_{f11}} M_{n,m} + P_{1,0}$ $P_{n,m} + M_2 \xrightarrow{k_{f12}} M_{n,m} + Q_{0,1}$ $Q_{n,m} + M_1 \xrightarrow{k_{f21}} M_{n,m} + P_{1,0}$ $Q_{n,m} + M_2 \xrightarrow{k_{f22}} M_{n,m} + Q_{0,1}$	

of polymer molecular weight, these molecular weight averages do not describe the complete characteristics of polymer MWD. Furthermore, for some polymers such as polypropylene with stereoirregularities, knowing the full MWD may not be always sufficient for many practical applications. It is possible that two polymer samples of different chain length distribution can have identical number and weight average molecular weights. Quite obviously, these polymers will exhibit different rheological properties under melt flow conditions. Also, bimodal or multi-modal MWD curves cannot be represented by molecular weight averages and polydispersity.

The major limitation in using the molecular weight moment technique is that only molecular weight averages are calculated and a complete MWD is not obtainable. Certain functions, such as the Schulz distribution and Wesslau distribution, are often adopted and fitted with molecular weight average. Certainly, such methods are no more than curve fittings, lacking any physical implications. Recently, Crowley and Choi [1997a, 1998a, b] developed the method of finite molecular weight moments to calculate the chain length distribution in free radical polymerization of vinyl monomers without using a MWD function *a priori*. This technique fully utilizes the convenience of the molecular weight moment technique but at the same time it enables the computation of full chain length distribution. In this method, instead of calculating the concentration or weight fraction of polymer with a certain chain length ($w(n)$), the weight fraction of polymers in a finite chain length interval (e.g.,

$n \leq r \leq m$) is calculated, resulting in the dramatic reduction of computational load. This method is different from simply discretizing the polymer population balance equations to finite difference form for numerical MWD calculations. In the following, the method of finite molecular weight moments is briefly presented.

The key component in the method of finite molecular weight is to define the following function:

$$f_{(m,n)} = \frac{\sum_{i=m}^n i M_i}{\sum_{i=2}^{\infty} i M_i} = \frac{\text{weight of polymer with chain lengths from } m \text{ to } n}{\text{total weight of polymer}} \quad (7)$$

Fig. 1 illustrates how the function $f_{(m,n)}$ is defined. As the number of chain length intervals is increased, the resulting chain length distribution will approach the continuous distribution. The function $f_{(m,n)}$ is different from the similar function used by Scali et al. [1995]: $F_i^w = nF(n)/\int nF(n)dn$ where F_i^w is a normalized weight fraction of polymer consisting of n monomer units. In their model, the instantaneous Schulz-Flory distribution function is adopted for $F(n)$. In the method of finite molecular weight moments, no such distribution is chosen *a priori* and the chain length distribution is directly computed from the kinetic model equations.

Having defined the function $f_{(m,n)}$, we can derive the following differential equation for $f_{(m,n)}$ using the dead polymer population

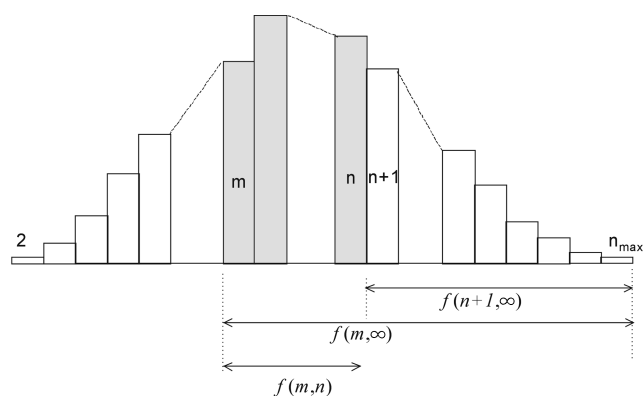


Fig. 1. Definition of function $f(m, n)$.

balance and the first moment equation:

$$\frac{df_{(m,n)}}{dt} = \frac{1}{\lambda_1} \sum_{i=m}^n \frac{dM_i}{dt} - \frac{\sum_{i=m}^n i M_i}{\lambda_1^2} \frac{d\lambda_1}{dt} = \frac{1}{\lambda_1} \sum_{i=m}^n \frac{dM_i}{dt} - \frac{f_{(m,n)}}{\lambda_1} \frac{d\lambda_1}{dt} \quad (8)$$

By applying the quasi-steady state assumptions to live polymer radicals and using the probability of propagation defined as

$$\alpha \equiv \frac{k_p M}{k_p M + k_t P + k_{fm} M + k_{fs} S} \quad (9)$$

we can derive the following equation:

$$\frac{df_{(m,n)}}{dt} = [\{m(1-\alpha) + \alpha\} \alpha^{n-2} + \{(n+1)(1-\alpha) + \alpha\} \alpha^{n-1} - (2-\alpha)f_{(m,n)}] \frac{k_p M P}{\lambda_1} \quad (10)$$

In Eq. (10), M is the monomer concentration and P is the total polymer radical concentration. Eq. (10) represents how the weight fraction of polymer in a chain length interval (m, n) changes with reaction time.

To calculate the polymer chain length distribution, Eq. (10) is solved with molecular weight moment equations and the kinetic modeling equations as illustrated in Table 4. It is necessary to assign appropriate values to m and n and to replace the infinite chain length domain with a finite range bounded by a maximum chain length (n_{max}). The maximum chain length is searched until a preset convergence criterion such as $f(2, n_{max})_f = \varepsilon$ where x_f is the final monomer conversion and ε is a number that is very close to unity (e.g., 0.999). This criterion indicates that polymer produced in the chain length range from 2 to n_{max} represents $100\varepsilon\%$ of all polymers that will be produced during the polymerization. Here, the minimum chain length of 2 is assumed but a larger value can be used if desired. Fig. 2 illustrates the experimentally measured and model predicted molecular weight distributions in solution polymerization of methyl methacrylate (MMA) in a batch reactor. Considering the simplicity of the computational method, we see that the agreement between the model predictions and the experimental data is excellent.

This technique has been extended to thermal polymerization of styrene [Yoon et al., 1998] and to an industrial process of continuous free radical polymerization of styrene in a series of reactors shown in Fig. 3 [Yoon, 2003]. In this process, three reactors are used: the

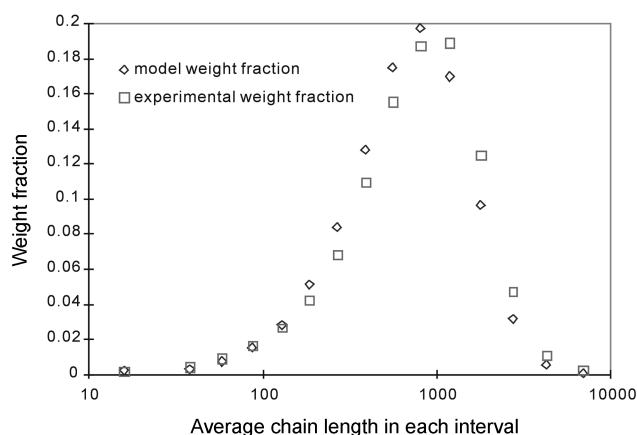


Fig. 2. Calculated and experimentally measured molecular weight distributions: solution polymerization of methyl methacrylate in a batch reactor [Crowley and Choi, 1997].

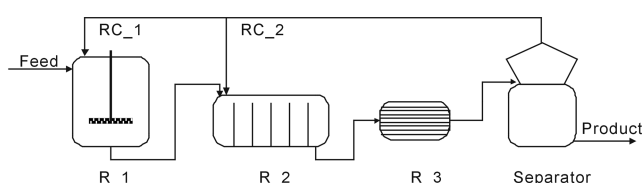


Fig. 3. Industrial continuous styrene polymerization process [Yoon, 2003].

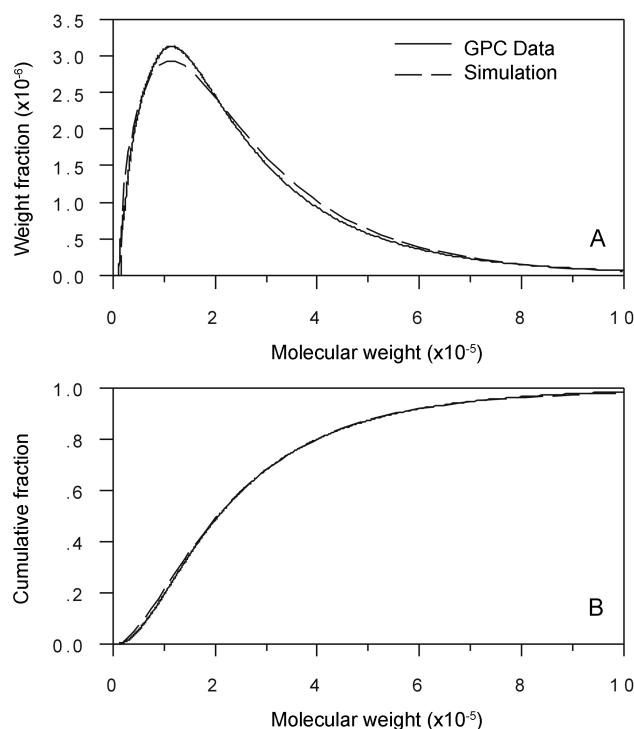


Fig. 4. Molecular weight distribution of polystyrene in a continuous process: solid lines-commercial plant data, dashed lines model simulations; reactor residence times $t_1=147$ min, $t_2=73$ min, $t_3=12$ min; reaction temperature $T_1=134$ °C, $T_2=168$ °C, $T_3=172$ °C.

first reactor (R_1: CSTR) is followed by a horizontal reactor (R_2) that consists of multiple compartments. Each compartment in R_2 can be approximated as a CSTR. The third reactor (R_3) is a plug flow reactor with short residence time that acts as a preheating unit for the reactor content before it is supplied to a separator. Fig. 4 shows the actual gel permeation chromatography (GPC) data and the model-calculated polymer molecular weight distribution of polystyrene at steady state. Note that excellent agreement has been obtained, demonstrating the practical utility of the finite molecular weight moment technique to compute polymer molecular weight distribution in a continuous process. The method of finite molecular weight moments has also been applied to the design of optimal operating conditions for a batch free radical polymerization process [Crowley and Choi, 1997b, 1998a, b].

