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The Value of Fundamental Modeling in the Design and Operation of Controlled Free Radical Polymerization Processes

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Summary: Free radical polymerization processes are some of the oldest in the history of synthetic polymers; however, there are still fundamental issues that are not well understood. As an example, the advent of living free radical polymerization involving free radical complexing agents and catalysts introduces new fundamental issues and many new applications involving complex behavior. In this paper, the main focus will be on living free radical polymerization. Examples will be used to illustrate how fundamental process modeling is essential in choosing the most appropriate reagents, reactor types and operating conditions for the application at hand.

Introduction

In free radical polymerization there are still important kinetic and process operation issues that require deeper fundamental knowledge before it is possible to have close control over molecular architecture, polymer morphology, and the polymerization process. These would include the details of chain branching structures, the practical consequences of chemical kinetic and equilibrium effects in living free radical polymerization, the influence of surface phenomena, thermodynamics, and flow on the morphology of multiphase polymers, the effects of mixing on polymer properties and process operation, etc. Because of limited space, the discussion here will focus on living free radical polymerization involving different mechanisms, for different products, and in different types of reactors.

Issues in Living Free Radical Polymerization

Table 1 shows the basic kinetic mechanisms for three principal types of living free radical polymerization: nitroxide mediated radical polymerization (NMRP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation transfer (RAFT) radical polymerization. The conventional steps as well as the special living free radical mechanisms for each type are shown.

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Table 1. Free radical homopolymerization kinetics

	Conventional Free Radical Polymerization
Initiation	$I \xrightarrow{k_d} 2R_i$ $R_i + M \xrightarrow{k_{pi}} P_1$
Propagation	
Chain Transfer	
To monomer	$P_n + M \xrightarrow{k_{trm}} P_n + R_m$
To solvent	$P_n + S \xrightarrow{k_{trs}} P_n + R_s$
To chain transfer agent (CTA)	$P_n + CTA \xrightarrow{k_{trCTA}} P_n + R_{cta}$
Termination	
Coupling	$P_n + P_m \xrightarrow{k_{tc}} D_{n+m}$
Disproportionation	$P_n + P_m \xrightarrow{k_{td}} D_n + D_m$
	Living Free Radical Polymerization
Initiation	
Nitroxide mediated Type	$R - N \overset{k_{capr}/k_{capf}}{\longleftrightarrow} R + N$
Atom Transfer Radical Polymerization	$R - X + Mt^n - Y/L \overset{k_{capr}/k_{capf}}{\longleftrightarrow} R + X\text{-}Mt^{n+1} - Y/L$
Reversible capping reaction	
Nitroxide mediated Type	$P_n + N \overset{k_{capr}/k_{capf}}{\longleftrightarrow} Q_n$
Atom Transfer Radical Polymerization	$P_n + X\text{-}Mt^{n+1} - Y/L \overset{k_{capr}/k_{capf}}{\longleftrightarrow} Q_n + Mt^n - Y/L$
RAFT Chemistry	$P_n + Q_m \overset{k_{capr}/k_{capf}}{\longleftrightarrow} Q_n - Q_m \overset{k_{capr}/k_{capf}}{\longleftrightarrow} P_m + Q_n$