For a copolymer system, comparing copolymer MWD predictions based on a first principles model to actual GPC measurements is not always straightforward. This is because the modeled variables are usually formulated in terms of the number of repeat units (chain length) of monomer or overall molecular weight averages in the copolymer, whereas GPC separates copolymer molecules based on their hydrodynamic volumes in dilute solutions. Goldwasser and Rudin [1983] derived the following general expression for the hydrodynamic volume of a copolymer in terms of the contributions of its distinct homo- and hetero-interaction segments as

$$v = \frac{4\pi}{3\phi''} \left(\sum_i w_i (K_i M_c^{1+c_i})^{2/3} \right)^{3/2} \quad (11)$$

where w_i is the weight fraction of the i -th type of interaction, K_i and c_i are the corresponding Mark-Houwink constants, ϕ'' is the universal constant, and M_c is the copolymer molecular weight. To relate hydrodynamic volume with chain length, we encounter the problem that there is no unique relationship between chain length and hydrodynamic volume for copolymers having different compositions except for the special case of a copolymer with constant and uniform copolymer composition. Strictly speaking, for statistical copolymerization, even this special case is physically unrealizable because there exists a copolymer composition distribution even for copolymer produced instantaneously. The sizes of solvated polymer molecules in the GPC mobile phase (solvent) depend on solvent interaction with the chain segments that consist of monomer and comonomer units with a certain sequence length distribution [Goldwasser et al., 1982; Goldwasser and Rudin, 1983]. For example, two copolymer molecules having different chain lengths and different copolymer composition could still conceivably elute at the same time because they have the same hydrodynamic volume. The overall degree of solvation may change with copolymer composition and use of a single average set of Mark-Houwink constants in column calibration may produce incorrect molecular weight data from the GPC analysis. In other words, there is no unique relationship between chain length and hydrodynamic volume for a copolymer with heterogeneity in the copolymer composition distribution. Therefore, it is not possible to measure the weight fraction of all copolymer molecules having the same chain length in a sample. This fact carries implications for the development of a copolymerization model which is compatible with MWD measurements using GPC.

Crowley and Choi [1999a] developed a computational technique

for modeling the hydrodynamic volume distribution of a copolymer in a batch free radical copolymerization process. Here, the method is similar to the finite molecular weight moment method: hydrodynamic volume distribution is calculated by computing the weight fraction of polymers over a number of hydrodynamic volume intervals. Chain length and copolymer compositions are related to hydrodynamic volume by using the bivariate distribution function and the universal calibration method with composition dependent Mark-Houwink constants. Experimentally, it is possible to measure the weight fraction of copolymer molecules in a fixed interval of hydrodynamic volume from a GPC chromatogram, given that a measurement of average copolymer composition in that same volume interval is also available. The corresponding copolymer chain lengths bounding the hydrodynamic volume interval can then be calculated to reconcile GPC measurements with model predictions based on chain length.

The following function is defined to represent the weight fraction of copolymers with hydrodynamic volumes between v_j and v_{j+1} :

$$f(v_j, v_{j+1}) \equiv \frac{\int_0^{\lambda_1} \left(\int_{l_j(F_1)}^{l_{j+1}(F_1)} l [w_1 F_1 + w_2 (1 - F_1)] \frac{dD(l)V}{dt} dl \right) dt}{\lambda_1} \quad (12)$$

where l is the overall copolymer chain length, w_1 (w_2) is the molecular weight of monomer 1 (monomer 2), F_1 is the instantaneous mole fraction of monomer 1 in the polymer, and $D(l)$ is the dead copolymer concentration of chain length l . To calculate the copoly-

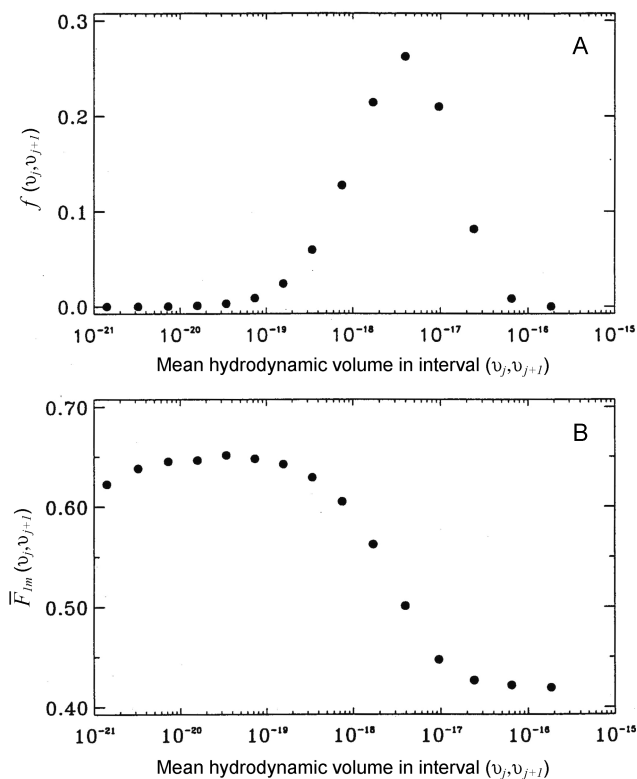


Fig. 5. Simulated weight hydrodynamic volume distribution and corresponding copolymer composition distribution for styrene and methyl methacrylate copolymerization [Crowley and Choi, 1999a].

mer weight fraction, the following equation is derived and solved with other copolymer kinetic equations:

$$\frac{df(v_p, v_{j+1})}{dt} = \frac{\int_{f_1 F_1}^{f_{j+1} F_1} l[w_1 F_1 + w_2(1 - F_1)] \frac{dD(l)V}{dt} dl}{\lambda_1} - \frac{f(v_p, v_{j+1}) d\lambda_1}{\lambda_1 dt} \quad (13)$$

Fig. 5 shows the copolymer weight hydrodynamic volume distribution (A) and the copolymer composition distribution (B) for styrene-MMA copolymerization in a semibatch reactor at the final polymer weight fraction of about 0.35. Notice in Fig. 5 (B) that the enrichment of monomer 1 (styrene) in the copolymer does not occur uniformly over the molecular size range but rather is concentrated in the higher molecular weight region.

The control of polymer MWD in industrial polymerization processes is a difficult task even with a high performance size exclusion chromatograph (SEC). The time required for sample conditioning and analysis is often unacceptably long for on-line process control purposes. For insoluble polymers (e.g., polytetrafluoroethylene), it is nearly impossible to directly measure the MWD. Recently, many attempts have been made to obtain the MWD from the rheological properties that are relatively easy to measure on-line. For example, correlations are made using the storage and loss moduli and the shape of the viscosity vs. shear rate curve. The modulus data can be transformed into a cumulative MWD function that is fitted with a hyperbolic tangent function and then differentiated to obtain the MWD [Lavallée and Berker, 1997; Carrot and Guillet, 1997]. For practical applications, the inverse MWD calculation methods have limitations in the accessible range of shear rate, experimental errors, and possibly ill-posed nature of the inverse integral transform of viscosity to MWD.

2. Design of MWD in Polyolefins

Catalytic polymerization of olefins is of enormous industrial importance since the first commercialization of Ziegler-Natta catalyzed ethylene polymerization started in the 1950s. Ethylene or propylene polymers synthesized with multi-site Ziegler-Natta type catalysts have broad MWDs (PD=5-20 or larger) and MWD control in industrial polyolefin processes was difficult. However, the MWD control problem in olefin polymerization processes changed dramatically with the development of single-site metallocene catalysts in the 1980s. It is now possible to tailor MWD by using ingenious catalyst and reactor technology.

In the current polyolefins industry, the major issues are: (1) precise control of polymer properties, (2) manufacturing cost reduction, and (3) development of new product grades and new applications. The research and development activities are divided broadly into the development of advanced catalyst systems, molecular design of polymers, and advanced polymerization process technology. High throughput catalyst screening technique or combinatorial chemistry technique is becoming popular in designing and screening polymerization catalysts [Keil, 2003].

With single site metallocene catalysts, it is possible to make polyolefins with narrow MWD that is very close to the theoretical Schulz-Flory most probable distribution. However, a narrow MWD polymer is not necessarily the most desirable. For high molecular weight polyethylene, too narrow MWD often causes difficulty in processing the polymer into blown films. To improve the flowability of such polymers, a bimodal MWD resin is made by adding low mo-

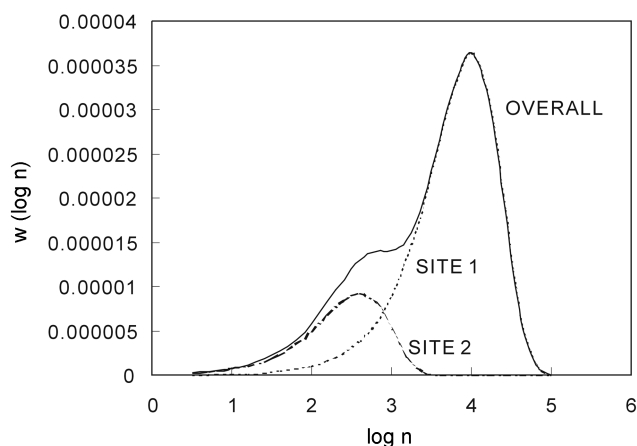


Fig. 6. Bimodal polyethylenes with two single site catalysts ($\phi_1=0.95$, $\phi_2=0.05$; $\tau_1=1.0 \times 10^{-4}$, $\tau_2=2.5 \times 10^{-3}$).

lecular weight fractions. A bimodal resin can be made in a series of two reactors operating at different reaction conditions. For example, the first reactor can be operated without hydrogen (chain transfer agent) to obtain a high molecular weight polymer. Then, polymerization is continued in the second reactor in the presence of hydrogen to produce lower molecular weight chains. Another technique is to use a combination of different catalysts in a single reactor. If we assume that molecular interactions between two different active sites or catalysts are negligible, we can describe the overall MWD by combining the two different Flory distributions for each catalyst [Kim et al., 1999]:

$$W(n) = \phi_1 n \tau_1^2 e^{-\tau_1 n} + \phi_2 n \tau_2^2 e^{-\tau_2 n} \quad (14)$$

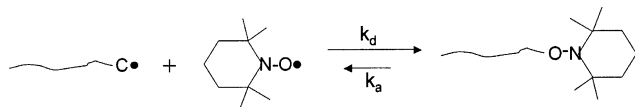
where $W(n)$ is the weight chain length distribution, ϕ_i is the weight fraction of polymer made on the i -th active site (or catalyst), and τ_i is the overall ratio of chain transfer rates to chain propagation rate for each type of active site. Fig. 6 illustrates how MWD can be modified by using two single site catalysts that have significantly different responses to chain transfer reactions ($\phi_1=0.95$, $\phi_2=0.05$; $\tau_1=1.0 \times 10^{-4}$, $\tau_2=2.5 \times 10^{-3}$).

3. Living Free Radical Polymerizations for MWD Control

Living free radical polymerization (LFRP) is a relatively recent development gaining popularity to synthesize the polymers with tailored macromolecular structure. Although true living polymerization conditions are only possible for ionic polymerizations, LFRP offers the convenience and versatility of free radical polymerization chemistry with living polymerization capabilities [Georges et al., 1993]. Unlike in conventional free radical polymerization systems where mean chain lifetime is about ~0.1-1 sec, irreversible bimolecular termination reactions are significantly suppressed in living polymerization, allowing for the synthesis of polymers with designed microstructure and MWDs. The applications of LFRP technique have also been extended to heterogeneous polymerizations such as emulsion polymerization, suspension polymerization, and dispersion polymerization [Bon et al., 1997; Hölderle et al., 1997; Butté et al., 2000; Brouwer et al., 2000; Cunningham, 2002].

The current living polymerization systems are based on either reversible termination (SFRP (stable free radical polymerization), ATRP (atom transfer radical polymerization)) or reversible transfer

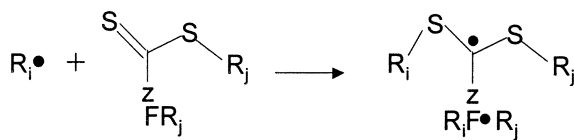
mechanisms (RAFT (reversible addition-fragmentation transfer), degenerative transfer) [Cunningham, 2002]. In SFRP and ATRP, a controlling agent is used to yield a dormant polymer chain by reacting reversibly with a propagating polymer radical. For example, in the nitroxide mediated living polymerization (NMLP), a nitroxide stable radical such as 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) is used to trap the propagating radicals in a reversible nonpropagating species. The trapping reaction can be represented as follows:



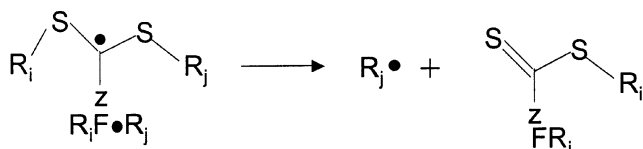
Since the reaction equilibrium is shifted toward the dormant species, the radical concentration becomes low and bimolecular termination rate is significantly reduced. Every polymer chain grows through a series of regularly alternating periods (i.e., active or dormant chains). Therefore, all of the chains grow at the same average rate to uniform chain length. A major drawback is that the overall reaction time becomes very large because of low active radical concentration. In ATRP the equilibrium between active and dormant chains is regulated by a redox reaction which involves metal ions ($\text{Cu}^{(I)}$, $\text{Ru}^{(II)}$, $\text{Mo}^{(0)}$, $\text{Fe}^{(III)}$) [Matyjaszewski et al., 1997]. Kinetic models were also developed for living free radical polymerization by NMLP and ATRP techniques [Butt  et al., 1999a; Zhang and Ray, 2002]. Table 6 shows the kinetic scheme for NMLP and ATRP [Butt  et al., 1999b]. Zhang and Ray applied the kinetic model to batch, semibatch, and continuous stirred tank styrene and n-butyl acrylate polymerization reactors. Their simulation shows that a semibatch reactor is most flexible to make polymers with controlled architecture.

In RAFT and degenerative transfer, a chain transfer agent is used. An end group originating from the chain transfer agent is exchanged between a dormant chain and an active polymer radical. Addition-fragmentation process is used to exchange a moiety such as a dithioester between the two chains.

Addition:



Fragmentation:



If a highly active chain transfer agent is rapidly consumed, few dead chains are formed from irreversible termination and as a result, a narrow MWD is obtained.

4. Chain Branching in Addition Polymerization

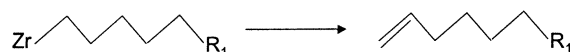
Branched polymers exhibit strongly different behaviors from linear polymers. For example, short chain branching in polyethylene impedes the crystallization and long chain branching influences the rheological properties. Although single site metallocene catalysts produce polyethylenes of narrow MWD (polydispersity ≈ 2.0), such

Table 6. Kinetic model for styrene polymerization by living free radical polymerization [Butt  et al., 1999]

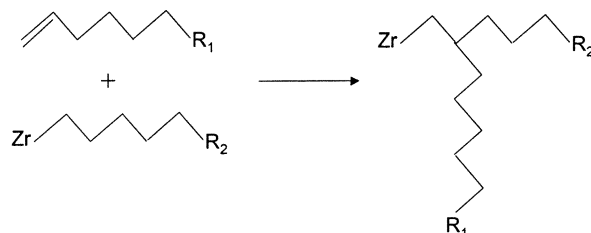
Kinetic scheme	Reaction rates	Remarks
Thermal initiation $3M \xrightarrow{k_{th}} 2R$	$R_{th} = k_{th}M^3$	
Initiator decomposition $I \xrightarrow{k_d} 2R$	$R_i = k_d I$	
Propagation $P_n + M \xrightarrow{k_p} P_{n+1}$	$R_p = k_p M \lambda_0$	$\lambda_i = \sum_{n=0}^{\infty} n^i P_n$
Exchange reaction $P_n + X \xrightleftharpoons[k_a]{k_d} D_n + Y$	$R_d = k_d X \lambda_0$ $R_a = k_a Y^{\alpha'} \mu_0$	$\alpha' = 0$ for NMLP $\mu_i = \sum_{n=0}^{\infty} n^i D_n$
Combination termination $P_n + P_m \xrightarrow{k_t} M_{n+m}$	$R_t = k_t \lambda_0^2$	
Chain transfer to monomer $P_n + M \xrightarrow{k_{fm}} M_n + P_1$	$R_{fm} = k_{fm} M \lambda_0$	
Dormant species decomposition $D_n + X \xrightarrow{k_{dec}} M_n + S$	$R_{dec} = k_{dec} X^{\alpha''} \mu_0$	$\alpha'' = 0$ for NMLP

narrow MWD polymers show inferior processability in extrusion and injection molding operations. Besides broadening the MWD by adding a small fraction of low molecular weight polymer chains, the processability of polyolefins, especially linear low density polyethylene (LLDPE) can also be improved by introducing long chain branching (LCB) to polymer chains. The long chain branching affects the polymer melt flow properties such as shear viscosity, extensional viscosity, and elasticity. In olefin polymerization, the LCB is formed when a dead polymer chain with a terminal double bond generated by β -hydride elimination reaction is incorporated into a growing polymer chain as shown below:

Step 1: Formation of vinyl end group



Step 2: Insertion into a growing polymer chain



Not all metallocene catalysts are known to produce the polyolefins with long chain branches. The most well-known metallocene catalyst system for LCB is a constrained geometry catalyst system (Dow Chemical) in a solution polymerization of ethylene at high temperatures and short reactor residence times. Recently, long chain branched isotactic polypropylene has also been synthesized by using metallocene catalysts [Weng et al., 2002, 2003]. The LCB content in polyolefins can be analyzed by ^{13}C NMR spectroscopy, multiple-detector SEC, SEC with multi-angle light scattering (SEC-MALS), and rheological measurements.

For a single site catalyst, a kinetic model for homopolymerization

of ethylene leading to LCBs can be modeled as:

Propagation



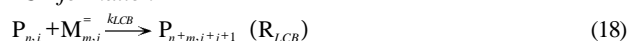
Chain transfer



β -hydride elimination



LCB formation



where $P_{n,i}$ is a live polymer of chain length n with i long chain branches, $M_{n,i}^=$ is a dead polymer of chain length n with i long chain branches having a terminal double bond, and X is a chain transfer agent (e.g., hydrogen). Since the dead polymer with a terminal bond ($M_{n,i}^=$) can be involved in the long chain branch formation, such dead polymer is often called a macromonomer. The mobility of dead polymer with a terminal double bond increases as the reactor temperature is increased. Hence, the rate of incorporation of $M_{n,i}^=$ species is higher in high temperature solution polymerization than in other processes such as gas phase or slurry phase polymerizations. The absence of hydrogen also favors the LCB formation [Chum et al., 1995]. In slurry polymerization processes changes in mass transfer properties of polymerization system may also influence branching formation.

At steady state, the weight chain length distribution of a homopolymer with LCBs is expressed as [Soares and Hamielec, 1996, 1997a, b; Zhu and Li, 1997]:

$$w(n, q) = \frac{1}{(2q+1)!} n^{2q+1} \tau^{2q+2} \exp(-\tau n) \quad (19)$$

where $\tau = (R_\beta + R_{fs} + R_{LCB})/R_p$. The τ value is in the range of 10^{-4} – 10^{-3} . Fig. 7 illustrates the weight chain length distributions of branched polyethylenes [Soares and Hamielec, 1996].