There has been some earlier work on modeling the kinetics of these living free radical polymerization processes. Yan et al.[1] developed a simple kinetic model for living free radical polymerization, discussing the effects of propagation and capping rate constants and reactant concentrations on polydispersity. Veregin et al.[2] presented a general solution for the molecular weight distribution as a function of conversion in nitroxide mediated styrene free radical polymerization, considering that the initiation is instantaneous and the termination reaction is negligible. They concluded that the polydispersity in this system is controlled by the exchange rate between the growing and dormant polymer chains. Greszta and Matyjaszewski et al.[3] proposed a detailed kinetic model for TEMPO mediated styrene polymerization and estimated the kinetic and thermodynamic parameters for the reversible reaction between growing and dormant species. Fukuda et al.[4] conducted computer simulations for nitroxide mediated styrene polymerization, concluding that thermal initiation is important in maintaining a reasonable polymerization rate in this system. Shipp and Matyjaszewski [5,6] studied styrene atom transfer radical polymerization through a kinetic model. They found that the termination is subject to diffusional control, which may conceal the persistent radical effect. The apparent external orders of reactants in this system were also studied. Ziegler and Matyjaszewski[7] studied atom transfer radical copolymerization of MMA and n-butylacrylate and used simulations to explain the observed results. Butté et al.[8, 9] developed a general kinetic model for living free radical polymerization. They assessed the model reliability by comparing simulations to experimental data for TEMPO mediated styrene polymerization and styrene atom transfer radical polymerization. They found their model a useful tool for analyzing living free radical polymerization processes. Zhu[10] presented a kinetic model for stable free radical polymerization. He discussed the effects of a variety of kinetic parameters and reactant concentrations on polymerization rate and polymer property development. Zhang and Ray[11, 12] developed a detailed process model for reversible addition-fragmentation chain transfer (RAFT) free radical polymerization which agreed well with experimental data and showed the effect of reactor choice and operating conditions on product properties and process productivity. Barner-Kowollik et al.[13] used a kinetic model for the RAFT free radical polymerization process to deduce the rate coefficients related to the addition-fragmentation equilibrium reaction. In contrast to deterministic models, He et al.[14] used a Monte Carlo method to study the kinetics and chain length distribution for living free radical polymerization. The effects of experimental variables such as initiation rate constant etc. were explored.

Sawamoto and coworkers[15] suggest that living free radical polymerization in aqueous suspensions should behave similarly to bulk polymerization. Some workers[9, 16-26] have studied living free radical polymerization in emulsion and miniemulsion reactors and suggest that this may be the most effective process for high reaction rates and close control of molecular architecture.

The consensus of this modeling work is that there are certain requirements for living free radical polymerization in bulk or solution:

- Chain transfer to monomer must be small for the chain lengths of interest.
- The rate of radical capping reactions compared to the chain propagation rate be

large enough that each polymer chain have many chain growth periods over the course of the polymerizations. This also means that the rate of radical capping must be sufficiently fast compared to propagation that the equilibrium between dormant chains and growing chains be established very early in the course of the polymerization.

- The equilibrium between growing and dormant polymer concentrations must allow the concentration of dormant polymer to be many orders of magnitude larger than that of growing polymer.

We will illustrate these and other points in the examples that follow using a general model capable of modeling experimental results for each of the living free radical mechanisms. This has been installed in the POLYRED™ polymerization process simulation package and used to generate all of the model predictions shown in this paper.

Table 2. Conditions for examples

For all cases, the ATRP system is used with primary capped species methyl 2-bromopropionate as seed. Cu^{I}Br is used as catalyst where the ligand could be 4,4'-di(5 nonyl)-2,2'-bipyridine (dNbpy) or similar. Parameters taken from various sources[27-32].

Example 1: Homopolymerization of n-butyl acrylate (BA) at 90°C in a batch reactor with batch charge of 6.5 mol/l BA, 0.065 mol/l of primary capped species and catalyst, $k_{capf} = 5\times10^{9}\,\text{l/mol/sec}, k_{capr} = 0.05\,\text{l/mol/sec}$ chosen as representative of the range for different ligands.

Example 2: Copolymerization of styrene (St) and n-butyl acrylate (BA) at 110°C in a semibatch reactor with initial 300 cm^3 charge of 6.77 mol/l St, 1.07 mol/l BA, 0.0814 mol/l of primary capped species and catalyst, and feed rate of 0.01 cm^3/sec composed of 6.77 mol/l St and 1.07 mol/l BA. The reactor has 1000 cm^3 volume.
$r_{St} = 0.79, r_{BA} = 0.26, k_{capf,St} = 1.15\times10^{7}\,\text{l/mol/sec}, k_{capr,St} = 0.45\,\text{l/mol/sec},$
$k_{capf,BA} = 8\times10^{7}\,\text{l/mol/sec}, k_{capr,BA} = 0.055\,\text{l/mol/sec}.$

Example 3: Copolymerization of stryrene (St) and n-butyl acrylate (BA) at 110°C in a series of continuous stirred tank reactors each with volume of 1 liter. Feed composition: 3.98 mol/l St, 3.24 mol/l BA, 0.0646 mol/l of primary capped species and catalyst. Feedrates: 4 tanks, 0.05 cm^3/sec; 8 tanks, 0.10 cm^3/sec; 16 tanks, 0.20 cm^3/sec. Kinetic parameters are the same as in Example 2.

Examples

We will present illustrative examples for three cases of living free radical polymerization under reaction conditions given in Table 2. First let us consider the example of atom transfer radical polymerization (ATRP) of n-butyl acrylate at 90°C in a bulk batch reactor where no conventional initiator is used, but all radicals come from primary capped species used as chain extension seeds. Figure 1 shows the effects of a change in the rate of the reversible capping reaction while the equilibrium constant was held fixed.

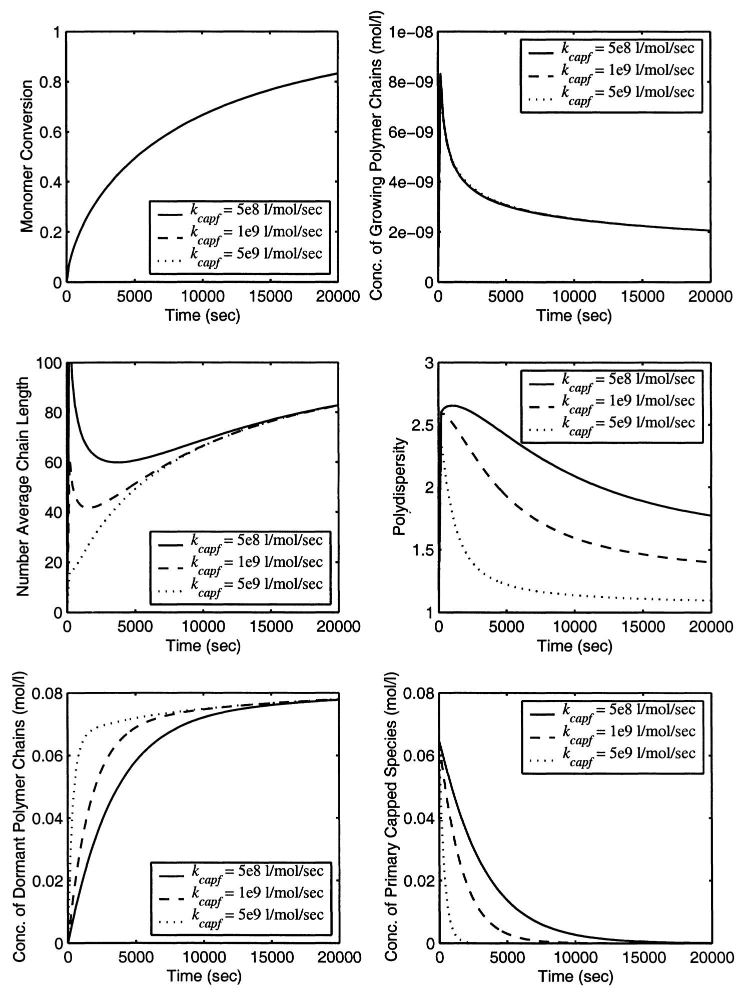

Figure 1 The effect of forward capping rate constant on the batch reactor polymerization of n-butyl acrylate (Example 1)

This could be accomplished by changing the capping species or catalyst. The fundamental effect is to increase the speed at which the primary capped species exchange their primary radicals for dormant polymer. Figure 1 shows that the growing radical concentration is not affected, so that monomer conversion is also unaffected. However, it is seen that only for rapid radical exchange that all of the chains (growing and dormant) grow at the same rate on average, and low polydispersity is possible. For