For a binary copolymerization, the following modified form of Stockmayer's bivariate distribution has been suggested for chains with q LCBs:

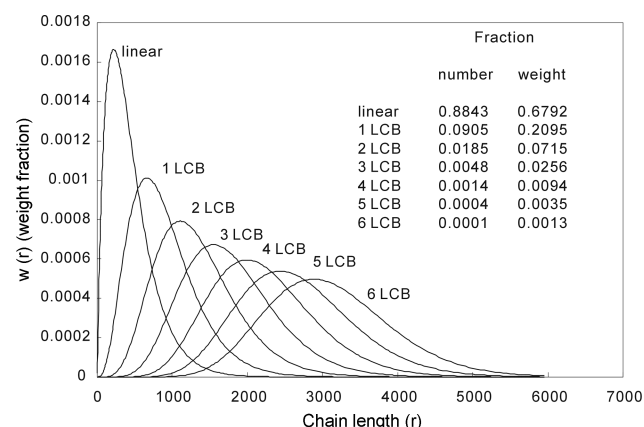


Fig. 7. Weight chain length distributions of branched polyethylenes ($\tau=0.004507$) [Soares and Hamielec, 1996].

$$w(n, y, q) dndy = \frac{1}{(2q+1)!} n^{2q+1} \tau^{2q+2} \exp(-\tau n) \cdot \frac{1}{\sqrt{2\pi\beta/n}} \exp\left(-\frac{y^2 n}{2\beta}\right) dy \quad (20)$$

where y is the deviation from the average copolymer composition (\bar{F}_1) and $\beta = \bar{F}_1(1-\bar{F}_1)[1+4\bar{F}_1(1-\bar{F}_1)(r_1 r_2 - 1)]^{0.5}$. r_1 and r_2 are the reactivity ratios. Eq. (20) can be integrated to:

$$w(y, q) = \int_0^\infty w(n, y, q) dn = \frac{\Gamma(2q+5/2)}{(2q+1)!} \frac{1}{\sqrt{2\pi\beta\tau}(1+y^2/2\beta\tau)^{2q+5/2}} \quad (21)$$

The frequency of LCBs in metallocene polyolefins is about 0.1–1.0 LCB per molecule, measured by analytical temperature rising elution fractionation (ATREF) [Soares and Hamielec, 1995a, b]. ATREF is a technique to fractionate semicrystalline polymers according to their solubility-temperature relationship (i.e., molecular structure).

Yiannoulakis et al. [2000] developed a dynamic model for the calculation of MWD and long chain branching distribution in a solution polymerization of ethylene with constrained geometry catalyst. They divided the total polymer chain population into a series of classes according to the LCB content (e.g., linear chains without LCB, chains with one LCB, chains with two LCBs, etc.). For each class of polymer chains, molecular weight moment equations were derived. Then, Schulz-Flory distribution function was used to reconstruct the MWD for each class of polymer chains. The overall weight chain length distribution was then calculated by the weighted sum of all polymer class distributions. Since molecular weight moment equations are solved with kinetic equations, this method can be used to simulate the changes in the MWD and LCB during the transition period of a polyethylene reactor.

Late transition metal catalysts such as Pd-based complexes containing bulky diimine ligands are also effective for ethylene polymerization. These catalysts are known as Brookhart catalysts and have a potential to generate branched polyolefins in the absence of α -olefin comonomer. Polyethylene with a broad spectrum of topologies (e.g., linear, hyperbranched, dendritic) can be synthesized by controlling the competition between monomer insertion and catalyst isomerization (catalyst walking) with these catalysts. Here, the coordination bond among the metal, olefin monomer and polymer chain stays together for a longer time than in a metallocene and the metal hydride can be re-added after some rearrangement in the polymer chain. The catalyst in the middle of the chain can start a branch [Tullo, 2001; Guan et al., 2003].

The long chain branching in metallocene catalyzed olefin polymerization does not lead to crosslinking reactions. But in free radical polymerization, long chain branching can lead to the broadening of MWD and the formation of nonlinear polymer chain through crosslinking reactions. In free radical polymerization, short chain branches are introduced by intramolecular chain transfer (back-biting reaction) and long chain branches by intermolecular chain transfer (e.g., high pressure free radical ethylene polymerization to LDPE). In LDPE processes, the relative rate of branch formation or the frequency of short chain branches is represented by the following equation:

$$SCB = \frac{R_b}{R_p} = \frac{k_b P}{k_p MP} \quad (22)$$

where R_b is the rate of intramolecular chain transfer, P is the total

live polymer concentration, and R_p is the rate of chain propagation. Notice that the short chain branch formation is independent of polymer molecular weight. The number of LCBs in LDPE may vary from 0.6-6.0 per 1000 carbon atoms. High reaction temperatures and low pressures favor the formation of LCBs.

The long chain branching in free radical polymerization can be represented by the following polymer chain transfer reaction:



where P_{mb} is the polymer chain of chain length m with a branch point in the backbone. It should be noted that chain transfer to polymer by hydrogen abstraction could occur at any position in the dead polymer chain, M_m . Note that the rate of formation of P_{mb} is given by

$$R_{fp} = k_{LB} m M_m \sum_{n=1}^{\infty} P_n$$

The overall branching density (number of branches per monomer molecule polymerized) can be calculated by using the following method. Let N_0 =total number of monomer molecules (both polymerized and unpolymerized), x =fraction of monomer molecules polymerized defined as $x=N_0-N/N_0$ where N =number of monomer molecules left when the fractional monomer conversion is x . Also, define v =total number of branches. Then, the following equations are derived:

$$\frac{dv}{dt} = k_{LB} P N_0 x \quad (24)$$

$$\frac{dx}{dt} = k_p P (1-x) \quad (25)$$

From these two equations, we obtain

$$\frac{dv}{dx} = \left(\frac{k_{LB}}{k_p} \right) N_0 \frac{x}{1-x} \equiv C_B N_0 \frac{x}{1-x} \quad (26)$$

Upon integration, the following is obtained

$$\rho \equiv \frac{v}{N_0 x} = -C_B \left[1 + \frac{1}{x} \ln(1-x) \right] \quad (27)$$

Fig. 8 illustrates the chain branches as a function of monomer conversion. Notice that branching frequency increases rapidly as monomer conversion increases high. Eq. (26) can also be written as

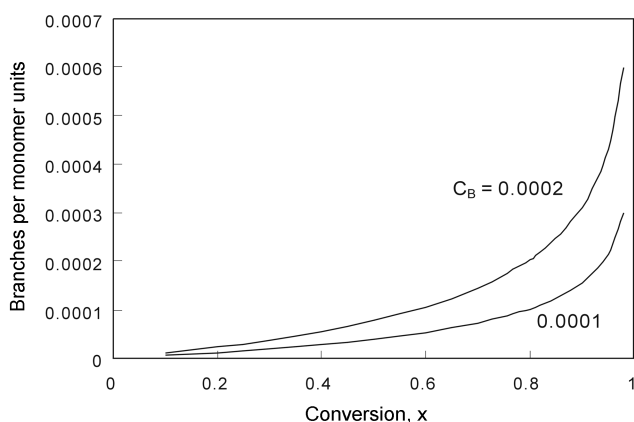


Fig. 8. Branching frequencies in the polymer chain.

$$\frac{dv}{dx} = C_B \left(\frac{x}{1-x} \right) [M]_0 \bar{M}_n \quad ([M]_0 = \text{initial monomer concentration}) \quad (28)$$

Pladis and Kiparrisides [1998] provide an excellent review of the mathematical modeling technique for LCB modeling.

The modeling of crosslinking and gelation in addition polymerization is a difficult computational problem. Recently, Teymour and Campbell [1994] developed a new computational method (numerical fractionation technique) to model the dynamics of gelation in addition polymerization systems. This method uses the kinetic approach and identifies a succession of branched polymer generations that evolve en route to gelation. In other words, polymer population is segregated into a series (generations) of unimodal subdistributions of similar structure (linear or branched) and size. As one moves from one generation to the next the average molecular size will grow geometrically, leading toward a generation of infinitely large polymer molecules. Numerical Fractionation has been applied successfully to a variety of nonlinear polymerization systems by a number of research groups [Arzamendi and Asua, 1995; Butté et al., 1999a; Papavasiliou et al., 2002].

5. Copolymer Microstructure

For a binary addition copolymer, the instantaneous average copolymer composition is described by the Mayo-Lewis equation using the reactivity ratios, r_1 and r_2 . Besides average copolymer composition, copolymer microstructure is represented by other attributes such as chemical composition distribution (the fraction of chains having a particular mole fraction of comonomer) and monomer sequence length distribution (the fraction of comonomer sequences of a particular length). For binary copolymers, Anantawaraskul et al. [2003] derived a bivariate distribution of kinetic chain length and chemical composition using a statistical approach:

$$f_{w,p}(r, n_A) = \sqrt{\frac{1}{2\pi r n_A (1-n_A)}} \left(\frac{P[A]}{n_A} \right)^{r n_A} \left(\frac{1-P[A]}{1-n_A} \right)^{r(1-n_A)} \times r^2 (1-\alpha)^2 \alpha^{r-1} \left[\frac{w_A n_A + w_B (1-n_A)}{w_A P[A] + w_B (1-P[A])} \right] \quad (29)$$

where r is the kinetic chain length, a is the probability of propagation, n_A is the mole fraction of comonomer A, $P[A]$ is the average mole fraction of comonomer A, w_A is the molecular weight of A, and w_B is the molecular weight of comonomer B. They generalized the chemical composition distribution [Eq. (29)] to describe the chemical composition distribution of multicomponent random copolymers (m -components) as follows:

$$f_w(r, n_1, n_2, \dots, n_{m-1}) = f_w(n_1, n_2, \dots, n_{m-1} | r) f_w(r) \quad (30)$$

where

$$f_w(r) = r(1-\alpha)^2 \alpha^{r-1} \quad (31)$$

$$f_w(n_1, n_2, \dots, n_{m-1}) = \sqrt{\frac{r^{m-1}}{(2\pi)_{m-1} n_1 n_2 \dots n_{m-1} (1-n_1-n_2-\dots-n_{m-1})}} \times \left(\frac{P[1]}{n_1} \right)^{r n_1} \left(\frac{P[2]}{n_2} \right)^{r n_2} \dots \left(\frac{P[m-1]}{n_{m-1}} \right)^{r n_{m-1}} \times \left(\frac{1-P[1]-P[2]-\dots-P[m-1]}{1-n_1-n_2-\dots-n_{m-1}} \right)^{r(1-n_1-n_2-\dots-n_{m-1})} \times \left[\sum_{i=1}^m (M_i n_i) \sqrt{\sum_{i=1}^m (M_i P[i])} \right] \quad (32)$$

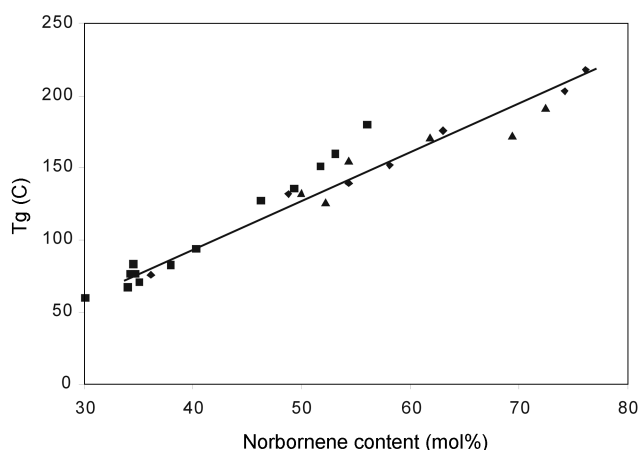


Fig. 9. Effect of norbornene content on glass transition temperature of ethylene-norbornene copolymer [Park, 2003].

For many copolymers, the effect of copolymer microstructure has little effect on the macroscopic copolymer properties. But for some copolymers, copolymer microstructure can be quite important. To illustrate this point, let us consider ethylene-cyclic olefin copolymers (COC). COC is emerging as a potential new class of engineering polymers for various interesting applications. Ethylene-norbornene copolymers (ENC) are the most well known of COCs having high glass transition temperature (up to 270 °C), low moisture absorbance, and excellent optical properties. This copolymer can be made over homogeneous metallocene catalysts such *rac*-Et(1-indenyl)₂ZrCl₂/methylaluminoxane catalyst. ENC is an interesting polymer in that the polymer's glass transition temperature varies with the amount of cyclic olefin monomer in the copolymer (Fig. 9). The microstructure of ENC depends on the nature of catalyst and the polymerization conditions [Tritto et al., 2001, 2002]. For example, when norbornene content in the copolymer is small (less than 6 mol-%), most of the norbornene units are present as isolated units with random sequence distribution [Bergström et al., 1998]. At norbornene mol-% larger than 45%, micronorbornene blocks of varying lengths (dyads, triads) can be formed. The copolymer becomes completely amorphous as norbornene content exceeds 14 mol-%.

For linear binary copolymerization with no penultimate effect, the monomer sequence distribution is represented by the following probabilities:

$$(M_1)_n = L_{11}^{n-1} (1 - L_{11}) \quad (33)$$

$$(M_2)_n = L_{22}^{n-1} (1 - L_{22}) \quad (34)$$

where L_{ij} is the probability that a growing chain ending in an i monomer unit ($i=M_1$ or M_2) will add a j ($j=M_1$ or M_2) monomer unit next. $(M_1)_n$ ($(M_2)_n$) is the probability of having exactly n units of M_1 (M_2) in a series of a growing chain. The average sequence lengths of M_1 and M_2 monomers are given by:

$$\bar{N}_1 = \sum_{n=1}^{\infty} n(M_1)_n = \frac{1}{1-L_{11}} = 1 + r_1 \frac{M_1}{M_2} \quad (35)$$

$$\bar{N}_2 = \sum_{n=1}^{\infty} n(M_2)_n = \frac{1}{1-L_{22}} = 1 + r_2 \frac{M_2}{M_1} \quad (36)$$

Note that the average chain length has a linear relation with the molar ratio of monomers in the bulk reaction phase.

Park et al. [2003] and Park [2003] report that penultimate effect cannot be ignored in quantifying the kinetics of ethylene-norbornene copolymerization with homogeneous *rac*-Et(1-indenyl)₂ZrCl₂/methylaluminoxane catalyst. They show that the penultimate norbornene has a strong effect on the propagation activity of the catalyst. With the penultimate model, the following equations are obtained:

$$(M_1)_n = \begin{cases} 1 - L_{211}, n=1 \\ L_{211} L_{111}^{n-2} (1 - L_{111}), n \geq 2 \end{cases} \quad (37)$$

$$(M_2)_n = \begin{cases} 1 - L_{122}, n=1 \\ L_{122} L_{222}^{n-2} (1 - L_{222}), n \geq 2 \end{cases} \quad (38)$$

where the probability function L_{ijk} is given by:

$$L_{111} = \frac{R_{p111}}{R_{p111} + R_{p112}} = \frac{r_{11}}{r_{11} + \frac{M_2}{M_1}} \quad (39)$$

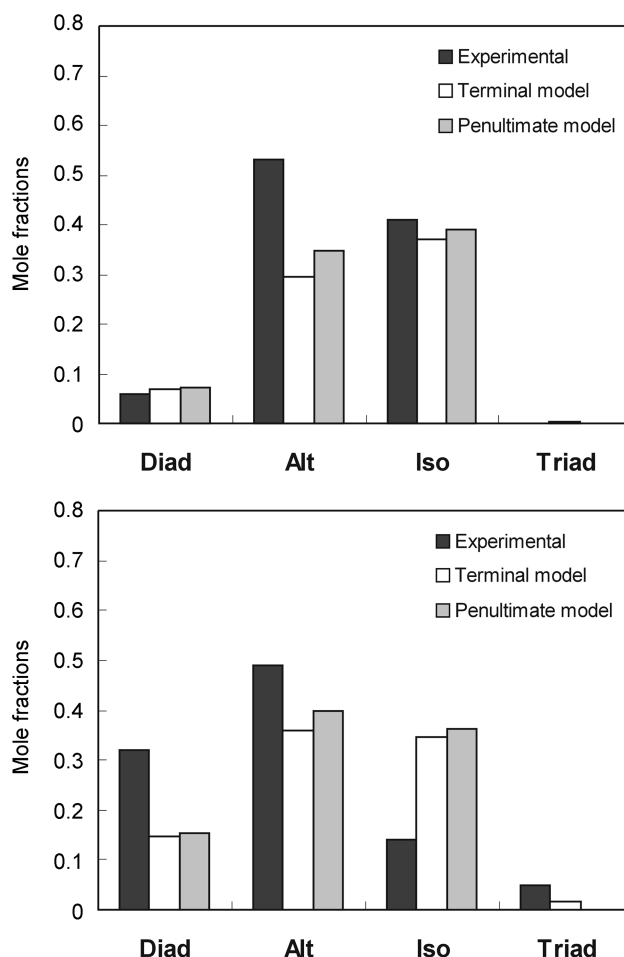


Fig. 10. Sequence distribution of norbornene in ENC at triad level: (a) 42 mol-% of norbornene in ENC; (b) 55 mol-% of norbornene in ENC. Here Diad, Alt, Iso, and Triad represent ENN, NEN, ENE, and NNN sequence, respectively [Park, 2003].

$$L_{121} = \frac{R_{p121}}{R_{p121} + R_{p122}} = \frac{1}{1 + r_{12} + \frac{M_2}{M_1}} \quad (40)$$

$$L_{211} = \frac{R_{p211}}{R_{p211} + R_{p212}} = \frac{r_{21}}{r_{21} + \frac{M_2}{M_1}} \quad (41)$$

$$L_{221} = \frac{R_{p221}}{R_{p221} + R_{p222}} = \frac{1}{1 + r_{22} + \frac{M_2}{M_1}} \quad (42)$$

Fig. 10 illustrates the comparison of experimental data and the model-predicted sequence length distributions at triad level. Although the rates of ethylene and norbornene copolymerization are strongly influenced by the penultimate unit in the propagating chains [Park et al., 2003], the penultimate effect on the comonomer sequence length distribution seems to be insignificant. It is expected from Eqs. (39)–(42) that only the monomer mole ratios and reactivity ratios, not individual rate constants, affect the development of sequence length distributions.

Recently, Teymour [2003] proposed an interesting technique (“digital encoding technique”) to calculate the monomer sequences in addition copolymerization processes. This method aims at profiling a complete chain sequence distribution for a given copolymer molecule by identifying chains at the level of “polymeric isomers.” The method uses symbolic binary arithmetic to represent the architecture of a copolymer chain. Thus, each binary number describes the exact monomer sequence on a specific polymer chain, and its decimal equivalent is a unique identifier for this chain. For example, if the binary digits 0 and 1 are assigned to monomers M_1 and M_2 , respectively, a chain with 6 monomer units in the sequence $M_1M_2M_1M_1M_2M_1$ is represented (excluding the chain end entities) as 010010 and its decimal equivalent $d=17$ identifies this particular chain. For chains with 6 monomer units, d ranges from 0 (i.e., 000000) to 63 (i.e., 111111). Using this scheme, the propagation reaction can be expressed as



Similarly, combination termination is expressed as



Consequently, population balances can be formulated to follow the evolution of chains of a decimal code ‘ d ’ and chain length ‘ j ’. Fig. 11 shows an example (adapted from Teymour [2003]) of such results for chains of length 6 and varying codes. This figure also shows the utility of this technique in following the effect of changing the reactor feed composition on the exact sequencing of monomers on the chains. As the fraction of monomer 1 in the feed is increased from 0.265 to 0.796, one observes a noticeable shift in the peaks from the high end of the code scale to the low end. This of course is a result of the more frequent appearance of 0s than 1s. It is thus clearly possible to accurately design the architecture of new copolymer products by simply manipulating the reaction conditions. The binary encoding technique has also been applied to the sequence analysis resulting from penultimate effects, azeotropic copolymerization and compositional drift [Teymour, 2003].

6. Polymer Particle Morphology

The control of particle morphology is important in many indus-

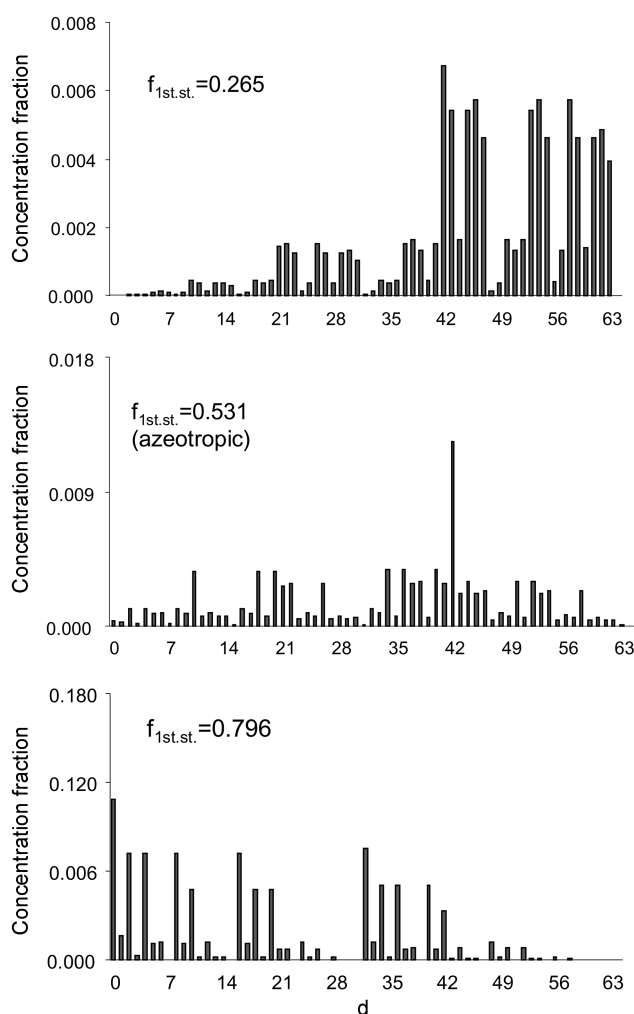


Fig. 11. Effect of feed monomer composition for a binary copolymerization of styrene and methyl methacrylate with disproportionation termination [Teymour, 2003].

trial polymerization processes. For example, for the production of high impact polypropylene, it is desired that the polymer particle should have high bulk density, large particle size, high rubber content, yet low degree of stickiness and improved flowability [Bouazid and McKenna, 2003]. The morphology of polymer particles also affects the operability of a gas phase fluidized bed polymerization reactor and the choice of the catalyst to be used. In free radical vinyl chloride polymerization, polymer particle morphology affects the diffusion of additives such as plasticizers.