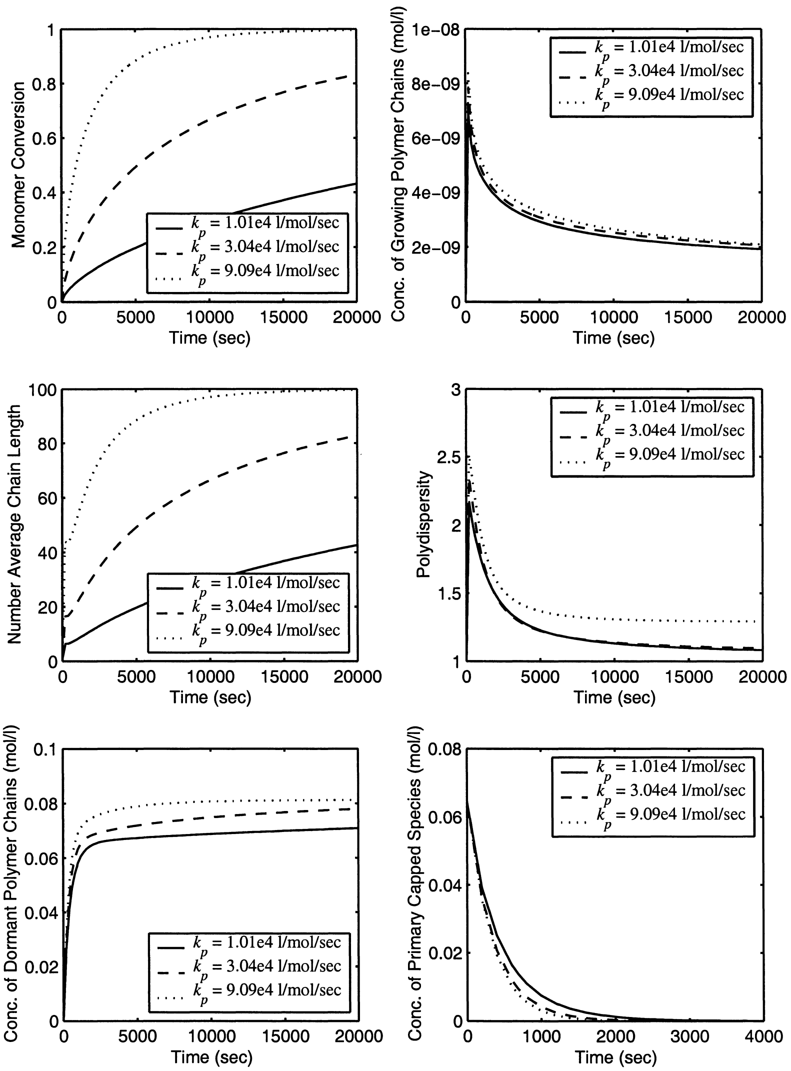

Figure 2 **The effect of propagation rate constant on the batch reactor polymerization of n-butyl acrylate (Example 1)**

slower radical exchange, a significant fraction of total polymer is produced before all of the dormant radicals have had a turn at growing.

Figure 2 shows the effects of an increase in the propagation rate constant, k_p. This can have the same effect on polydispersity as varying the capping rate because again a significant amount of polymer can be made before all of the dormant radicals have a turn at growing. The small effect of k_p on growing radical and dormant species concentration is due to reactor volume changes with conversion. Either small k_{capf} or

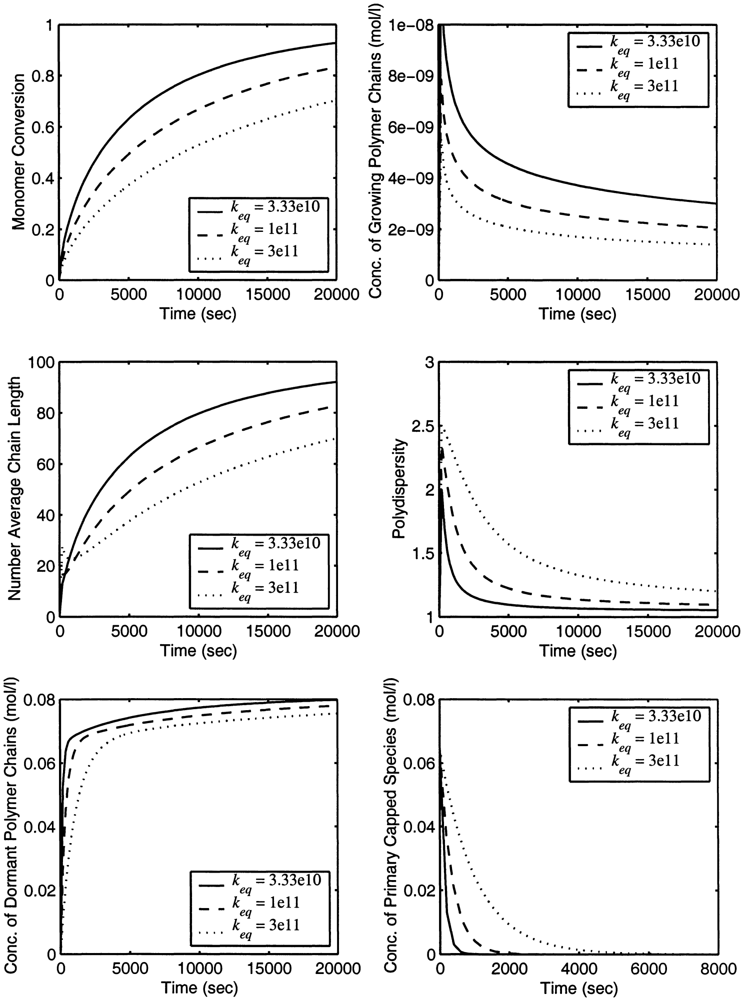

Figure 3 **The effect of varying the capping equilibrium constant on the batch polymerization of n-butyl acrylate (Example 1)**

large k_p can lead to high polydispersity even if the monomer concentration and other environmental conditions are held constant.

In reality, changing the capping agent could also change both the rate constant and equilibrium constant for capping, so that both possibilities should be considered. The effect of changing the radical capping equilibrium constant can be seen in Figure 3. Note that increasing the equilibrium constant shifts more growing radicals to the dormant state, thus decreasing the rate of polymerization and the rate of chain extension. Shifting the equilibrium results in more primary capped species that have to be converted to dormant polymer, and fewer growing radical "positions" to cycle all the dormant polymer through. Thus the polydispersity is higher for an increased equilibrium constant.

These idealized changes are impossible to achieve in experiment because changing the reagents can have multiple effects. Changing the capping agent can change both the rate and equilibrium of the capping reaction, while changing the monomers can affect all of the parameters of the system. Nevertheless, understanding the effects of kinetic and equilibrium parameters can allow better interpretation of experimental results.

For this example the only source of radicals has been the capped radical seeds. Now we explore the effects of adding small amounts of a conventional initiator. Figure 4 shows the influence of three levels of initiator addition to the batch charge. Notice that initially the growing radical concentration is much higher, but the termination reaction eventually drives this down to a value close to that with no additional initiator. The increased radicals have only a small effect on the conversion of primary capped species to dormant polymer because this requires the decomposition of primary capped species. The increase in growing radical concentration greatly increases the polymerization rate and the rate of chain extension; however, significant conversion occurs before most of the primary capped species are converted to dormant polymer. Thus true living polymerization is not achieved until about 50% monomer conversion, resulting in higher ultimate polydispersities than for the case without added initiator. It is this, and not the additional dead polymer, that causes the polydispersity increase.