The mechanism of polymer particle formation in any heterogeneous polymerization process is often quite complex and difficult to quantify. In heterogeneously catalyzed olefin polymerization processes, catalyst fragmentation and particle growth affect the catalyst activity and polymer properties. A catalyst fragmentation is practically very important to maintain the sufficiently fast access of the monomer to active catalyst sites located within the pores of the support. The traditional particle models such as polymeric flow model or multigrain model have been very successful in predicting the effect of mass and heat transfer limitations on the polymerization rate and molecular weight properties [Floyd et al., 1986, 1987; Hutch-

inson and Ray, 1987]. However, these macroscopic models are often inadequate to model the complex development of particle morphology such as hollow particles, pieces of shells and small fragments for very high activity catalysts [Kittilsen et al., 2000]. With very high activity catalysts, a rapid polymerization often results in local melting of the polymer inside a catalyst/polymer particle, blocking the access of monomer to active sites. Therefore, understanding the catalyst fragmentation and polymer particle growth phenomena is important for the optimal design of high activity supported olefin polymerization catalysts.

Some recent modeling work incorporates the convective flow effect inside the growing particles [McKenna et al., 2000; Kittilsen et al., 2000]. Grof et al. [2003] and Kosek et al. [2003] developed a new meso-scopic modeling technique to study the morphogenesis of polyolefin particles. In their modeling, they assume that cohesive forces keep the fragments of catalyst particle encapsulated in polymer together. The two driving processes for the growth and morphogenesis of polymer macro-particle are the growth of micro-grains and the binary and ternary visco-elastic interactions among micro-grains. They used various visco-elastic models to represent the interactions between micro-grains. Their work illustrates that the pore space reconstruction can be used to relate effective transport properties of porous catalyst/polymer particles to the geometry and topology of the pore obtained from microscope images.

PARAMETER ESTIMATION IN POLYMERIZATION REACTION MODELING

A modeling is never complete until all the relevant model parameters are determined or estimated. In fact, determining the parameters of a kinetic model by using laboratory, pilot plant, or plant data is perhaps the most critical step for the successful development of a process model and at the same time it might be the most time consuming, costly, and difficult process. Typical model parameters include rate constants (in Arrhenius form) and relevant transport and thermodynamic parameters such as mass and heat transfer coefficients, diffusivity, density, heat capacity, active site concentrations, etc. Some kinetic parameters may change with a changing reaction environment.

Parameter estimation is difficult because a multitude of reactions affect each other and relevant kinetic parameters are often masked by physical transport phenomena (e.g., diffusion, mass, and heat transfer effects). Practically, it is not always possible to design experiments to determine all the relevant kinetic parameters. Therefore, in modern kinetic modeling, pseudo-rate constant methods and computer aided parameter estimation techniques are widely used. Nonlinear multivariable regression techniques integrated with open kinetics equation-oriented models could significantly improve the speed and accuracy of the parameter estimation calculation [Chen, 2002].

A polymerization process model validated solely on the laboratory data may fail to provide accurate predictions of the behavior of a large-scale plant reactor because reaction environments can be quite different (e.g., impurities, efficiency of mixing, etc.). It is also important to realize that extracting process data from plant operations for process modeling purpose is not as easy as one may expect. It is because plant managers or plant engineers might be very reluctant to the idea of disturbing normal commercial operations to

generate some data for kinetic model development. In this regard, there is a need to develop advanced parameter estimation techniques using plant data without disturbing normal commercial production, particularly in a large-scale continuous polymerization process.

Another point to be made in modeling an industrial polymerization process is that one must decide the level of sophistication of the model. Unlike academic polymerization kinetic models, industrial process models should be developed with clear objectives or purposes for a given set of constraints (e.g., personnel, cost, time). There is absolutely no reason for an industrial process modeler to over-develop a process model. In this context, it is suggested that the goals of the reactor/process modeling project be clearly defined with specific applications laid down before the commencement of any modeling project. Sensible assumptions and/or simplifications are the keys to the successful modeling of an industrial polymerization process.

In transition metal catalyzed olefin polymerizations, the kinetic parameters are catalyst dependent. Therefore, whenever a new catalyst is employed, a new set of kinetic parameters must be determined. Considering the fact that the properties of polyolefins are mostly dictated by the nature of catalyst being used and that a large number of different types of catalysts are used for different polymer grades, we can easily understand the importance of having a well-established parameter estimation procedure that can be applied to any catalyst systems. In practice, the model parameters obtained from the laboratory data are used as a reference and actual plant data are used to adjust the model parameters. Sirohi and Choi [1996] presented on-line parameter estimation techniques where the extended Kalman filter and the nonlinear dynamic parameter estimation technique are used. In their method, dynamic process data during a grade transition in a continuous gas phase olefin polymerization reactor, by switching the catalyst type, are used to estimate several key kinetic parameters for the new catalyst which is assumed to exhibit similar polymerization characteristics. In their method, instead of re-determining all of the kinetic parameters for a new catalyst system, only a few selected rate constants that affect the polymerization rate and polymer properties (average copolymer composition and molecular weight averages) are determined.

In some polymerization processes, developing a first-principles model can be practically infeasible. For example, when several vinyl monomers are copolymerized using several free radical initiators, it is extremely difficult, if not impossible, to develop model equations to calculate the rate of polymerization and polymer properties such as molecular weight averages and copolymer composition. In such cases, building a statistical model based on experimental data would be a more pragmatic approach. Of course, the statistical model should be used with some cautions because it does not contain any physical or chemical information about the process itself and the applicable process range can be quite narrow. Nevertheless, statistical models are frequently used in the polymer industry for quality control purposes.

CONTROL OF POLYMER PROPERTIES

The primary goals of reactor control in industrial polymerization processes are to maintain stable reactor operations and product quality indices at their target values. For an existing plant, improved

reactor controls are needed to increase the polymer yield and to reduce production cost. Fig. 11 illustrates a typical industrial process control hierarchy [Congalidis and Richards, 1998]. Process knowledge, sensors, transmitters, and analyzers are the prerequisites for the design of basic control system to regulate pressure, temperature, level, and flow rate. With the regulatory control system in place, one can design advanced regulatory control, model based control and intelligent scheduling and optimization system.

There have been a large number of publications on the control of polymerization reactors in the past two decades. Many of these publications dealt mainly with reactor temperature control and polymer property control problems. It is not the objective of this paper to provide a comprehensive review of all aspects of polymerization reactor control. Instead, in the following discussion, the focus will be given on the issues relevant to the control of polymer properties based on some selected recent references.

Exothermic polymerization processes often exhibit strongly non-linear dynamic behaviors (e.g., multiple steady states, autonomous oscillations, limit cycles, parametric sensitivity, thermal runaway), particularly when continuous stirred tank reactors are used [Kiparisides, 1996; Kim et al., 1990, 1991, 1992]. Some polymerization processes are open loop unstable and susceptible to unmeasured disturbances, or upsets, even with a feedback controller in place. For example, in a transition metal catalyzed olefin polymerization process, unmeasured small amount of catalyst poisons can change the polymerization kinetics, and hence, the polymer yield and polymer properties. In worst cases, process disturbances may lead the reactor to instability [Choi and Ray, 1985, 1986].

Since many of the polymer properties are hard to monitor on-line, first-level process variables are controlled to follow a certain process recipe. Typical first-level reactor variables are polymerization temperature, pressure, feed rates of monomer(s), catalysts or initiators, chain transfer agents, solvents, etc. In principle, as long as these variables are tightly controlled, consistent product quality can be warranted. In general, polymerization rate and polymer properties are non-linearly correlated and hence a polymerization process control system is inherently a multivariable control system. In presence of unexpected process disturbances, or upsets, little can be done to correct the damages made on the product properties. In a batch process, the consequence of not being able to handle process upsets is a heavy economical loss.

The second-level control objectives include the direct control of polymer properties using on-line measurements or estimates of polymer quality indices. Any variations in the product quality can be corrected, in principle, if such quality indices are available during the polymerization.

Let us consider some issues concerning batch polymerization reactor control. A batch polymerization process is a multivariate and non-stationary or dynamic process. Quite often, direct on-line control of polymer properties is not feasible, or very difficult in many batch polymerization processes. For example, sampling from a reactor can be quite a challenge in some high-pressure batch reactor systems. For short batch reaction time, there is simply no time to analyze polymer samples off-line and use the result to make appropriate corrective control actions before the batch operation is terminated. A batch polymerization reactor should also be operated to maintain consistent batch-to-batch product quality and to maxi-

mize the product yield by increasing monomer conversion and/or reducing batch reaction time [Flores-Cerrillo and MacGregor, 2003].