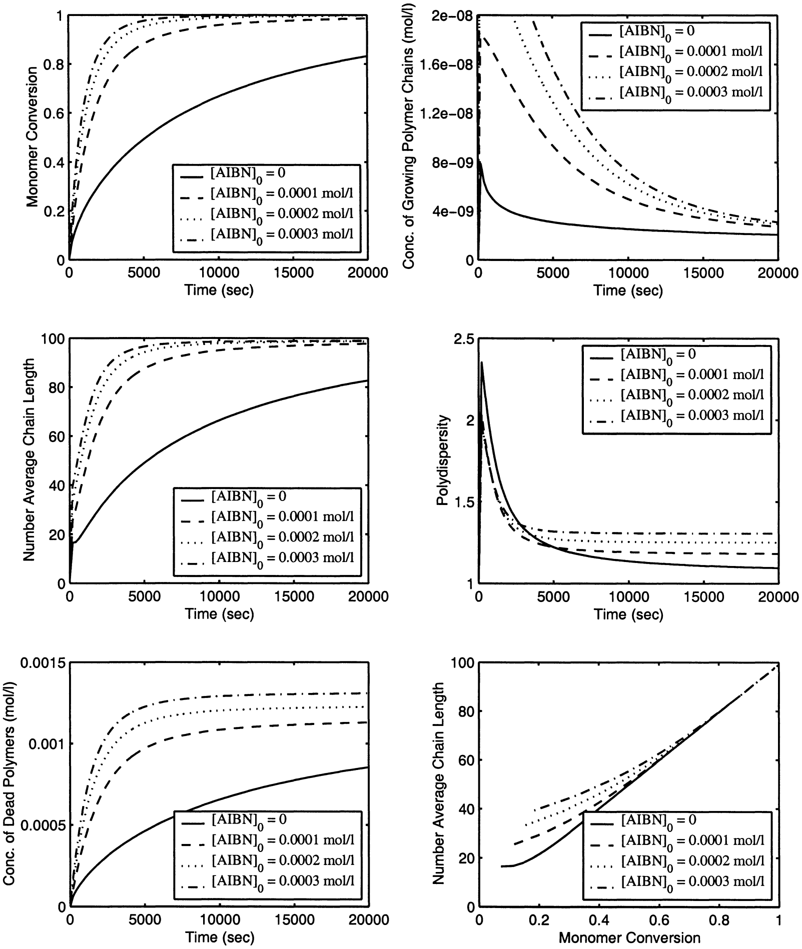

Figure 4 The influence of additional conventional initiator on the batch polymerization of n-butyl acrylate (Example 1)

We will now consider a second example: the case of the copolymerization of styrene and n-butyl acrylate using ATRP under the conditions described in Table 2. There is an initial charge of the two monomers plus the primary capping agent and a feed containing the two monomers. As seen in Figure 5, the reactor quickly reaches a "steady state" corresponding to starved feed operation and then produces a constant composition copolymer with steadily increasing chain length and decreasing polydispersity. Through this semibatch operation one obtains the narrow MWD of the batch reactor and the uniform composition of the CSTR. Other operations easily

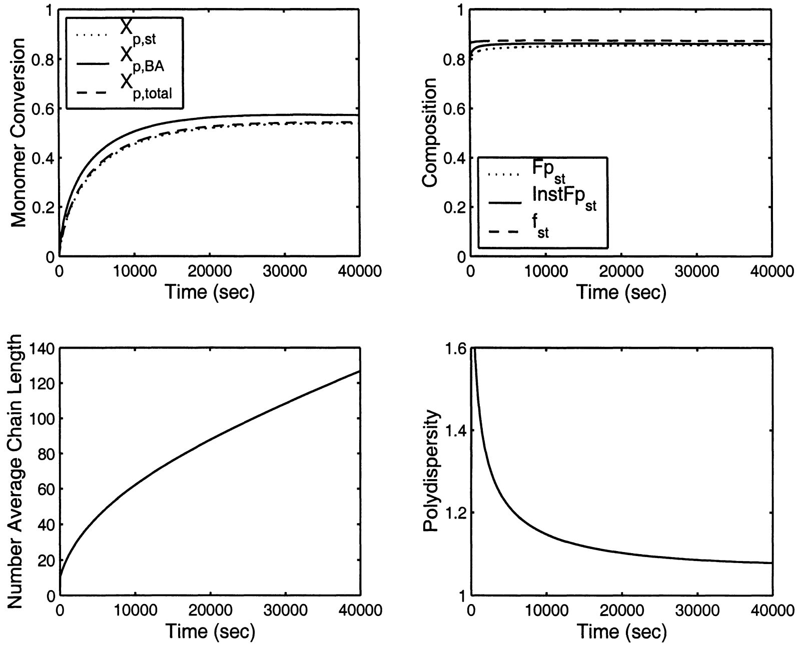

Figure 5 The semibatch copolymerization of styrene and n-butyl acrylate (Example 2)

carried out in the semibatch reactor can yield block copolymers or combinations of blocks and tapered segments in the polymer chain.