In many industrial batch polymerization processes, the design of a batch polymerization reactor control consists of two stages: 1) off-line design of a control trajectory (recipe), and 2) implementation and execution of the control trajectory. The control trajectory can be developed through experimentation, plant experience, or by using a process model [Butala et al., 1988; Scali et al., 1995; Crowley and Choi, 1997, 1999b]. There might exist some conflicting control objectives (e.g., polymer yield, molecular weight, composition, batch reaction time) that require special treatments. For example, multiobjective dynamic optimization techniques might be needed

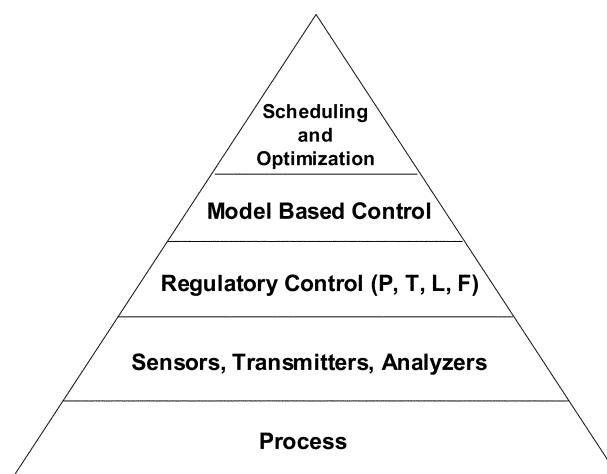


Fig. 12. Typical industrial process control hierarchy [Congalidis and Richards, 1998].

Table 7. Extended Kalman filter algorithm with on-line and off-line measurements

Process model	$\frac{dx}{dt} = f(x, u) + w(t), w(t) \sim N[0, Q(t)]$ $x(0) \sim N[x_0, P_0]$
On-line measurements	$y_{0,k} = h_0(x_k) + v_{0,k}; v_{0,k} \sim N[0, R_{0,k}]$
Delayed measurements	$y_{d,k-\tau} = h_0(x_{k-\tau}) + v_{d,k-\tau}; v_{d,k-\tau} \sim N[0, R_{d,k-\tau}]$
State estimation propagation	$\frac{d\hat{x}}{dt} = f(\hat{x}(t), u(t))$
Error covariance propagation	$\frac{dP}{dt} = F(t)P(t) + P(t)F^T(t) + Q(t)$
State estimate update with on-line measurements	$x_k(+) = x_k(-) + K_k[y_{0,k} - h_0(x_k(-))]$
Error covariance update with on-line measurements	$P_k(+) = [I - K_k H_{0,k}] P_k(-)$
Filter gain matrix with on-line measurements	$K_k = P_k H_{0,k}^T [H_{0,k} P_k(-) H_{0,k}^T + R_{0,k}]^{-1}$ where $F(t) = \frac{\partial f(x(t), u(t))}{\partial x(t)} \bigg _{x(t)=x(t)}$ $H_{0,k} = \frac{\partial h_0(x_k)}{\partial x_k} \bigg _{x_k=x_k(-)}$

to develop optimal reactor operating policies or target control trajectories in presence of conflicting control objectives [Butala et al., 1988, 1992].

Quite obviously, an accurate dynamic polymerization reactor model is a prerequisite for such advanced control designs. Many excellent dynamic optimization techniques have been developed and they are readily available to control engineers. A typical objective function (F) for reactor optimization takes the following form:

$$F = w_1 t_f + \sum_{i=1}^N w_i \left(\frac{Y_i}{Y_i^d} \right)^2 \quad (46)$$

where w_i is the weighting factor, t_f is the batch time, Y_i is the product quality parameter (e.g., M_n , average copolymer composition, etc.), and Y_i^d is the desired quality parameter value. The objective function is minimized subject to process model and constraints:

$$\frac{dx}{dt} = f(x(t), u(t), t); \quad c(x(t), u(t), t) \leq 0 \quad (47)$$

where x is the state variable and u is the control variable.

Recently, an attempt has been made to control the entire polymer molecular weight distribution curve by using a process model and optimization technique [Crowley and Choi, 1997b]. Fig. 13 illustrates the design of optimal reactor temperature trajectories to obtain a desired molecular weight distribution in a batch methyl methacrylate polymerization process. Here, feasible sequential quadratic programming (FSQP) technique is used to find the sequence of optimal reactor temperature set points which will yield the best match between target and actual polymer chain length distribution at the end of the batch. The graphs on the left in Fig. 13 represent the computed sequence of reactor temperature set points at selected iterations and the graphs on the right show the resulting chain length distribution compared with the target distribution. The final temperature set point program can be implemented and executed or the trajectory can be updated on-line if timely measurements or estimates of polymer molecular weight distribution are available dur-

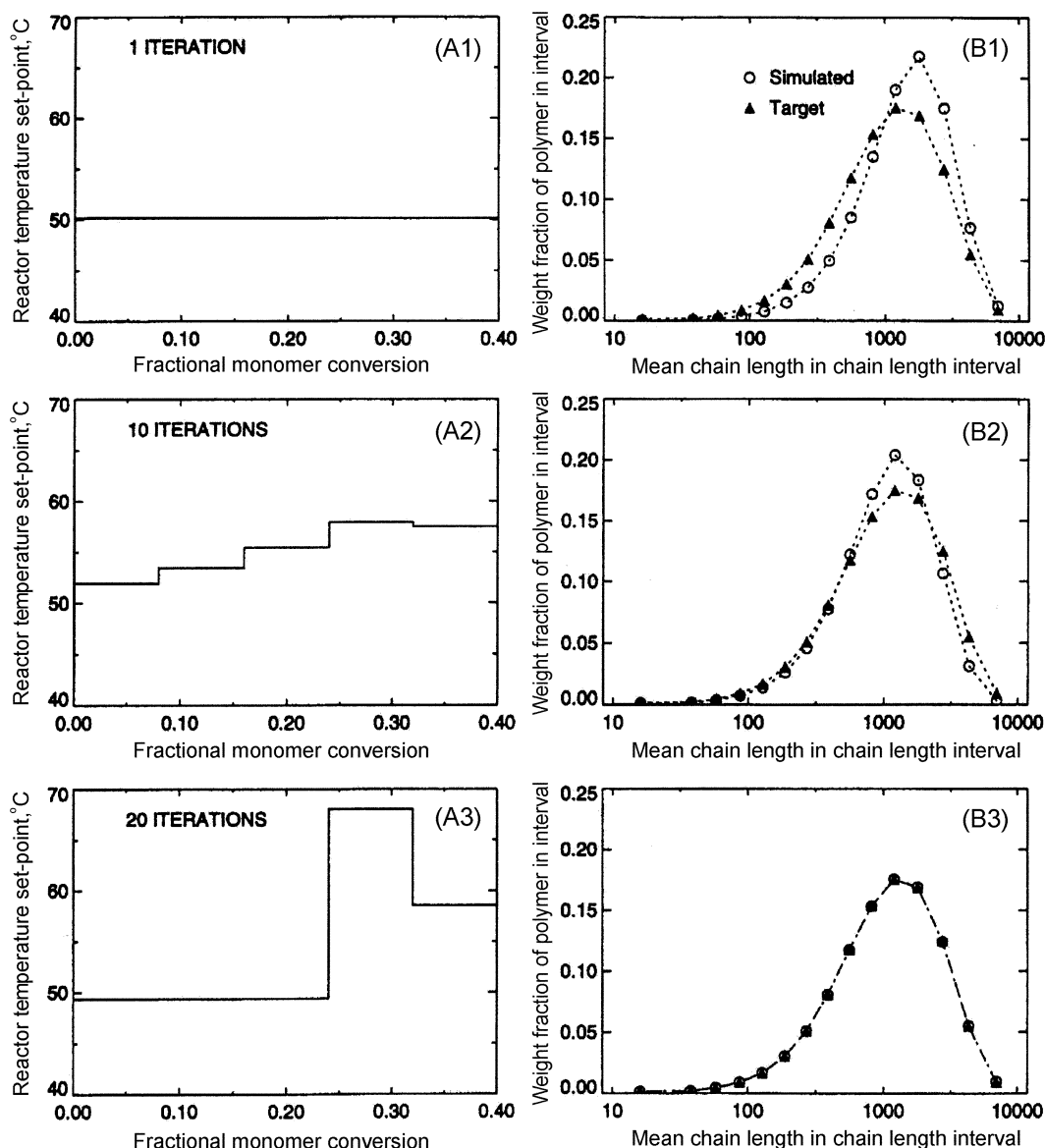


Fig. 13. Design of reactor temperature set point program to control polymer chain length distribution.

ing the batch operation [Crowley and Choi, 1998b].

Once the reactor control trajectory is designed, the next goal is to execute the trajectory as closely as possible. Traditional PID controllers are still widely used but model predictive controllers (MPC) are also used in some polymerization processes where the use of advanced reactor control can be economically justified. In MPC, a process model is utilized to predict the output into the future and minimize the difference between the predicted model output and the desired output using some open loop objective function. The measurement is used to update the optimization problem for the next time step. The MPC algorithms are reasonably well developed and utilized in many chemical processes including polymerization processes [Peterson et al., 1992; Ogunnaike, 1995; Seki et al., 2001; Jeong et al., 2001; Young et al., 2002; Doyle et al., 2002]. Since industrial polymerization processes exhibit strong nonlinearity the application of linear model predictive control (LMPC) is often limited, particularly for grade transition control and for regulatory control. In nonlinear model predictive control (NMPC) algorithms, a nonlinear programming problem has to be solved on-line and hence computational load is generally quite heavy. To reduce the computational burden, a successive linearization of the original nonlinear process model can be used to approximate the nonlinear process

behaviors [Seki et al., 2001; Young et al., 2002].

Continuous reactors are operated at steady state and hence the key objective in controlling a continuous polymerization reactor system is to maintain reactor stability in presence of any process upsets and during normal steady state operations and grade transition operations. In some continuous polymerization processes such as liquid slurry olefin polymerizations, reactor fouling may develop over a period of time, gradually deteriorating the control performance. In such a case, one may adjust the control variables to compensate for the changes in process characteristics. Then, some polymer property indices that are not directly measured or controlled on-line may drift from their specifications to result in poor product quality. Therefore, the development of on-line estimation techniques for polymer property indices that cannot be measured on line or only measured off-line with significant time delays becomes necessary [Chien and Penlidis, 1990].

In continuous polymerization processes, polymers of different properties are manufactured in a single product line. Therefore, designing efficient grade transition controls and optimal production scheduling becomes another important control design objective [McAuley and MacGregor, 1992; Debling et al., 1994; Sirohi and Choi, 1996; Wang et al., 2000; Chatzidoukas et al., 2003]. In some sense,

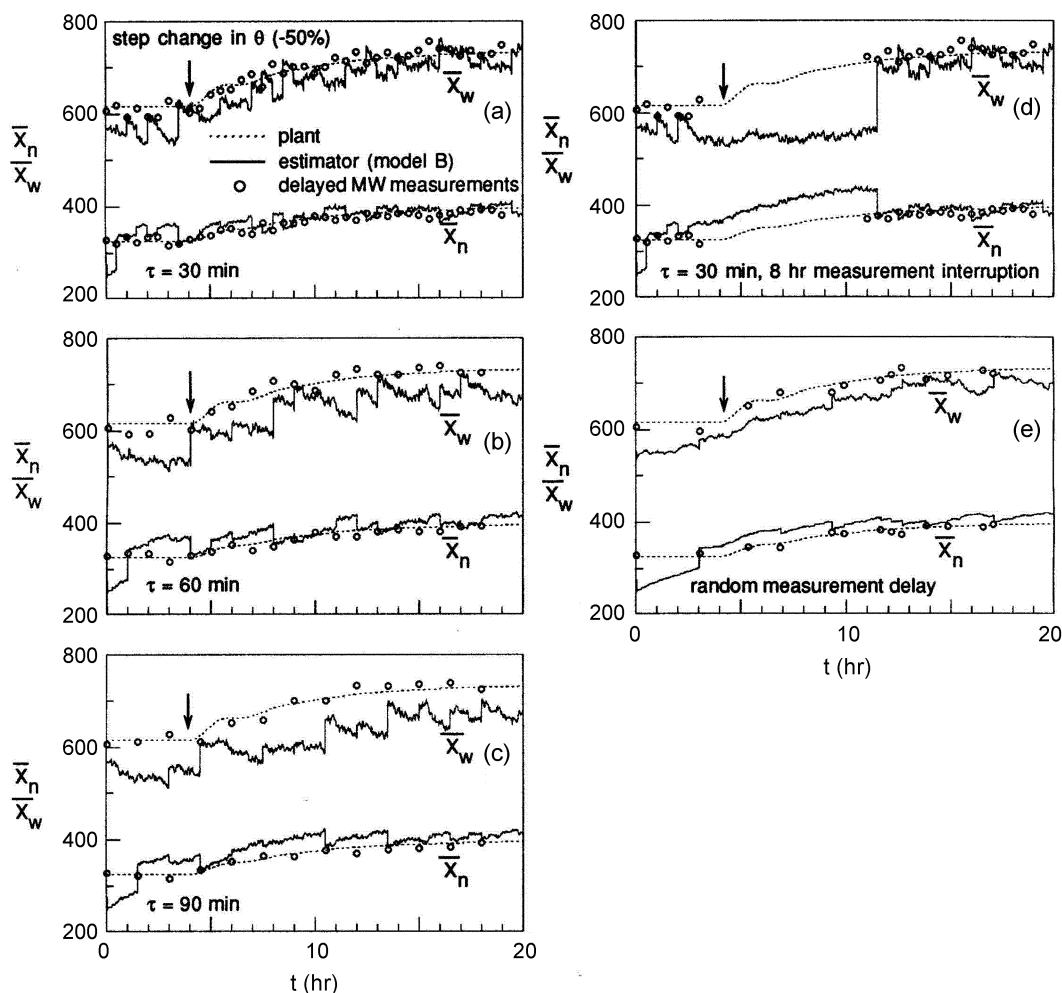


Fig. 14. Effect of molecular weight measurement time delay (τ) on estimation of MW during open loop transients to step change in reactor residence time (θ) [Kim and Choi, 1991].

the grade transition control problem is similar to the optimal design of a batch polymerization reactor control. Polymerization processes are nonlinear and multivariable systems in nature and thus significant control loop interactions are expected in conventional feedback control systems. The work by Congalidis and coworkers [1989] illustrates the value of a process model for the design of feedforward and feedback control of a continuous solution copolymerization reactor using a multivariable transfer function model. They analyzed control structure/loop pairings using singular value decomposition and relative gain array. Then, they determined the loop pairings and developed a combined feedforward/feedback strategy for servo and regulatory control problems. For a continuous terpolymerization process, Ogunnaiké [1995] illustrates the design of a two-tier control system. In the first tier level, the flow rates of monomer, catalyst, solvent, and chain transfer agent are used to regulate reactant composition in the reactor. Then, at the second tier level, set points for the composition of the reactor contents are used at a less frequent update rate to regulate final product properties. In the second tier, an on-line, dynamic kinetic model, running in parallel with the process, supplies estimates of product properties. The model predictions are updated by using delayed laboratory measurements and on-line stochastic filter.

A process model can be a powerful tool for the design of on-line polymer properties control system when it is used in conjunction with optimal state estimation techniques. Indeed, several on-line state estimation techniques such as Kalman filters, non-linear extended Kalman filters (EKF), and observers have been well developed and applied to polymerization process systems [Kim and Choi, 1991; Sirohi and Choi, 1996; Park and Rhee, 2003]. Table 7 shows the extended Kalman filter algorithm with delayed off-line measurements. In implementing the on-line state estimator, several issues may arise. For example, the standard filtering algorithm needs to be modified to accommodate time-delayed off-line measurements (e.g., MWD, chemical composition, conversion, etc.). The update frequency of state estimation needs to be optimally selected to compensate for the model inaccuracy. Fig. 14 illustrates the use of on-line state estimator (EKF) with delayed molecular weight measurements in a continuous stirred tank styrene polymerization reactor [Kim and Choi, 1991]. In this particular simulation, the minimum off-line measurement time for molecular weight averages is set as 30 min and irregular sampling intervals are assumed. The two models of different accuracies are used for plant simulations (dotted lines) and state estimation (solid lines). The simulation results shown in Fig. 14(d) and (e) indicate that unequal MW sampling gives much better estimates than with a large time delay of 90 min even with a model that exhibits a significant model-plant mismatch. Kim and Choi [1991] further show that when the modeling error is large, more frequent measurements of the molecular weight (or other polymer parameters) are required to obtain good estimates from the on-line state estimator. Fig. 15 illustrates the use of on-line estimate of polymer molecular weight for servo control with two models of different accuracies (Model A is more accurate than Model B). In this simulation, the set point of \bar{X}_w (weight average degree of polymerization) is step increased. The steady state model calculates the new set point values of other variables (e.g., reactor temperature, monomer conversion, feed initiator concentration). With the extended Kalman filter in place, the reactor reaches a new steady state in about

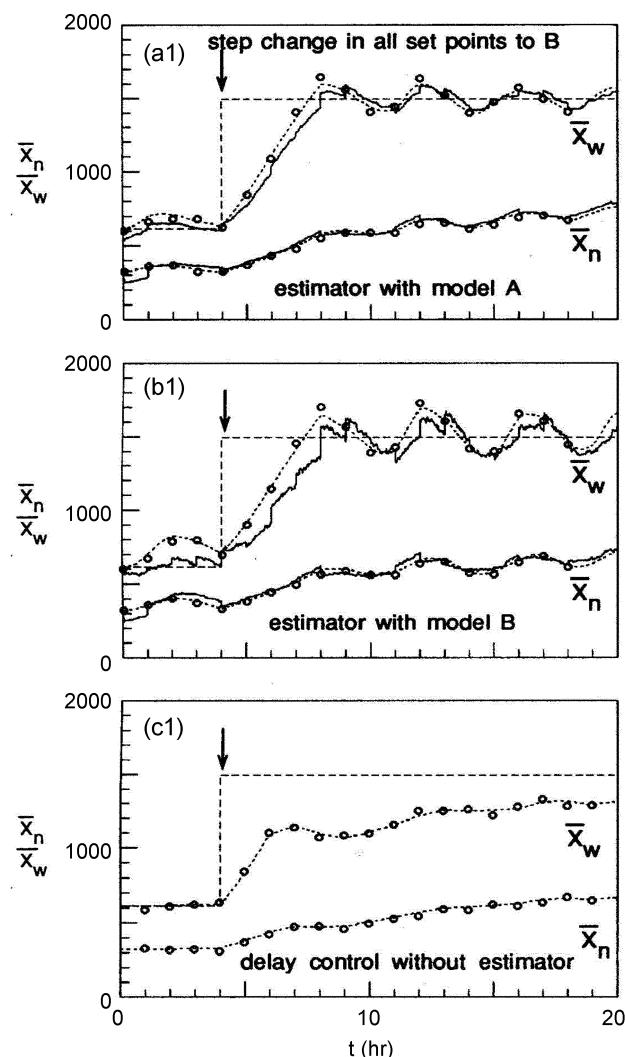


Fig. 15. Effect of model accuracy on MW control with 60 min delayed MW measurements [Kim and Choi, 1991].

3 hr [Fig. 14(a1), (b1)], whereas Fig. 14(c1) illustrates the failure of the grade transition control without on-line state estimator. Here, feedback control is carried out using time-delayed off-line measurements with PI controllers. Notice that the target MW is not attained in Fig. 15(c1) due to integral windup.

The state estimation technique can also be incorporated into the design of optimal batch polymerization control system [Crowley and Choi, 1997b, 1999b]. For example, a batch reaction time is divided into several control intervals and the optimal control trajectory is updated on-line using the molecular weight estimates generated by a model/state estimator. Of course, if batch reaction time were short, such feedback control of polymer properties would be difficult to implement. Nevertheless, the on-line stochastic estimation techniques and model predictive control techniques offer promising new directions for the improved control of polymer properties in batch polymerization reactors.

CONCLUDING REMARKS

Mathematical modeling is a powerful tool not only for the de-

velopment of process understanding, but also for the design of advanced process technology. In particular, a kinetic model plays an important role in designing polymerization conditions to tailor a polymer's molecular architecture. In this review, we discussed recent developments in modeling techniques for the calculation of polymer molecular weight distribution, copolymer composition distribution, sequence length distribution, long chain branching, and particle morphology. A few issues concerning the model parameter estimation and model-based polymer reactor control are also discussed. The modeling techniques for polymerization processes are reasonably well developed and several commercial simulation packages are available. However, modeling of polymerization reactions is still an active area of academic and industrial research. Although not discussed in this paper, the modeling of heterogeneous polymerizations such as precipitation polymerization and emulsion polymerization remains as a challenge. Many excellent design tools have also been developed for multiobjective optimization, on-line state estimation, and model predictive control of industrial polymerization reactors. These techniques are gaining favorable acceptance in the polymer industry. One of the outstanding issues is to develop more efficient parameter estimation techniques, particularly in a plant environment, without disturbing normal process operations. With these advanced computational and modeling tools, the question is how one can use them wisely and creatively to produce polymers of highest quality at lowest possible cost.

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