A continuous process such as a tubular reactor or a series of stirred tank reactors can provide a relatively narrow residence time distribution and higher productivity per unit volume than the batch or semibatch reactor. For our third example, consider the performance of a series of stirred tanks for the same copolymerization studied in Example 2. The conditions, given in Table 2, are for a 4, 8, and 16 tanks-in-series reactor train where each train has the same mean residence time. The results shown in Figure 6, indicate a slightly higher conversion and ultimate chain length from the larger number of tanks because of the narrowerer residence time distribution. Unfortunately, the series of stirred tanks also produces a tapered polymer chain because the monomer composition varies at each stage, as it would in a batch reactor. This could be remedied by feeding additional amounts of the more reactive monomer into each tank in order to keep the monomer composition constant along the train. For the series of stirred tanks,

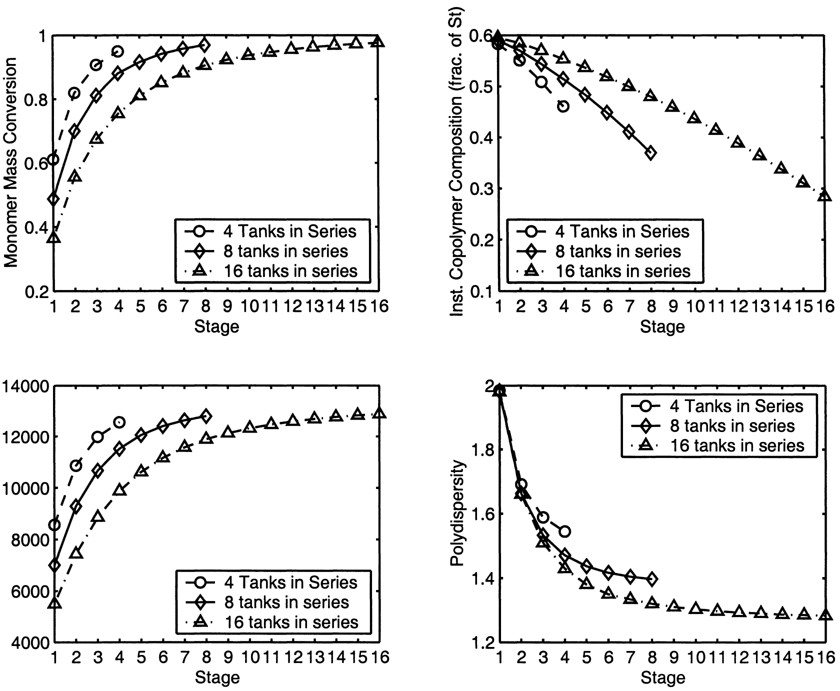

Figure 6 **The copolymerization of styrene and n-butyl acrylate in a series of stirred tank reactors (Example 3)**

the effect of the number of tanks on the polydispersity is dramatic: even with 16 tanks, the residence time distribution is still somewhat broader than that of the batch reactor, so that the polydispersity is limited to about 1.3. It is expected that a well-designed tubular reactor would have a much narrower residence time distribution and thus lower polydispersity. While the three examples discussed here involved ATRP systems, the general trends carry over to NMRP systems also. The case of RAFT systems is a little different and is treated in references[11-13].

Conclusions

Fundamental modeling of polymerization processes can play an important role in designing experiments and interpreting results. Then it becomes a key tool in developing an effective process for producing polymer in commercial quantities.

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